A review: bioactive compounds of macroalgae and their application as functional beverages

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Abstract. Macroalgae have the potential of a bioactive compound that can be used as the main ingredient in functional beverages. The content of bioactive compounds in macroalgae such as natural pigments, sulfated polysaccharides, antioxidants have been studied and it is very beneficial for health. Macroalgae, which are used as main ingredient in functional beverage, must be contain bioactive compound that are beneficial for health and also must be free from microbiological and heavy metal contamination. This study aims to determine bioactive compound activity and the potential of macroalgae as the primary raw material in the formulation of functional beverages. Studied on the formulation of functional beverages with macroalgae as raw materials have been carried out in the last few decades. All types of macroalgae have the potential to be used as raw material or main ingredient for functional beverage. The formulation of macroalgae functional beverages with other additives can improve the quality of the final product. The addition of natural scented ingredients and containing bioactive compounds can increase the value of taste and increase the nutrients in functional beverage products.

1. Introduction

Macroalgae can be used as the main ingredient for the fulfillment of functional food [1] Macroalgae has almost all types of essential amino acids needed by the body [2]. Macroalgae also contains bioactive compound that potential to counteract free radicals, prevent aging, prevent and treat other degenerate diseases [3–5]. The use of macroalgae has long been carried out by several Asian countries, namely China, Japan, Korea [6], Malaysia, Philippines, and Thailand [2]. Aside from being a main food ingredient [2,7], macroalgae are used as animal feed [8–11], organic fertilizer [10–12], cosmetic [2,3,13,14], medicines [2,15–18], to additional food ingredients [8,9,19,20]. Utilization of macroalgae in western countries also uses macroalgae as sea vegetables, salads, or cooked [18,21].

Indonesia has been long used macroalgae as the main food consumed daily [6,22] and for treatment [23]. The potential of macroalgae in the industrial sector only uses macroalgae to be directly dried and then exported. Type of processed macroalgae products (agar, carrageenan, alginate) exported are only around 20% and dry product as much as 80% [24]. Macroalgae resources, if carried out appropriately, can produce functional food products for the community [25], macroalgae as a cosmetic [26], biofuel [10,27], and animal feeding [8]. This review aims to provide information about the benefits of macroalgae as functional beverages, in order to increase the added value macroalgae products and to
make a good contribution not only as a daily food but also as a beneficial product for health that has a higher value.

2. Macroalgae characteristics

Taxonomically, macroalgae are classified into three classes, namely Rhodophyceae (red algae), Chlorophyceae (green algae), Phaeophyceae (brown algae). Cyanophyceae varieties are not considered as algae because Cyanophyceae is a prokaryotic organism, only eukaryotic organisms can be classified as macroalgae [28]. The characteristics contained in macroalgae can also be used to classify macroalgae. The most commonly used classification is based on the presence of special pigments other than chlorophyll which clearly identify macroalgae as one of the algal divisions [29]. Good temperatures for macroalgae growth range between 20-30°C. Macroalgae require sufficient light intensity to carry out photosynthesis, but the brightness required by each type of macroalgae is different [29]. Rhodophyceae and Chlorophyceae generally can live in limited sunlight while Phaeophyceae are generally able to absorb a lot of light and it abundant in coastal areas.

In the literature, all types of macroalgae contain chlorophylls-a, chlorophylls-b and β-carotene pigments (Table 1.) that can function as sources of bioactive components. Chlorophylls are the main pigments responsible for the photosynthesis process [30]. This pigment is very important for the survival of macroalgae. Chlorophylls are not only important for macroalgae growth but also can be potential as a natural coloring agent for food and beverage industry, in health sector and agriculture [31,32].

| Table 1. Macroalgae characteristics |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Division        | Common name     | Pigments         | Storage Product | Struktural cell wall | Intercellular mucilage | Flagella |
|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Rhodophyceae    | Red alga        | Chlorophylls a, b, phycocyanins, phycoerythrin, α- and β-carotenes, several Xanthophylls | Floridean starch | Cellulose, xylans, mannans | Sulfated polysaccharides | Not present |
| Chlorophyceae   | Green alga      | Chlorophylls a,b, β-carotenes, lutein, several Xanthophylls | Starch          | Cellulosa, xylans, mannans cellulose, chitin | Sulfated polysaccharides | Present |
| Phaeophyceae    | Brown alga      | Chlorophylls a,b, β-carotenes, fucoxanthins several other Xanthophyles | Starch          | Cellulose, xylans, mannans | Sulfated polysaccharides | Present |

[29,33]

Based on algaebase.org, Rhodophyceae is a macroalgal group with the highest number of species. Rhodophyceae has a varied appearance of thalus color. It contains a composition of pigments consisting of carotenoids, β-carotene and several xanthophylls and phycoerythrin. Phycoerythrin is the dominant pigment in Rhodophyceae which gives a red color. Chlorophyceae generally contains lutein, some xanthophyles, and carotenoids that function as antioxidants [3]. Carotenoids are able to protect organism and cells from oxidative damage caused by free radicals [34]. Carotenoids can inhibit free radical activity [34,35]. Inhibition of free radicals by carotenoids is carried out by β-carotenes, β-carotenes react with peroxy radicals, forming ROO-carotene radicals and electron delocalisation [3]. As with other macroalgae, the bioactive components of Chlorophyceae varies according to geographical location, harvest time, season, and species [36].
Phaeophyceae also has Chlorophylls a,b, β-carotenes and fucoxanthins pigments that displays a greenish brown color. Fucoxanthin has biological activity that functions as an antioxidant, anti-cancer, anti-inflammatory, anti-obesity, and antibacterial [37]. In addition, Phaeophyceae produces a variety of active components, secondary metabolic namely phlorothannins, which show specific biological activity [37,38]. The antioxidant in phlorothannins have higher antioxidant activity than vitamin E [39]. All of the content of polyphenols in macroalgae also differs according to geographical location, harvest time, season, and also species of macroalgae [36].

3. Nutritional compound from macroalgae
Carbohydrates in macroalgae are relatively high of each type (Table 2.), it cannot be considered as a food that contains a lot of energy, due to the low digestibility of carbohydrates in macroalgae. Macroalgae polysaccharides differ from those in terrestrial plants. There are three types of polysaccharides that have different functions: structural cell wall polysaccharides, inter-cell slime polysaccharides and storage polysaccharides [29]. The content of polysaccharides in macroalgae serves to reduce cholesterol levels, reduce blood lipid levels, and facilitate the digestive system. Polysaccharides in macroalgae show some biological activities that are very important for health. These activities are anticoagulant, antibacterial [22], antiviral, anticancer [36], antithrombotic, and anti-inflammatory [40].

| Table 2. Chemical compound of several types of macroalgae |
|-----------------------------------------------------------|
| Macroalga | Chemical composition |
| | Carbohydrates | Proteins | Lipids | Ashes | Fiber | Reference |
| Rhodophyceae | | | | | |
| Gracilaria gracilis | 9.52 | 20.2 | 3.58 | - | 24.8 | [41][42-44] |
| Gracilaria changii | 41.52 | 12.57 | 0.3 | 29.44 | 40.3 | [43] |
| Gelidiella acerosa | 68.67 | 10.05 | 3 | - | 13 | (45] |
| Gelidium pusillum | 40.64 | 11.31 | 2.16 | 21.15 | 24.7 | [46] |
| Gelidium pristoides | 43.1 | 11.8 | 0.9 | 14 | 0 | [47] |
| Hypnea pannosa | 22.89 | 16.31 | 1.6 | 40.59 | 46 | [48] |
| Hypnea musciformis | 20.6 | 18.64 | 1.27 | 37.92 | 21.6 | [48] |
| Kappaphycus alvarezii | 57.3 | 19.25 | 2.06 | 14.52 | 39.9 | [49-51] |
| Palmaria palmata | 11.2 | 12.3 | 1.39 | 45.3 | 42.2 | [52] |
| Eucheuma cottonii | 26.49 | 9.76 | 1.1 | 46.19 | 5.91 | [53] |
| Chlorophyceae | | | | | |
| Caulerpa racemosa | 52.81 | 17.36 | 2.21 | 3.11 | 23.8 | [40] |
| Caulerpa lentillifera | 59.27 | 12.49 | 0.86 | 24.21 | 3.17 | [54] |
| Enteromorpha compressa | 44.08 | 17.48 | 3.54 | 31.21 | 2.93 | [55] |
| Enteromorpha linza | 50.01 | 12.5 | 4.1 | 28.33 | 7.14 | [55] |
| Enteromorpha tubulosa | 51.05 | 19.09 | 5.56 | 17.01 | 6.82 | [55] |
| Halimeda opuntia | 0.22 | 1.47 | 0.7 | 39.67 | 5.84 | [56] |
| Ulva reticulata | 17.28 | 21.06 | 0.75 | 17.58 | 4.84 | [54] |
| Phaeophyceae | | | | | |
| Laminaria digitata | 76 | 82.2 | 0.85 | - | 31.6 | [52] |
| Laminaria hyperborea | - | 8.1 | 1.14 | - | 32 | [52] |
| Turbinaria conoides | 37.39 | 3.99 | 0.47 | 27.58 | 5.7 | [53] |
| Sargassum polycystum | 38.37 | 3.64 | 0.23 | 31.52 | 4.8 | [53,57] |
| Sargassum turbinaria | 37.39 | 6.9 | 0.47 | 27.58 | 5.7 | [53,57] |
| Sargassum duplicatum | 44.94 | 10.6 | 1.14 | 27 | 24 | [53,57] |
| Padina minor | 25.98 | 4.17 | 0.36 | 45.13 | 2.06 | [53] |
Undaria pinnatifida | 33.5 | 16.7 | 1.08 | 29.6 | 2.7 | [19,58]

Macrolalgae has a high fiber content but low in fat and calorie content, and it can be used as a main ingredient in functional beverages. The total fiber value in each macroalgae varies depending on geography, season, and time of harvest [36]. Fiber functions to maintain health and balance the digestive system functions. Dietary fiber is a part of plants that can be consumed and composed by carbohydrates, it resistant to the process of digestion and absorption in the small intestine and undergo fermentation in the large intestine [25].

High protein content is one of the determining factors in the of macroalgae as functional food. In general, Phaeophyceae protein level are lower when compared to Rhodophyceae and Chlorophyceae [18]. Macrolalgae have a high protein content compared to vegetables such as long beans, spinach and carrots [59]. This shows that macroalgae is good to be used as a food source of high protein content [60]. Macrolalgae protein levels depend on the type and period of season [8].

Lipids and fatty acids present in small amounts in macroalgae. The lipid content of the dry weight and composition of omega 3 and 6 fatty acids are only around 1-5% [29]. However, lipids containing omega 3 and omega 6 fatty acids play an important role in preventing various diseases. The lipid content of the Rhodophyceae, Chlorophyceae and Phaeophyceae are relatively low (Table 2) and the composition of fat in each type of macroalgae are varies. This is based on the season when harvesting or sampling and the environmental conditions [36,52].

The content of macroalgae lipids is different from land plants. Macroalgae has a higher proportion of saturated and unsaturated fatty acids [48]. In general, Phaeophyceae contains Alfa linoleate (omega 3), whereas in Chlorophyceae and Rhodophyceae it contains arachidonic acid and eikosapentanoic acid namely fatty acids with 20 carbon atoms [18,60]. In addition of fatty acids, macroalgae also contain sterols, terpenoids, and tocopherols [38]. Lipid extract from some edible commercial macroalgae show antioxidant activity and synergistic effects with tocopherol [48]. Phaeophyceae has higher sterol levels than Chlorophyceae and Rhodophyceae [8].

4. Bioactive compound from macroalgae

Raw materials for functional beverages do not came from animals and plants only. Raw materials originating from sea have started to develop rapidly. There are various ways to extract bioactive compounds from macroalga [61]. Several novel extractions without loss of bioactive activity have been applied. The new techniques are supercritical fluid extraction (SFE), ultrasound extraction (UAE), microwave assisted extraction (MAE) and pressurized fluid extraction (PLE).

| Macroalgae                  | Bioactive compounds                                      | references |
|-----------------------------|----------------------------------------------------------|------------|
| Gracilaria gracilis         | Antioxidant                                              | [64]       |
| Gracilaria changii           | Antiinflammatory, antiulcer, antioxidant                 | [65],[66]  |
| Gelidiella acerosa           | Antioxidant, antibacterial, strengthening of the immune system | [22,67]    |
| Gelidium pusillum            | Antimicrobial; antioxidant                               | [34,46]    |
| Gelidium pristoides          | Antimycrobacterial                                       | [68]       |
| Hypnea pannosa               | Antimicrobial                                            | [69]       |
| Hypnea musciformis           | Antibacterial, antifouling, ichthyotoxicity assays       | [70,71]    |
| Kappaphycus alvarezi         | Anti-hyperglycemic, antiproliferative, dietary fiber, anti-diabetic | [9,72–74] |
| Palmaria palmata             | Anti UV                                                  | [75]       |

Table 3. Bioactive compounds of several macroalgae


Eucheuma cottoni  Recognising blinding of carbohydrates, anti-diabetic  [9,19]

**Chlorophyceae**

*Caulerpa racemose*  Antibacterial, anti-inflammatory  [40]

*Caulerpa lentillifera*  Antibacterial, anti-inflammatory  [40]

*Enteromorpha compressa*  Antidepressant, reproductive health  [74–76]

*Enteromorpha linza*  Antibacterial, antioxidant  [50,76–78]

*Enteromorpha tubulosa*  Antioxidant,  [50]

*Halimeda opuntia*  Antimicrobial, antiplasmid, cytotoxicity activities  [79]

*Ulva reticulata*  Antimicrobial, antioxidant, palmitic acid  [80,81]

**Phaeophyceae**

*Laminaria digitata*  Antioxidant; anti-inflammatory activity  [64,82]

*Laminaria hyperborea*  Terpenes and phenols  [61]

*Turbinaria conoides*  Antioxidant, antibacterial, antifungal, anticancer  [16,83–85]

*Sargassum polycystum*  amino acids and amines, tannins, antioxidant  [86,87]

*Sargassum turbinaria*  Antioxidant  [88]

*Sargassum duplicatum*  Antioxidant  [89]

*Padina minor*  Anticancer, antioxiindat  [17,87]

*Undaria pinnatifida*  immunostimulatory, antiplasmodial, anti-allergi, antitumor  [90]

Based on the bioactive compounds, macroalgae can be as one of the potential raw materials for functional beverages. Phenolic compounds are one of the bioactive compounds included in natural antioxidants [39,61]. Catechins, phenolic acids, phlorotannins, flavonoids, flavonol glycoide and flavon [62,63] have been identified in *Rhodophyceae, Chlorophyceae, and Phaeophyceae*. They have potential as a bioactive compound as an antioxidant, anti-inflammatory, anticancer, antiulcer, antimicrobial (Table 3).

Macroalgae in Indonesia are widely available in nature and cultivation with good quality, qualifications, availability and varieties [91]. Bioactive compounds in macroalgae varies greatly depending on species, season, geographical conditions, environment, air temperature, harvest season and postharvest handling [7,92]. Macroalgae are more profitable compared to plants in terms of productivity, easier to extract, and unseasonal.

5. *Macroalgae as a functional beverages*

Macroalgae are source of agar, carrageenan and alginate. Agar has the ability to form a film or gel layer so that it can be used as a stabilizer, emulsifier, suspension, coating, gel forming and inhibitor [93]. In food industry, it is widely used in jelly, milk, ice cream and also fish and meat canning industry. This review discusses the benefits of macroalgae as the main ingredient of functional beverages. Macroalgae can be used as main ingredient because it contains bioactive compounds and prevents the disease [94,95].

There are several technique processing for functional beverages, one of them by the fermentation process. Fermented functional beverages using *E.cottoni* (Table 4) with the addition of 5% *L.plantarium* and 5% glucose and incubated at 37°C for 72 hours. The results is that the fermentation of *E.cottoni* produce slightly bitter flavored yogurts with a pH of 3, has a sour odor and the characteristic are yellow-green jelly [96]. The bitter taste is caused by washing of *E.cottoni* which is uncleaned, so there is still a salt component in the macroalgae. Washing and removal of salt need to be done, so the results of macroalgae fermentation are not bitter.
### Table 4. Functional beverages made from macroalgae

| Macroalga             | Functional beverages | Functional ingredient                                                                 | Result                                                                                                                                    | References |
|----------------------|----------------------|---------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------------------------------------------------|------------|
| **Rhodophyceae**     |                      |                                        |                                                                                                                                             |            |
| Eucheuma cottonii     | Yogurts              | *E. cottonii* by addition of 5% glucose & 5% inoculum of *L.plantarium*                | Yoghurt has a sour odor, sour taste and slightly bitter with a pH of 3                                                                       | [96]       |
|                      | Jelly drink          | *E.cottonii* by addition of culture-based *Spirulina platensis* and commercial *spirulina* | Type of spirulina (commercial & culture) gave no sign ificant effect to the hedonic test and antioxidant activity but affected significantly on protein content | [97]       |
|                      | Powder beverages     | *E. cottonii* by addition of 5% glucose and *essens*                                    | The best treatment was without addition of glucose                                                                                         | [98]       |
|                      | Beverages             | *E. cottonii* by adding different dosages of sugars                                    | Highest phosphor content                                                                                                                  | [99]       |
| Eucheuma spinosum     | Jelly drink          | *E.spiniosum* by addition of Sargassum sp                                              | The highest hedonic test result that jelly drink has a bright appearance and clean, bright purple, slightly felt and smell of seaweed overall acceptance and flavor, tasted a little sweet with sour flavor and a small amount of seaweed odor | [100]      |
| Gracillaria fisheri   | Fermented beverages  | Fermented *G.fisheeri* in four different fermentation process                           |                                                                                                                                             | [101]      |
| **Chlorophyceae**     | Tea                  | Dried *U.pertusa* extract                                                            | High antioxidant activity                                                                                                                 | [95]       |
| Fucus vesiculosus     | Yogurts              | *F. vesiculosus* 60% EtOH                                                            | No influence on chemical and microbiological characteristics Yoghurts lipid stability and shelf-life characteristics Overall sensory attributes were worsened | [102]      |
| Fucus vesiculosus     | Functional beverages | *F.vesiculosus* extract                                                              | Dietary fiber, antimicrobial                                                                                                               | [94]       |
| Ascophyllum nodosum   | Yogurts              | *A.nodosum* extract                                                                  | No influence on chemical characteristics Yoghurts had antioxidant activity before and after digestion                                      | [102]      |
| Sargassum polycystum  | Instant drink        | *S.polycystum* powder by addition of ginger and sugar                                 | More addition of S. polycystum extract, decreases the level of consumer preference fermentation time give the effect on physical properties (color and weight of nata/cellulose) and chemical properties (vitamin C content, total acidity, total sugar content, pH and alcohol content | [103]      |
| Sargassum sp          | Kombucha             | Fermented *Sargassum* with different fermentation time                                |                                                                                                                                             | [104]      |
| Sargassum binderi     | Seaweed tea          | *S.binderi* by addition of lemon essence                                               | Seaweed tea potential to be commercialised, thus, consumers may acquire the health benefit of fucoidan                                       | [105]      |
Fermentation times also very influential in making functional beverages. The result of kombucha beverage [104] with time treatment (Table. 5) showed decreased levels of vitamin C on the 4th day fermentation but increased on the 8th day to the 16th day. pH and total sugar decreased until the 16th day and alcohol levels increased until the 12th day and decrease until the 16th day. In accordance with the statement [(106)] fermentation effectively affects the taste, texture and also nutritional value.

Tea from macroalgae also have been widely studied, one of made from Sargassum binderi [105] (Table. 5). S.binderi powder as much as 5g in tea bag, brewed with 200 ml of boiling water for 20 minutes. This boiling water aims to maximize the extraction of fucoidan with higher secondary antioxidant activity. The fucoidan content, shows a significant positive correlation with the superoxide anion scavenging activity (r=0.99) [105]. The taste acceptance of the functional beverage was less favored by panelists. Addition of lemon juice to S.binderi tea can mask the fishy taste of tea produced from macroalgae. Similarly, research [103] showed greater addition of S.polycystum extract increase antioxidant activity, but panelists’ acceptance of taste was decreased.

### 6. Conclusion

Processing macroalgae into functional beverages can increase the nutrition value and bioactive compounds and it can be affect in human health. All types of macroalgae have the potential to be used as raw material or main ingredient for functional beverage, what must be considered are non toxic macroalgae types. A preliminary research should be conducted for non-commercial types of macroalgae to be processed into a product. This review about the use of macroalgae as functional beverage ingredients can open wider opportunities for the beverage industry to present functional beverage products with new innovations.

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