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Review

The development of seaweed-derived bioactive compounds for use as prebiotics and nutraceuticals using enzyme technologies

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ABSTRACT

Background: Seaweeds are a large and diverse group of photosynthetic macro-algae found across the world's oceans. There is a growing recognition that they are important sources of bioactive compounds with a variety of biological activities that could potentially contribute to functional food and nutraceutical industries.

Scope and approach: The complex structure and distinctive components of seaweed cell walls, which differ significantly from terrestrial plants, presents a major challenge for the effective extraction of bioactive compounds from inside the cells. Enzyme technologies have been used to improve the extraction, hydrolysis, and structure modification efficiently with a high degree of environmental sustainability. This review critically analyses the advances, challenges, and future directions in applying enzyme technologies to improve the extraction and processing of bioactive compounds from seaweeds and their potential applications in functional foods and nutraceuticals.

Key findings and conclusions: Different enzymatic processes have been demonstrated to (1) assist the extraction by breaking down the seaweed cell walls, and (2) degrade or hydrolyse macromolecules including polysaccharides and proteins. These enzymatic processes improve the yield and recovery of bioactive compounds and enhance their biological properties with regard to prebiotic, antioxidant, ACE inhibitory, anti-inflammatory, and antiviral effects. Seaweed-derived bioactive compounds from these processes present significant new opportunities in developing novel food applications. The current food regulations and safety requirements for seaweeds and their products are addressed for commercial product development.

1. Background

Marine macroalgae or seaweeds constitute approximately 25,000–30,000 species (Santos et al., 2015), with a great diversity of forms and sizes. They can be categorized into different taxonomic groups reflecting their pigmentation, including red algae (Rhodophyceae), brown algae (Phaeophyceae), and green algae (Chlorophyceae) (Mohamed, Hashim, & Rahman, 2012). Seaweeds have become an appealing source for commercial applications as they have fast growth rates and do not require arable land, fresh water, or even fertilizer when compared with terrestrial plants (Lorbeer, Tham, & Zhang, 2013). The cultivation of seaweeds has been growing rapidly and is now practiced in about 50 countries, and 28.5 million tonnes of seaweeds and other algae were harvested in 2014 to be used for direct consumption, or as a starting material for the production of food, hydrocolloids, fertilizers, and other purposes (FAO, 2016). Recently, the annual global production of alginate, carrageenan, and agar which are the most important seaweed hydrocolloids for various applications across the food, pharmaceutical, and biotechnology industries has reached 100,000 tonnes and a gross market value just above USD 1.1 billion (Rhein-Knudsen, Ale, & Meyer, 2015).

Seaweeds also contain a great variety of structurally diverse bioactive metabolites not produced by terrestrial plants (Gupta & Abu-Ghannam, 2011). Seaweeds are rich in carbohydrates, proteins, polyunsaturated fatty acids (PUFAs) including omega-3 fatty acids, and minerals as well as polyphenols, pigments (chlorophylls, fucoxanthins, phycobilins), and mycosporine-like amino acids (MAAs). These compounds possess various biological functions including antioxidant, anti-HIV, anticancer, antidiabetic, antimicrobial, anticoagulant, antivirus, anti-tumor, anti-inflammatory, immunomodulatory, prebiotic and cholesterol lowering effects (Holdt & Kraan, 2011). Although seaweed bioactive compounds are attractive for commercialisation in different

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functional food and nutraceutical products, the use of seaweed for this purpose is still not extensive.

The industrial use of enzymes to extract natural compounds from terrestrial plants for food and nutraceutical purposes has been developed and reported as a promising technology with a number of benefits such as saving process time and energy and improving the reproducible extraction process at the commercial scale (Puri, Sharma, & Barrow, 2012). However, the efficiency of enzymatic extraction procedures for the retrieval of active compounds from seaweeds may be inhibited by the more complex and heterogeneous structure and composition of seaweed cell walls in comparison to plants, which have a cell wall mostly consisting of cellulose and hemicellulose.

The main cell wall and storage polysaccharides of seaweeds vary with taxonomy. The structural polysaccharides of green seaweeds are sulphated polysaccharides, such as ulvans and sulphated galactans, xylans, and mannans, while the main storage polysaccharide is starch. Brown seaweeds contain laminarins as the storage polysaccharide, and the main cell walls are composed of alginic acids, fucoidans, and sargassans. On the other hand, red seaweed cell walls consist of agars, carrageenans, xylans, water-soluble sulphated galactans, and porphyrins (mucopolysaccharides), and the main storage polysaccharide is floridean starch (amylopectin-like glucan) (Kraan, 2012; Mišurcová, 2012). This is further complicated by a tightly-integrated network of biopolymers in seaweed cell walls, mainly polysaccharides, that are associated with proteins, proteoglycans, polymeric phenols, and various bound ions including calcium and potassium (Jeon, Wijesinghe, & Kim, 2012; Synytsya, Čopíková, Kim, & Park, 2015). An example of the structure model of a brown seaweed cell wall is shown in Fig. 1. In addition, marine algae have adapted to salty environments, unlike land plants. Charoensiddhi et al. (2016b) reported that salt buffers significantly reduced the extraction efficiency of carbohydrates from brown seaweed, compared with pure water. This may be due to the ability of pure water to cause an osmotic shock and the rapid influx of water into seaweed cells, which disrupts the structural integrity of the cell wall and facilitates extraction. The high salt content in seaweeds may inhibit enzyme-assisted extraction processes, particularly those requiring buffer systems.

This review aims to critically analyse the potential role of enzyme technology in assisting with the extraction and digestion of bioactive compounds from seaweeds, and to understand the advantages, limitations, challenges, and future development directions in the application of the seaweed-derived ingredients in functional food products and nutraceuticals.

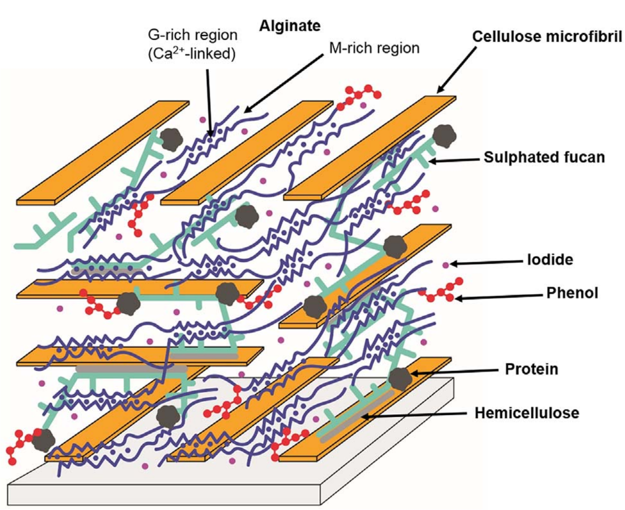

Fig. 1. Structure model of the brown seaweed cell wall; some sulphated fucans are tightly associated with cellulose microfibrils (flat ribbon-like shape), and they are embedded within the alginate network. Hemicellulose components (short chain form) link with the cellulose by hydrophobic interactions and connect with the sulphated fucans. Alginates and phenolic compounds are associated and can form high molecular weight complexes. Proteins are linked with sulphated fucans and covalently attached to phenolics (adapted from Kloareg & Quatrano, 1988; Michel, Tonon, Scornet, Cock, & Kloareg, 2010; Deniaud-Bouët et al., 2014).

2. Seaweed bioactive compounds and their potential as functional foods and nutraceuticals

Carbohydrates account for the majority of seaweed biomass. Polysaccharides and oligosaccharides have therefore been the key focus of many studies looking at seaweed-derived compounds. Aside from those, phenolic compounds and proteins from seaweeds have also been widely studied as potential functional ingredients. Therefore, these three classes will be the main focus of this review.

2.1. Polysaccharides

From an economic perspective, seaweed polysaccharides are the most important products produced from seaweeds (Michalak & Chojnacka, 2015). As the major components in seaweeds, polysaccharides account for up to 76% of the dry weight (DW) (Holdt & Kraan, 2011). Seaweeds contain a high total dietary fibre content: 10–75% for brown seaweed, 10–59% for red seaweed, and 29–67% for green seaweed. Seaweeds are particularly rich in soluble dietary fibre, which accounts for 26–38%, 9–37%, and 17–24% in brown, red, and green seaweed, respectively (de Jesus Raposo, de Morais, & de Morais, 2016). Most of these polysaccharides can be fermented by gut microbiota, which may provide a health benefit to humans through a prebiotic effect (O'Sullivan et al., 2010), which will be discussed in more detail later. Additionally, sulphated polysaccharides have shown anti-inflammatory, antioxidant, antibacterial, and immunological activity. These include fucoidans (L-fucose and sulphate ester groups) from brown seaweeds, agars and carrageenans (sulphated galactans) from red seaweeds, and ulvans (sulphated glucuronoxylorhamnans) and other sulphated glycans from green seaweeds (Synytsya et al., 2015).

2.2. Phenolic compounds

Phlorotannins are the major phenolic compounds found in brown seaweeds, constituting up to 14% of dry seaweed biomass, while other phenolic compounds are found at lower levels in some red and green seaweeds. Phlorotannins are highly hydrophilic components formed by the polymerization of phloroglucinol (1,3,5-trihydroxybenzene) monomer units with a wide range of molecular weights between 126 Da and 650 kDa. They can be categorized into four groups based on their linkages which are fuhalols and phlorethols (ether linkage), fucols (phenyl linkage), fucophloroethols (ether and phenyl linkage), and eckols (dibenzodioxin linkage) (Li, Wijesekara, Li, & Kim, 2011). Phlorotannins have been explored as functional food ingredients with many biological activities such as antioxidant, anti-inflammatory, antidiabetic, anti-tumor, antihypertensive, and antiallergic activities (Freitas et al., 2015).

2.3. Proteins

Bioactive proteins and peptides from seaweeds have been demonstrated to have antioxidant, antihypertensive, and anticoagulant activities (Harnedy & FitzGerald, 2011). Generally, a higher content of proteins is found in green and red seaweeds (10–47% of DW) compared to brown seaweeds (3–15% of DW) (Wijesekara & Kim, 2015). Important bioactive proteins from red and green seaweeds include lectin and phycobiliprotein and bioactive peptides from brown seaweeds have also been reported with angiotensin-I-converting enzyme (ACE-I) inhibitory potential (Fitzgerald, Gallagher, Tasdemir, & Hayes, 2011). Additionally, most seaweed species are a rich source of essential and acidic amino acids (Freitas et al., 2015).