Chapter

Introductory Chapter: Alginates - A General Overview

Leonel Pereira and João Cotas

1. Introduction

Alginate is an anionic polymer that occurs naturally in brown algae (Phaeophyceae), normally present on the cell walls of these organisms.

Alginate is a structural element designated to be the seaweed's main skeletal compound likewise the cellulose function in terrestrial plants, with the gel located in the cell walls and intercellular matrix conferring the mechanical strength and flexibility necessary to withstand the force of the water in which the seaweed grows [1]. Moreover, this function is reflected in the compositional difference of alginates in different seaweeds.

Alginate varies in composition of the algae from 20 to 60% dry matter, but on average brown algae species has 40% alginate. Alginate in brown algae occurs as gels containing sodium, calcium, strontium, magnesium, and barium ions [2].

Alginate is not a compound exclusively of brown algae because there are bacteria that can also produce alginate, but currently all commercial alginate is extracted from algae biomass [3].

Industrial applications of alginate are linked to the gelation, viscosity, and stabilizer properties that alginate attributes to the solutions and products in which it is present. Normally the alginate is a matrix of alginic acid bound cations, such as calcium, sodium, or magnesium. These ions give greater stability to the alginic acid molecule, where the divalent cations give alginate a very rigid conformation and a stable structure unlike the alginate with monovalent cations.

The biotechnological applications of alginate are based on specific effects of the alginate molecule and its variations depending on the covalent bonds with cations, such as calcium, sodium, or magnesium, and this allows for a great number of applications in several variations of the structure and conformation of the alginate molecule.

Alginates are in vogue for specialized knowledge as a pharmaceutical or biomedical ingredient or as compound for advanced biotechnology, and these investigations are turning to a more detailed study of the properties and structure of alginate, leading to points of scientific innovation that, associated with empirical knowledge, will benefit the traditional techniques of alginate exploitation.

2. History

Alginic acid was first discovered and patented (patent date: 12 January 1881) by the British chemical scientist E. C. C. Stanford, and he continued the work on its discovery, contributing to the elucidation of the chemical structure of alginic acid [3]. The Stanford patent explains how the alginate can be extracted by soaking the algae with water or diluted acid, then extracting with sodium carbonate, and then precipitating the alginate present in the solution by addition of acid [4].

In the second decade of the twentieth century, some scientific groups working separately with alginate found that uronic acid was one of the constituents of alginic acid. Moreover, this discovery led to further study in the years to come. These investigations led to the discovery of D-mannuronic acid in hydrolyzed alginate samples. The nature of the bonds in the uronic acid residues in the alginate was identical to that in the cellulose, through the β 1, 4 bond.

It was only in the 1950s that with the work of Fischer and Dörfel [5], through a chromatographic study of uronic acids, the presence of a different uronic acid from what had been identified was discovered, identifying this new acid with L-guluronic acid. And that acid had a considerable quantity in the sample analyzed, and as such, a quantitative method was developed to determine the two acids present in alginate, mannuronic acid and guluronic acid.

Thereafter, alginate was identified as a binary copolymer composed of residues of guluronic and mannuronic acids, but in general, it was reported that alginic acid was chemically homogeneous and of equal chemical structure, independent of the raw material from which it was extracted.

This principle had to be scientifically proven, and the alginate had to be fractionated chemically from different sources to prove the theory. The development of fractionation techniques was done mainly by Haug [6], who helped the characterization alginate as a block copolymer and in the correlation between the block structure and the physical properties of an alginate with that composition.

3. Chemical structure

The alginate is an unbranched biopolymer family. The alginates consist of 1,4-β-D-mannuronic acid (M) and 1,4 α-L-guluronic acid (G) monomers, with a homogeneous (poly-G, poly-M) or heterogeneous (MG) block composition, which was proven by partial acid hydrolysis. That is, each alginate-producing species may exhibit different alginate compositions and as such differences in the ratio of mannuronic and guluronic acid blocks, varying in composition and sequence [7]. The proportions of the two acids vary from species to species and from different parts of the same seaweed [8].

It was proven that the alginates do not have regular repeating units and that the distribution of the monomers along the polymer chain could not be described; hence the knowledge of the monomeric composition was not sufficient to determine the sequential structure of alginates from diverse species.

Alginate is found in seaweeds as salts of different metals, primarily sodium and calcium, in the intercellular regions and cell walls. Its biological functions in seaweeds are of structural and ion exchange type. Alginate enriched in polymannuronic acid is found in young cell wall tissue and/or intercellular regions, whereas polyguluronic-rich alginate is found in the cell wall having a high affinity for Ca^{2+}, which is mainly responsible for gel strength [9]. Alginate polymer is synthesized in the cytoplasm and then transported to the cell surface [10].

The principal differentiation between algal and bacterial alginates at the molecular level is the presence of O-acetyl groups at C_2 and/or C_3 in the bacterial alginates [11].

4. Alginate extraction

The extraction methodology of alginate is recurring on the transforming of the insoluble mixture of the alginic acid salts prevenient of the cell wall in a soluble alginate salt, which is naturally recommended for aqueous high-affinity polysaccharide obtained from the main species of brown algae (e.g., Fucales and Laminariales). The industry uses brown seaweeds mainly from the genus *Macrocystis*, *Laminaria* (**Figure 1a**), *Lessonia*, *Ascophyllum*, *Alaria*, *Ecklonia*, *Eisenia*, *Nereocystis*, *Sargassum*, *Cystoseira*, and *Fucus* (**Figure 1b**), with *Macrocystis pyrifera* (**Figure 1c**) and *Ascophyllum nodosum* (**Figure 1d**) being the principal resources utilized.

Various species are harvested, and some are even cultivated offshore (e.g., *Laminaria* and *Alaria* (**Figure 1e**)) for alginate production, between southern and northern hemispheres. The species used are generally harvested from natural resources. China and some northern hemisphere countries, however, cultivate these species, which is an expensive way of alginate production. In this case, *Laminaria* is mostly used as food, and if surplus amounts are cultivated, then it can be used for alginate production.

Brown seaweeds that grow in cold water and those growing at a temperature up to 20°C are more used because they have more alginic acid content than the brown seaweeds found in more warm waters. And due to more turbulent waters, the seaweeds produce more content than the same species in calmer waters [12].

The alginic acid appears in the seaweeds as an insoluble mixed salt. To extract it, it is necessary to convert the alginic acid into its soluble salt forms such as sodium or potassium [12]. The alginate is made alternately insoluble and soluble in solvent by ion exchange reactions to separate out from the other constituents of algae. As large molecules must diffuse out from the plant tissues, the seaweed is preferably reduced to small particles as a preliminary step. Therefore, the first step is to wash (dry, if necessary) and mill the seaweed. Alginate isolation is essentially an ion exchange process, and alginate is brought into solution as sodium alginate by treating it with a strong alkali, after a pre-treatment with hydrochloric acid before the extraction with sodium carbonate [13, 14]. There are several methods to separate the alginate from other soluble substances from the crude alginate extract solution.

For example, addition of alcohol [2] would precipitate out sodium alginate. Adding a solution of calcium chloride with good stirring would precipitate out calcium alginate, whereas adding hydrochloric acid would precipitate out alginic acid.

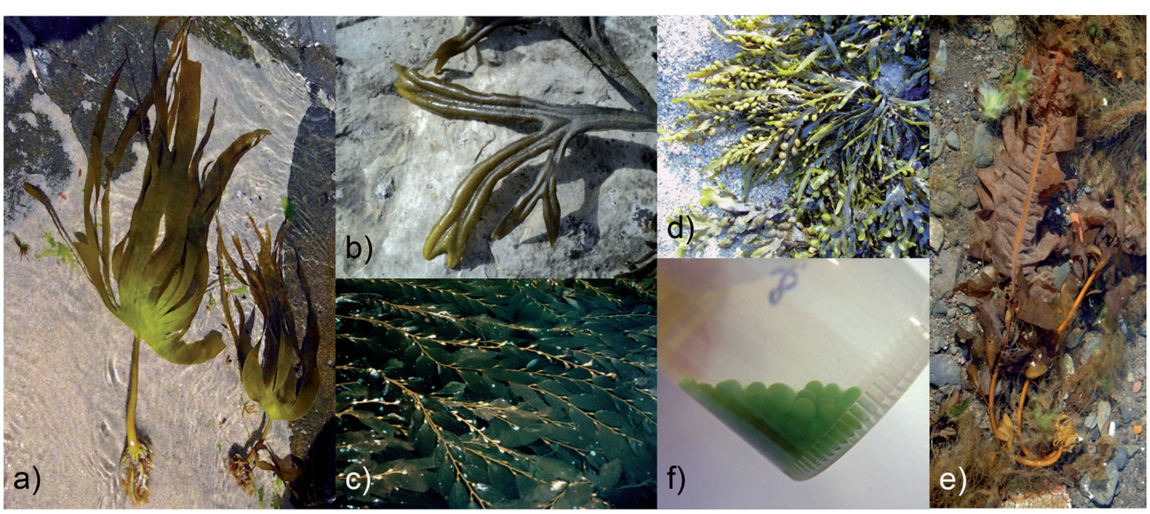

Figure 1.
(a) Laminaria ochroleuca from Ínsua beach, afife, north of Portugal; (b) Fucus ceranoides from mondego river estuary (coordinates: 40° 7'31.39"N, 8°46'15.76"W), center-north of Portugal; (c) Macrocystis pyrifera; (d) Ascophyllum nodosum from Praia do norte, Viana Do Castelo, north of Portugal; (e) Alaria esculenta from Eskifjördur, Iceland; (f) Chlorella vulgaris immobilized in calcium alginate gel beads. Original images: (a, d, and e) University of Coimbra (MACOI), (b and f) João cotas images in public domain: (c) Shane Anderson.

The extraction of alginate is done by mild acid treatments that remove undesirable compounds (normally, hydrochloric acid) and modify the cell wall alginate into alginic acid to obtain the best extract efficacy because the intercellular mucilage has been regarded as the principal site of alginic acid [15]. The alginic acid is recovered as a soluble sodium form by neutralizing with sodium carbonate or sodium hydroxide. The insoluble residue is removed by filtration, flotation, or centrifugation, and the soluble alginate is precipitated by conversion into alginic acid or calcium/sodium alginate. The alginic acid is then converted into the required counter ion by neutralization with appropriate hydroxides or chlorites. The difference in the alginate recovery process depends on the source and structure of constituents of alginate [13].

5. Alginates as valuable resource

Alginates are used in the food, cosmetic, paper, agricultural, pharmaceutical, and biomedical industries and in other various industries; some are now starting to apply the alginates. The alginates overall are the main seaweed polymer, in terms of quantities, used by industry. There are different purity classes of alginates ready to apply for different uses; with that, the price of alginates varies according to the purity state and applications on the industry. For instance, the alimentary grade sodium alginate is priced at USD 6.5 and 11.0/kg, while pharmaceutical grade is valued at USD 13 and 15.5/kg. In Asia, more specifically in the Korean peninsula and in Japan, *Saccharina japonica* (formerly *Laminaria japonica*) has a big demand which resulted in a higher price, which resulted in the introduction of buying alginates from other countries [16]. Alginate market is expected to grow annually between 2 and 3%. The uses of alginate in the industry, such as textile printing, account for nearly half of the global market. On the biomedical, medical, and pharmaceutical industries, it has an implication of nearly 20% of the global market, and it is expected to grow between 2 and 4% in the global market, lying on the applications of alginic acid derivatives in wound healing and regular basis innovations and developments in controlled-release technologies. Paper industry only reports to nearly 5% of the global market [17].

Alginates are mainly used as thickeners and stabilizers in the food, pharmaceutical, and cosmetic industries, because they are easy to use, has a low cost, are well tolerated in the human, and can be easily modified for determined objective and in the different fields.

Today, the global seaweed industry is worth more than USD 6 billion per annum (approximately 12 million tons per annum in volume) of which 85% is in the food area for human consumption. Seaweed-derived polysaccharides (carrageenan, agar, and alginates) make up almost 40% of the world's hydrocolloid market [18].

The global alginate market size was valued at USD 624.0 million in 2016. The demand for alginates in the food industry will be increasing by consumption of frozen desserts, ice creams, beer, and yogurt; with that, it is anticipated to push a salient market growth of alginate value and use.

The application of the alginates in the food industry is permitted and regulated by the major regulatory agencies including the FDA and European Commission, which stimulates the high interest in alginate. The increasing of food industry in Asia, due to the growth in habitants, is expected to run a higher demand of alginate in that area. Therefore, this alginates-based products acceptance by the manufacturing industries is expected to growth, such as biomedical industry and its high demand for alginate with high quality. The product is mainly used in the pharmaceutical industry for the production of controlled-release drugs due to superior product performance [19].

Corporations in the market devote to the investigation and development of new advanced product grades to captivate costumers. Extraordinary financing by national governments and alginate industries on route to the growth of seaweed processing is predicted to help the alginate-based industry's expansion and success. Nevertheless, such high search for alginate can have as outcome a limited raw material availability, and the alginate industry is now evaluating the production of alginate with seaweeds of aquaculture (mainly offshore, at this moment in the North Atlantic Area and China).

There is a large market for any brown seaweed that has an alginate of medium to high viscosity or high gel strength [20].

5.1 Agricultural applications

Alginate present in the brown algae (in the form of alginic acid) constituted a functional element of the traditional fertilizers, allowing the water retention in the soils. So, the principal function of alginate on agricultural area was as a soil conditioner. Being a superabsorbent (SAP) or water-retaining material is an advantage of alginate. They are natural materials that can absorb large amounts of water, as much as hundreds of times their own mass. These alginates are generally known in agriculture as nonionic or ionic moisture-holding hydrogels for increasing soil water retention, which is a basic soil property.

The reservation of moisture or water in the soil is the major process consequence in which all plantations depend. The large pore spaces in arenaceous soils restrain the soil from holding water, and the soil dries out regularly, and precious nutrients wash away past the plant roots. The inclusion of alginate can solve the lack of retention of water and raise nutrient disponibility. High-capacity absorbents definitely can upsurge the water-retention capacity in such soils.

Superabsorbents (SAP) in agricultural areas have been designed and developed to provoke an enrichment of the abiotic properties of soil by rising their water-retention ability, developing a better water usage efficiency, enhancing soil permeability and infiltration rates, contributing to lower the irrigation frequency, lowering the compaction shift, preventing erosion and water drainage, enhancing plant performance, increasing soil aeration, lowering the dissolution of fertilizers, developing a better adsorption capacity or enhancing the uptake of some nutrient elements by the plants, and provoking a raise of the microbial activity [21].

The alginate of seaweed directly suppresses the pathogens [22]. Indeed, alginate pellets developed as carrier material for biocontrol agents have been reported to reduce multiplication of *Rhizoctonia* (fungi) disease in potato [23], while incorporation of *Ascophyllum nodosum* extract into the planting medium caused delay and reduced incidence of *Verticillium* (fungi) wilt of pepper plants [24]. Therefore, it's proven that alginates are involved in host defense mechanisms [25]. Of particular interest in agriculture are those that elicit defensive responses resulting in protection against pathogens or insect damage [26].

In other cases, the alginate will have other particular function, as the main characteristic of alginate as product principal emulsifier and to delivery control of actives ingredients in agricultural field. The active ingredient is mixed with alginates for their safer, easier, and more accurate handling as well as for their effective application in the field and, at the same time, preventing the immediate release of the active ingredient, so the main drawback associated with these formulations can be avoided. These alginate-based systems are able to deliver the active ingredient gradually for a long period of time in a specified target with a desired rate [27–29]. The controlled-release systems do not release the active ingredient at once; this technique therefore lowers the pesticide residues in soil and thus reduces the direct effect of pesticide. After their degradation, these are helpful as compost in the field [30].

Alginate is also used as an inoculant carrier for plant growth-promoting bacteria [31, 32] and for bacteria with biodegradation ability [33].

5.2 Biomedical applications

The conventional role of alginate in the biomedical area includes being used as thickening, gel-forming, and stabilizing agents, as alginate can play a significant role in controlled-release drug products. But the main use of alginate in the biomedical area is actually in hydrogel form, used in the wound healing [34], drug delivery, and tissue engineering applications. Alginate hydrogels are biocompatible and structurally identical to the macromolecular-based components in the human body and can regularly be convoyed into the body by minor invasive techniques of administration to the select human body [35].

In this area, there is a need that the alginate used and tested is pure as maximum as possible, because the impurities will compromise the biocompatibility of the biomaterial with alginate [36].

The utmost captivating characteristics of alginate for the biomedical applications involve the natural biocompatibility, mild gelation conditions, and easy adaptation to assemble alginate derivatives with new properties and characteristics. Alginate has a safe clinical sheet for biomedical applications as a wound dressing material and pharmaceutical component and has been harmlessly inserted in a wide range of utilizations.

The conception of new biomaterials is centralized on the resemblance in the functions of the extracellular matrices of body tissues, as these can manage the host feedback/responses in an accurate behavior, and materials derived from natural sources have gained a lot of interest, mainly because of their inherent biocompatibility. At this moment, alginate and its derivatives are one of the best chemically known biopolymers in the world, and it has been extensively investigated and used for many biomedical applications, due to its biocompatibility, low toxicity, relatively low cost, and mild gelation by addition of divalent cations such as Ca^{2+} [37].

The great challenge in this area is complementing the physical feature of alginate gels with specific use in a precise utilization. Taking in consideration the great range of different possible cross-linking approaches, employing molecules with diversified chemical structures, molecular weights, and cross-linking capabilities will usually turnout gels applicable for specifics different types of application [36].

Alginate-based wound dressings keep the physiologically humid microenvironment, lowering the risks of a bacterial infection at the wound location and promoting an easy wound healing. Drug compounds, from small chemical drugs to macromolecular proteins, can be liberated from alginate gels in a skillful way, revolving around in the cross-links types and cross-linking methodology applied.

The therapy of acute and chronic wounds is a major need in various areas of medicine, and alginate-based wound dressings have various beneficial properties. Traditional wound dressings, such as gauze, provide principally a good barrier property—maintaining the wound dry by granting the evaporation of wound exudates and preventing the passage of pathogens into the wound [38]. In the opposite way, the modern dressings, likewise the alginate dressings, contribute to a moist wound environment and aid an easy wound healing [39].

New wound dressing types with alginate that are more functional and bioactive have been studied and developed up to this date.

Alginate gels are additionally an excellent compound for cell transplantation in the tissue engineering area. The main objective of tissue engineering was to develop and produce man-made tissue and organ replacements for patients who suffer the loss or failure of an organ or tissue [40]. In this field, hydrogels are used to deliver cells to the specific location, providing an area for new tissue formation and, moreover, controlling the structure and function of the engineered tissue [41].

Even with recent developments in the area, the treatment of bone injuries is restricting because of the poor healing and complex bone healing system. In this case, alginate gels have been tested with success in bone regeneration by delivery of osteoinductive factors, bone-forming cells, or a mixture of both [42].

Alginate gels have been described to be effective for transplanting chondrogenic cells to recover damaged cartilage in animal models [43].

Alginate gels are also being actively investigated for their ability to mediate the regeneration and engineering of a variety of other tissues and organs, including skeletal muscle, nerve, the pancreas, and the liver. Actual plans for skeletal muscle regeneration involve the cell transplantation, growth factor delivery, or a combination of both approaches [44, 45], and alginate gels have been described as potential hypothesis in these strategies.

Alginate derivatives containing cell-adhesive peptides have been gaining significant attraction in the last years. These derivatives are normally prepared by chemically including peptides as side chains, applying carbodiimide chemistry to connect via the carboxylic groups of the sugar residues. Considering that alginate intrinsically do not have mammalian cell adhesiveness, pertinent ligands are essential to develop and manage cellular interactions, principally for cell culture [36].With that, the alginate gels are now being utilized much more as a model system for mammalian cell culture in this field. And one of the advantages is that the gels can be adapted to 2D or more physiologically relevant 3D culture systems.

The absence of mammalian cell receptors joined with the low protein adsorption to the gels enables the utilization of these materials in many ways as an ideal blank slate, with highly specific and quantitative modes for cell adhesion that can be incorporated. Also development demonstrated with in vitro studies can be readily translated in vivo, because of the inherent biocompatibility and easy introduction of alginate into the body [36].

Alginate hydrogels have been widely investigated to date in many drug delivery applications, due to their adjustable swelling properties in response to temperature changes, leading to on-demand modulation of drug release from the gels [46].

Alginate is a nondegradable material in mammals, as the mammals do not have enzymes (i.e., alginase) that can break the alginate chains, but ionically cross-linked alginate-base gels can be disassociated by release of the divalent ions cross-linking the gel into the surrounding media. Despite the gel dissolution, the average molecular weights of many commercially available alginates are higher than the renal clearance threshold of the kidneys, and presumably dissolved alginate isn't removed from the body with 100% efficiency [47].

Alginate has also been greatly explored in plenty drug delivery systems merged with chitosan, and this blend forms ionic complexes. Chitosan is a derivative of chitin [48].

Alginate is an attractive and exceptional contender for the protein drug delivery systems, considering that alginate-based materials/gels can incorporate proteins [49, 50]. The delivery in this scenario can be easily exploited by modifying the degradation rate of the gels [50].

Also, alginate can serve as an agent against heavy metal poisoning, and it is proven that it can be an effective coadjuvant in the case of food poisoning [51].

On the medical side, there has been an increment of interest to use alginate as a pharmaceutical ingredient to treat some diseases or health problems:

Diabetes—This bioactivity is related to the hypoglycemic activity from alginate [52].

Cholesterol—The alginate on the assay in article [52] with rats provides interesting results, with cholesterol excretion from the rats and hypocholesterolemic effect from alginate.

Obesity—The capacity of alginate to swell and so occupy space on the stomach of the patient provides a satiety effect which can help people lose weight and provide a management tool for the medical personnel [53];

Digestive tract problems—The alginate is used as dietary fiber and can regulate the intestinal tract.

5.3 Bioremediation applications

Environmental bioremediation is a profitable and promising technology, which can lead to complete mineralization of organic pollution. Bioaugmentation (introduction of selected microorganisms to supplement indigenous populations) is one of the bioremediation approaches [54]. Entrapment in alginate gel is a widely used approach for immobilization of microorganisms to improve their viability (**Figure 1f**) [55].

Alginate is a natural chelating agent and a bio-adsorbent of heavy metals in aqueous solution; it has high affinity and binding capacity for metal ions and, thus, is widely used as a heavy metal adsorbent for environmental protection [56]. Alginate-clay composites are suitable for environmental remediation as sorbents of heavy metals [57] and persistent organic pollutants [58].

5.4 Cosmetic applications

Alginates are an omnipresent ingredient of cosmetics. They usually are utilized as emulsifiers, consistency enhancers, and thickening agents in cosmetic formulas, forming a moisture-retaining surface film. They can have some kind of active effect, such as skin protection, because they retain water and maintain the skin rehydrated [59].

Alginates are water-insoluble; however, they can swell, as mentioned before. Thus, they are like hyaluronic acid, so they can absorb more water as much as several hundreds of times its weight.

They are used in hand jellies and lotions, ointment bases, pomades and other similar preparations, greaseless creams, dentifrices, and other products that became more green and environmentally friendly [60, 61].

Alginate has also been described as an anti-oxidative agent and can be applied to prevent skin aging and cutaneous disorders. Additionally, antioxidants can help to maintain the organoleptic properties of cosmetic products by inhibiting lipid oxidation, thus avoiding changes in appearance, odor, and flavor [62].

5.5 Food applications

Alginates are commonly used in the food industry as natural additives; they have codes from the European Union as food additives, and these codes vary with the ion type associated with alginic acid [15, 63].

European codes for alginates are as follows: alginic acid, E400; sodium alginate, E401; potassium alginate, E402; ammonium alginate, E403; calcium alginate, E404; and propylene glycol alginate, E405.

Seaweed polysaccharide applications in food industries are based mainly on their stabilizing, emulsifying, and gel-forming ability. They are widely used as food additives in jams, jellies, ice creams, dairy products, etc., to improve and stabilize the structure of food.

Water-in-oil emulsions likewise the mayonnaise and the salad fillings are less liable to fractionate toward their original oil and water phases if thickened with alginate. When the emulsion is acidic, the sodium alginate will precipitate into insoluble alginic acid forms; to resolve this problem, propylene glycol alginate (PGA) is used for acidic emulsions, because this compound is stable in mild acid conditions [63].

The advantage of alginate in the food industry is that humans do not have enzymes to break the molecule; therefore, alginate behaves as a dietary fiber, enhancing the satiety and reducing the food intake of humans, lowering the energy intake by human, and preventing obesity [53].

5.6 Dental medicine applications

Hydrocolloids were the first elastic materials to be used in the dental field, and their results are fundamental to form a first "idea" about the patient's oral health status.

The alginate is used as irreversible footprint compound to emulate a footprint faithfully, giving details in a high-definition footprint although there is an existence of undercuts.

The main alginate advantages are the fact that they are low cost, do not react adversely on the patient, and can be easily manipulated and that the technique can be performed within a short period of time and has simple execution, lack of instrumentation, and high-definition footprint, even with the presence of undercuts, in a single-step methodology.

Alginate picking reaction is a chemical reaction of irreversible precipitation; therefore they cannot return in soluble form using physical means, such as temperature, as with reversible hydrocolloids [64].

5.7 Other areas of alginate application

Packaging dominates the waste generated from plastics. Since the European Union synthetic plastic ban, alginate is one of the most suitable alternatives to fabricate packaging material due to their nontoxicity, biodegradability, and derivability from renewable natural resources.

With the bibliography analysis, it can be resumed that additives such as nonmaterial and antimicrobial compounds can improve various characteristics of the films and the packaging with antimicrobial activity is highly desirable in films to improve the shelf life of packed food products [56].

In textile printing, alginates are used as thickeners for the paste containing the dye. These pastes may be applied to the fabric by the use of either screen or roller printing equipment. These combine chemically with cellulose in the fabric. Alginates don't interact with the dyes; also they can be washed out of the finalized textile and are considered the first-rate thickeners to the reactive dyes [20].

The principal alginate application in the paper industry is in surface sizing. Alginate is mixed with starch sizing giving a smooth uninterrupted film and a surface with less fluffing. The oil resistance derivate from alginate films allows a size with improved greaseproof and oil-resistant properties. This can enhance the gloss obtained with high gloss inks.

If papers or boards need to be waxed, alginate in the size maintains the wax at the surface.

Alginates provide a better coating runnability than other similar compounds/products, specifically in hot, on-machine coating applications.

They are also exceptional film formers and enhance the ink printability and resistance. In the size, the normal mixture of alginate is 5–10% of the total weight of starch. Alginate is used in the starch adhesives to form corrugated boards, because it stabilizes the viscosity of the adhesive and allows control of its rate of penetration [20].

The applications of alginates in new areas has proven the multi-role capacity of alginates, such as supportive agent for silicon nanopowder to yield a stable battery anode that possesses reversible capacity eight times higher than that of the state-of-the-art graphitic anodes. Improved performance characteristics prevent the dramatic volume changes during electrochemical alloying and de-alloying with Li, which typically leads to rapid anode degradation [65].

In the specialized clothing industry, the alginate anti-fire capacity was proven to be effective. The new alginate-based materials are showing enormous potential to be applied in building insulation materials and textile industry [66–68]

6. Conclusion

Humans use seaweed since the inception of civilization due to its medicinal properties and other properties, such as manure for the infertile soils. There is also a long history of alginate usage in foods as additives and as emulsifying, gelling, and stabilizing agents. And those characteristics open new areas and industries where alginate can be harnessed and used with success.

In bioremediation, the alginate can act as heavy metal chelating agent and support new technology to rehabilitate the degraded ecosystems.

This function can also serve as medical support to patients poisoned with heavy metals.

Although it was discovered in 1881, one of the main characteristics of alginate was used for a long time without notice: this was as soil conditioner by Europeans and other people since the Bronze Age.

Alginate is one of the easiest and low-cost natural polymers, and because of these particularities, alginate is the most researched polymer among all seaweed polysaccharides. Alginate advantages are now being explored for innovations on other areas, and that is improving the knowledge about alginates.

On the biomedical area, the alginate-based compounds/products will be on the front line of the new emergent methods and techniques evolving the human and animal health in various medical areas. This is happening now with wound dressings and the addition of regeneration factors in the alginate-based ones.

It is believed that with the new demand of natural polymers to substitute synthetic polymers, the alginate from various forms will be harnessed and will gain new types of applications in the industries that work with polymers. That demand is now sorting effects with the increment of investigation and development of new techniques and methods to work with alginate and its subforms, such as alginate-nanoclay complexes.

Acknowledgements

This work had the support of Fundação para a Ciência e Tecnologia (FCT), through the strategic project UID/MAR/04292/2019 granted to MARE. This work also received funding from the European Structural and Investment Funds through the COMPETE Programme and from National Funds through Fundação para a Ciência e a Tecnologia (FCT) under the program grant SAICTPAC/0019/2015.

This work is also co-financed by the European Regional Development Fund through the Interreg Atlantic Area Programme, under the project NASPA.

Conflict of interest

The authors declare no conflict of interest.

Author details

Leonel Pereira and João Cotas*
Marine and Environmental Sciences Centre (MARE), Department of Life Sciences, Faculty of Sciences and Technology, University of Coimbra, Coimbra, Portugal

*Address all correspondence to: jcotas@gmail.com

References

[1] Sudha PN, editor. Industrial Applications of Marine Biopolymers. Boca Raton: CRC Press; 2017. 626 p

[2] Haug A, Smidsrød O. Strontium–calcium selectivity of alginates. Nature. 1967;**215**(5102):757

[3] Draget KI, Smidsrød O, Skjåk-Bræk G. Alginates from algae. Biopolymers. 2005:1-30

[4] Hoagland DR, Lieb LL. The complex carbohydrates and forms of Sulphur in marine algae of the Pacific coast. The Journal of Biological Chemistry. 1915;**23**(1):287-297

[5] Fischer FG, Dörfel H. Die Polyuronsäuren der braunalgen (kohlenhydrate der algen I). Hoppe-Seyler's Zeitschrift für Physiologische Chemie. 1955;**302**:186-203

[6] Draget KI, Skjåk Bræk G, Smidsrød O. Alginic acid gels: The effect of alginate chemical composition and molecular weight. Carbohydrate Polymers. 1994;**25**(1):31-38

[7] Szekalska M, Puciłowska A, Szymańska E, Ciosek P, Winnicka K. Alginate: Current use and future perspectives in pharmaceutical and biomedical applications. International Journal of Polymer Science. 2016;**2016**:1-17

[8] Haug A, Larsen B, Smidsrød O. Uronic acid sequence in alginate from different sources. Carbohydrate Research. 1974;**32**(2):217-225

[9] Arunkumar K. Extraction, isolation, and characterization of alginate. In: Sudha PN, editor. Industrial Applications of Marine Biopolymers. Boca Raton: CRC Press; 2017. pp. 19-35

[10] Abe K, Sakamoto T, Sasaki SF, Nisizawa K. In vivo studies of the synthesis of alginic acid in ishige okamurai. Botanica Marina. 1973;**16**(4):229-234

[11] Skjåk-Bræk G, Grasdalen H, Larsen B. Monomer sequence and acetylation pattern in some bacterial alginates. Carbohydrate Research. 1986;**154**(1):239-250

[12] Clare K. Algin. Industrial Gums. 1993:105-143

[13] McHugh DJ. Production and Utilization of Products from Commercial Seaweeds. FAO Fisheries Technical Paper No. 288. Vol. 1891987

[14] Sime WJ. Alginates. In: Harris P, editor. Food Gels. Dordrecht: Springer Netherlands; 1990. pp. 53-78

[15] Pereira L, Gheda SF, Ribeiro-Claro PJ. Analysis by vibrational spectroscopy of seaweed polysaccharides with potential use in food, pharmaceutical, and cosmetic industries. International Journal of Carbohydrate Chemistry. 2013;**2013**(vi):1-7

[16] Gillespie RD, Critchley AT. Phenology of *Sargassum spp.* (sargassaceae, phaeophyta) from Reunion rocks, KwaZulu-Natal, South Africa. Hydrobiologia. 1999;**398-399**(April):201-210

[17] Kraan S. Algal polysaccharides, novel applications and outlook. In: Chang C-F, editor. Carbohydrates—Comprehensive Studies on Glycobiology and Glycotechnology. InTech; 2012. pp. 489-532. DOI: 10.5772/51572

[18] Ferdouse F, Holdt SL, Smith R, Murúa P, Yang Z. The global status of seaweed production, trade and utilization. FAO Globefish Research Program. 2018;**124**:120

[19] Alginate Market Analysis By Type (High G, High M), By Product (Sodium Alginate, Calcium Alginate, Potassium Alginate, Propylene Glycol Alginate), By Application, And Segment Forecasts. 2018-2025 [Internet]. 2017. p. 127. Available from: https://www.grandviewresearch.com/industry-analysis/alginate-market

[20] McHugh DJ. A guide to the seaweed industry. In: FAO Fisheries Technical Paper 441. 2003. pp. 1-105

[21] Abd El-Rehim HA. Characterization and possible agricultural application of polyacrylamide/sodium alginate crosslinked hydrogels prepared by ionizing radiation. Journal of Applied Polymer Science. 2006;**101**(6):3572-3580

[22] Sultana V, Baloch GN, Ambreen AJ, Rajput Tariq M, Ehteshamul-Haque S. Comparative efficacy of a red alga *Solieria robusta*, chemical fertilizers and pesticides in managing the root diseases and growth of soybean. Pakistan Journal of Botany. 2011;**43**(1):1-6

[23] Jacobs H, Gray SN, Crump DH. Interactions between nematophagous fungi and consequences for their potential as biological agents for the control of potato cyst nematodes. Mycological Research. 2003;**107**(Pt 1):47-56

[24] Jayaraj J, Wan A, Rahman M, Punja ZK. Seaweed extract reduces foliar fungal diseases on carrot. Crop Protection. 2008;**27**(10):1360-1366

[25] Craigie JS. Seaweed extract stimuli in plant science and agriculture. Journal of Applied Phycology. 2011;**23**(3):371-393

[26] Chatzissavvidis C, Therios I. Role of algae in agriculture. In: Pomin VH, editor. Seaweeds: Agricultural Uses, Biological and Antioxidant Agents. New York: Nova Science Publishers; 2014. pp. 1-37

[27] Nair R, Varghese SH, Nair BG, Maekawa T, Yoshida Y, Kumar DS. Nanoparticulate material delivery to plants. Plant Science. 2010;**179**(3):154-163

[28] Gogos A, Knauer K, Bucheli TD. Nanomaterials in plant protection and fertilization: Current state, foreseen applications, and research priorities. Journal of Agricultural and Food Chemistry. 2012;**60**(39):9781-9792

[29] Campos EVR, de Oliveira JL, Fraceto LF. Applications of controlled release Systems for Fungicides, herbicides, acaricides, nutrients, and plant growth hormones: A review. Advanced Science, Engineering and Medicine. 2014;**6**(4):373-387

[30] Kumar S, Bhanjana G, Sharma A, Sidhu MC, Dilbaghi N. Synthesis, characterization and on field evaluation of pesticide loaded sodium alginate nanoparticles. Carbohydrate Polymers. 2014;**101**:1061-1067

[31] Bashan Y. Alginate beads as synthetic inoculant carriers for slow release of bacteria that affect plant growth. Applied and Environmental Microbiology. 1986;**51**(5):1089-1098

[32] Trivedi P, Pandey A, Palni LMS. Carrier-based preparations of plant growth-promoting bacterial inoculants suitable for use in cooler regions. World Journal of Microbiology and Biotechnology. 2005;**21**(6-7):941-945

[33] Li H, Li P, Hua T, Zhang Y, Xiong X, Gong Z. Bioremediation of contaminated surface water by immobilized *Micrococcus roseus*. Environmental Technology. 2005;**26**(8):931-940

[34] Pielesz A, Machnicka A, Sarna E. Antibacterial activity and scanning electron microscopy (sem) examination of alginate-based films and wound dressings. Ecological Chemistry and Engineering S-Chemia I Inzynieria Ekologiczna S. 2011;**18**(2):197-210

[35] Sakiyama-Elbert S, Hubbell J. Functional biomaterials: Design of Novel Biomaterials. Annual Review of Materials Research. 2001;**31**(1):183-201

[36] Lee KY, Mooney DJ. Alginate: Properties and biomedical applications. Progress in Polymer Science. 2012;**37**(1):106-126

[37] Gombotz WR, Wee S. Protein release from alginate matrices. Advanced Drug Delivery Reviews. 1998;**31**(3):267-285

[38] Boateng JS, Matthews KH, Stevens HNE, Eccleston GM. Wound healing dressings and drug delivery systems: A review. Journal of Pharmaceutical Sciences. 2008;**97**(8):2892-2923

[39] Queen D, Orsted H, Sanada H, Sussman G. A dressing history. International Wound Journal. 2004;**1**(1):59-77

[40] Langer R, Vacanti J. Tissue engineering. Science. 1993;**260**(5110):920-926

[41] Lee KY, Mooney DJ. Hydrogels for tissue engineering. Chemical Reviews. 2001;**101**(7):1869-1879

[42] Kolambkar YM, Dupont KM, Boerckel JD, Huebsch N, Mooney DJ, Hutmacher DW, et al. An alginate-based hybrid system for growth factor delivery in the functional repair of large bone defects. Biomaterials. 2011;**32**(1):65-74

[43] Thornton AJ, Alsberg E, Albertelli M, Mooney DJ. Shape-defining scaffolds for minimally invasive tissue engineering. Transplantation. 2004;**77**(12):1798-1803

[44] Saxena AK, Marler J, Benvenuto M, Willital GH, Vacanti JP. Skeletal muscle tissue engineering using isolated myoblasts on synthetic biodegradable polymers: Preliminary studies. Tissue Engineering. 1999;**5**(6):525-531

[45] Levenberg S, Rouwkema J, Macdonald M, Garfein ES, KohaneDS,DarlandDC,etal.Engineering vascularized skeletal muscle tissue. Nature Biotechnology. 2005;**23**(7):879-884

[46] Roy D, Cambre JN, Sumerlin BS. Future perspectives and recent advances in stimuli-responsive materials. Progress in Polymer Science. 2010;**35**(1-2): 278-301

[47] Al-Shamkhani A, Duncan R. Radioiodination of alginate via covalently-bound tyrosinamide allows monitoring of its fate in vivo. Journal of Bioactive and Compatible Polymers. 1995;**10**(1):4-13

[48] Sandford PA, Steinnes A. In: Shalaby SW, McCormick CL, Butler GB, editors. Water-Soluble PolymersBiomedical Applications of High-Purity Chitosan. Vol. 467. Washington, DC: American Chemical Society; 1991. pp. 430-445

[49] Lee KY, Peters MC, Mooney DJ. Comparison of vascular endothelial growth factor and basic fibroblast growth factor on angiogenesis in SCID mice. Journal of Controlled Release. 2003;**87**(1-3):49-56

[50] Silva EA, Mooney DJ. Effects of VEGF temporal and spatial presentation on angiogenesis. Biomaterials. 2010;**31**(6):1235-1241

[51] Eliaz I, Weil E, Wilk B. Integrative medicine and the role of modified citrus

pectin/alginates in heavy metal chelation and detoxification - five case reports. Forschende Komplementärmedizin. 2007;**14**(6):358-364

[52] Mariya V, Ravindran VS. Biomedical and pharmacological significance of marine macro algae-review. Indian Journal of Marine Sciences. 2013;**42**(5):527-537

[53] Brown EM, Allsopp PJ, Magee PJ, Gill CI, Nitecki S, Strain CR, et al. Seaweed and human health. Nutrition Reviews. 2014;**72**(3):205-216

[54] Hassanshahian M, Emtiazi G, Caruso G, Cappello S. Bioremediation (bioaugmentation/biostimulation) trials of oil polluted seawater: A mesocosm simulation study. Marine Environmental Research. 2014;**95**:28-38

[55] Zommere Ž, Nikolajeva V. Immobilization of bacterial association in alginate beads for bioremediation of oil-contaminated lands. Environmental and Experimental Biology. 2018:105-111

[56] Abdul Khalil HPS, Saurabh CK, Tye YY, Lai TK, Easa AM, Rosamah E, et al. Seaweed based sustainable films and composites for food and pharmaceutical applications: A review. Renewable and Sustainable Energy Reviews. 2017;**77**(January):353-362

[57] Shawky HA. Improvement of water quality using alginate/montmorillonite composite beads. Journal of Applied Polymer Science. 2011;**119**(4):2371-2378

[58] Barreca S, Orecchio S, Pace A. The effect of montmorillonite clay in alginate gel beads for polychlorinated biphenyl adsorption: Isothermal and kinetic studies. Applied Clay Science. 2014;**99**:220-228

[59] Pereira L. Seaweeds as source of bioactive substances and skin care therapy—Cosmeceuticals, algotheraphy, and thalassotherapy. Cosmetics. 2018;**5**:68

[60] Malinowska P. Algae extracts as active cosmetic ingredients. Zesz Nauk/Uniwersytet Ekonomiczny w Poznaniu. 2011;**212**:123-129

[61] Fabrowska J, Łęska B, Schroeder G, Messyasz B, Pikosz M. Biomass and extracts of algae as material for cosmetics. In: Kim S, Bażyńska-Chojnacka K, editors. Marine Algae Extracts. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2015. pp. 681-706

[62] Wang HMD, Chen CC, Huynh P, Chang JS. Exploring the potential of using algae in cosmetics. Bioresource Technology. 2015;**184**(December):355-362

[63] Pereira L. A review of the nutrient composition of selected edible seaweeds. In: Seaweed: Ecology, Nutrient Composition and Medicinal Uses. 2012. pp. 15-47

[64] Cervino G, Fiorillo L, Herford AS, Laino L, Troiano G, Amoroso G, et al. Alginate materials and dental impression technique: A current state of the art and application to dental practice. Marine Drugs. 2019;**19**(1):1-15

[65] Kovalenko I, Zdyrko B, Magasinski A, Hertzberg B, Milicev Z, Burtovyy R, et al. A major constituent of brown algae for use in high-capacity Li-ion batteries. Science. 2011;**334**(6052):75-79

[66] Chen H-B, Shen P, Chen M-J, Zhao H-B, Schiraldi DA. Highly efficient flame retardant polyurethane foam with alginate/clay aerogel coating. ACS Applied Materials & Interfaces. 2016;**8**(47):32557-32564

[67] Liu Z, Li Z, Zhao X, Zhang L, Li Q, Liu Z, et al. Highly efficient flame retardant hybrid composites based on

calcium alginate/nano-calcium borate. Polymers (Basel). 2018;**10**(6):625

[68] Liu Y, Zhang C-J, Zhao J-C, Guo Y, Zhu P, Wang D-Y. Bio-based barium alginate film: Preparation, flame retardancy and thermal degradation behavior. Carbohydrate Polymers. 2016;**139**:106-114