CHAPTER-III

LITERATURE REVIEW:

Marine environment occupies about two third of the earth’s surface and the future of the world population depends mainly on this environment for its food, industrial raw materials and other live saving drugs (Santhanam et al., 1990). Seaweeds or marine macro algae are plants and ecologically, commercially valuable living marine resources that belong to the primitive groups of non-flowering plants without true root, stem and leaves in the division Thallophyta of Plant kingdom. Seaweeds are categorized into four groups such as Chlorophyceae (Green seaweeds), Phaeophyceae (Brown seaweeds), Rhodophyceae (Red seaweeds) and Cyanophyceae (Blue green algae) especially on the basis of pigments, stored food materials, morphological and anatomical characters. (Kaliaperumal, 2009).

Diversity of seaweed:

About 6,000 species of red seaweeds (Rhodophyceae), 2,000 species of brown seaweeds (Phaeophyceae) and 1,200 species of green seaweeds (Chlorophyceae) occur globally of which approximately 220 species are economically important. The world production of seaweeds is estimated as 21, 65,675 mt/year and India is contributing only 3,003 mt/year (Kaliaperumal, 2009). The total standing crop varied from 6,77,308.87 to 6,82,758.87 tons (fresh weight) along the Indian coast, while the world natural resources were estimated to be 2,00,54,590 tons (fresh weight) (Zemke-white and Ohno, 1999). There are about 8,000 species of marine macro algae along the world’s coast line and they may extend as deep as 270 m (Luning, 1990). India has a vast coastline of more than 7000 km, which harbours a large diversity of marine algal species (Sahoo et al., 2003). The seaweed flora of India is highly diversified and
comprises mostly of tropical species but boreal, temperate and subtropical elements have also been reported. Many of the rocky beaches, mudflats estuaries, coral reefs and lagoons along the Indian coast provide ideal habitats for the growth of seaweeds (Rao and Mantri, 2006); rich seaweed beds occur around Visakhapatnam in the eastern coast, Mahabalipuram, Gulf of Mannar, Tiruchendur, Tuticorin, Kanyakumari and Kerala in the southern coast; Veraval and Gulf of Kutch in the western coast; Andaman and Nicobar Islands and Lakshadweep (Kaliaperumal and Pandian, 1984; Selvaraj and Selvaraj, 1997; Sahoo, 2001; James et al., 2004; Manilal et al., 2009; Christobel and Jeeva, 2009; Paul and Raja, 2011; Jeeva et al., 2012; Satheesh and Wesley, 2012). Distribution of seaweed species in India are, Gujarat, Maharashtra, Goa, Karnataka, Kerala, Lakshadweep, Tamil Nadu, Andhra Pradesh, Orissa, West Bengal and Andaman and Nicobar Islands. India presently harvests only about 22,000 tonnes of macro-algae annually compared to a potential harvest of 870,000 tonnes, a mere 2.5 per cent (NAAS, 2003).

Gulf of Mannar marine province is situated between India and Sri Lanka. It runs on its Indian side at its head from Pamban Islands, southern coastline which includes the famous pilgrim centre Rameshwaram to Kanyakumari. The Gulf of Mannar reserve was one of the six areas chosen on the basis of seriousness and diversity of threats on one hands and the richness of biological wealth on the other. It has unique ecological systems mainly contributed by coral reefs (as spawning grounds), sea grass beds (as nursery grounds) and mangroves (as shelter and feeding grounds) for many species of commercially important fin fish and shell fish. There are 21 Islands which extend between 8° 47’ to 9° 15’ N latitude and 78° 12’ to 79° 14’ E longitude from Pamban to Thoothukudi and these Islands are arranged northeast from Thoothukudi.
Several species of green, brown, red and blue algae with luxuriant growth occur along the south coast of Tamil Nadu from Rameswaram to Kanyakumari. Diversity and seasonal distribution of seaweeds are known from different coastal regions of Gulf of Mannar (Chacko et al., 1955; Umamaheswara Rao, 1969, 1972, 1973; Subbaramaiah et al., 1977; Kalimuthu et al., 1992; Kaliaperumal et al., 1995, 1996; Sreekala Devi et al., 2004; Domettila and Jeeva, 2013; Mary Josephine et al., 2013). The total standing crop of seaweeds in the intertidal region of Tamil Nadu was estimated as 22,044 tons (fresh weight) in a potential area of 9891.35 ha of the 20,000 ha total area surveyed. As of now, among the coastal states and union territories, Tamil Nadu ranks first in resource potential (Subba Rao et al., 2006).

The southern most Island (Hare Island) is now connected with the main land following the construction of the major port. Hare Island is an island which lies adjoining the Tuticorin port. It is a very good picnic spot for holiday seekers and the domestic tourist. Muyal Theevu is also called as Hare Island, situated 20 km away from Thoothukudi city. Muyal Theevu is known for its healthy ecosystem of coral, seaweeds and sea grasses. Some of the species like Ulva lactuca, Ulva reticulata, Enteromorpha compressa (Chlorophyceae), Spathoglossum asperum, Stoechospermum marginatum, Turbinaria ornata, Turbinaria conoides (Phaeophyceae) and Hypnea musciformis, Acanthophora spicifera, Corynomyorpha prismatica and Kappaphycus alvarezii (Rhodophyceae) were found most abundant. It is situated 4.5 km away from Tuticorin Port Beach with a variety of substrata-rocky, silty, muddy and sandy. The diversity of seaweed species of Hare Island was reported by (Sarojini Menon et al., 1993; Mary Josephine et al., 2013)
Seaweeds as food:

Seaweeds have been traditionally used in human and animal nutrition. Seaweeds are rich source of bioactive compounds such as carotenoids, dietary fiber, protein, essential fatty acids, vitamins and minerals. Important polysaccharides such as agar, alginates and carrageenans obtained from seaweeds are used in pharmaceutical as well as in the food industries (Bocanegra et al., 2009). Seaweeds have been used as a part of human diet in China, Japan, Thailand and South Korea for many years (Mabeau and Fleurence, 1993; Wong and Cheung, 2000). Some seaweeds are generally suitable for making cool, gelatinous dishes or concoctions (Ito and Hori, 1989; Manivannan et al., 2009). In general, seaweeds are considered as low calorie food item, but rich in vitamins, minerals and dietary fibre (Ito and Hori, 1989). Seaweeds are also utilized as animal feed ingredient, raw material for fertilizer and as well as in various industrial applications (Mabeau and Fleurence, 1993; Fleurence, 1999; Rupérez, 2002; Kumari et al., 2010). Marine algae have been utilized in Japan as raw materials in the manufacture of many seaweed food products, such as jam, cheese, wine, tea, soup and noodles and in the western countries, mainly as a source of polysaccharides for food and pharmaceutical applications. Human consumption of green algae, brown algae and red algae were 5, 66.5 and 33 per cent respectively and it was high in Asia mainly in Japan, China and Korea (Dawes and Mathieson, 2003). Use of seaweeds as food has been traced back to the fourth century in Japan and the sixth century in China. Today those two countries and the Republic of Korea are the largest consumer of seaweeds as food. Japanese have been consuming sea vegetables for more than 10,000 years. In ancient Chinese culture sea vegetables was noted as a delicacy. Some species of seaweeds like nori (*Porphyra sp*), wakame (*Undaria*)
were used in every day cookery in Japan. The most important food species in Japan are nori, Kombu (*Laminaria japonica*) and wakame. The mean intake of seaweed in Japanese diet has been reported to be approximately 7g/person/day (CFSAN, 2003). Low income families who reside near tidal areas may rely exclusively on ocean resources and eat seaweeds as part of their regular diet (Ostraff, 2006). Red algae like *Porphyra* and nori are used in soups and salads. There are many types of seaweeds available commercially in the Malaysian market. Only four types are commonly used for food preparation in the Japanese restaurants in Malaysia namely nori (*Porphyra* sp.), kumbu (*Laminaria japonica*), wakame (*Undaria pinnatifida*) and hijiki (*Sargassum fusiforme*). Nori has the highest amount of protein compared to the other types. Wakame has the highest amount of calcium. Sea lettuce (*Ulva lactuca*) is very high in iron. Hijiki (*Sargassum fusiforme*) is high in calcium and fiber. Dulse (*Rhodymenia palmata*) is rich in vitamins B₆ and B₁₂. Almost all types contain iodine, sodium, potassium, magnesium, copper, zinc, and vitamins A, B, C, E and K. (Amin Ismail and Tan Siew Hong, 2002). Nori is the Japanese name for edible genus of red seaweed *Porphyra*, which includes species like *P. yezoensis*, *P. umbilicalis*, *P. haitaensis* and *P. tenera*. Nori has about one-third protein and one-third dietary fiber and contains high proportions of iodine, vitamins A, B, and K and iron. *P. yezonsi* has been found to contain sufficient vitamin B₁₂ to prevent vitamin B₁₂ deficiency in rats. (Takenaka *et al.*, 2001; Fumio Watanabe, 2007). Laver (*P. laciniata*) is reddish purple, crinkly seaweed that is gathered off the shores of British Isles. This ancient food has been valued for centuries by the Scots, Welsh, and Irish. When cooked, it turns to greenish brown. In Scotland, it is dipped in oat meal and fried or made into a puree. The water in which laver is cooked turns into a thick jelly that, when combined with potatoes and other vegetables, makes a delicious and
healthy soup. (Teas, 1981). Irish moss is another red alga used in producing various food additives along with *Kappaphycus*. Alginate, agar, carrageenan and gelatinous substances are collectively known as hydrocolloids or phycocolloids and have attained commercial significance especially in food production. Most of the carrageenan is extracted from *Kappaphycus alvarezii* and *Euchema denticulatum*. The original source of carrageenan was *Chondrus crispus*. Carrageenan was a family of linear sulphated polysaccharide extracted from red seaweeds. The name is derived from a type of seaweed that is abundant along the Irish coast line (Buck *et al*., 2006). Carrageenan and agar are used as thickening and gelling agents in food, pastry, yoghurts, chocolate, milk and as growth medium for microorganisms (Chandini *et al*., 2008). These are widely used in food and other industries as thickening and stabilizing agent and also used in desserts, ice cream, milk shake and sauces (Buck *et al*., 2006). In India however seaweed consumption is negligible except in the preparation of porridge from *Gracilaria sp* and *Acanthophora sp* in coastal status of Kerala and TamilNadu (Dhargalkar and Neelam pereira, 2005).

**Nutritive components of seaweeds**

The nutritional value of a food depends on its chemical composition such as carbohydrates, proteins, lipids, sugars, and also the minerals present in them. Seaweeds are the excellent source of bioactive compounds such as carotenoids, dietary fiber, protein, essential fatty acids, vitamins and minerals (Bhaskar and Miyashita, 2005) and they contain many biologically active substances like lipids, proteins, polysaccharides and polyphenol (Chandini *et al*., 2008). Christine Dawczynski *et al*., (2007) analysed the nutritional compositions of 34 edible seaweed products of *Laminaria sp*, *Undaria pinnatifida*, *Hizikia fusiforme* and *Porphyra sp*. 

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**Carbohydrate**

Carbohydrates are polyhydric alcohols, having potentially active aldehyde and ketone groups. When carbohydrates are oxidized in the body, they liberate carbon dioxide water and energy utilized in various biochemical and physiological processes in the cell. The carbohydrates in a living cell are in a constant flux participating in many enzyme catalyzed reactions. It is necessary to convert bond energy into chemical energy for the growth and development of the cell (Gangadevi et al., 1996). Carbohydrate level was determined in many species of Phaeophyceae and Chlorophyceae. Hypnea musciformis contained considerable amount of carbohydrate (Poopy Mary Vimala bai et al., 2003). Seaweeds also contain storage polysaccharides, notably laminarin (β-1.3- glucan) in brown seaweeds and floridean starch (amylopectin like glucan) in red seaweeds. When faced with human intestinal bacteria, most of these polysaccharides (agar, carrageenans, ulvans and fucoidans), are not digested and therefore can be regarded as dietary fibres. (Lahaye, 1991). Water-soluble and water insoluble fibres have been associated with physiological
effects. Many viscous soluble polysaccharides (pectins, guargum, etc.) have been correlated with hypocholesterolemic and hypoglycemic effects, whereas water insoluble polysaccharides (cellulose) are mainly associated with a decrease in digestive tract transit time (Southgate, 1990). Among polysaccharides, fucoidans were particularly studied as they showed interesting biological properties such as anti-thrombotic, anti-coagulant, anticancer, anti-proliferative, antiviral and anti-inflammatory activities (Angstwurn, 1995; Charreau, 1997; Nasu, 1997). Seaweeds could be a good source of dietary fiber in the diet. Soluble and insoluble dietary fibers were recognized to have different physiological response (Weiwang et al., 2001). Seaweeds have high fiber content, making up 32 per cent to 50 per cent of dry matter. The soluble fiber fraction accounts for 51 to 56 per cent of total fibers in green (ulvans) and red algae (agars, carrageenans and xylans) and for 67 to 87 per cent in brown algae (laminaria, fucus, and others). Dietary fiber of seaweeds range from 33 per cent to 75 per cent of dry weight and mainly consist of soluble polysaccharide in the range of 17 per cent to 59 per cent (Buck et al., 2006).

**Protein**

Proteins are complex nitrogenous substances and they are biopolymers containing large number of amino acids. All the biochemical reactions in a cell are catalyzed by enzymes, all of which are proteins, peptides and amino acids. Protein content varied among the different genera and also in the different species of same genera. Protein content in marine algae was reported to vary from 10 to 33% dry weight (Dhargalkar et al., 1980). Kaliaperumal (1994) investigated maximum protein content in green algae followed by red algae and brown algae from Lakshadweep. Broader variations in the protein content of marine algae in Arockiapuram coast was
reported (Stella Roseline, 2003). Protein content of various classes of macro algae were reported in other studies (Fleurence, 1999; Kolb et al., 1999; Ruperez and Saura-Calixto, 2001; Polat and Ozogul, 2008, 2009). Seaweeds belonging to the Rhodophyta possess high levels of proteins (10–30% dw) (Darcy-Vrillon 1993). In some red seaweed, such as *Palmaria* and *Porphyra tenera*, the protein contents are 35 and 47% dw, respectively. These levels are even comparable to that of the soybeans (35% dw). (Morgan et al., 1980). The protein level of *Ulva sp* is in the range of 15-20 % of the dry weight. (Kaliaperumal et al., 2002). Studies showed that phycobiliproteins having antioxidant properties would be beneficial in the prevention or treatment of neurodegenerative diseases caused by oxidative stress such as gastric ulcers and cancers (Gonzalez et al., 1999; Remirez et al., 1999). Green algae belonging to the genus *Ulva* contain 18-26% protein and *Enteromorpha intestinalis* occurring abundantly in the Gulf of Mannar have 20-26% of protein (Nisizawa et al., 1987). Nirmal kumar et al., (2010) studied the variation of biochemical composition of eighteen marine macro algae collected from Okha coast, Gulf of Kutch. The study revealed that protein content was rich in the sequence of members belonged to Rhodophyta> Chlorophyta> Phaeophyta. Protein content was generally high in green and red algae on an average 21-35 per cent of fresh weight. Manivannan et al., (2009) studied the proximate composition of different group of seaweeds from Vedalai coast. The result revealed that protein content was maximum in *Gracilaria acerosa* and minimum in *Dictyota dichotoma*. Wong and Cheung, (2001) evaluated the nutritive value of seaweed protein concentrates isolated from red seaweeds *Hypnea charoide* and *Hypnea japonica* and green seaweed *Ulva lactuca* and determined their in vitro protein digestibility and amino acid profile. All the three seaweeds protein concentrates were rich in leucine, valine and threonine but lacked in sulphur
containing amino acid, cystine and lysine. All essential amino acids were found to be higher than those of FAO/WHO requirement pattern.

For good growth and survival of fish, essential amino acids as well as unsaturated fatty acids of omega - 3 series are essential which are found in seaweeds (Bell et al., 1986). Many marine animals have a limited ability to synthesize these compounds from precursor molecules (Kanazawa et al., 1979; Watanabe et al., 1983). Seaweeds contain high levels of methionine and cystine, both are lacking in animal products. So it is highly recommended that seaweeds should be eaten with food to enhance the biological effect of proteins. Wong and Cheung, (2000) reported relatively higher amount of free amino acids in most of the seaweeds. These amino acids provide different types of flavours to several edible seaweeds. Glycine and alanine give a sweet flavour to edible seaweeds (McLachlan, 1972) and aspartic and glutamic acids are responsible for the special flavour and taste of seaweeds (Mabeau et al., 1992). Christine Dawezynski et al., (2007) examined different seaweed products and reported the presence of amino acids, protein and dietary fibre. Further, they detected all essential amino acids in the seaweed species tested and red algae species featured uniquely high concentrations of taurine. Rajasulochana et al., (2010) mentioned that the dried sample of Kappaphycus alvarezi was found to contain 18 amino acids with lysine as the major constituent followed by phenylalanine, glutamic acid, isoleucine, histidine, tryptophan, methionine and asparagine. Further, it can be noted that glycine is much less compared to all other components available in Kappaphycus sp. The nutritional value of some seaweeds such as Hypnea musciformis, Acanthophora spicifera and Gracilaria corticata as a complete source of
dietary protein and amino acid for human and animal nutrition was evaluated (Vinoj Kumar and Kaladharan, 2007).

Lipid and Fatty acids

Lipid and fatty acids are constituents of all plants cells. They function as membrane components, storage products, source of energy and quantitatively represent the best calorific value of all foods. Lipids exist as important structural constituents of cellular membranes and are the insulators of delicate internal cell organelles (Ahluwallia and Paul, 1987). Manivannan et al., (2008) studied the biochemical composition of seaweeds from Mandapam coastal region and they found low lipid concentration in Enteromorpha intestinalis (1.33%) followed by Padina gymnospora (1.4%), Sargassum tenerrimum (1.46%) and Ulva lactuca (1.6%). The nutritional composition of edible seaweed Durvillaea antartica and Ulva lactuca were evaluated. High lipid content was accounted in Durvillaea antartica than Ulva lactuca (Ortiz et al., 2006). Bhaskar et al., (2005) documentated the conjugated fatty acids in seaweeds from the Indian Ocean. They revealed that Acanthophora spicifera Gracilaria edulis and Gracilaria folifera were rich in glycolipids followed by neutral and phospholipids. Fatty acid composition of these seaweeds revealed C16:0 as the predominant fatty acid. Generally green algae contain high level of alpha linoleic acid, brown and red algae are particularly rich in fatty acids, such as eicosapentaenoic acid and docosahexaenoic acid. They have very little fat ranging from one to five per cent of dry matter; they contain higher proportion of essential fatty acids when compared to land plants (Dhargalkar and Neelam Pereira, 2005). Padina boergesnii contains high amount of palmitic acid and unsaturated fatty acids like oleic acid and linolenic acid (Vasanthi et al., 2003). High lipid content was reported in
**Stoechospernum marginatum** (Gangadevi et al., 1996). Seaweeds contain more than 50 kinds of unsaturated fatty acids. Eicosapentaenoic acid (EPA), docosahexaenoic acid (DHA) and γ-linolenic acid are three common types of unsaturated fatty acids found in seaweeds. Eicosapentaenoic acid has health benefits, such as lipid – lowering, antiplatelet aggregation, delayed thrombosis; cardiovascular protectant. Docosahexaenoic acid is an important substance involved in the growth and development of brain. γ-linolenic acid regulates blood pressure, softens blood vessel, relieve arteriosclerosis, prevents coronary heart disease, inhibits cholesterol synthesis and helps human body to maintain normal cholesterol levels. Lipid extracts of some edible seaweed showed antioxidant activity and synergistic effect with tocopherol (Le Tutour, 1990).

Seaweed products represent an important source of long chain poly unsaturated fatty acids that are fundamental for the formation of important structural lipids and elements of cell membranes. In addition, these long chain poly unsaturated fatty acids are precursors of eicosanoids, which influence inflammation processes and immune reactions (De Pablo and Alvarez de Cienfuegos, 2000; Calder and Grimble, 2002). Seasonal variation of fatty acids in seaweeds has also been studied (Floreto et al., 1993; Nelson et al., 2002). Some macro algal biomass can store large amounts of oil, which can be exploited for the production of biodiesel (John and Anisha, 2011). Xiancui Li et al., (2002) examined the fatty acids composition of 22 species of marine macrophytes by using capillary gas chromatography, and reported high levels of fatty acids. They also reported the presence of arachidonic and eicosapentaenoic acids in red algae.
Minerals

Seaweeds are known to be one of the richest sources of minerals. The most common minerals found in seaweeds are iodine, magnesium, calcium, phosphorus, iron, potassium copper and fluoride (Ensminger et al., 1995). Minerals are very important for the biochemical reactions in the body as co-factors of enzymes. Calcium, potassium and magnesium build and maintain bones and teeth, whereas, sodium and potassium help to maintain balance of water, acids and bases in fluids outside of cells, and involve in acid-base balance and transfer of nutrients in and out of individual cells (Ensminger et al., 1995). Deficiency in minerals leads to severe impairment of health. For instances, calcium malnutrition causes abnormal bone formation, namely osteoporosis and anemia caused from iron deficiency (Reinhold, 1988; Martinez – Navareete et al., 2002). Deficiency in magnesium can lead to numbness, tingling, muscle cramps, and abnormal function of the heart. Numerous studies have reported the presence of trace metals and other micro nutrients in seaweeds (Black and Mitchell, 1952; Young and langille, 1958; Bryan, 1969; Yamamoto and Ishibashi, 1972; Saenko et al., 1976; Munda, 1978; Fleurence and Le Coeur, 1993; Karthikai Devi et al., 2009). Manivannan et al., (2009) reported the mineral composition of different seaweeds such as Ulva lactuca, Enteromorpha intestinalis, Turbinaria ornata, Padina gymnospora, Hypnae valentiae, Gracilaria folifera from Mandapam coastal regions. Padina gymnospora contained considerable amount of minerals such as copper, iron, sulphur, calcium and potassium. Karthikai Devi et al., (2009) estimated the element concentration of various seaweeds such as Codium tomentosum, Enteromorpha clathrata, Enteromorpha compressa Turbinaria conoides, Colpomenia sinuosa, Sargassum tenerimum, Sargassum wightii and
*Acanthophora spicifera* from Gulf of Mannar southeast coast of India. *Gracilaria* is represented by 32 species in Indian coast, of which 31 species are found in different parts of the Bay of Bengal contained calcium, potassium, nitrogen, phosphorus and magnesium in excess (Krishnamurthy, 1991).

Seaweeds as source of antioxidants

Phenolic compounds can act as antioxidants by chelating metal ions, preventing hydroxyl, superoxide and peroxide radicals formation and improving the antioxidant endogenous system (Al-Azzawie and Mohamed, 2006). The term “phenolic compound” describes several hundred biomolecules found in edible plants that possess on their structure a benzene ring substituted by at least, one hydroxyl group (Manach *et al*., 2004). These phenolic compounds are commonly found in plants, including seaweeds (Duan *et al*., 2006). Polyphenols represent a diverse group of compounds such as flavonoids (i.e. flavonones, flavonols, flavanones, flavononols, chalcones and flavan-3-ols), lignins, tocopherols, tannins and phenolic acids (Shukla *et al*., 1997). Dhamotharan, (2002) estimated the total phenol content in brown algae. Flavonoids, the largest groups of phenolic compounds are known to contain a broad spectrum of chemical and biological activities including antioxidant and free radical scavenging properties (Kahkonen *et al*., 1999). Flavonoids include flavonols, flavones, catechins, proanthocyanidins, anthocyanidin and isoflavonoids (Ndhlala *et al*., 2007). Phenolic compounds are important in plant defence mechanisms against invading bacteria and other types of environmental stress, such as wounding and excessive light or ultraviolet radiation (Herrmann, 1989; Harbourne, 1994; Wallace and Fry, 1994). Occurrence of five different flavonoids namely acanthophorin A, acanthophorin B, tiliroside, catechin and quercetin has been reported in *Acanthophora*
spicifera (Hannah et al., 2004). Antitumor and antioxidant properties have been ascribed to the flavonoids based on in vivo and in vitro studies both in human and in animals (Cody et al., 1988). Cyanobacteria are known to produce bioactive compounds which include peptides, lipopeptides, aminoacids, sulfolipids, polysaccharides, glycoproteins, phenolic compounds, antinogenins, alkaloids and macrocyclic compounds like pyrroles, amides and fatty acids (Borowitzka, 1995; Allnutt, 1996; Burja et al., 2001). These metabolites were reported to have antibacterial, antifungal, anticancer, anti parasitic, antiproliferative, anti-HIV, anti-inflammatory, cytotoxic, photoprotective and enzyme inhibition activity (Patterson, 1996; Banker and Carmeli, 1998; Harrigan et al., 1998; Jaki et al., 1999; Stevenson et al., 2002). Hexane extract of Gracilaria edulis afforded several new proliferestane derivatives along with cholesterol and clinasterol (Das et al., 1992). Vegetable tannins are secondary plant metabolites, subdivided into condensed and hydrolysable compounds. The condensed tannins are polymeric flavonoids and hydrolysable tannins are gallic acid and/or egallic acid. They easily hydrolyse in acidic media (Huang et al., 2008). In contrast to terrestrial tannins, phlorotannins are tannin compounds found only in marine algae. Phlorotannins are formed by the polymerization of phoroglucinol (1, 3, 5-trihydroxy benzene) monomer units and synthesized in the acetate-melonate pathway in marine algae (Ragari and Glombitza, 1986; Arnold and Targett, 1988; Waterman and Mole, 1994). Phlorotannins obtained from several brown algae have been reported to possess strong antioxidant activity which may be associated with their unique molecular skeleton. Phlorotannins from brown algae have up to eight interconnected rings. They are therefore more potent free radial scavengers than other polyphenols derived from terrestrial plants, including green tea catechins, which only have three to four rings (Hemat, 2007). Plants contain
high concentrations of numerous redox-active antioxidants, such as polyphenols, carotenoids, tocopherols, glutathione, ascorbic acid and enzymes with antioxidant activity, which fight against hazardous oxidative damage of plant cell components. In animal cells, antioxidant production is much more limited and oxidative damage is involved in the pathogenesis of most chronic degenerative diseases including cancer, heart diseases and aging (La Vecchia et al., 2001). According to Chapman and Chapman, (1980) 100 g seaweed contains more than the daily requirement of vitamin A, B and B₁₂ and two third of vitamin C. Enteromorpha contains vitamins C and β-carotene which among the nutrients protect cells against powerful oxidizing agents (Krinsky, 1992). Seaweeds are rich sources of vitamin C, vitamin B- complex, e.g folic acid and vitamin A precursors, such as β-carotene (Takenaka et al., 2001; Watanabe et al., 2002; Mc Dermind and Stuercke, 2003; Yon and Hyun, 2003). Vitamin C is an antioxidant protecting hydrogen/electron carriers within the cell and maintains suitable redox levels for enzyme systems. Ascorbate is also involved in the biosynthesis of hormones and deoxyribonucleic acid. The algae belonging to Chlorophyceae and Phaeophyceae have higher annual mean contents of the vitamin C than Rhodophyceae (Qasim and Barkati, 1985). Seasonal variations in ascorbic acid concentrations are apparently dependent on hydrographic parameters and solar radiation and growth intensity of plants (Poppy Mary Vimalabai et al., 2003; Vasanthi and Rajamaniakam, 2004). Vitamin E is a generic term applied to tocopherols and tocotrienols, which show similar nutritional properties to α-tocopherol. Sanchez-Machado et al., (2002) reported higher levels of α-tocopherol in commercially important brown alga Himanthalia elongata. Durmaz et al., (2008) quantified α-tocopherol level in Cystoseira sp. and Ulva sp.
Antioxidant activity of seaweeds

Membrane lipid peroxidation is induced by free radicals or reactive oxygen species, which are formed as by-products of many biochemical reactions as well as in electron transport (Ewing et al., 1989). Reactive oxygen species have the potential to cause several cellular disorders if not scavenged properly (Halliwell and Gutteridge, 1986). Reactive oxygen species and free radicals are capable of causing damage to biomolecules, such as nucleic acids, lipids, proteins and other cellular constituents (Kubo et al., 1992 and Halliwell, 1996). Degradation and modification of these molecules have been associated with various chronic diseases such as cancer, coronary heart disease, atherosclerosis, cataracts, ageing, muscular dystrophy and some neurological disorders (Finkel and Holbrook, 2000; Cooke et al., 2002). Natural antioxidants such as α-tocophenol, phenols and β-carotene found in higher plants are being used in the food industry to inhibit lipid peroxidation and they can protect human body from free radicals and retarding the progress of many chronic diseases (Matsukawa et al., 1997; Qi et al., 2006).

Gey (1990) has reported that the synergistic action of wide spectrum of antioxidants is better than the activity of single antioxidant. Antioxidants from natural sources primarily as food have a higher bioavailability and therefore have higher protective efficacy against oxidative stress than synthetic antioxidants. Most of the isolated compounds from marine resources belong to sulfated polysaccharides, phenols, terpenoids, carotenoids, lactones, sterol and fatty acids (Mc Dermid and Stuercke, 2003; Qi et al., 2005; Duan et al., 2006). The antioxidant activity of these compounds are mainly attributed to scavenging activity against superoxide and hydroxyl radicals, chelating ability, quenching singlet and triplet oxygen and reducing
power (Ruberto et al., 2001; Athukorala et al., 2006). Marine algae, like other photosynthesizing plants, are exposed to a combination of light and oxygen that leads to the formation of free radicals and other strong oxidizing agents. However, absence of oxidative damage in the structural components of macroalgae like polyunsaturated fatty acids and their stability to oxidation during storage suggest that their cells have protective anti-oxidative defense systems (Matsukawa et al., 1997). In vitro antioxidant activities of methanol extracts of three seaweeds viz., Euchema kappaphycus, Gracilaria edulis and Acanthophora spicifera exhibited dose dependency and the scavenging activity increased with increasing the concentration of the extract in DPPH assay (Ganesan et al., 2008). Studies established that Turbinaria ornata and Padina tetrastromatica exhibited similar DPPH scavenging activity (Chew et al., 2008; Kumar et al., 2008; Kuda and Ikemori, 2009). Seaweeds like Porphyra sp (Nori), Laminaria sp (Kumbu) Undaria sp (Wakame) and Hijikia sp (Hijiki) had significant antioxidant properties (Amin Ismail and Tan Suw Hong, 2002). Total flavonoids and antioxidant activity of Sargassum wightii and Ulva lactuca were estimated (Meenakshi et al., 2009). Ganesan et al., (2011) studied the antioxidant activity of three edible species of Enteromorpha. Excellent DPPH radical scavenging activity was observed in methanolic extract of Enteromorpha compressa, whereas acetone extracts of Enteromorpha tubulosa showed good reducing power and higher antioxidant activity. Some of the marine plants have been investigated and reported to have antioxidant and radical scavenging potential (Meenakshi et al., 2012; Vijayabaskar and Shiyamala, 2012). Chandhini et al., (2008) studied the antioxidant activity of three Indian brown seaweeds Sargassum marginatum, Padina tetrastromatica and Turbinaria conoides and reported increased activity with increasing concentration of the methanolic extracts. Superoxide anion is one of the
most effective free radical, implicated in cell damage as precursors of reactive oxygen species, contributing to the pathological process of many diseases. Superoxide anion scavenging activity of seaweed extracts was determined using a non-enzymatic system described by Lim et al., (2002). In reducing power assay, substances (antioxidant), which have reduction potential react with potassium ferricyanide (Fe³⁺) to form potassium ferrocyanide (Fe²⁺) then react with ferric chloride forming the ferric ferrous complex through electron transfer ability, with change in color from yellow to bluish, showing an absorption maximum at 700nm. The intensity of color depend on potential of the compounds (antioxidants) present, consequently will be the antioxidant activity (Zou et al., 2004). Selvaraju et al., (2011) reported that Sargassum wightii possessed higher antioxidant activity.

**Antimicrobial properties of seaweeds**

The ocean contains a vast repository of the plant systems producing diverse antimicrobials (Oleson et al., 1963). Sreenivasa Rao et al., (1982) established that crude extract of seaweeds were active against Gram-positive and Gram-negative pathogenic bacteria. Pesando and Caram (1984) reported that ethanolic extracts of brown seaweeds had highest antibacterial potential. Sargassum sp. played against both Gram-positive and Gram-negative bacteria. It was found that environmental factors have also influenced the production of antibacterial substance (Rao et al., 1988). Ethanolic extract of Sargassum johnstonii, Enteromorpha sp, and Corallina officinalis showed high activity against Staphylococcus aureus. Halymenia floresia extract inhibited the growth of Gram-positive and Gram-negative bacteria (Vanitha et al., 2003). Acetone extract of Gelidiella indica had inhibitory activity against Salmonella arbory and Citrobacter sp. Further, Cheilosporium spectabile and
*Chnoospora minima* showed antibacterial activity against human pathogens such as *Staphylococcus aureus, Streptococcus mutans, Proteus vulgaris* and *Salmonella typhimurium* (Suresh Kumar *et al*., 2002). Crude extract of *Sarconema furcellatum* showed higher range of inhibitory activity against *Providensi sp.* and *Escherichia coli* (Kannapiran *et al*., 2002). Acrylic acid isolated from *Ulva fasciata* was found to have antibacterial activity (Maya *et al*., 2005).

Antibacterial activity varied with different species collected at various locations and with extraction procedure. Evaluation of marine algae for antibacterial activity as fresh and lyophilized forms were carried out by Salvador *et al*., (2007) and reported red algae being more effective in comparison with other classes. Study on extracts from fresh and dried samples of *Ulva rigida* remarkably varied in their antibacterial capacity. Extracts from fresh materials inhibited *Staphylococcus aureus, Enterococcus faecalis* and *Escherichia coli* (Tuney *et al*., 2007). Methanolic and chloroform extracts of *Jania rubens* had significant antimicrobial activity (Karabay-Yavasoglu *et al*., 2007). The highest activities were obtained by dichloromethane extracts of *Asparagopsis armata* (Bansemir *et al*., 2006). Ethanolic extracts of *Caulerpa spp* were highly active against *Staphylococcus aureus* and *Vibrio sp* (Freile Pelegrin and Morales, 2004). Methanolic extract of *Corallina officinalis* was highly active against *Enterobacter aerogenes, Escherichia coli* and *Enterococcus faecalis* (Taskin *et al*., 2007). Chloroform, ethyl acetate, methanol and ethanol extracts of *Chaetomorpha linum, Enteromorpha compressa* and *Polysiphonia subtilissima* showed species specific activity in inhibiting the growth of Gram-negative bacteria (*Shigella flexneri, Vibrio* and *Escherichia coli*) and Gram-positive bacteria (*Bacillus substilis* and *B. brevis*) (Patra *et al*., 2009).
Vijayabaskar and Shiyamala, (2011) tested the methanolic extracts of brown algae, *Sargassum wightii* and *Turbinaria* against various Gram positive and Gram-negative human pathogenic microbes and suggested *Turbinaria* as a good source of antimicrobial agent in pharmaceutical industry. Chiheb Ibtissam *et al.*, (2009) evaluated the antibacterial activity of methanolic extracts of 32 macro algae for the production of antibacterial compounds against *Escherichia coli*, *Staphylococcus aureus*, *Enterococcus faecalis* and *Klebsiella pneumoniae*. Bouhlal Rhimou *et al.*, (2010) screened the antibacterial activity of extracts of 26 marine Rhodophyceaeen members to assess their potential in the pharmaceutical industry. It was observed that *kappaphycus*, red seaweed showed maximum activity against *Pseudomonas flouresences*, *Staphylococcus aureus* and less inhibition on *Vibrio* and *Proteus mirabilis*. Antibacterial agents found in algae include aminoacids, terpenoids, phlorotannins, acrylic acid, phenolic compounds, steroids, halogenated ketones, alkanes, cyclic polysulphides and fatty acids. Antimicrobial activity was attributed to the presence of acrylic acid, phlorotannins, terpenoids and steroids found in a large number of marine algae (Gonzalez Del Val *et al.*, 2001). Compounds with cytostatic, antiviral, antihelmintic, antifungal and antibacterial activities have been detected in green, brown and red algae (Lindequest and Schweder, 2001; Newmann *et al.*, 2003). Cox *et al.*, (2010) revealed that the extraction of antimicrobials from different species of seaweeds was solvent dependent, and found methanol as good solvent for extraction of antimicrobials from brown seaweeds and acetone for red and green species.

Antibacterial halogenated compound such as bromophenols, have been isolated from many types of seaweeds. *Colpomenia sinuosa* having fatty acids and
sterols, especially fucosterol exhibited significant antitumoral, antileukemic, antiprototozoan and hypolipidemic activity. Dolabellane derivatives isolated from Dictyota dichotoma possessed antimicrobial activity against bacteria (Demirel et al., 2009). Ulva species are rich in essential nutrients and they exhibit antiperoxidative and anti-hyperlipidemic activities (Sathivel et al., 2008). Jaki et al., (2000) reported that algal extracts were found to have antibacterial properties against three bacterial strains Escherichia coli, Salmonella typhimurium and Streptococcus facialis. It was reported that Oscillatoria sp., Phormidium sp. and Lyngbya sp. have antibacterial effect against human pathogenic bacteria such as Streptococcus mutants, Staphylococcus aureus, Pseudomonas aeruginosa, Bacillus subtilis and Klebsiella pneumoniae.

Ouattara et al., (2011) investigated that phenolic content were active as antibacterial agents against different types of microorganisms like Salmonella typhi. Flavonoids are reported to be active against species like Streptococcus, Escherichia coli and Staphylococcus aureus. Methanol extracts of Oedogonium sp., Ulothrix sp. and Oscillatoria sp. showed no inhibitory effect against Gram negative bacteria, Escherichia coli (Goud et al., 2007). Tuney et al., (2006) demonstrated that methanol extract of Gracilaria gracilis exerted inhibitory effects against Gram positive bacteria Streptococcus epidermidis at a concentration of 25 µl. Uma maheshwari et al., (2009) found that methanol extract of Halophila ovalis exerted antibacterial effect against Salmonella typhi and Salmonella paratyphi-B. Irie et al., (1966) tested halogenated metabolites from the red alga Laurencia species for antibacterial activity against 22 strains of human pathogenic bacteria, including seven strains of antibiotic–resistant bacteria and found a wide spectrum of antibacterial activity against Gram positive
bacteria including methicillin-resistant *Staphylococcus aureus*, penicillin–resistant *Streptococcus pneumoniae* and vancomycin–resistant *Enterococcus faecalis* and *E. faecium*. It was stated that Laurinterol and allo-laurinterol were particularly effective against the tested organisms.

Marine planktonic algae have been recognized as potential source of antibacterial and antifungal substances. Since 1960 several workers have documented about the antifungal activity of marine planktons against *Trichophyton* and *Candida sp* (Gueho *et al.*, 1977). Extracts from *Laurencia flagellifera*, *Gelidiella indica* and *Chnoospora minima* inhibited the fungus strain *Candida albicans* (Suresh Kumar *et al.*, 2002). *Valonia argrophia* extract was more active against *Candida albicans* than pneumonia G. Extracts of *Halimeda optuntia* and *Halimeda tuna* showed mild activity (Mtolera and Semesi, 1996). Lipid fraction of *Enteromorpha compressa* exerted inhibitory activity over *Candida tropicalis* and *Aspergillus niger*. Lipophilic fraction of *Ulva fasciata* had maximum inhibitory activity against *Candida albicans*, *Trichophyton mentagorophytes* and *Aspergillus fumigatus*. Lipid fraction of *Caulerpa scalpelliformis* could reduce *Candida kursci* and *Trichospermum marginatum*. *Hypnea valentiae* extracts were active against *Aspergillus flavus* and *Candida albicans* (Selvaraj *et al.*, 2006). Ethanolic extract of *Ceramium rubrum* and *Acanthophora spicifera* exerted their inhibitory effect on *Cercospora arachidicola*, *Pyricularia oryzae*, *Aspergillus niger* and *Macrophomina phaseolina* (Sudha and Maria Victorial Rani, 2009; Flora and Maria Victorial Rani, 2012). Min Hee Lee *et al.*, (2010) studied the antifungal activity of dieckol isolated from *Ecklonia cava*, against *T. rubrum*. Fluorescent microscopic observation indicated that dieckol exhibited fungicidal activity against *Trichophyton rubrum* by destroying cytoplasmic
membrane integrity. Tuney et al., (2006) found that ethanolic extract of Padina pavonia was active against Candida albicans, however methanol and acetone extracts of the same alga were inactive against Candida albicans. Efficiency of algal extracts against microorganisms is influenced by factors such as location and seasonality. Padmakumar and Ayyakkannu, (1997) reported that Rhodophyta (red algae) had highest antimicrobial activity than Phaeophyta (brown algae).

**Utilization of seaweeds in silver nano particles synthesis**

Many scientists have been attracted recently towards biosynthesis of gold and silver nanoparticles using various plant sources and obtained nanoparticles with an average size of 20-30 nm (Gardea-Torresdey et al., 2003; Shankar et al., 2003; Rai et al., 2007; Singaravelu et al., 2007). Green synthesis of nanoparticles provides advantage over chemical and physical methods as it is cost effective, environment friendly, easily scaled up for large scale synthesis. Further, there is no need to use high pressure, energy, temperature and toxic chemicals. Biosynthetic methods employing either biological microorganisms or plant extracts have emerged as simple and viable alternative to chemical methods but most of the methods are still in developmental stages (Veerasamy et al., 2011). Kumar et al., (2012) reported seaweed mediated reduction of silver into silver nanoparticles using Gracilaria corticata and its antifungal activity against Candida sps. These silver nanoparticle possess several biomedical properties such as antimicrobial, antiprotozoal, anti-inflammatory, antioxidant, cytotoxic, contraception, gastro intestinal, cardiovascular, hypoglycemia, anti-enzymes, spasmyotic and allelophatic effects (Almeida et al., 2011). Ragupathi Raja Kannan et al., (2013) demonstrated the formation of silver nanoparticles by reduction of aqueous silver metal ions during exposure to seaweed,
Chaetomorpha linum extract. Dhanalakshmi et al., (2012) reported higher amount of phytochemicals in Sargassum plagiophyllam and their role in silver nanoparticles synthesis. Rajeshkumar et al., (2012) used Padina tetrastromatica for green synthesis of silver nanoparticles. Sahaya raj et al., (2012) reported the synthesis of pure and stable metallic nanoparticles of silver by the reduction of aqueous Ag⁺ ions with thallus broth of marine alga, Padina pavonia (Phaeophyceae) and further investigated the impact of the synthesized nanoparticles against Fusarium oxysporum and Xanthomonas campestris using agar well diffusion method. Rai et al., (2009) suggested that when silver ions penetrated inside the bacterial cell DNA molecules turn into condensed form and lose their replication ability leading to cell death. Song et al., (2006) suggested that nanoparticles release silver ions into the bacterial cell, resulting in bactericidal activity. Jeong et al., (2005) demonstrated that silver nanoparticles are non-toxic to human beings and most effective against bacteria, virus and other eukaryotic micro-organism at low concentrations and without any side effects. Mohandass et al., (2013) reported the synthesis of silver nanoparticle from Sargassum cinereum and examined its antibacterial potential. Vivek et al., (2011) reported the synthesis of silver bio nanoparticles using Sargassum wightii, Kappaphycus alvarezii and Gelidelia acerosa. Many companies utilizing nanotechnology in nutritional sciences, has marketed a new product called Nanoceuticals which is a colloid (or emulsion) of particles of less than 5 nm in diameter. These products will scavenge free radicals, increase hydration and balance pH in body fluid. Nano clusters, a nanosize powder combined with nutritional supplements when consumed, enhance the absorption of nutrients. Nanoceutactical delivery system for transmucosal administration of dietary supplements has resulted in increased-bioavailability in comparison with gastrointestinal absorption (Food
Standards Agency, 2006). Seaweeds are being used for its rich nutrient content, antioxidant property and antimicrobial activity in treating major degenerative and deficiency diseases. Though seaweeds are consumed extensively by Indonesians, Japanese and Koreans having understood the nutritional properties and valuable health benefits of seaweeds, Indians are still juvenile to explore their benefits.