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Seaweed based sustainable films and composites for food and pharmaceutical applications: A review

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ABSTRACT

Various studies have been focused on seaweeds derived polysaccharides based composites because of its renewability and sustainability for food packaging and pharmaceutical applications including tissue engineering, drug delivery, and wound dressing. Alginate, carrageenan, and agar are widely used for this purpose due to their biocompatibility, availability, gelling capacity, and encapsulation efficiency. Essential oils (like oregano, clove, lemongrass, etc.) as antimicrobial and antioxidant agent, biopolymer (like starch, cellulose, chitosan, etc.), and nanoparticles (organically modified and unmodified inorganic nanoclays, nano-cellulose, carbon nanotubes) as reinforcing material are frequently used for the fabrication of seaweed based materials. Composites have an edge over pure polymer based material in terms of mechanical and barrier properties, controlled release of drugs, and adsorption efficiency. This review comprehensively addresses different types of additives and their impact on various functional properties of seaweed based composites, their methods of incorporation, and applications with special emphasis on food and pharmaceutical usage.

1. Introduction

Packaging dominates the waste generated from plastics. Major hurdles against increasing use of plastics are non-biodegradability and derivability from non-renewable natural resources. This has put tremendous pressure on the environment due to the accumulation of plastic products in natural surroundings which adversely affect wildlife, wildlife habitat, and humans. Thus there is need to derive packaging for novel polymers to address the shortcomings of conventional plastics. Biopolymers such as starch, gluten, and guar gum are suitable alternatives to fabricate packaging material due to their nontoxicity, biodegradability, and derivability from renewable natural resources. Seaweed based polysaccharides are an interesting example of biopolymer and films derived from such source have good oxygen vapor barrier properties and are impervious to fats and oils. However, the major limitations in the use of biopolymers as packaging materials are their relatively poor mechanical and barrier properties as compared to their nonbiodegradable counterparts [1]. One of the most frequently used methods to overcome this drawback is to fabricate composite films by mixing of one polymer with another polymer and/or hydrophobic component and/or nanoparticles. This approach enables one to utilize the distinct functional characteristics of every component of the composite film. Thus such hybrid films have improved mechanical and barrier properties over the pure polymeric film [2,3].

For the development of food packaging when seaweed based polysaccharides films reinforced with organically modified or unmodified nanoclay an improvement in mechanical strength of the film was observed [4,5]. Moreover, strong inhibitory activity against foodborne pathogens in seaweed based food packaging is developed by incorporating natural or synthetic antimicrobial agents like grapefruit seed extract, silver nanoparticles etc. [6,7]. Through the vast literature survey, it can be concluded that additives like nonmaterial and antimicrobial component effectively improves various properties of composite films. Besides food packaging, seaweed based composites are also studied for pharmaceutical applications owing to its excellent properties.

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In recent years pharmaceutical firms have started looking towards marine organisms including seaweeds for novel drugs delivery systems from natural products. Due to excellent hydrogel-forming capability under relative pH [8], biocompatibility, and hypoallergenic nature seaweed offer a broader platform for medicinal purpose especially in drug delivery and tissue engineering. Seaweed polysaccharides have hydrophilic groups like carboxyl, sulfate, and hydroxyl groups on the surface which can easily interact with biological tissues. Sulfated polysaccharides have anionic sulfate groups which are not present in polysaccharides of terrestrial and animal origin. Such polysaccharides avoid aggregation during blood circulation by reduced interaction with serum proteins. Owing to these properties the usage of seaweed polysaccharides in biomedical applications are increasing. However, due to poor mechanical strength, there is limited use of pure seaweed derived polysaccharides in pharmacy including bone tissue engineering. Poor functional characteristics of seaweed polymers also lead to rapid release of drugs and loss of bioactive compounds under formulating environments such as heat, sonication, or exposure to organic solvents. Various studies have shown that composite materials can effectively address such issues, for example, nanoclay or biopolymer addition in seaweed matrix resulted in a sustained release of drugs [9,10]. Herbal or biopolymer incorporated seaweed scaffolds had improved cell adhesion and proliferation as compared to scaffolds without herbal extract or biopolymer [11,12]. Thus we can conclude that seaweed based composites have many added advantage over pure biopolymer-based material in various pharmaceutical applications.

Although both food and pharma sector have parallels between their overall production practices, they also have their own discrete challenges. Extensive reviews are available on food and pharma applications of biopolymers like starch, cellulose, polylactic acid (PLA), polycaprolactone (PCL), etc. However, comprehensive review on seaweed for food packaging and pharmaceutical applications is lacking. Thus there is a need to provide an insight on this with current trends and future prospect. The objective of this review is to discuss comprehensive scenario about the types and properties of seaweed based composites along with their preparation procedure and applications with special emphasis on pharmaceuticals and food packaging.

1.1. Chronological event in the field of seaweed based composites

Humans use seaweeds since the time immemorial and date back to some of the earliest records in human history (Table 1). Agar was discovered around 1658 in Japan and its first chemical analysis was done in 1859. Carrageenan was used as food additives since the 15th century. However, as an industrial crop, seaweed cultivation is still a recent development following its rapid increase in production and technological developments during the past half century. Seaweed as a crop has established itself as one of the most transitional industries with rapid development potential that can address the long-term issue of environmental sustainability.

1.2. Seaweed properties and extraction for food packaging and pharmaceuticals

Seaweed refers to several species of macroscopic, multicellular, marine algae that live near the seabed. The term includes some members of the red, brown, and green algae. They are the most abundant source of polysaccharides including alginate, agar, fucoidan, agarose, carrageenan, and ulvan. Agar is derived from a polysaccharide called agarose, which forms the supporting structure in the cell walls of red algae of Rhodophyceae class [23]. Agarose is accountable for the gelling capacity of agar which makes it very useful in skin care, herbal medicines, and has excellent film properties. Due to this agar and agar-based composites are widely used in food and pharmaceutical applications [5]. Most of the large brown seaweeds are potential sources of alginate. Alginic acid is a linear copolymer with homopolymeric blocks of (1-4)-linked β-D-mannuronate and its C-5 epimer α-L-guluronate residues, respectively, covalently linked together in different sequences. It has been shown that the physical properties of alginates depend on the sequencing of its monomers [24]. The ability of alginates to react with divalent and trivalent cations is widely being utilized in alginate film formation. Alginic acid is insoluble in water but swells when placed in water. This property makes it a useful disintegrating agent in tablets. Carrageenans are linear sulfated polysaccharides that are extracted from red edible seaweeds. It has three main commercial classes: Kappa (κ) forms strong, rigid gels in the presence of potassium ions and due to such properties it has been used for the formation of cohesive and transparent films [25]. Iota (ι) forms soft gels in the presence of calcium ions. Lambda (λ) does not form the gel and is used to thicken dairy products. Carrageenans are widely exploited due to its hydrophilic and anionic properties. It has been extensively used in food packaging and pharmaceutical industries as gelling, emulsifying, stabilizing agents, and base material for packaging films. According to FAO's report on Global Aquaculture Production published in 2013, the worldwide production of seaweed was around 27 million tons (Table 2).

Seaweeds are mainly harvested for human consumption. Besides that, they are also being cultivated for the extraction of gelatinous substances collectively known as hydrocolloids: alginate, agar, and carrageenan. Alkali is used for the extraction of carrageenans because it induces chemical modification that leads to increased gel strength in the final product. There are two methods for recovering carrageenans

Table 1
Chronological event of seaweed usage and recent technological development.

Period	Stage of development in applied seaweed research and industry
≥35,000 BCE	Water carriers were made using hygroscopic properties of kelp by Tasmanian aboriginal (Dillehay et al. [13]).
13,000 BCE	Ancient civilizations in Chile used seaweed for nutrition and health (Dillehay et al. [13]).
0–300 CE	In China it was used for iodine supplement (Dillehay et al. [13]).
1716	Alginate was reported to be used in wound dressings (Martin [14]).
1940s	Industrial development of hydrocolloids from seaweeds; research on seaweed as food (Craigie [15]).
1948	Incorporation of antioxidants to the carrageenan based coatings for improved quality and microbiological stability of muscle foods (Stoloff et al. [16]).
1950s	First international seaweed symposium on seaweed held at Scotland (Dillehay et al. [13]).
1961	Calcium alginate coatings reduced dehydration of cut-up poultry (Mountney and Winter [17]).
2000	Inhibition of *Salmonella* on broiler skin using agar based films containing nisin (Natrajan and Sheldon [18]).
2010	Development of chitosan/carrageenan composite nanoparticles for drug delivery applications (Grenha et al. [19]).
2012	Alginate based nanocomposite film reinforced with nanocrystalline cellulose was prepared (Huq et al. [20]).
2013	Agar film incorporated with silver nanoparticles exhibited improved water vapor, gas barrier and mechanical properties (Rhim et al. [7]).
2014	Carrageenan based composite films incorporated with grape seed extract showed strong inhibitory activity against food borne pathogens (Kanmani and Rhim [6]).
2015	Alginate/pullulan based composite films were developed (Xiao et al. [21]).
2016	Nanocomposites were prepared using cellulose nanofibrils and alginate biopolymer (Deepa et al. [22]).

Table 2
World production of seaweed (FAO report Global Aquaculture Production, 2013).

Country	Seaweed (fresh weight million tons)	World production (%)
China	13.5	50.1
Indonesia	9.3	34.6
Philippines	1.6	5.8
South Korea	1.1	4.2
North Korea	0.44	1.7
Japan	0.42	1.6
Malaysia	0.27	0.9
Others	0.37	1.1

(Fig. 1**a**). Alcohol precipitation method can be used for all types of carrageenans, however, gel method can only be used for kappa-carrageenan. Hilliou et al. [26] reported that by increasing the alkaline pre-treatment duration PT leads to κ/ι-hybrid carrageenans containing fewer sulfate groups and biological precursor monomers. Consequently, gel properties in the presence of KCl were improved as demonstrated by an increase in Young's modulus with parameter PT. Thus carrageenans with improved gel properties can be suitably used in food and pharma industries. There are mainly two different ways of recovering the alginate. The first one is to add acid, which causes alginic acid to form and the second way of recovering the sodium alginate from the initial extraction solution is to add calcium salt (Fig. 1**b**). Fertah et al. [27] demonstrated that high yield temperature of 40 °C and sample size of less than 1 mm are appropriate conditions for extraction of sodium alginate. Furthermore, they observed that the M/G ratio of alginates was 1.12 which led to the formation of soft and elastic gels thus it can be used as polyelectrolyte complexes for the production of drug delivery micro and nano-particles. Agar can be extracted by acid or by alkali treatment as shown in Fig. 1**c**. Alkali treatment during the extraction process of agar increases the gel strength from 72 g/cm^2 (which is not appropriate for industry) to 1064 g/cm^2 [28]. On the basis of these studies, it can be concluded that by modifying the extraction procedure of seaweed based polysaccharides researcher can effectively alter the properties of seaweed based composites which subsequently widens its applicability.

2. Different types of seaweed based composites and their preparation procedure

2.1. Seaweed incorporation with biopolymers

Biopolymers can be produced by chemical synthesis starting from renewable bio-based monomers such as polylactic acid. It can also be produced by microorganisms such as polyhydroxyalkanoates or from vegetal or animal biomass such as polysaccharides (starch, cellulose) and proteins (gelatin, chitosan). Starch is a carbohydrate consisting of a large number of glucose units joined together by glycosidic bonds. It is frequently used for the development of seaweed based composites due to the formation of an extensive network of hydrogen bonds between polymers. Thus various studies on seaweed polysaccharides and starch-based composites have been conducted in past. Alginate along with starch was processed into films with excellent mechanical and barrier properties for food packaging [30,31]. Furthermore, composite beads of alginate-starch for controlled release of drug was efficiently achieved and successfully demonstrated by Kim et al. [32]. Developed composite beads could also adsorb and remove heavy metals such as lead from the body. Thus it can be concluded that composites made up of same types of biopolymers (like alginate and starch) have the potential to be used in wide range of applications owing to its excellent characteristics. With the addition of one or more components in such composite can further be impregnated with desirable characteristics. For example, by adding clays in alginate-starch bead formulation the release of fungicide can be retarded [33]. The release of pesticides from such beads occurred in a controlled way which is necessary for agrochemicals. The slower the release, the lower will be the amount of active ingredient available for leaching and volatilization, hence, it may be useful for safe handling of pesticides and preserves the environment. Similarly like alginate, agar/starch based films also have excellent mechanical properties [34,35]. On the basis of above-mentioned reports, it can be concluded that the seaweed/starch-based composites not only have applicability in the field of food and pharmacy but can also be useful in environmental preservation techniques.

Besides starch, cellulose is also often used with alginate, agar, and carrageenans for the development of composite materials. It is a

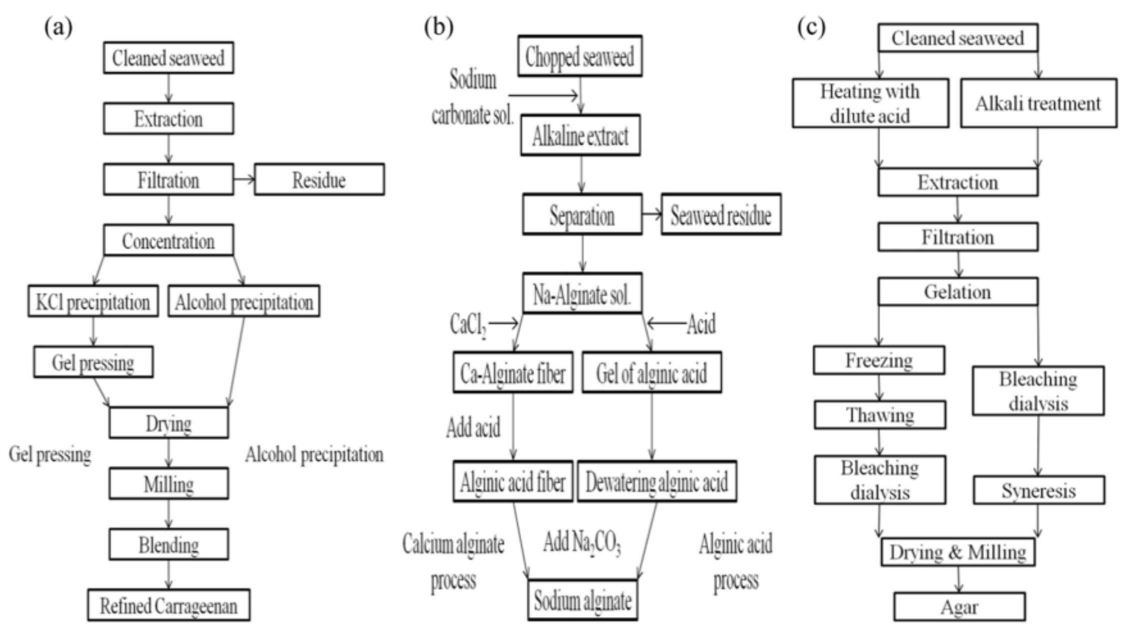

Fig. 1. Flow chart for extraction process of (a) refined carrageenan; (b) sodium alginate; (c) agar [29].

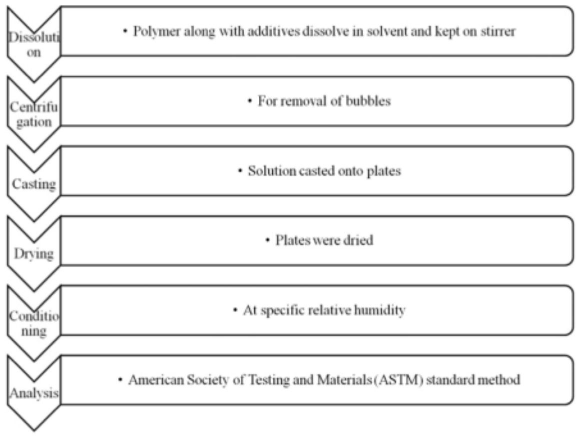

Fig. 2. Flow chart of solvent casting method for biodegradable film preparation.

polysaccharide consisting of a linear chain of several hundred to many thousands of β(1→4) linked D-glucose units. Composites based on alginate/cellulose matrices demonstrated skin tissue compatibility for use as a non-adherent hydrogel dressing [36]. Furthermore, alginate/cellulose-based composites with antimicrobial activity were also developed by adding copper for potential application as dressing materials [37]. Moreover, composites of different types of carrageenans with cellulose were also studied and it was observed that the mechanical properties of the developed composites were better than those of the hydrogels of carrageenans and cellulose gels [38]. Thus it can be concluded that seaweed and cellulose based composites are widely researched as dressing materials owing to its human tissue compatibility, water retention capacity, mechanical strength etc.

Gelatin is an animal protein and has been widely used along with seaweed for various applications. Balakrishnan et al. [39] showed that hydrogel can be prepared from alginate and gelatin in the presence of small amount of borax. The developed composite matrix has wound healing feature of alginate, hemostatic effect of gelatine, and antiseptic property of borax which make it a potential wound dressing material. Alginate/gelatin and whey protein isolate based composite films were also developed with improved mechanical and barrier properties for food packaging application [40]. Alginate/gelatin composites have wide applicability ranging from the wound dressing to packaging materials. Furthermore, the addition of gelatin into agar matrix hindered the release of various compounds from the developed composite [41–43]. The improved and controlled release of compounds from gelatine/agar composites can be explained by the specific interaction between polymer components, their network structure, and polymer drug interaction. Gelatin is also widely researched with carrageenan based composites for various applications. The addition of gelatin in carrageenan matrix was found to improve the thermal stability of the fabricated composite hydrogels for sustainable drug delivery system [44–46]. The in vitro drug release studies showed that an enhancement in porosity resulted in the improved drug release due to the tuning of pore size distribution. On the basis of vast literature, it can be suggested that seaweed and gelatin based composites have very wide applicability especially in the field of pharmaceuticals.

Chitosan is the most abundant cationic polysaccharide and there are numerous studies on seaweed/chitosan composites. A composite microparticle drug delivery system based on alginate, chitosan and pectin were developed by Yu et al. [47] for oral delivery of protein drugs, using bovine serum albumin as a model drug. Substantial reports are available on the utility of alginate polymer-based composites for bone tissue regeneration. Among them, alginate-chitosan composite for bone tissue repair is one of the most considered materials [48]. Beside health sector, alginate/chitosan composites can also be used for packaging applications. Biopolymer composite films of κ-carrageenan and chitosan were prepared by co-dissolving them into different organic acids [49]. The mechanical strength, elasticity, and water vapor permeability of developed κ-carrageenan/chitosan composite films demonstrated dependency on the organic acid solvent. Available literature suggests that addition of various biopolymers in seaweed based matrices can tailor the release rate of drugs and fertilizers or pesticides from the matrix and enhances the mechanical and barrier properties of biodegradable food packaging and coating materials. However, in spite of numerous studies on the development of biopolymer based composites, their commercial exploitation is still lacking.

2.2. Preparation procedure of seaweed/biopolymer composites

There are various methods available in the literature for the preparation of seaweed based composites depending on their applications such as wall material for drug release or biodegradable packaging film. For drug delivery system there are wide varieties of methods available depending on types of polymeric matrix and encapsulated drug. Alginate-starch-chitosan microparticles containing stigmasterol solubilised in canola oil as a drug delivery vehicle were effectively produced by one stage external ionic gelation process [50]. Another popular method of encapsulation is spray drying. This technique was used for alginate/starch blends as wall material to controls the release of encapsulated fish oil [51]. In another study, optimization of various components for film formation was done by central composite design to study the effects of sodium alginate and cationized starch as independent process variables on drug encapsulation and drug release [52]. Composite gels of carrageenan with cellulose were prepared by using an ionic liquid, 1-butyl-3-methylimidazolium chloride by a heating-cooling process to check the release of drugs and fertilizers from wall material [38]. For food packaging application, alginate/starch film was prepared by slowly dissolving starch and alginate in a constantly stirred mixture of distilled water, ethanol, and glycerine. Further tocopherol was added into the film for inhibition of lipid oxidation in packed pre-cooked ground beef patties [53]. Solvent casting method is one of the most popular methods for development of biodegradable films. A series of agar/starch blends were processed into films by casting method [34]. A general flow chart of solvent casting method is depicted in Fig. 2 [1]. This method was also used for the improvement of water vapor and gasses (CO_2 and O_2) barrier properties of the polymeric matrix composed by κ-carrageenan and pectin along with mica flakes [25]. A similar methodology was used in several other studies for seaweed polysaccharides based food packaging applications [54].

2.3. Seaweed based nanocomposite material

The Europe Union adopted a definition of a nanomaterial in 2011. According to the EU "Nanomaterial" means: "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1–100 nm". It can be particles, tubes, rods, or fibers. Table 3 demonstrates the two classes of nanomaterials which are frequently used for the development of biopolymer based nanocomposite films.

Beside biopolymers, nanoclays are one of the most commonly used additives in seaweed based composite materials. Montmorillonite (MMT), a typical example of nanoclay, consists of several hundred nanometers long inorganic layered silicates having layer spacing of few nanometers and hundreds of such layered platelets stacked into particles or tactoids. Chemically, MMT consists of two silicate tetrahedral sheets sandwiching an octahedral sheet of either magnesium or aluminum hydroxide. For packaging application nanocomposites based

Table 3
Types of nanomaterials employed in development of biopolymer based nanocomposites.

Inorganic	Organic
Nanoclays • Montmorillonite (MMT) • Bentonite • Kaolinite	**Organically modified nanoclays** • MMT modified with a quaternary ammonium salt and tallow group
Silver nano-particles	**Cellulose** • Nanocrystalline cellulose • Cellulose nanowhiskers • Cellulose nanofibers **Carbon nanotubes** • Single wall nanotubes • Multi wall nanotubes **Chitin nanofibrils**

on κ-carrageenan/MMT [55] and agar/κ-carrageenan/MMT [56] was earlier studied. Agar-based nanocomposite films were also developed by using natural MMT clay [5] and organically modified and unmodified MMT [57]. Incorporation of nanoclay resulted in improvement in mechanical and barrier properties of a film due to the transfer of stress from polymeric matrix to nanoclay sheets and introduction of the torturous path in a film. However, active packaging with antimicrobial activity is highly desirable in films for improving the shelf life of packed food products. In this regard film with high mechanical and antimicrobial properties were developed when organically modified nanoclay dispersed in the biopolymer matrix composed of mixtures of κ-carrageenan and locust bean gum [4]. Organically modified nanoclay has better compatibility with organic biopolymer as compared to unmodified inorganic nanoclay this further enhances properties of nanocomposites. Antimicrobial activity is another added advantage of modified nanoclay due to its quaternary ammonium salt. Besides packaging application, seaweed based nanocomposites are also widely developed for biomedical applications. Sodium alginate based nanocomposites for drug delivery system was developed by using inorganic clay kaolin [58] or MMT [59]. Incorporation of nanoclays led to improvement in physical characteristics and alters the rate of drug release from composite materials.

Seaweed based nanocomposites incorporated with nanocellulose is widely studied because of its improved and unique characteristics. Nanocellulose refers to nanostructured cellulose and this may be either cellulose nanofibers (CNF) also called microfibrillated cellulose (MFC), nanocrystalline cellulose (NCC), bacterial nanocellulose or cellulose nanowhiskers (CNW). In one study, characteristics of alginate based films were enhanced by the addition of inorganic MMT and organic cellulose nanoparticles and the developed biodegradable films have potential to be used in packaging of agricultural produce [60]. Similarly, alginate based nanocomposite films were also prepared for the preservation of food by reinforcing NCC [20] and cellulose nanoparticles [61]. Agar-based stand alone films were also developed by incorporating crystalline nanocellulose [62–64]. It is widely known fact that the addition of nanoparticles resulted in improved physical properties of composite films. Apart from packaging, seaweed based composites also have potential application in therapeutic treatment. Soft composites consisting of κ-carrageenan gel reinforced with two types of nanocellulose (MFC and NCC) for many applications including drug release system was developed [65]. In other studies, hybrid injectable hydrogels comprising of alginate and nanocellulose were synthesized for delivery of cells and bioactive molecules [66,67]. Park et al. [68] developed bacterial nanocellulose alginate hydrogel for cell encapsulation. Overall it can be concluded that seaweed and nanocellulose based composites has wide potential to be used in field of food packaging and biomedical field.

Carbon nanotubes have enormous potential to be used in nanocomposites due to the very high surface area/weight ratio and strong adsorption affinities. It is allotropes of carbon having cylindrical nanostructure with length to diameter ratio up to 132,000,000:1. Alginate and carbon nanotube based composite for the fabrication of biomaterial scaffold [69,70], antibodies based immunosensor [71], and adsorbent for wastewater treatment [72] was earlier studied by various authors. Composites having therapeutic applications were earlier developed by using carbon nanotubes and two oppositely charged biopolymers (chitosan and carrageenan) [73], agar [74], or agarose [75]. Furthermore, for packaging applications free standing composite films were prepared by using κ-carrageenan and carbon nanotubes [76], or single and multi-walled carbon nanotubes [77]. There are inadequate studies has been conducted on seaweed/carbon nanotubes composites in spite of excellent potential shown by carbon nanotubes.

Chitin nanofibrils as nanocrystals represent the pure and sugary molecular portion of α-chitin obtained after the elimination of proteins. In several studies, it is incorporated in seaweed polysaccharides for the development of composites with desirable features. Shankar et al. [78] reported that incorporation of chitin nanofibrils in carrageenan based nanocomposites resulted in films having strong antibacterial activity against gram-positive foodborne pathogens. Various mixtures of chitin nanocrystals and oppositely charged carrageenan [79] and alginate [80,81] were developed with improved mechanical properties for therapeutic applications including wound dressing. Further studies on seaweed and chitin nanofibrils based composites are needed to be done to explore its possible industrial application in food and biomedical fields.

Silver nanoparticles incorporation often induces strong antimicrobial activity in the composites as reported by various authors for carrageenan-based nanocomposites [82,83] along with organically modified clay mineral [84]. In another study, agar based silver nanoparticles composites for packaging applications were developed by Shukla et al. [85]. Among seaweed based polysaccharides/silver nanocomposites, alginate is the most studied polymer for pharmaceutical applications. Incorporation of nanosilver into alginate fibers increased antimicrobial activity and improved the binding affinity of composite for wound treatment [86]. In another study, biocomposite films containing alginate and sago starch impregnated with silver nanoparticles was prepared as a dressing material [87]. On the basis of above literature it can be that alginate based silver nanoparticles mainly developed for biomedical application as a wound dressing material, however, their potential use in other areas is yet to be explored.

2.4. Preparation procedure of seaweed based nano-composites

Nanoclays are one of the most frequently used components in the development of nanocomposites. However, prior to their incorporation nanoclays are intercalated to increase the basal spacing between their parallel sheets and this will facilitate the crawling of more amount of biopolymers among those sheets. This phenomenon enhances the interaction between nanoclays and polymer matrix which resulted in improved properties of nanocomposites. A general flowchart of intercalation of nanoclay in biopolymer matrices is given in Fig. 3 [2]. Based on similar methodology as depicted in Fig. 3, the researcher developed agar/κ-carrageenan blend film incorporated with nanoclay [56]. Water as a solvent is mainly used for the solubilization of biopolymer and intercalation of nanoclays. Furthermore, water is also used for chemical modification of nanoclays. In one study, untreated bentonite was dispersed in a solution of NaCl and washed with de-ionized water until the supernatant is free from chloride ion to obtain MMT in MMT-Na form [59]. Further authors added diclofenac as a drug into a homogeneous solution of alginate followed by addition of MMT-Na and the beads were prepared from obtained emulsion by gelation method. Intercalation is only desirable in nanoclays due to their parallel sheets however other nanoparticles are free from such restrictions. In another study, for the synthesis of silver nanoparticles agar as a reducing agent was dissolved in deionized water and $AgNO_3$ was added [85]. The

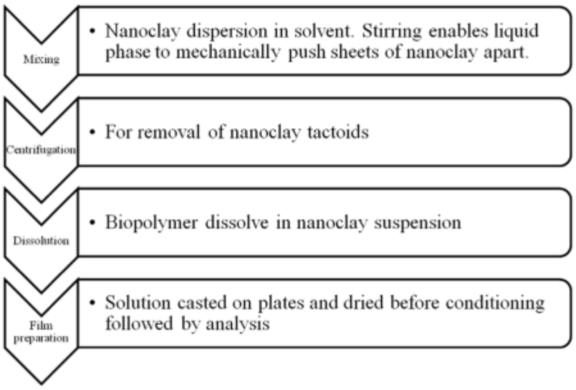

Fig. 3. Process of intercalation of nanoclay in biopolymer matrices.

obtained mixture was incubated in dark at constant stirring and the acidic pH was set. Thereafter, obtained solutions were centrifuged to get a clear solution of silver nanoparticles. Furthermore, to make agar/silver nanocomposite, agar was added into silver nanoparticles solution followed by heating. Subsequently, the viscous solution of agar/silver nanocomposite was poured into plastic plates and dried at room temperature before the analysis of films. Chitin nanofibrils were isolated from chitin after being hydrolyzed with HCl under strong agitation [78]. The unhydrolyzed fibers were filtered and the filtrate was centrifuged. The obtained precipitate washed with distilled water and the suspension was homogenized followed by sonication and then subjected to dialysis for obtaining chitin nanofibrils. Carrageenan-based chitin nanofibrils composite films were prepared using a solution casting method. In another study, single wall carbon nanotubes were poured into a mixture of sulfuric acid and nitric acid, followed by sonication and then vacuum filtration [69]. The treated carbon nanotubes were solubalize in water and dispersed in sodium alginate solution in presence of cross-linker EDSI and 1-ethyl-3-3-dimethylaminopropyl)-carbodiimide hydrochloride for the preparation of alginate-based nanocomposite gel for tissue engineering. In another study, onion skin was bleached with sodium chlorite solution and then boiled with sodium sulfite [64]. The resulting component was treated with sodium hydroxide solution followed by filtration and acetic acid treatment. Finally, extracted cellulose was dried to get cellulose microfiber. Agar-based cellulose microfiber composite films were prepared using a solution casting method. Thus based on methodology available in literature it can be concluded that there are various methods for the synthesis of different types of nanoparticles and its subsequent reinforcement in seaweed nanocomposite materials.

2.5. Seaweed and essential oil based composite material

Essential oil is a concentrated hydrophobic liquid containing volatile aroma compounds from plants. Their incorporation often leads to high antimicrobial activity in the composite materials which in turn will have wider applicability, especially in food packaging. Main components of clove essential oil are eugenol, β-caryophyllene, α-humulene, and eugenyl acetate. Studies on clove essential oil incorporated into an alginate-based edible film assured the safety and quality of fresh-cut 'Fuji' apples [88] and silver carp fillet [89]. The observed increase in shelf life extension of fresh-cut food products packed in alginate-based active nanocomposite was due to the antimicrobial activity of clove essential oils against common foodborne pathogens [90]. Turmeric essential oil is another widely studied active components having ar-turmerone (2-methyl-6-(4-methylphenyl)-2-hepten-4-one) as the main constituent. Beside composite preparation essential oil usually encapsulated for the development of delivery system either in food or in the drug. Encapsulation of turmeric essential oil as a model drug using alginate matrix was prepared as potential drug delivery system [91–93]. Further study on turmeric essential oil entrapment in alginate gel to control *Callosobruchus maculates* was also performed [94].

Oregano essential oil is primarily composed of monoterpenoids and monoterpenes and has potential use in foods or pharmacy as an antibacterial agent. Incorporation of oregano essential oil in alginate films significantly improve physical properties of film and induce strong antibacterial activity [95]. Various studies demonstrated the effectiveness of oregano essential oil when incorporated in alginate composite films for improving the shelf life of fish [96], bologna, and ham slices [97]. Lemongrass essential oil is also studied because of its constituents including myrcene, citronellal, and geranyl acetate. Earlier various authors investigated the effect of lemongrass as a natural antimicrobial agent by incorporating it in edible alginate film to improve the shelf life of fresh-cut 'Fuji' apples [98], "Piel de Sapo" melon [99], and pineapples [100]. Besides food packaging, alginate-based composite films with notable antimicrobial and antifungal properties were developed by incorporation of various essential oils including lemongrass essential oil for wound dressing application by Liakos et al. [101]. Alginate/chitosan composite as nano-carrier for encapsulated lemongrass essential oil was also developed for biomedical and pharmaceutical applications [93]. Another antimicrobial agent savory essential oil mainly consists of savory carvacrol, p-cymene, and γ-terpinene. Savory essential oil when incorporated into agar-based nanocomposite films it acts as a plasticizer which resulted in increased percent elongation at break and induces high antimicrobial activity against gram-positive bacteria as compared to gram-negative bacteria [102]. Oussalah et al. [97] also reported the application of savory essential oil containing alginate films for controlling the growth of pathogenic bacteria *L. monocytogenes* and *S.typhimurium* on bologna and ham slices. Zataria essential oil has a high content of phenolic oxygenated monoterpenes. Because of its hydrophobicity, the addition of zataria essential oil reduced the water vapor permeability and enhanced the mechanical properties of κ-carrageenan films [103]. Available literature suggests that alginate is widely used with essential oils to develop active composite materials for food packaging applications. Essential oils are highly effective against gram positive bacteria since it inhibits the bacterial cell wall synthesis. Furthermore, essential oils are also hydrophobic in nature and highly rich in fatty acids thus its addition often resulted in improved water barrier properties and percentage elongation of composites. Incorporation of essential oils in seaweed-based polysaccharides are frequently used for the shelf life extension of fresh-cut fruits, however, their usage in biomedical industries is still needed to be explored.

2.6. Preparation procedure of seaweed/essential oil based active composites

Generally essential oil (hydrophobic) mixed with aqueous biopolymer solution (hydrophilic) with the help of emulsifier to facilitate compatibility between them. Oregano essential oil mixed with tween-80 as emulsifier and then added into a sodium alginate aqueous solution, further the mixture was homogenized followed by ultrasonication [95]. Finally, dispersion composed of $CaCO_3$ glucono-δ-lactone was added to the film-forming mixture and the resultant solution was casted onto Petri dishes and allowed to dry in an oven to obtain film. Similar method was also used for the preparation of alginate/gelatin film containing oregano essential oil for fish preservation [96]. In another study, oregano and savory essential oil was added into a preheated aqueous solution containing alginate, poly(ε-caprolactone) diol, and glycerol as plasticizer [104]. Obtained solution was then casted and dried. Further dried films were treated by $CaCl_2$ solutions followed by washing in distilled water and again dried at room temperature before testing. In another set of experiments, the suspension of nanocrystalline cellulose dispersed in agar solution

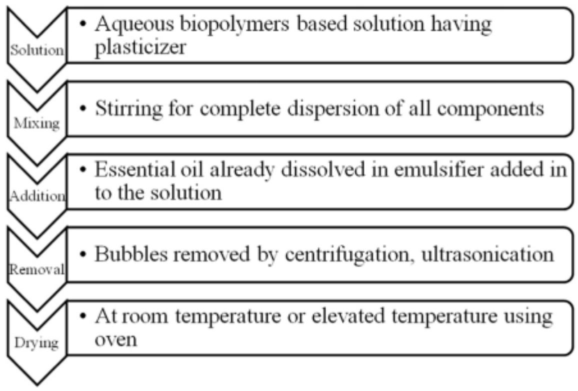

Fig. 4. Flow chart demonstrating steps involved in the preparation of active films.

containing glycerol followed by addition of tween-80 along with savory essential oil [102]. Obtained solution was degassed for removal of bubbles and then casted into Petri dishes and dried in an oven. Thus by analysing above methods for preparation of bioactive films general steps for film formation procedure is demonstrated in Fig. 4. Shojaee-Aliabadi et al. [103] also use the similar methodology as described above for the production of κ-carrageenan films incorporated with *Zataria multiflora Boiss* and *Mentha pulegium* essential oils. Rojas-Graü et al. [98] prepared film coating suspension for 'Fuji' apples by mixing apple puree with alginate solution containing glycerol followed by incorporation of oregano or lemongrass essential oil. 'Fuji' apples were washed, sanitized by immersion in sodium hypochlorite solution, rinsed, and dried prior to cutting. The apple pieces were first dipped into coating solutions and packaged into polypropylene trays subsequently stored in darkness and chemical as well as the microbial analysis was done periodically. A similar methodology was used for the preparation of edible alginate based film incorporated with malic acid and essential oils of cinnamon, palmarosa, and lemongrass for the shelf life extension of fresh-cut melon [99]. In another study, an aqueous solution of sodium alginate was prepared and added into the MMT clay solution followed by incorporation of marjoram, clove, and cinnamon essential oils already mixed with tween-80 [90]. The final solution was homogenized, degassed, casted, dried, and later conditioned at 25 °C and 52.89% relative humidity prior to testing. Thus it was observed that tween-80 is one of the most frequently used emulsifiers to solubilise hydrophobic essential oils into hydrophilic seaweed polysaccharide aqueous solution.

3. Applications

Seaweed based polysaccharides are one of the most abundant biopolymers in nature that can be used in food and biomedical industries as a scaffold, dispersant, coating, stabilizing, packaging, and thickening agent due to its biocompatibility, biodegradability, high water-retaining capacity, and excellent film characteristics.

3.1. Food industries

Seaweed polysaccharides applications in food industries are based mainly on their stabilizing, emulsifying, and gel forming ability. It is widely used as food additives in jams, jellies, ice creams, dairy products etc to improve and stabilize the structure of food. Furthermore, seaweed-based composite films and coatings are also used for food packaging. Researchers developed alginate/polyethyleneimine and biaxially oriented poly(lactic acid) based multilayer barrier films as a promising alternative to nonbiodegradable synthetic packaging materials [105]. Table 4 summarizes the types of seaweed-based composites for various food packaging and coating applications.

3.2. Pharmaceutical industries

Seaweed-based polysaccharides can easily form gel thus they are widely used in drug delivery system. Numerous studies have shown that the gel forming kinetics has a significant impact on several of its functional properties including stability, biodegradability, gel's immunological characteristics, and biocompatibility. One of the major limitation of using seaweed polymer in drug delivery system is that the active compound loss during beads preparation by leaching through the pores of beads. To overcome this drawback many composites based on seaweed have been fabricated and tested for drug delivery applications. Besides that, seaweed-based composites also have potential application in bone tissue engineering, wound dressing materials, tablet dispersant, scaffolds, cells encapsulation etc. Table 5 summarizes the types of seaweed based composites for various biomedical and pharmaceutical applications.

3.3. Others

Seaweed based composites also used for various other purposes and in this section; their important applications are club together. Alginate has high affinity and binding capacity for metal ions thus widely used as a heavy metal adsorbent for environmental protection. They are also used for the slow release of fungicides, pesticides etc under safe agricultural practices. Table 6 summarizes various applications of seaweed-based composites especially in wastewater treatment and environment protections.

The focus of seaweed composites in the past has been on the food, pharma, biomedical, and environment protection. A greater emphasis on exploring new horizons for seaweed based composites like oxygen, carbon dioxide, and pathological sensors may be the next area of development in packaging technology. Technical challenges exist while seeking new goals, however, current trends suggest that seaweed based composite material will continue to improve functionally and characteristically. Researchers have focused mainly on designing new

Table 4
Applications of seaweed-based polysaccharides in food packaging and coatings.

Types of composites	Applications	References
Alginate/Nanocrystalline cellulose	Polymeric packaging films for food	Huq et al. [20]
Alginate/Starch	Packaging of Precooked Ground Beef Patties	Wu et. al. [53]
Carrageenan/Locust Bean Gum/ organically modified nanoclay	Shelf life extension of food	Martins et al. [4]
Carrageenan/grapefruit seed extract	Active food packaging	Kanmani et al. [6]
Agar/nanoclay	Biodegradable food packaging	Rhim [5]
Alginate/Polycaprolactone/Oregano or savory or cinnamon essential oils	Edible film for food	Salmieri et al. [104]
Alginate/Oregano or cinnamon or savory essential oils	Preservative coating on bologna and ham slices	Oussalah et al. [97]
Alginate/Apple puree/Lemongrass or oregano or vanillin essential oils	Prolong shelf life of fresh cut 'Fuji' apples	Rojas-Graü et al. [98]
Alginate/Lemongrass essential oil	Quality retention of fresh cut pineapples	Azarakhsh et al. [100]
κ-carrageenan/Montmorillonite/Zataria multiflora Boiss essential oil	Antimicrobial packaging for food	Shojaee et al. [106]
Agar/Nanocrystalline cellulose/savory essential oil	Active packaging for improving the safety and shelf life of foodstuff	Atef et al. [102]

Table 5
Applications of seaweed-based polysaccharides in biomedical and pharmaceuticals.

Types of composites	Applications	References
Carrageenan/Chitosan nano-particles	Carriers of therapeutic macromolecules	Grenha et al. [19]
Alginate/Montmorillonite	Delivery system of vitamin B_1 and B_6	Kevadiya et al. [9]
Alginate/O-carboxymethyl chitosan/*Cissus quadrangularis* extract	Osteoinductive 'herbal' scaffold for bone tissue engineering	Soumya et al. [11]
Carrageenan/Graphene oxide	Bone regeneration and implantation	Liu et al. [107]
Fucoidan/Chitosan micro complex hydrogel	Carrier for fibroblast growth factor-2	Nakamura et al. [10]
Ulvan/Chitosan polyelectrolyte nanofibrous membranes	Substrate material for the cultivation of osteoblasts	Toskas et al. [12]
Oxidized alginate/Gelatin	Hydrogel wound dressing	Balakrishnan et al. [39]
Alginate/Starch	Removal of heavy metals from body	Kim et al. [32]
Agar/Gelatin	Vehicle for controlled drug release/Control release of salbutamol tablets	Wakhet et al. [42]; Saxena et al. [43]
Carrageenan/Gelatin hydrogels	Drug delivery applications	Varghese et al. [46]

Table 6
Various applications of seaweed-based polysaccharides.

Types of composites	Applications	References
Alginate/Starch/Kaolin/Bentonite	Controlled release of the fungicide thiram	Singh et al. [33]
κ-carrageenan/Poly(acrylamide)/Sepiolite clay	Removal of cationic crystal violet dye from water	Mahdavinia et al. [108]
Alginate/Illite/Smectite clays organified	Adsorption of methylene blue	Wang et al. [109]
Sodium alginate/Carbon nanotubes	Immunosensor for *Shigella flexneri*	Zhao et al. [71]
Calcium alginate/Carbon nanotubes	Removal of copper from aqueous solution	Li et al. [72]
Carrageenan/Multi walled carbon nanotubes	Adsorption of crystal violet from aqueous solution	Hosseinzadeh [110]

approaches and applying new methods on model systems for drug delivery vehicle, but efforts toward commercialization of seaweed in food packaging and pharma products are still lacking.

4. Conclusion

Seaweed was used by humans since the inception of civilization due to its medicinal properties. It also has a long history of usage in foods as additives, emulsifying, gelling, and stabilizing agent. Most frequently used polysaccharides of seaweed are agar, alginate, and carrageenan. However, alginate is the most researched polymer among all seaweed polysaccharides due to its ability to react with di- and tri-valent cations thus form sodium or calcium alginate which in turn has wide applicability in food and pharmaceuticals. Functional characteristics of isolated seaweed polymers significantly depend on extraction procedure. Mainly seaweed-based polymers assorted with essential oils as antimicrobial agents, other biopolymers, and nanoparticles to develop a novel composite material having high mechanical and barrier properties as well as high encapsulation efficiency, gel strength, adsorption capacity, and conductivity. Depends on the usage various methodology for preparation of seaweed composites has been proposed in past like solvent casting method for film development, intercalation of nanoclays for nanocomposites, and emulsification of essential oils for active composites. Recent advances in the field of seaweed-based composites enable their usage in food packaging and coating along with the development of new drug delivery system, biomedical scaffolds, and cell encapsulations.

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