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The Extraction of Alginate from Brown Seaweeds

1.1 Introduction

Alginic acid is an anionic polysaccharide distributed widely in the cell walls of brown seaweeds, where it exists in the cell walls and extracellular matrix in the form of a mixed salt of sodium, calcium, magnesium, strontium, and barium alginate. The British chemist E C C Stanford first described the extraction of alginic acid from brown seaweed in a patent dated 12 January 1881 [28]. In the following years, Stanford carried out the initial studies on the chemical nature of alginic acid, which he named "algin." [29] Due to the protein components in the seaweed extract, Stanford initially believed that alginic acid contained nitrogen.

Brown seaweeds are distributed in many parts of the world, and following Stanford's initial work, many other scientists around the world made further studies on this novel biomaterial. In 1926, Atsuki and Tomoda [2] and Schmidt and Vocke [27] reported that uronic acid was a constituent of alginic acid. Shortly after these two studies, other scientists found D-mannuronic acid in the hydrolysate of alginate [3, 17, 19–21].

The chemical nature of alginate was further clarified in 1955, when Fischer and Dorfel found that in addition to D-mannuronic acid, the hydrolysates of alginic acid also contained L-guluronic acid [6]. This finding is important to illustrate the nature of alginic acid as a copolymer composed of two types of monomers, i.e. D-mannuronic acid (M) and L-guluronic acid (G). Figure 1.1 shows the chemical structure of these two monomers.

It is now widely known that as a natural copolymer, the proportions of D-mannuronic acid and L-guluronic acid vary widely for alginate extracted from different types of brown seaweeds, resulting in variations of the physical properties of alginate-based materials. As a polymeric acid, alginic acid can form salt with various types of metal ions to form alginate salt, with alginate being a term commonly used as a general description for the various types of alginic acid based salts, as well as all the derivatives of alginic acid and alginic acid itself. These seaweed-derived polymeric materials have thickening, gelling, emulsifying, film, and fiber-forming properties that are widely utilized in many diversified industries.

Alginate Fibers and Wound Dressings: Seaweed Derived Natural Therapy, First Edition. Yimin Qin.

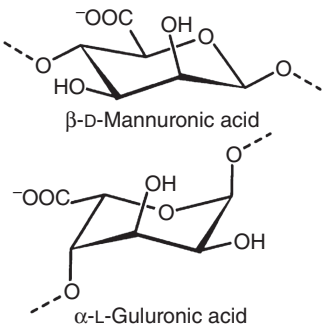


Figure 1.1 The chemical structures of β-D-mannuronic acid and α-L-guluronic acid.

1.2 Global Distribution of Brown Seaweeds

Although alginic acid is present in several types of bacteria such as *Azotobacter vinelandii* and many species of *Pseudomonas* [7] and alginate can be successfully extracted from the biomass of the soil bacterium *A. vinelandii* ATCC 9046 cultivated on crude glycerol as an alternative carbon source [10], up to the present time, all commercially available alginates have been extracted from brown seaweeds, mainly *Laminaria hyperborea, Macrocystis pyrifera, Laminaria digitata, Ascophyllum nodosum, Saccharina japonica, Ecklonia maxima, Lessonia nigrescens, and Durvillaea antarctica*. The chemical composition of alginate extracted from different types of seaweeds varies according to seasonal and growth conditions, as well as within different parts of the plant [1, 13]. This variability in composition shows the biological role of alginate in seaweeds whose mechanical properties can be regulated partly by the variations in the M/G composition of alginate. For example, the brown seaweed *L. hyperborea* grows in very exposed coastal areas, where high mechanical rigidity is required in the stipe and holdfast, whereas high flexibility is needed in the leaves that float on streaming water. The stipe and holdfast contain alginate with a high content of L-guluronic acid, which is responsible for high gel strength, while the leaves contain alginate with a high content of D-mannuronic acid, which is related to softness and flexibility.

Figure 1.2 shows the distribution of the main species of wild brown seaweeds around the world. Globally, brown seaweeds, or Phaeophyceae, are a large group of multicellular algae that play an important role in the marine environment, both as a source of marine vegetables and for the habitats they form, which provide a natural environment for other marine organisms. For example, the brown seaweed *M. pyrifera* may reach 60 m in length and form prominent underwater forests. In the Sargasso Sea, the brown seaweed *Sargassum* creates unique habitats in a vast area of tropical water. In many parts of East Asia, the brown seaweed *S. japonica* is widely used as food for human consumption. Overall, there are about 1500–2000 species of brown seaweed in the world [11].

Figure 1.3 shows the main types of brown seaweeds used for alginate production. In 2015, the worldwide annual industrial production of alginate was estimated to be

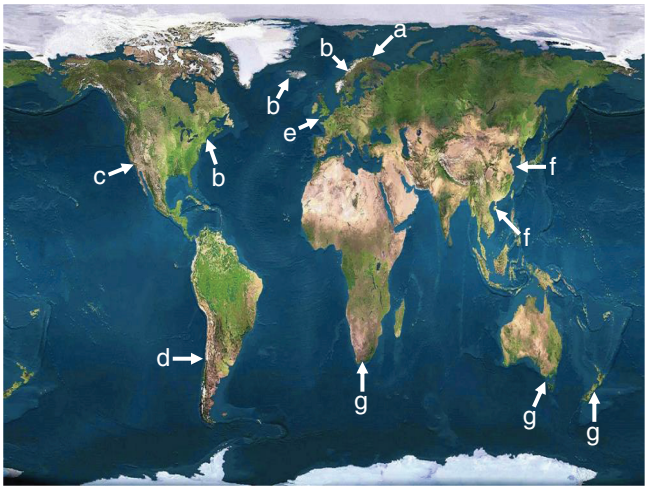


Figure 1.2 Distribution of wild brown seaweeds around the world, (a) *Laminaria hyperborea*; (b) *Ascophyllum nodosum*; (c) *Macrocystis pyrifera*; (d) *Lessonia nigrescens*; (e) *Laminaria digitata*; (f) *Saccharina japonica*; (g) *Ecklonia maxima*. Source: Adapted with permission from fig. 1.4, Qin [26].

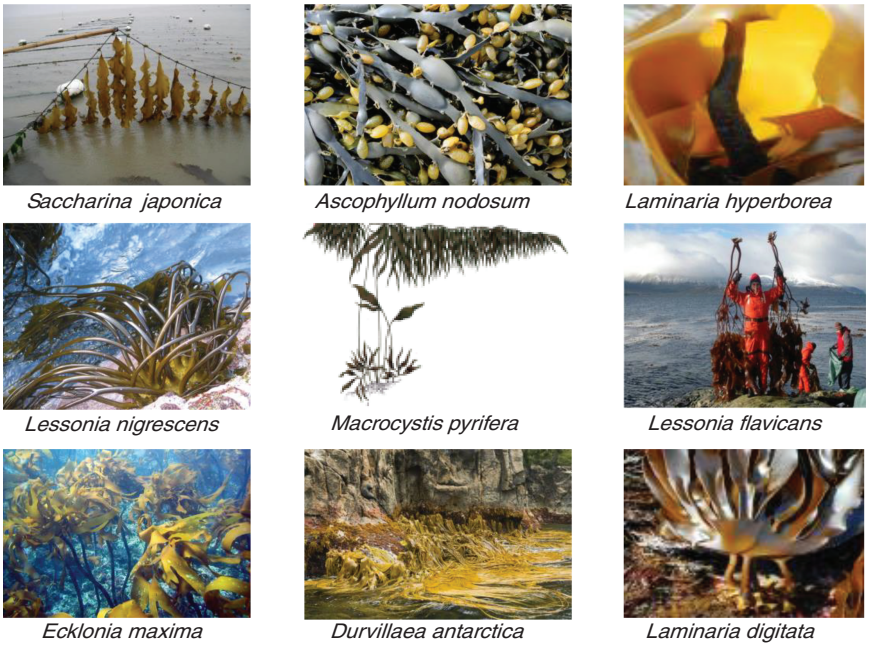


Figure 1.3 Main types of brown seaweeds used for alginate production. Source: Adapted with permission from fig. 1.2, Qin [25].

55 500 metric tons, utilizing 236 820 tons of dry brown seaweeds [26], which represents a small percentage of the biosynthesized material in naturally occurring wild brown seaweeds. It is estimated that the total quantity of wild seaweed stock on the Norwegian Sea coast is around 50–60 million tons, with 7 million tons washed to the shoreline annually. During the algae bloom in 2019, 20 million metric tons of brown seaweed, known as the Great Atlantic *Sargassum* Belt, stretched almost 9000 km. These naturally available seaweed biomasses are complemented by the cultivated seaweeds, and it is reasonable to assume that alginate is an unlimited and renewable resource even for a steadily growing industry.

The properties of alginate vary from one species to another, and the choice of which seaweeds to harvest and cultivate is based on both the availability of particular species and the properties of the alginate that they contain. For example, alginate extracted from *S. japonica* is not suitable for the production of food gel due to its high content of mannuronic acid. At present, the main commercial sources of wild brown seaweeds are species of *Ascophyllum, Durvillaea, Ecklonia, Laminaria, Lessonia, Macrocystis, Sargassum,* and *Turbinaria*. Of these, the most important are *Macrocystis, Laminaria,* and *Ascophyllum*.

Macrocystis pyrifera grows best in calm, deep waters with temperatures of 15 °C or less. It is sensitive to water temperature and does not withstand a rise above 20 °C. It grows on rocky bottoms where its holdfast can become established and can be found as large underwater forests, with plants rising to and growing along the surface, at times up to 20 m in length.

Laminaria species are harvested principally in Norway, Scotland, Ireland, and France. *L. hyperborea* grows on rocky seabeds, usually at depths from 2 to 15 m. In Norway, where this type of seaweed is particularly abundant, fresh seaweed is harvested with specially designed equipment before being used for alginate production. *L. digitata* is found on either side of the low water mark and is usually harvested by hand when the plants are exposed at low tide. It is collected in France, Norway, and Scotland but the quantities are small in comparison with *L. hyperborea*. In France, it is harvested using small boats with a hydraulic arm fitted with a hook device at the end, which is lowered into the bed of *L. digitata* and rotated so that the weed wraps around it. The arm is then raised to the surface, bringing the seaweed with it.

Ascophyllum nodosum grows in the intertidal zone. It has been harvested by hand in Scotland and Ireland for more than a century. A mechanized harvesting technique was developed in Norway, whereby the seaweeds are cut and then pumped through a large diameter pipe into a net bag on a shallow-draught water jet-propelled vessel. The operation is carried out at high tide, and the bags can be left floating for later collection.

Other types of brown seaweeds for alginate production include *Lessonia*, *Ecklonia*, and *Durvillaea* species. *Lessonia* is collected in Chile, where it is cast up after storms. This particular species of brown seaweed has been popular in the alginate industry for the production of food-grade alginate due to its relatively high content of guluronic acid. *Lessonia trabeculata* grows in the sublittoral at a depth of 1–20 m. It has a very thick holdfast and stands up underwater, rather like *L. hyperborea*. Figure 1.4 shows an illustration of the brown seaweed *L. trabeculata*.

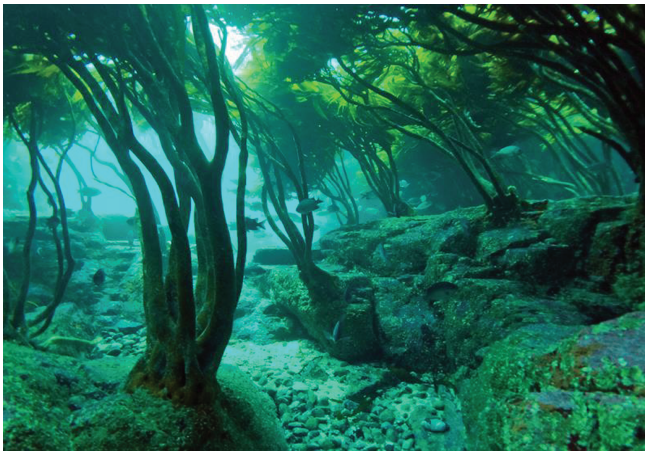


Figure 1.4 An illustration of the brown seaweed *Lessonia trabeculata*.

Ecklonia cava grows in deep water up to 20 m and is harvested by divers in both Japan and Korea. *Eisenia bicyclis* grows in a similar location and is collected along with *Ecklonia* in Japan. *Ecklonia* that has been cast up by storms is collected in Korea and South Africa. In Korea, it is used by the local alginate producer. The Korean industry also uses waste *Undaria* that is unsuitable for food uses, just as the Japanese industry uses similar waste from *S. japonica* seaweeds.

The alginate obtained from *Sargassum* and *Turbinaria* has a poor viscosity, so these species are used only when the above colder water species are not available. The Indian alginate industry is based on *Sargassum* that grows in the south, for example, along the coasts of Kerala and Tamil Nadu states. The species that grow in the north give a low-viscosity alginate, unsuitable for the main Indian market of textile printing. *Turbinaria* is used only when supplies of *Sargassum* are unavailable. The Philippines has large resources of *Sargassum*, but this is exported mainly to Japan for use in animal feeds and fertilizers.

Sargassum species are found worldwide in both the eulittoral and upper sublittoral zones. They exhibit a wide variety of shapes and forms. The alginate content is usually low, and the quality of the alginate is poor. For alginate extraction, they are regarded as the raw material of last resort.

None of the common seaweeds for alginate production are cultivated. They cannot be grown by vegetative means but must go through a reproductive cycle involving an alternation of generations. For alginate production, this makes cultivated brown seaweeds too expensive when compared to the costs of harvesting and transporting wild seaweeds. The only exception is *S. japonica* (formerly known as *Laminaria japonica*), which is now widely cultivated in China for food but is also used for alginate production. Since its initial development in the 1950s, the cultivation of *S. japonica* has been very successful in China, reaching about eight million tons of wet seaweed annually, of which about two-thirds is used as food and the rest is available for alginate production. Figure 1.5 shows an illustration of the cultivation of brown seaweed, *S. japonica*.

Figure 1.5 An illustration of the cultivation of brown seaweed, *Saccharina japonica*.

1.3 The Extraction of Alginate from Brown Seaweeds

1.3.1 General Description of the Extraction Process

Figure 1.6 shows an illustration of the wet and dry structures of brown seaweed, where alginic acid is the main structural component, accounting for up to 40% of the dry seaweed biomass. Alginate exists mainly in the intercellular mucilage and algal cell wall as a water-insoluble mixture of calcium, magnesium, potassium, and sodium salts, which provide the mechanical strength and flexibility of the seaweed as a marine bio-organism. In addition, as a hydrophilic biopolymer, alginate

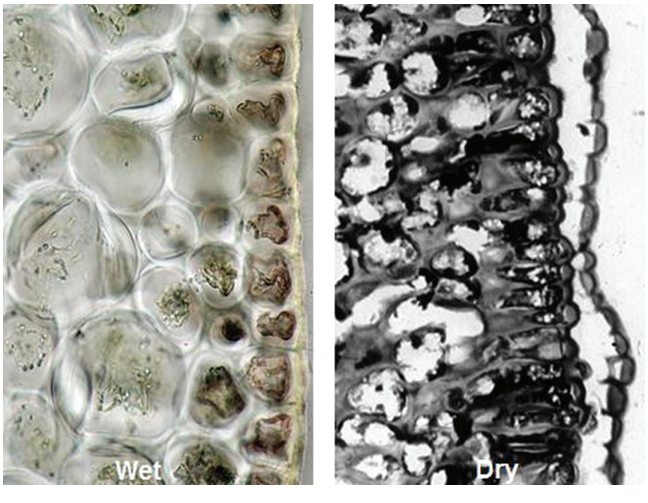


Figure 1.6 An illustration of the wet and dry structure of brown seaweed.

acts as a water reservoir, preventing dehydration when part of the seaweed is exposed to air. In general, the biological role and morphophysiological properties of alginate in brown seaweeds are similar to those of cellulose and pectin in terrestrial plants.

For the commercial extraction of alginate from brown seaweeds, F C Thornley first established a business based on using alginate as a binder for anthracite dust in 1923, and when that was not successful, he moved to San Diego. By 1927, his company was producing alginate for use in sealing cans. After some difficulties, the company changed its name to Kelp Products Corp., and in 1929, it was reorganized as Kelco Company.

Prior to the establishment of Kelco, there were a few companies established in the United Kingdom following the discovery of alginate by Stanford in 1881, such as British Algin Company Ltd. (1885), Blandola Ltd. (1908), Liverpool Borax Ltd. (1909). In 1934, Cefoil Ltd. was established to extract alginate from seaweeds in order to make fibers for military uses [18, 31]. World War II stimulated the alginate industry when production units were set up in Scotland and California using local seaweed resources of wrack and kelp. After the war, other production units followed suit and were constructed close to natural seaweed beds in the United States, Norway, France, the United Kingdom, Japan, and, more recently, China. The raw materials are mainly *M. pyrifera* in California, *L. hyperborea* in Norway, *L. digitata* in France, and *A. nodosum* in Scotland. In China, the kelp *S. japonica* was introduced from Japan and has been successfully cultivated on a large scale, usually grown on ropes along the Pacific coast.

Yields of alginate from different types of brown seaweeds vary greatly [24]. It has been reported that the yields of alginate as a percentage of dry seaweed biomass are, respectively, 18–45% for *M. pyrifera* [8, 30], 16–36% for *L. digitata* [4, 16], 14–21% for *L. hyperborea* [4], 17–25% for *S. japonica* [12], 16–34% for *Saccharina latissima* [16], 13–29% for *L. trabeculata* [5], 24–28% for *Ecklonia arborea* [9], 45–55% for *Durvillaea potatorum* [15, 23] and 12–16% for *A. nodosum* [22].

Figure 1.7 shows a process flow chart for the extraction of alginate from brown seaweeds. During the extraction process, the goal is to obtain dry, powdered sodium alginate. The natural calcium and magnesium salts of alginic acid in the seaweed biomass do not dissolve in water, while the sodium salt does. Therefore, the rationale behind the extraction of alginate from the seaweed is to convert all the alginate salts to sodium salts and dissolve them in water. After removing the seaweed residue by filtration, alginic acid can be recovered from the aqueous solution.

During the extraction process, once the alginate component of seaweed is in the aqueous extraction medium, there are two different ways to recover it. The first is to add acid to the extraction solution to convert sodium alginate into alginic acid, which does not dissolve in water and hence can be separated from the water. The alginic acid separates as a soft gel, and some of the water must be removed from this. After this has been done, alcohol is added to the alginic acid, followed by sodium carbonate, which converts the alginic acid into sodium alginate. Since sodium alginate does not dissolve in the mixture of alcohol and water, it can be separated from the mixture, dried, and milled to an appropriate particle size.

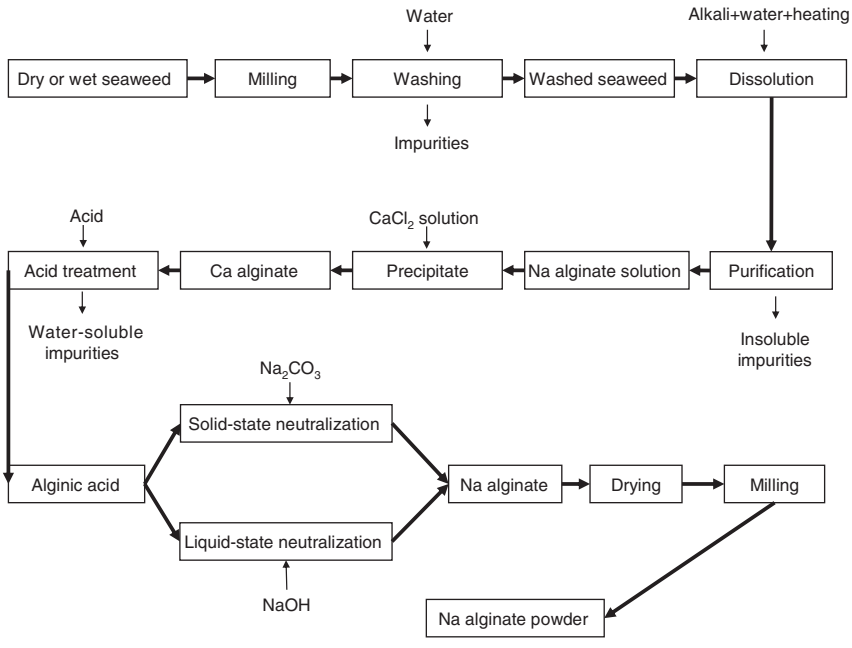


Figure 1.7 Process flow chart for the extraction of alginate from brown seaweeds. Source: Adapted with permission from fig. 3.4, Qin [26].

The second method of recovering sodium alginate from the initial extraction solution is to add a calcium salt, which results in the formation of water-insoluble calcium alginate that can be separated from the aqueous medium. In order to further purify the alginate material, acid is added to convert it into alginic acid before adding sodium carbonate to convert alginic acid to sodium alginate, which is extruded into pellets that are then dried and milled.

These two processes are straightforward, and the chemistry is simple, i.e. convert the water-insoluble alginate salts in the seaweed into soluble sodium alginate and precipitate it either in the form of alginic acid or calcium alginate so that alginate can be separated from the extract solution. The difficulties lie in handling the materials encountered in the process. In order to extract alginate, the seaweed biomass should be broken into pieces and stirred with a solution of an alkali, usually sodium carbonate. Over a period of time, alginate dissolves as sodium alginate to produce a thick slurry, which also contains parts of the seaweed that do not dissolve, mainly cellulose. The solution is often too viscous to be filtered and must be diluted with a very large quantity of water before it passes through a filter cloth. However, the pieces of undissolved residue are very fine and can quickly clog the filter cloth. Therefore, before filtration is started, a filter aid, such as diatomaceous earth, must be added, which holds most of the fine particles away from the surface of the filter cloth and facilitates filtration. Since the filter aid is expensive and in order to reduce the quantity of filter aid needed, some processors force air into the extract as it is being diluted with water, where fine air bubbles attach themselves to the particles of

residue. During this time, the diluted extract is left standing for several hours while the air rises to the top, taking the residue particles with it. This frothy mix of air and residue is then removed from the top, and the solution is withdrawn from the bottom and pumped to the filter. The next step is the precipitation of the alginate from the filtered solution, either as alginic acid or calcium alginate.

1.3.2 A Comparison of Alginic Acid Method and Calcium Alginate Method

The alginic acid method uses acid to convert alginate in the filtered extract into alginic acid, which is water insoluble in the form of soft and gelatinous pieces. This jelly-like mass of alginic acid contains only 1–2% alginic acid and 98–99% water. At this stage, it is too soft to allow the use of a screw press. By centrifuging, the solid content can be increased to 7–8% before alcohol (usually ethanol or isopropanol) is added to produce a 50 : 50 mixture of alcohol and water. Solid sodium carbonate is then added gradually until the resulting paste reaches the desired pH. The paste of sodium alginate can be extruded as pellets or oven dried and milled.

In the calcium alginate method, calcium alginate is formed when calcium chloride is added to the filtered extract. The resultant calcium alginate precipitate can be readily separated and washed with water to remove excess calcium. It is then stirred in dilute acid and converted to alginic acid, which can be squeezed in a screw press to remove excess water. The product coming out of the screw press contains about 20–25% alginic acid, which is then mixed with sodium carbonate to convert it into sodium alginate.

The advantage of the calcium alginate method is that calcium alginate can be precipitated in a fibrous form that can be readily separated and then converted into alginic acid, which is still fibrous and can be readily separated. In addition, the final sodium alginate product may contain some calcium ions, which help control the viscosity of the final product. The alginic acid method saves one step, i.e. the formation of calcium alginate; however, when alginic acid is precipitated in this process, it forms a gelatinous precipitate, which is very difficult to separate, and the overall losses of alginic acid are generally greater than in the calcium alginate method. It is also more difficult to remove water from within the gel structure of the separated alginic acid. The water content in the dewatered alginic acid is often high so that alcohol must be used as a solvent for the conversion to sodium alginate, which makes the process more expensive.

1.3.3 Process Control

During the production of alginate from brown seaweeds, appropriate process control is needed for color control of the product, water supply, and waste disposal. If the original seaweed is highly colored, such as with *Ascophyllum* seaweeds, the alkaline extract will also be highly colored, and a dark product is produced, which is not suitable for high-value applications such as medical devices. Lighter colored seaweeds, such as *Macrocystis*, yield light-colored alginate suitable for food and other applications.

Sodium hypochlorite can be used to bleach alginate in the filtered alkaline extract or during the final conversion stage. As an oxidant, the excessive use of sodium hypochlorite can lower the molecular weight of alginate and reduce its value. An alternative method to reduce color is to apply formalin in the extraction solution, whereby colored compounds are bound to cellulose in the seaweed cell walls so that much of the color is left behind in the seaweed residue when the alkaline extract is filtered.

The extraction of alginate from brown seaweeds requires a large amount of processing water, in particular when the viscous alkaline extract is diluted to a low viscosity suitable for filtration. Up to 1000 tons of water are required to produce 1 ton of alginate, and a reliable source of water supply is important for alginate production. In addition, a large amount of wastewater also needs to be treated and preferably recycled. It should be pointed out that the wastewater from the alginate extraction process is relatively harmless, and in some countries, the waste is pumped out to sea. Where environmental concerns are greater, or when water supplies are limited, recycling is not too difficult and its costs may be partly offset by the lowering of the quantity and cost of water used by the factory.

In addition to wastewater, there are also solid wastes in the form of seaweed residues, which contain cellulose, protein, minerals, and other organic and inorganic components. The residues are rich in bioactive substances, and they are now commonly used as raw materials for the production of fertilizers.

1.3.4 Key Process Parameters

The extraction of alginate from brown seaweeds involves the dissolution of alginic acid in an alkaline solution and its precipitation with an acid or calcium salt. Although the chemistry is simple, a number of process parameters need to be addressed and controlled within appropriate ranges. Some of the key process parameters are discussed below.

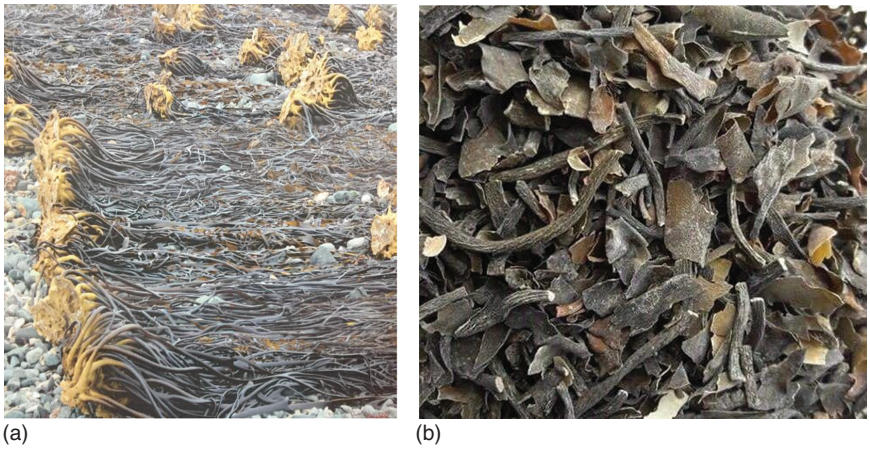
1.3.4.1 Size Reduction of Raw Materials

The seaweeds that are fed into the extraction process can be in many forms. They can be freshly collected from the sea such as those used in Norway, while those collected in Chile are usually dried and broken up into small pieces of about 5–10 mm square, which makes it easy to wet the seaweed when they are soaked in water at the beginning of the extraction process. It also helps to facilitate the penetration of formalin, acid, and alkali more thoroughly and more rapidly. In addition, process flow is also smoother when the seaweeds are in small pieces that can be pumped and transported through the process pipeline. Figures 1.8 and 1.9 show a whole plant of dried seaweed and broken pieces of dried brown seaweed, respectively.

1.3.4.2 Acid Treatment

Alginate exists in mixed calcium, magnesium, potassium, and sodium salts in the seaweed biomass, and it has been shown that a pretreatment with dilute mineral acid can remove the metal ions, leading to a more efficient extraction process. In the

Figure 1.8 The author holds a whole plant of dried seaweed.



(a) (b)

Figure 1.9 An illustration of the broken pieces of dried brown seaweed. (a) Seaweeds being sun dried on the beach and (b) broken pieces of brown seaweed.

pretreatment, the alginate is first converted into alginic acid before being converted into sodium alginate following the addition of alkali (usually sodium carbonate), as illustrated below:

$$Ca(Alg)_2 + 2H^+ = 2HAlg + Ca^{++}$$

$$HAlg + Na^+ = NaAlg + H^+$$

During the acid treatment, all the acid-soluble phenolic compounds are removed, which is important in that the phenolic compounds can form brown oxidation/polymerization products with alkali and are largely responsible for the brown discoloration, which occurs during alkaline extraction. Hence, pretreatment of the seaweed with acid before alkaline extraction gives a more efficient extraction, a less colored product, and a reduced loss of viscosity during extraction. During the treatment, the seaweed is stirred with 0.1 M sulfuric acid or hydrochloric acid for 30 minutes, with treatment temperature ranging from room temperature to about 50 °C depending on the seaweed used. Little degradation of alginate occurs with most species of seaweed at temperatures up to 40–50 °C. At the end of the treatment, the slurry of seaweed and acid solution can be separated on a rotary drum screen.

1.3.4.3 Formaldehyde Treatment

The discoloration of alginate can be further reduced by pretreatment with formaldehyde. It has been found that phenolic compounds and formaldehyde can react to form insoluble products, which remain in the seaweed residue during the extraction process. In practice, a 0.1–0.4% commercial formalin solution is used to treat the seaweed, usually at room temperature for 15–30 minutes. After the treatment, the seaweed is separated using a rotary drum screen, and the solids are used in the alkaline extraction.

1.3.4.4 Alkaline Extraction

The addition of alkali to the extraction solution converts alginate to a soluble form that can be separated from the rest of the seaweed biomass. Sodium carbonate (soda ash) is usually used as the alkali because of its low cost. During the production process, the seaweed is stirred in a tank with the sodium carbonate solution at about 1.5% concentration. When the seaweed has undergone size reduction and acid pretreatment, a good extraction can be achieved for two hours at 50 °C with little degradation of alginate, although the time can be reduced by using higher temperatures, usually with some loss of viscosity in the final product. As extraction proceeds, the extract becomes thicker, requiring dilution during the subsequent processes.

1.3.4.5 Separation of Alginate from Insoluble Seaweed Residue

The separation of alginate from insoluble seaweed residue involves several steps, including flotation, filtration, precipitation, bleaching, conversion, dewatering, drying, and milling.

Flotation When sodium alginate is dissolved in the extract solution, a viscous mixture is formed where the alkali-insoluble seaweed residue is usually slimy and finely divided and can rapidly clog filter cloths if conventional filtration methods are used. Although some of the residues can be removed using centrifuges, the clarity of the resulting solution is usually poor. During commercial production, the major portion of the insoluble residue is usually removed by a flotation process, where the extract is first diluted with 4–6 times its volume of water to produce a suitable viscosity of about 25–100 cps. A small quantity of flocculant is then added, and air is forced into the liquid. After being left to stand for several hours, the fine particles of insoluble residue are raised to the surface by the rising air bubbles and are scraped from the surface and the clarified liquor beneath it. Since the cellulose residue has a negative charge, cationic flocculants such as polyacrylamides and chitosan are often used.

Filtration After the flotation process, the remaining insoluble residue is filtered to give the final product good quality. Because the residue is very fine, filter cloths are rapidly blocked and the best method is to use a rotary precoat vacuum filter where the rotating drum of the filter is coated with a 2–3 cm layer of precoat material, preferably perlite because it gives a more porous medium than diatomaceous earth and so does not block as easily. During filtration, a blade on the rotary filter continually removes the top surface of the precoat so that a clean filter surface is always available. After 9–10 hours, most of the precoat has been removed by the scraper, filtration is stopped, and a new layer of precoat is deposited. Great care is necessary in selecting the appropriate grade of perlite and the correct cloth to support the precoat medium.

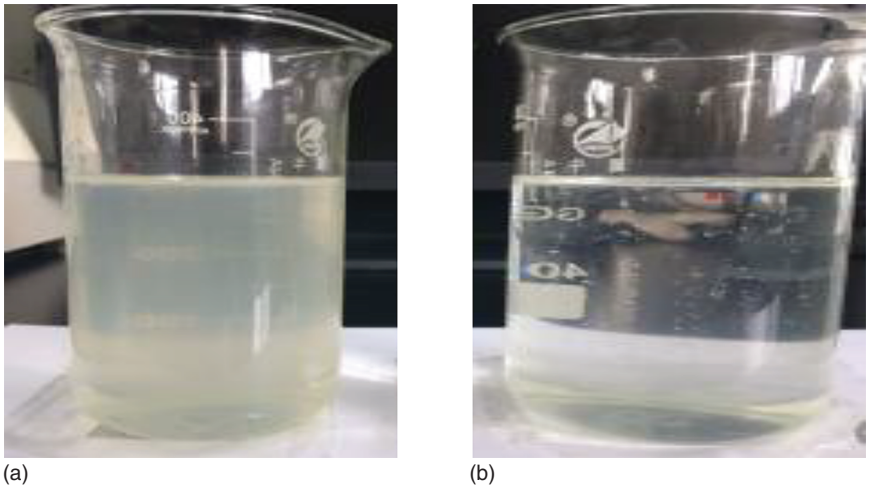
Precipitation of Calcium Alginate The purified alginate after filtration is a dilute aqueous solution of sodium alginate, and because of the presence of a large percentage of water, it is not economical to dry it with conventional methods such as heat evaporation. It must be precipitated out either as calcium alginate or as alginic acid. The process is normally carried out by adding the diluted extract to a 10% calcium chloride solution, resulting in fibrous precipitate that can be easily handled on a metal screen. If calcium chloride solution is added to the extract, a soft gel is formed, which is more difficult to process further. After washing with water, the fibrous calcium alginate is then treated with dilute mineral acid when the Ca^{2+} ions are exchanged for H^{+} ions to produce fibrous alginic acid, which is dewatered using a screw press. The dewatered product should contain at least 25% solids if it is to be used in the conversion process.

Bleaching For food- and medical-grade alginate, it is necessary to use bleaching for the improvement of color and odor. In order to avoid degradation, the bleaching process is best carried out with calcium alginate since it is chemically more stable than alginic acid. The bleaching process is normally carried out by adding a 12% sodium hypochlorite solution to a suspension of calcium alginate in water.

Conversion of Alginic Acid to Sodium Alginate Alginic acid is converted into sodium alginate in two ways. In the dry method, the dewatered alginic acid is mixed with solid alkali, usually sodium carbonate, in a mixer suitable for blending heavy pastes. A thick paste is formed when the resultant sodium alginate is dissolved in the limited amount of water in the system. If the alginic acid content is less than 25%, the resulting paste may be too fluid for the next step when the paste is forced through small holes and the extrusions are chopped into pellets and dried. The dried pellets with about 10% moisture can be milled to an appropriate particle size, usually about 60 mesh or 250 μm. In the wet conversion method, NaOH is dissolved in ethanol before reacting with alginic acid to produce sodium alginate.

1.4 Ultrapure Alginate

Alginate obtained in the above-described procedure contains several mitogens and cytotoxic impurities, making it unsuitable for biomedical applications. Ultrapure and amitogenic alginates suitable for biomedical purposes are prepared by using more rigorous extraction processes. For example, free flow electrophoresis was applied as one technique to remove mitogenic impurities from commercial alginates [32]. This method was, however, not suitable for large-scale processing because it was time consuming and required expensive electrophoresis equipment. A chemical extraction method was therefore described by using Ba-alginate gels [14]. Ba^{2+} ions show higher affinity toward alginates compared to Ca^{2+} ions. Ba-alginate gels are stable in acidic and neutral pH environments but disintegrate under alkaline pH conditions. During the purification process, mitogenic contaminants are first eluted from Ba-alginate beads by treatment with various solutions followed by ethanol extraction, after which the pure alginate beads are dissolved in an alkaline



(a) (b)

Figure 1.10 Alginate solutions (a) before and (b) after purification.

solution, which is then dialyzed. Once Ba^{2+} ions are fully exchanged for Na^{+} ions, the purified sodium alginate is precipitated from the solution by the addition of ethanol. Figure 1.10 shows alginate solutions before and after purification.

1.5 Summary

Many species of brown seaweed are commercially available from many parts of the world, which gives the alginate extract industry a wide variety of raw materials for the production of alginate with different chemical and physical properties. Some may yield an alginate that gives a strong gel, another a weaker gel; one may readily give a cream/white alginate, another may give that only with difficulty and is best used for technical applications where color does not matter. Alginate producers often prefer to buy a mixture of species of seaweed that allows them to blend their products to give them properties suitable for specific end uses.

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