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Review Article

Seaweed Antioxidants as Novel Ingredients for Better Health and Food Quality: Bangladesh Prospective

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Abstract: The known medicinal effects of seaweeds have been known for thousands of years. Also, a wide range of recent studies have described the high antioxidant capacity of a range of edible seaweeds. In this review article, the application of seaweed antioxidants in foods, food supplements, nutraceuticals and medicine is considered from the perspective of benefits to human health. The underlying physiology of algal antioxidant compounds is reviewed in the context of seaweed biology and utilization. It is found that direct consumption of seaweed products for their antioxidant composition provides a useful alternative to non-natural substances, while simultaneously providing worthwhile nutritional benefits. Economic utilization of seaweeds for their antioxidant properties is also inquired. Overall, the review confirmed that seaweeds antioxidants have huge potential in providing major health benefits through subsequent investigative studies relating to this in literature.

Keywords: Antioxidants, macroalgae, micronutrients, polyphenols, oxidative stress, ROS

1. INTRODUCTION

Seaweed is the common name for countless species of marine plants and algae that grow mostly on rocks and other plants in the ocean as well as in rivers, lakes, and other water bodies. It is chock-full of vitamins, minerals, and fiber, and can be tasty. In many countries, fresh seaweed are used as food by coastal communities, and considered as a traditional food item due to their nutritional value and characteristic [1, 2]. Seaweeds are a valuable source of proteins, polysaccharides and fiber; and they are also rich in antioxidants and micronutrients, such as vitamins and trace elements [3].

Among the most relevant components found in seaweeds are antioxidants which have attracted major interest due to their positive effects. Antioxidant vitamins and trace elements are usually obtained from the diet, since some organisms are unable to synthesize them. The beneficial effects of antioxidants are due to their capacity to scavenge and neutralize reactive oxygen species (ROS) [4] An excessive ROS production and/or low antioxidant defense can cause oxidative damage to biomolecules, such as proteins, lipids and DNA [8]. Antioxidants may reduce ROS production by scavenging free radicals through various mechanisms [4, 7].

Antioxidant has a potential to prevent cancer and cardiovascular diseases. The nature of these substances varies a lot whereas the most powerful antioxidants are polyphenols, phycobiliproteins, vitamin C, α-tocopherol and some carotenoids (xanthophylls). Furthermore, seaweed contains a high concentration of polysaccharides of various structure and functionality. The indigestible polysaccharides of macroalgae could be important sources of dietary fibres. These fibres can be insoluble such as cellulose, mannans and xylans or water soluble such as agar, alginic acid, laminarin, fucoidan and their derivatives which may potentially

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be exploited as prebiotics for applications in both human and animal health.

Seaweeds are a potentially good source of micronutrients and may be beneficial for human health, given their reportedly high vitamin and trace element content [1, 9]. Many published studies on seaweeds are focused on seaweed antioxidant vitamins and their medicinal effects. The objective of this study was to assess the potential of seaweeds as novel ingredients for better health and food quality in the Bangladesh perspective.

2. ECOLOGY AND USES OF SEAWEEDS

2.1. Ecology

Two specific environmental requirements dominate seaweed ecology. These are the presence of seawater (or at least brackish water) and the presence of light sufficient to drive photosynthesis. Another common requirement is a firm attachment point. As a result, seaweeds most commonly inhabit the littoral zone and within that zone more frequently on rocky shores than on sand or shingle. Seaweeds occupy a wide range of ecological niches. The highest elevation is only wetted by the tops of sea spray, the lowest is several meters deep. In some areas, littoral seaweeds can extend several miles out to sea. The limiting factor in such cases is sunlight availability. The deepest living seaweeds are some species of red algae.

A number of species such as Sargassum have adapted to a fully planktonic niche and are free-floating, depending on gas-filled sacs to maintain an acceptable depth. Others have adapted to live in tidal rock pools. In this habitat seaweeds must withstand rapidly changing temperature and salinity and even occasional drying.

2.2. Edible Seaweeds

Biologically, seaweeds are classified as macroalgae, with sub-classification as brown (Phaeophyta), red (Rhodophyta) or green algae (Chlorophyta). Some examples of these edible algae are outlined in Table 1. In 1994/95 over 2,000,000 tonnes (dry weight) of seaweed was harvested [10]. Much of this may be consumed as whole seaweed products, while a large proportion is also used in the production of over 85,000 tons of viscous polysaccharides for various food and industrial applications. Historically, seaweed is a readily available food source that has been consumed by coastal communities [11]. Seaweed is consumed habitually in many countries in South-East Asia [12]. However, it is not considered a habitual component of the Western diet [13].

Table 1. Eexamples of edible seaweeds.

Sub-classiicaton	Genus	Common Name
Brown Algae (Phaeophyta)	Alaria	Kelp/bladderlocks
	Himanthaia/ Bifurcaria	Sea spaghetti, fucales
	Limiliaria	Kelp/kombu/kumbu/ sea tangle
	Saccharina	Sugar wrack
	Uiularia	wakaae
	Ascophyllum	Egg wack
	Fucus	Bladder wack, rockweed
	Sargassum	Mojaban/Indian brown seaweed
	Hizikia	Hijiki
	Sargassum	Sea holly
	Diciyotales	
	Eisenia	Arame
Red algae (Rhodophyta)	Rhodymenia/ Palmaria	Dulse
	Porphyra	Noi/ haidai/ kim/ gim
	Chondrus	Irish moss/ carrigeen
	Mastocarpus/	Gigartiiia Stackhousc, Guir,
	Gracilaria	
	Asparagopsis	Limu Kohu
	Graleloupia	
Green algae (Chlorophyta)	Ulvaia/Enteroniorpha	Laver/sea lettuce/ sea grass/nori

In the West, seaweed isolates (e.g. alginate from brown algae and agar or carrageenan from red algae) are typically used industrially. Seaweed consumption has gained a measure of acceptance in some Westernized cultures such as Hawaii, California and Brazil, where there are large Japanese communities who have had a tangible influence on the local dietary practices [14, 15]. Low consumer awareness regarding potential health benefits and a lack of previous experience of seaweed challenges its use in the daily diet.

Average Fresh Seaweed composition is 13% dry matter and 87% water. The dry matter is made of proteins, lipids, antioxidants, fiber and minerals (Fig.1).

2.3. Herbalism

Alginates are commonly used in wound dressings, and production of dental molds. In microbiology research, agar - a plant-based goo similar to gelatin and made from seaweed - is extensively used as culture medium. Carrageenans, alginates and agaroses (the latter are prepared from agar by purification), together with other lesser-known macro algal polysaccharides, also have several important biological activities or applications in biomedicine.

Seaweed is a source of iodine, necessary for thyroid function and to prevent goiter. However, an excess of iodine is suspected in the heightened cancer risk and even bigger risks in post-menopausal women. Thus Japanese people, who consume a lot of seaweeds (Fig. 2), have high risk of cancer.

Seaweeds may have curative properties for tuberculosis, arthritis, colds and influenza, worm infestations and even tumors [87]. Nori, a seaweed, is known as a remedy for radiation poisoning in Japan. Seaweed extract is also used in some diet pills [16]. Other seaweed pills exploit the same effect as gastric banding, expanding in the stomach to make the body feel fuller.

3. MAJOR ANTIOXIDANT COMPOUNDS IN SEAWEEDS

Most of the Seaweeds possess considerable antioxidant activity. However, presence of antioxidant doesn't completely ensure that a beneficial response will be the result of consumption of seaweeds by humans. The potential human health advantages depend upon both the respective intake of the plants, and the bioavailability of anticipated anti-oxidant activities [17]. Some examples of perceived health benefits related to specific antioxidant compounds from seaweeds are shown in Table 3. All energy-producing metabolic processes are intrinsically driven by an electron transport chain, maintenance of which is essential to the health and integrity of an organism. The hazards of a prolonged imbalance include formation of reactive species, unstable molecules or molecular fragments that, if not neutralized, can react with non-target molecules, causing a variety of (negative) cellular impacts [18]. These may include the initiation of increased cell proliferation, mitochondrial damage, excessive DNA strand breakage and deleterious chemical chain reactions leading to lipid peroxidation, enzyme inhibition and protein degradation [4, 8]. In healthy biological systems, reactive oxygen species (ROS) are continually produced. Alscher et al [18] highlighted

Table 2. The major groups of antioxidant compounds in seaweeds with specific examples and potential algal sources for utilization.

General Category	Example Compounds	Algal Source
Carotenoids	β-carotene	Chondrus crispus [19]
	Fucoxanthin	Mastocarpus stellatus Brown algae [20]
	Antheraxanthin,	Red algae [21]
	lutenin	
Phenolic compounds	Stypodiol, isoepitaondiol	Taonia atomaria [22]
	Terpenoids	Cystoseira sp. [23]
Phycobilin pigments	Phycoerythrin, phycocyanin	Red algae in general [24, 25]
Polyphenols	Catechin, gallate	Halimeda sp. [26]
	Flavonoids Phlorotannins	Palmaria palmate [27] Fucus vesiculosus
Sulphated polysaccha-rides	Fucoidan, alginic acid,	Turbinaria conoides [28]
	Fucoidan Sulphated-galactans Galactans	Laminaria japonica [29] Some marine red algae [30] Most red algae [31]
Vitamins	Ascorbate	Chondrus crispus [19]
		Mastocarpus stellatus Sargassum sp.
	Vitamin A	Kappaphycus alvarezii [32]

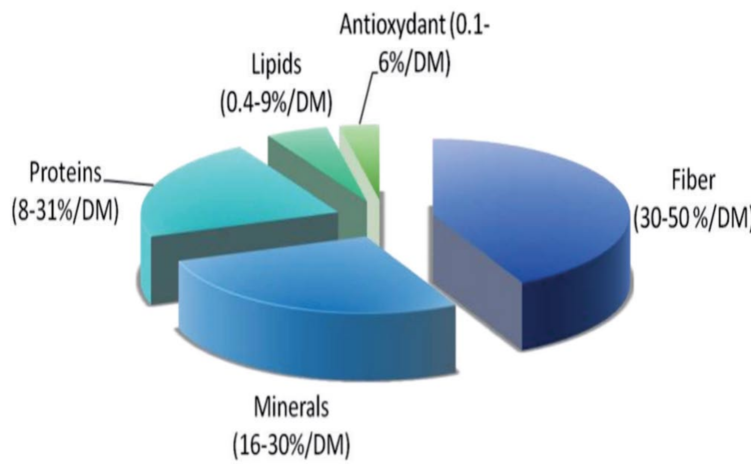

Fig. 1. Dry matter of antioxidant.

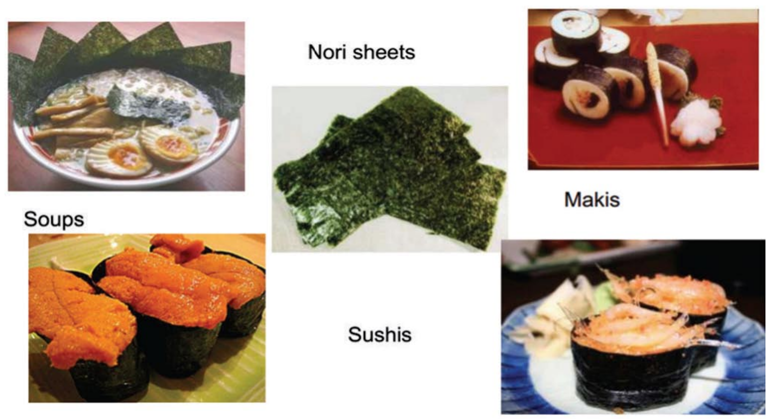

Fig. 2. Some popular seaweed based foods from Japan.

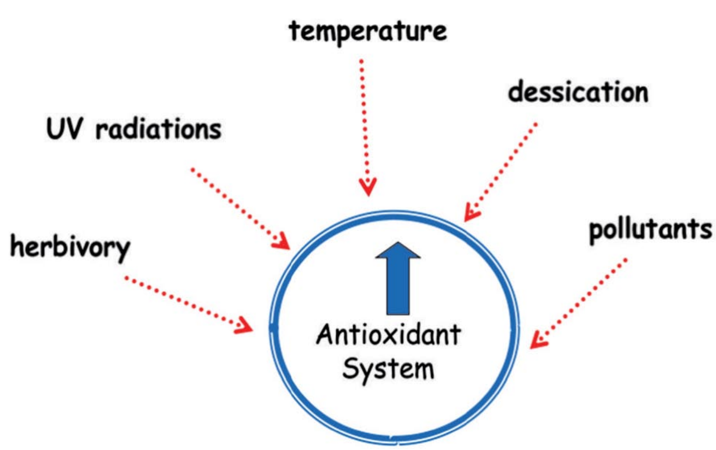

Fig. 3. Antioxidants : protective agents from various environmental stresses.

the role of reactive oxygen metabolism (ROM) in seaweeds, the stress factors that trigger it and details of the antioxidant response mechanisms.

The functional complexities associated with antioxidant defense mechanisms are diverse, and their relative importance against reactive species in vivo depends upon how, where and which reactive species (RS) is generated and what target of damage is measured. If commercialization of seaweeds for their antioxidant activity is to be considered, additional research is required to establish bioavailability of specific compounds [34] and to then guarantee production of standardized products containing them [35, 36]. This review will focus primarily on the potential health benefits and therapeutic properties purported to be associated with consuming seaweed and seaweed based products (Table 3).

Table 3. Salient examples of perceived health benefits of specific antioxidant compounds from seaweeds.

Antioxidant compound	Perceived health benefit	Reference
β-carotene, lutein	Antimutagenic Protective against breast cancer	[37] [38]
Carrageenan	Anti-tumor	[39]
Fucoidan	Anti-HIV Anticancer Protection against neurodegenerative disorder	[40] [41] [29]
Fucoxanthin	Antiangiogenic, Protective effects against retinol deficiency	[42]
Galactan-sulfate	Anti-viral	[43]
Phlorotannins	Anti-inflammatory,	[27]
	Bactericide, Hypertension Vascular chemoprotection	[44] [45]
Polyphenols	Antimicrobial	[46]

There is some concern about toxicological effects of seaweed. However, most edible seaweeds are marine algae whereas most freshwater algae are toxic. While marine algae are not toxic, some do contain acids that irritate the digestion canal, while some others can have a laxative and electrolyte-balancing effect [33].

4. SEAWEED AND HOMEOSTASIS

The stress-coping mechanisms of intertidal seaweeds are diverse and include antioxidant production, and free radical scavenging activities [19, 22, 47]. Two major stress coping mechanism include, maintaining the level of ROS and maintaining a metabolic oxidation / reduction balance. In [19], the author reported that the activity of three antioxidant enzymes, e.g. superoxide dismutase (SOD), ascorbate per-oxidase, and glutathione reductase in Chondrus crispus and Mastocarpus stellatus was greater in winter than in summer, suggesting that levels of reactive oxygen species (ROS) were also higher in winter as a result of cold stress. A gradual and continued accumulation of ROS in most macroalgae occurs as a result of environmental conditions such as dessication, freezing, low temperatures, high irradiance, ultraviolet radiation, heavy metals and salinity fluctuations [18, 19, 48, 49]. These stresses compromise photosynthesis, forming singlet oxygen that can cause damage to the photosynthetic apparatus [18]. To cope with such stresses, seaweeds deactivate the ROS by utilizing a high cellular content of antioxidant compounds, or by increasing the activity of antioxidant enzymes. This robust antioxidant potential of seaweeds helps minimize the hazardous effects of ultraviolet light or oxidation by ROS [50, 51].

Marine seaweed often experience exposure to high levels of both UVB and UVA radiation. While irradiance is required for the photosynthetic conversion of energy via light harvesting, electron transport, and ATP / NADPH synthesis, maintaining a metabolic oxidation / reduction balance is essential to the health and productivity of the system [52]. To quench the excess production of harmful radical species, seaweeds have evolved mechanisms such as photo-inhibition which leads to a slowly reversible reduction in photosynthetic rate from the maximum saturation level. This is brought about by either a reduction in the number of photosynthetic units, or by an increase in the maximum turnover time. The up-regulation of antioxidants and antioxidant enzymes, such as carotenoids and SODs and methods of cellular repair by photo-reactivation and nucleotide excision are also strategies for maintaining homeostasis [47, 52]. In a comprehensive literature review [51] identified a number of compounds in marine algae to which antioxidant activity has been attributed. These included polyphenols, phycocyanins, various enzymes, carotenoids, catechins, and ascorbic acid (Table 1).

5. ANTIOXIDANTS IN HUMAN HEALTH

ROS, along with reactive nitrogen species (collectively labelled RS) have been identified as agents in various pathogenic diseases and deleterious clinical conditions related to human health. These include cancer, cardio-vascular disease, hemorrhagic shock, AIDS, atherosclerosis, hypertension, ischemia / re-perfusion, diabetes mellitus, hyperoxaluria, neuro-degenerative diseases such as Alzheimer's and Parkin-son's diseases, rheumatoid arthritis, ageing and even male-pattern baldness [6, 8, 46, 53-54]. The defense response to excess RS metabolism can involve preventative mechanisms, repair mechanisms and up-regulation of endogenous antioxidant defenses [8].

Melanoma and non-melanoma skin cancers are among the most prevalent cancers in the human population. They are often caused by large, or prolonged doses of UV radiation that overwhelm the natural protective antioxidant capacity of the skin [55, 56]. Using whole tissue ex-tracts in a naked mouse study, polyphenols derived from certain brown algae (e.g., Ecklonia spp.; see Appendix A) and applied either topically or administered through the diet provided highly protective effects against UVB induced skin carcinogenesis [57]. The dietary effects of non-seaweed derived commercial supplements of D-alpha-tocopherol and L-ascorbic acid on the sunburn reaction in humans is evaluated as a potential elicitor for skin cancer [58]. They determined that large doses of the two antioxidants acted synergistically to protect against sunburn damage. However, the effects of long-term administration of megadoses of these anti-oxidants requires more investigation.

In a study of female nurses and dietary intake of vitamins A, C, and E, folate and certain carotenoids, [59] could not conclusively demonstrate that these antioxidants protected against basal cell carcinoma un-der their experimental conditions. More recently, it is suggested that regular dietary anti-oxidant supplementation may even be associated with harmful effects, especially in women.

However, results of a two-year cohort study refuted this conclusion and that group observed no increased melanoma risk with supplementation of comparable doses of beta carotene and selenium [60]. Although these trials relate to non-seaweed sources of antioxidants, marine macroalgae possess complements of such active compounds in various amounts and ratios [51]. Ex-periments showed human and monkey cancer cell lines were inhibited by extracts of various seaweeds, especially by the brown algae Hydroclathrus clathratusand Padina arborescences [61]. The extracts, either in a crude state or after purification, demonstrated antioxidant activity and tumor suppression in a mouse model.

Cardiovascular disease (CVD) encompasses a broad range of primary and secondary conditions and its manifestation is a major cause of death −30%worldwide [5]. Risk factors for CVD include age, male gender, elevated low-density lipo-protein cholesterol levels, low high-density lipoprotein cholesterol levels, diabetes mellitus, smoking, chronic overeating and obesity. The adverse complications of obesity and unhealthy lifestyle factors are heightened by oxidative stress [62–64].

Extensive studies in pathophysiologic research clearly suggest that CVD represents a continuum of processes which include oxidative stress, endothelial dysfunction, inflammatory processes and vascular remodeling [64]. Foods rich in antioxidants have long been touted as aids in disease prevention. [65] assessed the association between the traditional Japanese dietary patterns and CVD. They concluded that a diet high in antioxidant foods, including seaweeds, de-creased the risk of CVD mortality. Kang et al [46] undertook an eightweek human clinical trial to assess the effect of orally administered polyphenolic compounds. From brown algae on erectile dysfunction. Compounds from the five algae tested, Eisenia bicyclis, Ecklonia stolonifera, Ecklonia cava, Ecklonia kurome, and Hizikia fusi formis demonstrated positive effects against the risk factors associated with CVD. Deterioration of erectile function is a key in vivo indicator of cardiovascular health. Results from this trial showed significant improvement in erectile function and associated vascular health based on peripheral blood circulation.

Numerous studies into the synergistic effects of antioxidants and antioxidant enzymes and their interplay with RS suggest that the ideal protective mechanisms against clinical aspects of cellular damage should involve combinations, or whole suites of antioxidant compounds. Cellular homeostasis is thus more readily assured, and the possibility of profound imbalances brought about by high doses of single compounds can be effectively averted [55].

Considerable research demonstrates the human health benefits of naturally occurring antioxidant com-pounds. Claims of anti-viral, anti-inflammatory, anti-cancer, anti-mutagenic, anti-tumour, and hepatoprotective properties have been substantiated, albeit mostly from in vitro trials [27, 32, 57, 66-68] (Table 2).

6. FOOD VALUE AND HEALTH POTENTIAL OF SEAWEED

Seaweeds play an important role in this business which remains a growing, vibrant, and important production sector for healthy human food [90]. Intensive marketing programs and the popular health food press has recently raised the public profile of seaweed antioxidants considerably. However, clinical trials must be under-taken and publicized in order to educate and maintain consumer confidence. Aside from the direct health benefits, antioxidants from natural sources that combat lipid oxidation of foods, especially during processing and storage, are in high demand. The current use of synthetic antioxidants such as butylated hydroxyanisole, butylated hydroxy-toluene, and propylgallate is strictly regulated in many countries because they can in themselves pose potential health hazards, including carcinogenic effects [61, 69].

As part of a balanced diet, seaweeds can provide fibre, protein, minerals, vitamins and low fat carbohydrate content [27]. Seaweeds contain significant amounts of insoluble and soluble polysaccharides, and hence offer potential for fortification of food products with Dietary fibrs (DF) for technological and physiological purposes [89]. *The versatil*ity of seaweed as food allows consumption in fresh, dried, pickled or cooked forms and as a component in a wide assortment of other products. However, Seaweeds are eaten as whole foods by a relatively small percentage of the world population [27], in a relatively limited geography. Japanese form the largest consumer group eating on average, 1.6 kg dry weight per person, per year and they eat seaweed in great variety (fig.2). Scientists in Asian countries have demonstrated the health benefits derived from eating seaweeds [70], and the official Japanese Food Guide (see [71] for discussion) promotes seaweed as a nutritional foodstuff. Research is advancing into using marine macroalgae for production of novel foods, such as health beverages and processed meat products.

Several medicines and nutrients based on seaweeds are already available in market (Fig. 4, 5). The objective is to take advantage of their naturally occurring antioxidant compounds and other nutritive components [72]. This is a more holistic approach, based upon the observation that supplements of manufactured vitamins do not significantly decrease levels of oxidative damage in well-nourished individuals who already eat a balanced diet [5-6] . The extracted brown algal polyphenols from Eckloniasp decreases UVB-induced skin tumor development in mice regardless of whether the polyphenols were administered topically, or ingested as a dietary component, suggesting that the viability of these seaweed based antioxidants is unaffected by digestive processes [57]. A growing awareness of the functionality of

Fig. 4. Some Popular Seaweed based nutrients available in the market.

Fig. 5. Some medicines based on seaweed antioxidants.

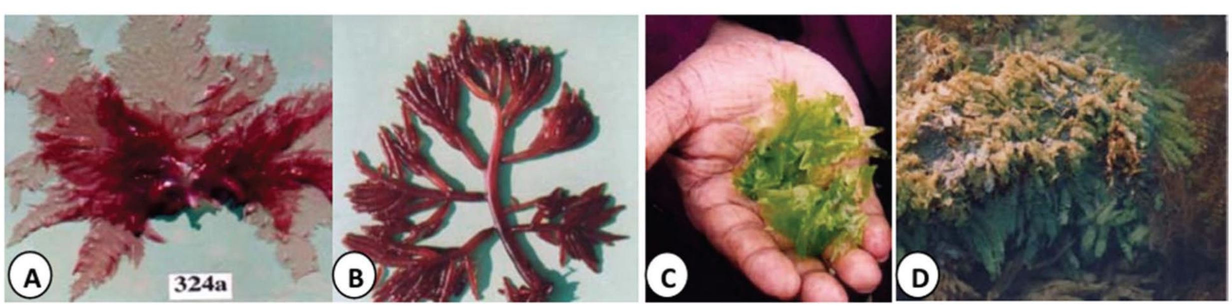

Fig. 6. Edibleseaweeds: (A) *Halymenia floridana*; (B) *Chrysymenia enteromorpha*; (C) *Ulva lactuca*, var. Rigidaand; (D) *Caulerpa racimosa*.

seaweeds beyond basic nutritive value will enhance the development of science and technology in this area of study.

7. ANTIOXIDANTS IN SEAWEEDS EXTRACTED USING COMPRESSED FLUIDS

In the search for feasible new sources of natural antioxidants that can be used in the food industry, seaweeds may be suggested as possible raw materials. These organisms are widely known and consumed in certain countries, and numerous health benefits have been associated with their use. Different compounds with antibacterial, antiviral and antifungal activity can be found in these types of organisms [73], along with compounds with antioxidant activity. Multifunctional antioxidant potential of several brown and red edible seaweeds has been evaluated in organic and aqueous soluble extracts and suitable sources of phytochemicals from seaweeds for further nutraceutical applications has been reported [88].

Spirulina is a blue-green microalga from Cyanobacterium gender. It is well known by its high content in proteins. Among them, phycobili proteins are known by its pharmaceutical and antioxidant properties. These proteins were characterized by using CE-ion trap-MS and CE-time of flight-MS. Later, the usefulness of CE-MS to monitor and optimize the pressurized liquid extraction of proteins from Spirulina platensis microalga was demonstrated [74]. The combined use of PLE and CE-MS allowed the attainment of extracts rich in phycobiliproteins in short extraction times (namely, yields of 20% can be obtained in less than 2 h under the optimum PLE process in an automatic way).

Moreover, Spirulina has been studied as an alternative source of functional ingredients, especially antioxidants. [75] studied the possibilities of using Spirulina supercritical extracts as both, antioxidants and antimicrobials. In this case, the best antioxidant extract was obtained in the first fraction when using intermediate pressures and temperatures (220-320 bar, 55 °C), with CO2 plus 10% ethanol as cosolvent, whereas higher pressures and temperatures (320 bar, 75 °C) were needed when pure CO2 was used. In order to provide a more in depth characterization of the antioxidant fraction, we used HPLCDAD-MS/MS with two different interfaces (ESI and APCI) that revealed the presence in the extracts of several carotenoids previously identified in Spirulina platensis microalga along with chlorophyll a and some degradation products [76]. Also, the structure of some phenolic compounds could be tentatively identified. Moreover the enrichment in vitamin E of extracts from microalga Spirulina platensis was studied [75]. The optimal conditions for the extraction of vitamin E from Spirulina platensis were achieved working at maximum temperatures, being the optimum value predicted, by using advanced statistical tools, of 29.4 mg/g extract which implies a tocopherol enrichment of more than 12 times the initial concentration of tocopherol in the raw material.

But also the subcritical fluid extraction of Spirulina has been studied in our research group. Different extraction temperatures (115°C and 170°C) and four different solvents (hexane, light petroleum, ethanol and water) were tested using extraction times ranging from 9 to 15 min. The antioxidant activity of the different extracts was determined by means of an in vitro assay using a free radical method. Moreover, a new and fast method was developed using micellar electrokinetic chromatography with diode array detection (MEKC-DAD) to provide a preliminary analysis on the composition of the extracts. It was observed that the optimum conditions that maximize yield and minimize EC50 depend on the polarity of the solvent used to perform the extractions. Extraction temperature had an enormous influence in both responses while the effect of extraction time was almost negligible. Ethanol was finally selected as the extracting solvent for its GRAS (Generally Recognized as Safe) status and because it provided higher yields with medium antioxidant activities [74]. Also, a new procedure was developed to separate and characterize antioxidant compounds from Spirulina platensis microalgae based on the combination of pressurized liquid extraction(PLE) and different chromatographic procedures, such as TLC, at preparative scale, and HPLC-DAD [77]. TLC analysis of the best ethanolic extract obtained at 115°C for 15 min was carried out and the silica layer was stained with a DPPH solution to determine the antioxidant activity of different chromatographic bands. Next, these colored bands were collected for their subsequent analysis by HPLC-DAD, revealing that the compounds with the most important antioxidant activity present in Spirulina extracts were carotenoids, as well as phenolic compounds and degradation products of chlorophylls.

Another important microalgae well known by its antioxidant properties is *Dunaliella salina* [78]. This microalga has been studied in our research group considering both, supercritical fluid extraction and pressurized liquid extraction. In terms of PLE, the optimization of the extraction of antioxidants [74] and antimicrobials was carried out using experimental design with three different solvents (hexane, ethanol, and water) and two main factors (extraction temperature (40, 100, and 160°C) and extraction time (5, 17.5, and 30 min)). As response variables, the extraction yield (percent dry weight/initial weight) and the antioxidant activity of the extracts, determined using the trolox equivalent antioxidant capacity (TEAC) method, were considered. The parameters of the model were estimated by multiple linear regressions. Results showed that the extraction temperature was the factor having the strongest influence (positive) on the two response variables. The best yields were obtained with ethanol at the higher extraction temperature and time tested. Besides, although hexane extracts provided the best antioxidant activity, ethanol extracts were also very active. The chemical characterization of ethanol extracts was carried out using HPLC-DAD, and attempts were made to correlate their chemical composition with the antioxidant activity measured. Results pointed out that the extracts contained, besides all-trans-ß- carotene and isomers, several different minor carotenoids that seemed to make a strong contribution to the antioxidant activity of the extracts. By using supercritical CO2 different compositions of ß-carotene isomers were identified in the extracts by using HPLC-DAD. Also, antioxidant activity of the extracts was measured using a trolox equivalent antioxidant capacity (TEAC) assay. Higher yields were obtained at high pressures and low temperatures, that is, at higher CO_2 densities. Attempts were made to correlate the antioxidant activity of the extracts with their chemical composition by means of principal component analysis. A certain relationship was found between their antioxidant activity and the isomeric composition of ß-carotenes. As a result, an original equation was proposed to predict the antioxidant activity of extracts from *D. salina* in terms of the ratio 9-cis-ß-carotene/all-trans-ß-carotene, the concentration of a -carotene, and, especially, the concentration of 9-cis-ß-carotene.

8. SEAWEED AS A SOURCE OF OMEGA FATTY ACIDS

Apart from the abundance of minerals in seaweeds, it is their low, but very distinctive, fat content that attracts our attention. It can vary quite widely across the species, for example, being on the order of1-2% in dulse and konbu and up to 4-5% in wakame. Within a given species, it also depends on the time of year and the place where it grows. Most of the fats in seaweeds are made up of fatty acids with long hydrocarbon chains.

There are two relationships that are particularly interesting, namely, the relationship between the saturated and the mono- and polyunsaturated fats and that between omega-3 and omega-6 tatty acids.

A common trait of all seaweed species is that they contain about twice as much saturated as monounsaturated fat, but the combined total of unsaturated fat is greater than that of saturated fat. The crucial difference is the content of polyunsaturated fats, especially the super unsaturated fatty acids EPA (eicosapentaenoic acid) and AA (arachidonic acid), which are omega-3 and omega-6 fatty acids, respectively. The polyunsaturated fats make up 30-70% of the total fat content, with omega-3 and omega-6 fatty acids accounting for most of it. It is an interesting point of comparison that no plants contain AA.

The most noteworthy aspect of the fat composition of seaweeds is the balance between the essential tatty acids omega-3 and omega-6. Essential fatty acids are those that our body cannot make and, therefore, has to ingest.

In the different species of seaweeds, the proportion of omega-3 to omega-6 typically falls between 0.3 and 1.8, with variations within a particular species, again dependent on where the seaweeds are grown and the time of year. From a nutritional standpoint, this is close to the ideal proportion for a human diet. Some nutritionists cautiously recommend that the figure should be about 0.2, but others think that it should be close to 1. , These recommendations should be contrasted with the proportion of 0.05 to 0.1, which is typical of the aver-age Western diet. As a consequence, this diet is far too rich in omega-6 fats and far too poor in omega-3 fat's.

Whereas seaweeds contain fair amounts off EPA (eicosapcntacnoicacid), the content of the other important omega-3 fatty acid found in the various seaweed species, DHA (docosahexaenoic acid), is often too small to be measured. This is in contrast to fish, which can have large quantities of both EPA and DHA. These two substances generally make up 30% and 20%, respectively, of the content of the fish oil sold as a dietary supplement. Unlike the macroalgae, the microalgac contain significant quantities of DHA in addition to FPA.

The omega-3 fatty acids found in fish and shellfish are not produced by these organisms themselves but obtained via the food chain from algae. Sterols are a particular type of fat, which seaweeds, like other higher organisms, utilize to strengthen their cell membranes. Two of these sterols, fucosterol and desmosterol, are elated to cholesterol. 'I he brown algae have an especially large sterol content, up to ten times as great as that in red algae. Normally, humans cannot make use of these seaweed sterols and less than 5% of the total is absorbed in the intestines. At the same time, however, they act to reduce the amount of cholesterol that is absorbed from other food. Studies have indicated that seaweed sterols help to decrease free and bound cholesterol levels and, in addition, to lower blood pressure.

Seaweeds contain up to 2% of dry weight of lipids and much of this lipid content is made up of polyunsaturated fatty acids (PUFA) [79, 80]. Table 4 illustrates that PUFAs account for almost half of this lipid content, with much of it occurring in the form of omega-3 and omega-6 lipids. The omega-3 to omega-6 ratio is closely matched, a factor that has been found to be important in a balanced diet. Both omega-3 and omega-6 fatty acids are essential, i.e., humans must consume them in the diet. Omega-3 and omega-6 compete for the same metabolic enzymes; thus, the omega-6:omega-3 ratio will significantly influence the ratio of the ensuing eicosanoids. This means omega-3 and omega-6 should be consumed in a balanced proportion, with the ideal ratio of omega-6:omega-3 ranging from

Table 4. Polyunsaturated fatty acid (PUFA) contents of seaweed*.

	Fatty Acid (% of Total fatty acid content)					
Seaweed	**Saturated**	**Monounsaturated**	**PUFAs**	**ω6 PUFAs**	**ω3 PUFAs**	**ω6:ω3 Ratio**
Himanthalia elongata	39.06	22.75	38.16	15.08	18.7	0.81
Laminaria ochroleuca	33.82	19.23	46.94	20.99	25.08	0.83
Undaria pinnatifida	20.39	10.5	69.11	22.1	44.7	0.49
Palmariaspp.	60.48	10.67	28.86	2.14	25.52	0.13
Porphyraspp.	64.95	18.91	16.1	7.97	7.2	1.21

*__Source__: Sanchez-Machado et al [80].

3:1 to 5:1. Seaweeds contain many essential fatty acids, which may add to their efficacy as a dietary supplement or as part of a balanced diet [81]. Seaweeds are also normally tested after drying, but the effects of other types of food processing, such as canning, have been found to have a detrimental post-processing effect on fatty acid levels [80].

9. SEAWEED CULTURE: BANGLADESH PERSPECTIVE

The sophisticated technology and financial investment required to enter the emerging marine biotechnology market, results in dominance by wealthy countries. However, a focus on marine resources involving low-cost technology requirements, such as seaweed, provides an opportunity for developing countries like Bangladesh to access this emerging market. Seaweed aquaculture, growing at 7.5% per year, is becoming an important component of marine aquaculture, propelled by a diversification of the demand for seaweed products from traditional uses to bio-energy, cosmetics and biomedicine applications [91].

In Bangladesh, the natural abundance of commonly cultured tropical seaweeds of commercially important species is reported to be very low. Only small portion of the south-eastern part of the mainland covering only 30 km of the coast line in Ukiya and Teknaf and St. Martin Island have got rocky substratum and are suitable for naturally growing sea weeds.

Seaweeds are found mainly in the St. Martin Island and in mangrove forests. Seaweeds, having protein, amino acids, vitamins and minerals, are used as different purposes such as fodder, fertilizer, human food, industrial and pharmaceutical raw materials etc. Seaweeds reduce high blood pressure,

Table 5. Status of seaweed resources in Bangladesh.

S. No.	Species Scientific name	Abundance in Different Months					
		Type	Dec.	Jan.	Feb.	Mar.	Apr
1.	*Actinotrichia fragilis*	RSW	+	+	+		
2.	*Asperogapsis taxiformes*	RSW		+	++	++	+
3.	*Calliblepharis sp.*	RSW	++	+			+
4.	*Caulerpa sp.*	RSW	+	+	+	+	+
5.	*Ceramium sp.*	RSW	+		+	+	+
6.	*Chrysymenia sp.*	RSW		+	+	+	+
7.	*Cthonoplastis sp.*	RSW	+	++	++	++	++
8.	*Dictyota sp.*	BSW	+	+	+		+
9.	*Eucheuma sp.*	RSW		+			
10.	*Galauxara sp.*	RSW	+	+			+
11.	*Halymenia sp.*	RSW		+	+	+	+
12.	*Hydroclathara sp.*	BSW	++	+	+	+	+
13.	*Hypnea sp* (a)	RSW		+	+	++	++
14.	*Hypnea sp* (b)	RSW		++	+++	+++	+++
15.	*Hypnea sp* (c)	RSW		++	+++	+++	+++
16.	*Hypnea sp* (d)	RSW		+	++	++	++
17.	*Liagora sp*	RSW	+	+			+
18.	*Lobophara sp.*		+	+	+	+	+
19.	*Padina sp.*	BSW	+	+	+	+	+
20.	*Sargassum* (2 sp).	BSW		++	++	++	++
21.	*Scinnaia complanta*	RSW	+	+			+
22.	*Vanvorstrea coccinea*	RSW	+				

Source: Sarker [92]
RSW = Red Seaweeds; BSW = Brown Seaweeds
+ Normally available; ++ Moderately available; +++ Commercially available

cholesterol, and prevent strokes. They can also be used as remedy for rheumatism, diarrhea, and for controlling the growth of tumors. Study [82] and [83] reported 133 species of seaweed from the St.Martin's Island. [84] made 4 new records of seaweed from the coast of St. Martin's Island. And now more than 140 species of seaweed still found in the coastal area of Bangladesh. There are red and brown seaweed resources in Bangladesh. Among them the 5 most commercially important and available species of Bangladesh are *Hypnea sp., Cthonoplastis sp., Aspergapis taxiformes, Calliblepharis sp., Sargassum sp*.

Bangladesh have a variety of edible marine algae, such as *Halymenia floridana* (Fig. 6A), *Chrysimenia enteromorpha* (Fig. 6B), *Ulva lactuca var. rigida* (Fig. 6C) and *Caulerpa racimosa* (Fig. 6D). Researches should be carried out for growing these algae along the coastal belt starting from Teknaf to Sundarbans, using above mentioned algae as seed materials (inocula) from St. Martin Island adopting Chinese/Japanese technology. The St. Martin Island is being used as a cultivation site by most of the marine researchers of Bangladesh. To explore the full seaweed potential of Bangladesh, the south coastal belt starting from Teknaf to Sundarbans should be used, as the cultivation area of St. Martin Island is very small, compared to the population of Bangladesh.

Drifted seaweeds in the SMI are collected, dried and sold to neighboring country by local people. The people of St. Martin collect drifted seaweeds during Jan. to April, dry them in sun (Fig. 7A-B) and sell to Myanmar, at the rate of tk 5-8 per kg. The amount of harvest varies from 4-6 ton per day, being highest in March. There is a very good potentiality of cultivating edible seaweeds (which are present in the St. Martin) in the vast coastal areas of Bangladesh.

In recent years, sea weed cultivation has been an issue of much importance all over the world. Culture of sea weed is a maiden concept for the people of Bangladesh. The people of Bangladesh are very new about the systematic and cultivator techniques of seaweed. The red sea weed Hypnea sp. is widely distributed in the intertidal and sub-tidal water of St. Martin's island. A recent trial on Hypnea sp. cultivation in the St. Martin's island, funded by the SUFER (Support for University Fisheries Education and Research) project of Department for International Development (DFID), and Ministry of Science and Information and Communication Technology (MSICT), Government of Bangladesh, technically assisted by the Institute of Marine Sciences (IMU), University of Chittagong, has opened a new avenue in the aquaculture industry of the country.

Natural status quo and research endeavor show that Hypnea sp. (commonly known as maiden hair) is a fast growing species, found attached to objects like corals, stones, boulders, rope, bamboo, and even to other seaweed. One of the magnificent achievements of this research (which was carried out for the first time in Bangladesh) is that a number of locally adaptive seaweed culture technologies have been developed, which are easy to set-up and very much within the reach of the poor farmer. Another prominent feature of these seaweed culture technologies is that all the components used to prepare the culture systems are organic and eco-friendly.

However, this edible plant is used to prepare jellies. It has a mild flavor and delicate texture. Hypnea is high in carrageenan, which can thin the blood and lower cholesterol, helping to prevent strokes. It is also used against diarrhea. Compounds that stop the growth of tumors have been found in Hypnea. This sea plant also can be used as raw materials for pharmaceuticals and industrial products, animal feed or fertilizer.

A number of species of *Hypnea* sp. have so far been recorded from the cost of St. Martin's island. These are: *Hypnea boergesenii*, *H. coenomyce, H. musciformes, H. valentiae, H. cornuta*. Pertinently, *Hypnea sp*. culture in the coastal water of this country (especially along the inshore water of St. martin's Island) holds good promise for the farmers and private entrepreneurs. Already there exists a

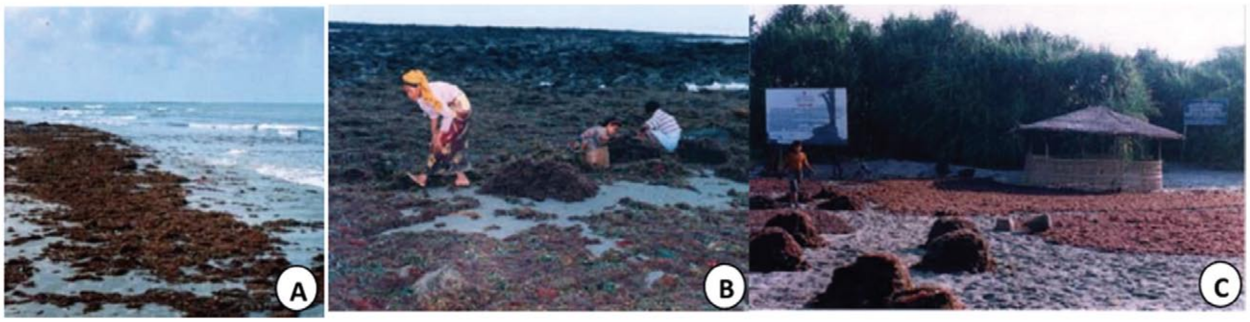

Fig. 7a-c. Seaweed Harvesting: A. Drifted seaweeds on the West coast of SMI. B. Members of a family collecting the seaweeds (mainly Hypnea and other red algae). C. Sun drying of seaweeds on the sandy beach.

Fig. 8a. Cultivated Hypnea sp. ; Fig. 12b. Growth observation *Hypnea sp.* on net in the Coastal water of St. Martin's Island.

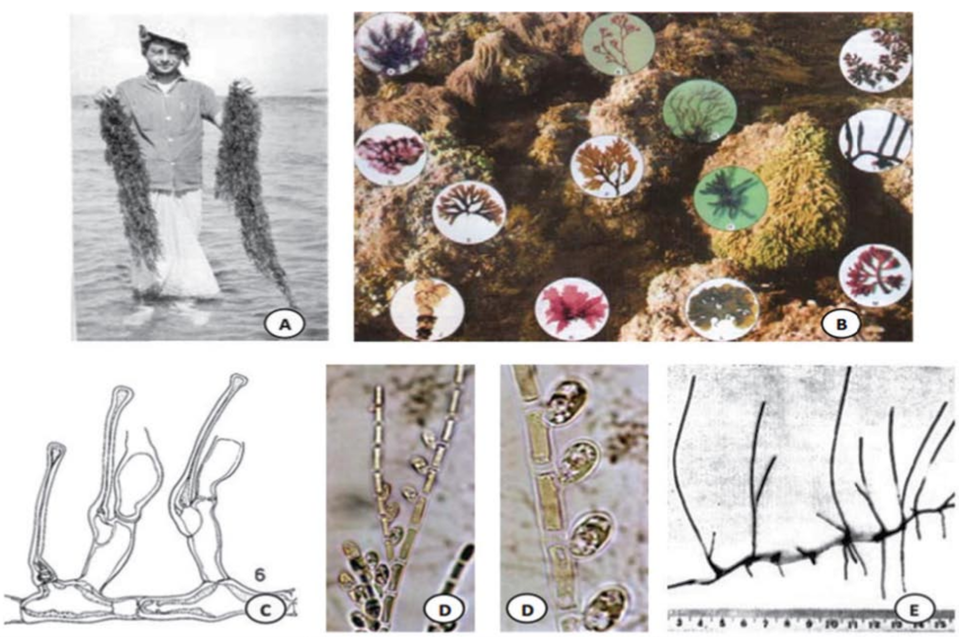

Fig. 9. Seaweeds and a "Sea grass" in the SMI. (A). A view of the seaweed flora in the west coast of SMI (B),1 March 1995 (right) Acrochaetium bengalicumIslametAziz (C). A. nurulislamiiA. Aziz et S. Islam (D) and Halodule uninervis Forskal (E).

seaweed marketing chain in the St. martin's Island. If initiatives are taken by the government and also by the privet agencies, a legal and stable marketing channel for seaweed can be established in the country.

In the marine environment it is the hard rocks, boulders, etc. where marine algae (seaweeds) grow. Thus it is the SMI, extended part of Teknaf and Inani beach where the seaweeds grow abundantly. All these collections and studies were made in the littoral zone (area exposed during low tide) of the St. Martin Island. But it appears that a lot more seaweeds occur in the sub-littoral zone of the area mentioned. The island is very rich in seaweeds and [85] have recorded two new species- Acrochaetium bengalicumIslam etAziz and A. nurulislamiiA. Aziz et S. Islam (Fig. 9C-D). Only two marine angiosperms, such as Halodule uninervis andHalophyla decipienswere recorded from the SMI (Fig. 9E).

Bangladesh can earn huge foreign exchange by exporting seaweed said Dr. Mohammad Zafor, prof of Institute of Marine Sciences and Fisheries of Chittagong University. In a research paper Dr. Zafar mentioned that, worldwide seaweed has been considered as one of the important economic resources [84]. It is used as industrial raw materials and edible item for human in many countries. It is reported that seaweed plays significant role in the economy of Japan. There are more than 140 species of seaweed found in the costal water of Bangladesh, especially in the St. Martin's Island. But these resources are a vital for maintaining ecological balance. Considering the nutritional and medicinal values of seaweed as well as it's possibility of being used as a human food, an attempt was taken to carry out research on seaweed cultivation in the inter tidal water of St. Martin's Island. If the initiative is taken to materialize this research breakthrough, coastal poor people can improve their economic and livelihood condition. Mass production of seaweed adds a new export item for Bangladesh.

10. CONCLUSIONS

The potential for commercialization of seaweed based, antioxidant compounds as food supplements or nutraceuticals ensures continued dedicated efforts to eventually develop functional, condition-specific, antioxidant products. Seaweeds are indeed suitable natural agents for producing and delivering these products based on the multi-functional aspects of secondary seaweed metabolites and the presence of a wide variety of associated non-toxic antioxidants [63, 86]. Such relatively non-toxic associations can enhance the synergistic effects of multiple antioxidants and provide buffering capacity if necessary for those compounds which may have been intentionally increased. Algae are efficient harvesters and proficient managers of electromagnetic energy and as highly nutritional food-stuffs, can be regularly consumed without fear of metabolic toxicities. We advocate the regular consumption of a variety of marine algae, primarily for their anticipated in vivo antioxidant capacities and associated synergistic effects. Rather than striving for targeted cause and effect mechanisms, which are developed in isolation and are generally fraught with the complexities of endogenous cellular activities, a diet rich in a diversity of seaweeds would provide healthy, whole food sustenance and competent antioxidant balance. Ideally, algae destined for human use would be derived from managed, sustainable sources, thus ensuring traceability and a high level of food safety and security. Core research avenues should include investigations into the bioavailability of seaweed based antioxidants [34]. Organisms, in general do not normally function in isolation at any metabolic level, and oxidation-reduction reactions and subsequent cellular exposures to RS are fundamental to all living things. It is the imbalance of RS that can compromise homeostasis, and it is a legion of relevant seaweed antioxidants that may mitigate, and even help reduce the impacts of cellular impairment.

Seaweed cultivation holds good promise in the coastal water of Bangladesh. Like other countries of the world, Bangladesh can boost its economic dimension through commencing seaweed cultivation. People should include it in their daily food ration. Nutritional deficiency can well be met, if the people of Bangladesh will change their habit and consider seaweed as a comestible commodity. To materialize the seaweed research outcome, patronization from government sources and private entrepreneurs is a demand of the time.

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