Review

Pioneering Role of Marine Macroalgae in Cosmeceuticals

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Abstract: Cosmetics are broadly used by people to protect the skin from external environmental stresses and for beauty purposes globally. A recent trend towards cosmetics with natural formulations has emerged. The cosmetic industry uses the term ‘cosmeceutical’ to refer to a cosmetic formula that has drug-like applicative advantages. Recently, macroalgae have received increased attention as natural ingredients for cosmeceutical applications. Many marine algae are rich in biologically active components that have been reported to exhibit strong benefits to the skin, mainly for photoprotection, skin whitening, moisturization, anti-aging, anti-wrinkle, antioxidants, and antimicrobial uses. The present review provides a detailed study of the literature on the cosmetic potentials of marine algae-derived polysaccharides, peptides and amino acids, pigments, phenolic components, and fatty acids. We provide an overview of different types of macroalgae with their biologically active constituents and potential cosmetic benefits. In addition, the bioactive molecules of cosmetic products containing marine macroalgae as well as their mechanisms of action are briefly discussed.

Keywords: seaweeds; bioactivity; cosmeceuticals; skin care; anti-inflammatory; photoprotection

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1. Introduction

In cosmeceuticals, cosmetic products are a topical combination of cosmetic and pharmaceutical with bioactive molecules to have medicinal or drug-like applications to improve health and texture of skin [1,2]. Due to modernization and skin care attention, cosmetic companies are enlarging gradually each year worldwide. To fulfill the requirements of customers, these cosmetic companies are moving towards unbeatable exploitation of synthetic cosmetics and constituents. Due to the ineffectiveness of synthetic components, it may cumulate in skin and produce toxic effects and may cause harm to healthy skin structure. Hydroxybenzoic acid esters (parabens) reported its adverse effect to the skin as well as increase incidence of malignant melanoma and breast cancer since it is widely used in cosmetic formulations [3]. Another substance is phthalate, which is highly found in different cosmetic formulations that can cause DNA mutations and damage, as found in human male gamete [4,5]. Some of these synthetic chemical compounds can cause detrimental effects in animals such as reduction of sperm counts, changed pregnancy outcomes, congenital disabilities of male genitalia, etc. [6]. As a result, users have changed their liking and selected natural cosmetic products for usage [7]. Hence, the enlarging market for skincare formulations and constant look for an alternative natural constituents led to the production of a different types of cosmeceutical skin products [8]. Cosmetics has had a commanding role in society, mainly for traditional and conventional purposes, since immemorial times. In ancient times, people were aware of natural compounds extracted from milk, flowers, fruits, seed, vegetables, herbs, marine algae, and minerals from clay, ash, etc. [5]. In different parts of the world, there is still a practice of utilizing marine macroalgae as an alternative natural sustainable remedy by making it into a promising natural raw material in skin cosmetics [9].

Marine macroalgae (seaweeds) are macroscopic, multicellular, eukaryotic organisms that can perform photosynthesis due to presence of Chlorophyll and some other photosynthetic pigments. They are widely distributed along the coastal line (the intertidal and sub-tidal regions) and in brackish water [10]. Based on pigment composition, they can be classified into three types. Brown alga belongs to Ochrophyta phylum (Phaeophyceae class), red alga belongs to Rhodophyta phylum, and green alga belongs to Chlorophyta phylum. Among these three types, brown algae belong to the Chromista kingdom, whereas green and red algae belong to the Plantae kingdom [10,11]. Seaweeds have a more highly diversified bioactive constituents than terrestrial organisms [12]. These bioactive compounds have a wide range of biological activities which can be used in product preparation as an ingredient [13,14]. The applications of macroalgae in cosmeceutical formulations depends on their constituents (such as polysaccharides, carbohydrate derivatives, proteins, peptides, amino acids, phenolic compounds, vitamins, minerals, fatty acids, pigments, etc.) [15,16]. Many previous findings have reported the role of seaweed based bioactive compounds which offer antitumor, antiallergic, antimicrobial, antioxidant, antiinflammation, antilipidemic activity, antiwrinkle, anti-aging, moisturizing, and photoprotection activities [5,15,17–19]. The present study aims to reveal the role of marine macroalgae-derived polysaccharides, peptides, and amino acids, pigments, phenolic compounds as well as lipid and fatty acids in skin cosmetic benefits.

2. Seaweed Derived Metabolites in Cosmetics

Due to presence of the above-mentioned bioactive constituents and their potential biological activities, they can be broadly use in cosmeceutical products. For the preparation of cosmeceutical products, macroalgae-derived compounds have been noted as being of significant importance [20]. Polysaccharides have a great role in cosmetics including in moisturizers, emulsifiers, wound healing agents, and thickening agents [21]. Fernando et al. [22] have reported anti-inflammation activity of Fucoindan from *Chnoospora minima* (Phaeophyceae) by inhibition of Lipopolysaccharides induced nitric oxide production, inducible nitric oxide productions, Cyclooxygenase-2, and Prostaglandin E2 levels in an experimental study by targeting RAW macrophages. Likewise, Ariede et al. [23], Wang et al. [24], and Teas and Irhimeh, [25] reported beneficial activities of *Fucus vesiculosus* (Figure 1a) (Phaeophyceae) derived polysaccharides such as anti-aging, anti-melanogenic, anti-cancer, and antioxidant activity by stimulating collagen production, tyrosinase inhibition, decreasing melanoma growth and by preventing oxidation formation, respectively. In addition, the anti-inflammation activity of sulphated polysaccharide from *Padina tetrastrum* (Phaeophyceae) by COX-2 and iNOS inhibitions in an experimental model of Paw edema in rats [26]. Moreover, Khan et al. [27] reported the anti-inflammation activity of polyunsaturated fatty acids derived from *Undaria pinnatifida* (Figure 1b) (Phaeophyceae) on mouse ear edema and erythema. In vitro, the antioxidant activity of methanolic extracts from *Osmundaria obtusiloba* and *Palisada flagellifera* (Rhodophyta) was studied by DPPH, ABTS, metal chelating, Folin ciocalteu, and beta-carotene bleaching assays [28,29]. Phenolic compound Sargachromanol E revealed antiaging activities from *Sargassum horneri* (Phaeophyceae) by inhibition of matrix metalloprotein expression on UVA irradiated dermal fibroblast [30]. Likewise, the Anti-melanogenic activity of Sargachromanol E from *Sargassum serratifolium* (Phaeophyceae) was studied by downregulation of microphthalmia-associated transcription factors on B16F10 melanoma cells [31]. Along with this, Yoon et al. [32] showed inhibition of tyrosinase and melanin and expressed anti-melanogenic activity of the brown macroalga *Petalonia binghamiae*'s ethanolic extract. Besides, mycosporine amino acids (MAAs) from *Porphyra* sp. (Rhodophyta) reported collagenase inhibition as well as control expression of MMP (on human fibroblast cell lines) in vitro [33]. Additionally, antioxidant activity revealed by *Neopyropia yezoensis* (formerly *Porphyra yezoensis*) (Rhodophyta) derived Mycosporine amino acids by ROS scavenging potential and MMP expression on human skin fibroblast [34]. The antiaging activity was found by collagenase inhibition of *Palmaria palmata* (Figure 1g) (Rhodophyta) derived MAAs [35]. Some species

of macroalgae *Laurencia pacifica*, *Laurencia rigida*, *Wilsonosiphonia howei* (formerly *Polysiphonia howei*), *Rhodomela confervoides*, *Schizymenia dubyi* (Figure 1c) (Rhodophyta), etc. were found to be a good source of phenolic compounds [11,31,36].

Figure 1. Seaweed species images: (a)—*Fucus vesiculosus* (P); (b)—*Undaria pinnatifida* (P); (c)—*Schizymenia dubyi* (R); (d)—*Ulva linza* (C); (e)—*Bryopsis plumosa* (C); (f)—*Laminaria digitata* (P); (g)—*Palmaria palmata* (R); (h)—*Himanthalia elongata* (P); (i)—*Porphyra umbilicalis* (R); (j)—*Jania rubens* (R); (k)—*Gracilaria gracilis* (R); (l)—*Ceramium virgatum* (R); (m)—*Kappaphycus alvarezii* (R); (n)—*Ulva lactuca* (C); (o)—*Ascophyllum nodosum* (P); (p)—*Eucheuma denticulatum* (R); C—Chlorophyta; R—Rhodophyta; P—Phaeophyceae; Scale = 1 cm.

3. Polysaccharides

Marine macroalgae derived polysaccharides are well known for their biological benefits. Many previous research studies have suggested the presence of polysaccharides (ulvan, fucoidan, alginate, laminarin, carrageenan, sulphated polysaccharides, agar, and

agarose) in macroalgae and noted their cosmeceutical benefits. Other examples of macroalgae derived polysaccharides and their cosmetic benefits are presented in Table 1. Wang et al. [37] suggested important bioactivities of fucoidan (including antioxidant, antimicrobial, anti-inflammatory, anticancer, antihyperlipidemic, and other bioactivities). Some studies suggested the utilization of polysaccharides as bioactive constituent in skin care formulations, played a major role in cosmetics such as moisturizers, emulsifiers, wound healing, and as a thickener [38]. The chemical structures of marine algae derived polysaccharides are illustrated in Figure 2.

Figure 2. Chemical structures of marine macroalgae derived polysaccharides. (a) Ulvan, (b) agar, (c) kappa-carrageenan, (d) porphyran, (e) laminaran, and (f) fucoidan.

Table 1. Application of macroalgae derived polysaccharides in skin cosmetics.

No.	Name of Macroalgae	Polysaccharides	Cosmetic Benefits	References
1	<i>Ulva lactuca</i> (Figure 1n) (C)	SP (Ulvan)	Antioxidant, Moisturizer, Photoprotective	[39]
	<i>Neopyropia yezoensis</i> (R)	Porphyran	Antiinflammation	[40,41]
2	<i>Porphyridium</i> sp.* (R), <i>Costaria costata</i> (P), <i>Ulva lactuca</i> (Figure 1n) (C)	Sulphated polysaccharides	Antioxidant, Anti-inflammatory, Antiaging	[42]
3	<i>Fucus vesiculosus</i> (Figure 1a)	Fucoidans	Antiaging, Antiwrinkle	[43]
4	<i>Ascophyllum nodosum</i> (Figure 1o), <i>Chnoospora minima</i> , <i>Sargassum fusiforme</i> , <i>Saccharina japonica</i> , <i>Sargassum polycystum</i> , <i>S. vachellianum</i> , <i>S. hemiphyllum</i> (P)	Fucoidans	Photoprotection, Anti photoaging Anti-inflammatory, Anti-elastase, Anti-collagenase, Skin whitening	[44–47]
5	<i>Fucus vesiculosus</i> (Figure 1a) (P)	Fucoidan	Anticoagulant Antioxidant, Enhancer of Skin fibroblast formation	[48]
6	<i>Neoporphyra haitanensis</i> (R)	Porphyran	Antioxidant	[49,50]
7	<i>Saccharina longicuris</i> (P)	Laminaran	Anti-inflammation, Antioxidant, Reconstruction of dermis	[51,52]
8	<i>Saccharina longicuris</i> (P)	Galactofucans	Enhance fibroblast formation, Increase synthesis of matrix metalloproteinase (MMP) complex and collagen-1	[53]
9	<i>Eucheuma denticulatum</i> (Figure 1p) (R)	Carrageenan	Antioxidant, photoprotection	[54]
10	<i>Gelidium</i> sp. (R)	Agar	Thickener	[55]
11	<i>Ascophyllum</i> sp., <i>Fucus</i> sp., <i>Sargassum</i> sp., <i>Undaria</i> sp. (P)	Laminaran	Anticellulite	[56]
12	<i>Saccharina cichorioides</i> (P)	Fucoidan	Anti-atopic dermatitis	[57]
13	<i>Corallina officinalis</i> (Figure 4a) (R)	Sulphated polysaccharides	Antioxidant	[58]
14	<i>Ulva australis</i> (C)	Ulvan	Antiaging	[59,60]
15	<i>Acanthophora muscoides</i> (R)	Sulphated polysaccharides-Carrageenan	Anticoagulant, Antinociceptive, antiinflammation, Gel agents	[61–63]
17	<i>Chondrus crispus</i> (R)	Carrageenan	Gel and Thickening agent, Skin moisturizer	[64]
18	<i>Ulva rigida</i> (Figure 4m), <i>U. pseudorotundata</i> (C)	Sulphated polysaccharides	Antioxidant, Chelators, Gel agents, Moisturizer	[65]
19	<i>Ascophyllum nodosum</i> (Figure 1o) (P)	Fucoidan	Anti-inflammation, Antiviral, Antiaging, Anti elastase, Photoprotective, Tyrosinase inhibition, Anticellulite	[66]
20	<i>Gracilaria</i> sp. (R)	Agar	Thickener	[67]
21	<i>Padina boergesenii</i> (P)	Sulphated polysaccharides	Formation of collagen	[68]

Table 1. Cont.

No.	Name of Macroalgae	Polysaccharides	Cosmetic Benefits	References
22	<i>Macrocystis</i> sp., <i>Lessonia</i> sp., <i>Laminaria</i> sp. (P)	Alginate	Gelling and Stabilizing agent, Moisturizer, Chelator	[69,70]
24	<i>Kjellmaniella crassifolia</i>	Fucoidan	Antiaging, Antiwrinkle	[71]
25	Brown algae (P)	Alginate	Thickening agent Gelling agent	[72]
27	<i>Sargassum</i> <i>vachellianum</i> (P)	Polysaccharides	Skin moisturizer and protectors	[73]
28	<i>Fucus vesiculosus</i> (Figure 1a), <i>Laminaria digitata</i> (Figure 1f), <i>Undaria pinnatifida</i> (Figure 1b) (P)	Fucoidan	Antioxidant, Antiaging, Anticoagulant, Increase skin fibroblast formulation	[74,75]
29	<i>Ascophyllum nodosum</i> (Figure 1o) (P)	Fucoidan	Anti-elastase, gelatinase A inhibition, Inhibition of interleukin-1 beta in fibroblast cells	[76]
30	<i>Ecklonia cava</i> (P)	Phlorotannins	Photoprotectors against UV-B	[77,78]
31	<i>Neoporphyra haitanensis</i> , <i>Gracilaria chouae</i> , <i>G. blodgettii</i> (R)	Agar	Antioxidant, Thickeners Antitumor, Radiation protector, Antiaging	[79,80]
32	<i>Turbinaria conoides</i> (P)	Laminarin, Alginate, Fucoidan	Antioxidant	[81]

SP, Sulphated Polysaccharides; C, Chlorophyta; R, Rhodophyta; P, Phaeophyceae; * Microalgae.

Many previous studies demonstrated that fucoidan obtained from brown algae, *Fucus* sp., *Sargassum* sp., as well as brown alga, *Laminaria* sp. (Phaeophyceae) can be utilized as an inhibitor of tyrosinase [82]. Brown algae such as *Chnoospora minima* and *Sargassum polycystum* derived fucoidan can inhibit tyrosinase, collagenase, and elastase [83]. Park and Choi, [84] also demonstrated the improved inhibition of low molecular weight fucoidan in a melanoma cell.

Polysaccharides report a key role in collagenase and elastase inhibition. Sulphated polysaccharides obtained from brown alga, *S. fusiforme* (formerly *Hizikia fusiformis*) (Phaeophyceae) potentially inhibited collagenase and elastase by regulating different pathways in HDF cells radiated by UVB [85]. In a dose-dependent manner, *Chnoospora minima* and *Sargassum polycystum* derived fucoidan showed elastase and collagenase inhibition activities [40]. Furthermore, Moon et al. [86,87] studied the inhibitory activity of MMP1 promoter and increase the expression of Type-1 procollagen synthesis of Fucoidan.

Polysaccharides have the greatest amount of water retention time and can act as humectant and moisturizer in cosmetic products. Many research studies suggested greater hydration capacity and moisturizing effects of polysaccharides from *Saccharina japonica* (formerly *Laminaria japonica*) (Phaeophyceae) than hyaluronic acid [88]. Isolation of sulphated polysaccharide was carried out from the green macroalgae *Ulva linza* (formerly *Ulva fasciata*) which revealed higher moisture absorption and retention for 96 h in comparison to glycerol [89]. *Saccharina japonica*, *Neoporphyra haitanensis* (formerly *Porphyra haitanensis*) (Rhodophyta), *Codium fragile*, *Ulva linza* (Figure 1d) (formerly *Enteromorpha linza*), and *Bryopsis plumosa* (Figure 1e) (Chlorophyta) derived polysaccharides showed good amount of moisture absorption and retention [90]. They also reported the role of sulphate content and molecular weight in the moisture-holding capacity.

Oligosaccharide zinc complex derived from *Laminaria digitata* (Figure 1f) (Phaeophyceae) reported anti-acne activity (i.e., reduction of acne signs) by reducing sebum pro-

duction [91]. Sebaaly et al. [92] reported bactericidal activity of *Corallina* sp. (Rhodophyta) derived sulphated galactan against *Enterococcus faecalis* and *Streptococcus epidermidis*.

4. Amino Acids

Protein is considered a macromolecule and polymer of amino acids. Pereira [76] reported the role of amino acids as a natural moisturizing factor that prevents water loss in the skin. Marine macroalgae are a satisfactory resource of various amino acids, such as glycine, alanine, valine, leucine, proline, arginine, serine, histidine, tyrosine, and some other mycosporine amino acids (MAAs). Marine macroalgae derived peptides and amino acids and its skin cosmetic benefits are illustrated in Table 2. In cosmeceutical products, amino acids usually function as a hydrating agent as a natural moisturizing factor in human skin [93].

Stengel et al. [94] reported that macroalgae are a quality source of essential amino acids, such as histidine, tyrosine, tryptophan, and non-essential amino acids such as alanine, serine, and proline. Antioxidant activity was reported by *Ulva australis*-derived amino acids, histidine, and taurine [95]. On the other hand, red macroalgae *Palmaria palmata* (Figure 1g) (Dulse) and brown alga *Himanthalia elongata* (Figure 1h) are plentiful in glutamic acid, alanine, and serine [96]. The chemical structures of marine algae derived amino acids are illustrated in Figure 3.

Figure 3. Chemical structures of amino acids derived from marine macroalgae. (a) Alanine, (b) serine, (c) proline, (d) histidine, (e) tyrosine, (f) tryptophan, (g) glutamic acid, and (h) mycosporine glycine.

Table 2. Applications of macroalgae derived peptides and amino acids in skin cosmetics.

No.	Name of Macroalgae	Compounds	Cosmetic Benefits	References
1	<i>Scytosiphon lomentaria</i> (P)	Amino acids	Antioxidant, Radical scavengers, Chelators	[97–99]
2	<i>Gracilaria vermiculophylla</i> (R)	Porphyra-334, Palythine, Asterina-330, Shinorine	Antioxidant, UV protector	[100]
3	<i>Ulva lactuca</i> (Figure 1n) (C), <i>Asparagopsis armata</i> (Figure 4c) (R)	MAAs, Amino acids	Antiaging, Anti wrinkles, Improves collagen formation	[101]
4	<i>Pelvetia canaliculata</i> (Figure 4d) (P)	Amino acids	Antioxidant, Collagen formation, Proteoglycan's synthesis	[102]
5	<i>Gracilaria chilensis</i> , <i>Pyropia plicata</i> , <i>Champia novae-zelandiae</i> (R)	MAAs	Anti UV, Antioxidant	[103]
6	<i>Ulva lactuca</i> (Figure 1n) (C)	Arginine, Aspartic acid, Glycine	Enhance collagen and elastin synthesis	[103]
7	<i>Porphyra umbilicalis</i> (Figure 1i) (R)	MAAs, (2:1 ratio of Porphyra-334 and Shinorine)	Antiaging	[104]
8	<i>Palmaria palmata</i> (Figure 1g), <i>Catenella caespitosa</i> (R)	MAAs	UV and UV-A protection	[105]
9	<i>Porphyra</i> sp., <i>Catenella caespitosa</i> (R), <i>Padina crassa</i> , <i>Desmarestia aculeata</i> (P)	MAAs such as Aminocyclohexenone-type, Aminocyclohexene imine-type	Photoprotection, Antiaging, Anti-inflammatory, Antioxidant	[106]
10	<i>Curdiea racovitzae</i> , <i>Iridaea cordata</i> (R)	Palythine, asterina-330	Antioxidant, Anti-UV, Antiaging	[107]
11	<i>Porphyra</i> sp. (R)	Protein and hydrolysates	Moisture retention capacity and viscosifying agent	[108,109]
12	<i>Palmaria</i> sp., <i>Porphyra</i> sp. (R)	High amounts of Glycine and Arginine	Natural moisturizing factor	[110]
13	<i>Chondrus crispus</i> (Figure 4b), <i>Mastocarpus stellatus</i> (Figure 4e), <i>Palmaria palmata</i> (Figure 1g) (R)	Palythine, Usujirene, Porphyra-334, Shinorine, Asterina, palythinol	Antioxidant, Anti-proliferation	[111]
14	<i>Pelvetia canaliculata</i> (Figure 4d) (P)	Amino acids	Antioxidant, Collagen synthesis, Proteoglycan synthesis stimulation	[112]
15	<i>Laminaria digitata</i> (Figure 1f) (P)	Proteins	Lipolytic	[113]
16	<i>Neopyropia yezoensis</i> (R)	Peptide PPy1	Anti-inflammatory	[114]
17	<i>Palmaria palmata</i> (Figure 1g) (R)	MAAs	UV protector	[115]

Table 2. Cont.

No.	Name of Macroalgae	Polysaccharides	Cosmetic Benefits	References
18	<i>Sargassum polycystum</i> (P)	Amino acids and amines	Anti-melanogenic or skin whitening effect	[116–118]
19	<i>Porphyra umbilicalis</i> (Figure 1i) (R)	Porphyra-334, Shinorine	Moisturization, Skin protector, Antiwrinkle, Protect against roughness	[119]
21	<i>Porphyra yezoensis</i> f. <i>coreana</i> (R)	Peptides, PYP1-5, porphyra-334	Enhance Elastin and collagen formation, reduce MMP expression	[119]
22	<i>Palmaria palmata</i> (Figure 1g), <i>Porphyra umbilicalis</i> (Figure 1i) (R)	MAAs	Antiaging, Collagenase inhibition	[120,121]

C, Chlorophyta; R, Rhodophyta; P, Phaeophyceae.

A natural moisturizing factor, arginine has been reported in Rhodophyta *Palmaria* sp. and *Porphyra* sp. and can be used in cosmetic products [76]. Seaweed-derived mycosporine amino acids play a role in potential photo protector against UV radiation damage, in radical scavenging, and in DNA repair systems. Hence, it can be applicable in UV protection and antioxidant activity in cosmeceutical applications [122]. Due to their selective affinity to the target cells and their capacity to change physiological roles in the skin drawn attention to skincare products. Ryu et al. [119] found increased elastin and collagen production as well as decreased the expression of matrix metalloprotein (MMP) from *Neopyropia yezoensis* (formerly *Porphyra yezoensis*) (Rhodophyta) derived peptides such as PYP1-5 and porphyra-334. In addition, PYP1-5 increases expression of TIMP-1,2 and TGF- β 1 protein expression, which induced collagen synthesis [123]. Mycosporine amino acids from different species of Gracilaria genus (*G. tenuistipitata*, *G. domingensis*, *G. birdiae*) (Rhodophyta) exhibited photoprotection activity [124]. It can also absorb ultraviolet light and also played its role as a photoprotector [125,126]. As compared to synthetic sunscreens, Porphyra-334 obtained from the *P. umbilicalis* (Figure 1i) (Rhodophyta) lower the intracellular radical oxygen species increased by UVA damage and also conquered the expression of MMP complexes which proved a better UV filter [127]. Suh et al. [128] revealed the role of MAAs in antioxidant, antiaging, and anti-inflammatory activities by ROS scavenging potential, by increasing UV suppressed genes expression, and by reducing COX-2 and involucrin expression in HaCaT cells. Red algae *P. umbilicalis* contain MAAs and hence act as photoprotective [128]. Other examples include *Dixonella grisea* (formerly *Rhodella reticulata*) (Rhodophyta), *Ecklonia cava* and *Undaria pinnatifida* (Figure 1b) (Phaeophyceae) have been reported for antioxidant activity [129–132]. Some algae such as *Jania rubens* (Figure 1j) and *Meristotheca dakarensis* (Rhodophyta) that produce glycosaminoglycans, type 1 and type 3 collagen synthesis, and keratin have been widely utilized for their antiaging benefit [133]. Subramaniyan et al. [134] and Kim et al. [123] reported *Neopyropia yezoensis* (formerly *Pyropia yezoensis*) (Rhodophyta) derived peptides in the stimulation of collagen synthesis in antiaging activity (by enhancing expression of TGF β 1 protein), elastin synthesis, and by suppressing the expression of MMP-1 protein.

Figure 4. Seaweed species images: (a)—*Corallina officinalis* (R); (b)—*Chondrus crispus* (R); (c)—*Asparagopsis armata* (R); (d)—*Pelvetia canaliculata* (P); (e)—*Mastocarpus stellatus* (R); (f)—*Laminaria ochroleuca* (P); (g)—*Saccharina latissima* (P); (h)—*Cystoseira compressa* (P); (i)—*Gongolaria nodicaulis* (P); (j)—*Ericaria selaginoides* (P); (k)—*Gongolaria usneoides* (P); (l)—*Fucus spiralis* (P); (m)—*Ulva rigida* (C); (n)—*Fucus serratus* (P); C—Chlorophyta; R—Rhodophyta; P—Phaeophyceae; Scale = 1 cm.

5. Pigments

Marine macroalgae have a broad diversity of photosynthetic pigments that capture light for the photosynthesis process. Chlorophyta (green algae) contain chlorophyll *a*, chlorophyll *b*, and carotenoids; Rhodophyta (red algae) contain chlorophyll *a*, phycobilin (phycocyanin, phycoerythrin), and carotenoids (carotene, lutein, zeaxanthin), and Phaeophyceae (brown algae) contain chlorophyll *a*, chlorophyll *c*, fucoxanthin, and different carotenoid pigments. Different macroalgae-derived pigments and cosmetic applications are reported in Table 3. These pigments provide a shield to the skin cells against harmful UV radiations [135].

Hama et al. [136] reported cosmetic formulation containing astaxanthin exhibit potential antioxidant and photoprotection effect against the cell damage caused by UV B. Marine macroalgae are widely known for different ranges of pigments; chlorophylls, carotenoids, and phycobilin are the three major classes of pigments. Carotenes, fucoxanthin, xanthophylls, and peridinin belong to carotenoids, whereas phycocyanin and phycoerythrin belong to phycobilin pigment.

Pereira et al. [137,138] suggested the biological role of pigments in photoprotection as well as an antioxidant activity through the elimination of ROS. Carotenoids used as natural dyes have been reported to benefits such as antioxidant, anti-inflammatory, and radical sequestering properties [139]. Carotenoids have pro-vitamin A activity that protects the healthy skin from damaging effects as well as photooxidation from UV light [140]. Astaxanthin has various skin cosmetic benefits such as antiinflammation and antioxidants in photodamage [141]. Peng et al. [142] and D' Orazio et al. [143] showed the main biological benefits of fucoxanthin such as antitumor, anti-inflammatory, antitumor, anti-obesity, and antiangiogenic activities. Carotenoids such as alpha-carotene, beta carotene, and lycopene are categorized as carotenes whereas astaxanthin, fucoxanthin, lutein, and zeaxanthin are categorized as xanthophylls. These pigments have skin benefits such as anti-inflammatory and antioxidant properties, and are useful as natural dyes. Mularczyk et al. [144] reported the antioxidative, anti-inflammation, and immunomodulatory activity of astaxanthin and suggested it as an interesting candidate for the cosmetic industry. R-phycoerythrin is commonly found in different algae such as *Polysiphonia stricta*, *Palmaria palmata* (Figure 1g), *Gracilaria gracilis* (Figure 1k), *Gracilaria tikvahiae*, and *Neopyropia yezoensis* (Rhodophyta). This R-phycoerythrin together with phycobiliproteins can be used as a natural color enhancer as well as in cosmetic formulations.

Cardoso et al. [145], Kim et al. [146], and Sekar and Chandramohan [147] reported the role of pigments such as phycocyanin and phycoerythrin in daily routine cosmetic products such as lipsticks, eyeliner, as well as photoprotection, antimicrobial, anti-inflammatory properties. The chemical structures of pigments found in marine macroalgae are presented in Figure 5.

Table 3. Applications of macroalgae derived pigments in skin cosmetics.

No.	Name of Macroalgae	Pigment	Cosmetic Benefits	References
1	<i>Sargassum</i> spp.	Carotenoids, Astaxanthin, Beta-carotene, Fucoxanthin	Anticellulite, Antiaging, Antiphotoreaging, antioxidant, antiviral	[148]
2	<i>Saccharina japonica</i> (P)	Fucoxanthin	Inhibition of tyrosinase and Melanogenesis in UVB irradiated	[149]
3	<i>Cladosiphon okamuranus</i> (P)	Fucoxanthin	Antioxidant, DPPH inhibition	[150]
4	<i>Neopyropia yezoensis</i> ®	Phycoerythrin	Antioxidant, Anticancer, Antiinflammatory	[34]

Table 3. Cont.

No.	Name of Macroalgae	Pigment	Cosmetic Benefits	References
5	<i>Gracilaria gracilis</i> , <i>Porphyridium</i> sp. (R)	Phycobiliprotein pigment such as R-phycoerythrin, Phycocyanin, Allophycocyanins	Antioxidant, Skin whitening activity by Antimelanogenic activity	[151]
6	<i>Cladophora glomera</i> ® (C)	Chlorophyll a, Chlorophyll b, Chlorophyll c, Chlorophyll d	Antibacterial, Antioxidant, Colorants, Deodorizer	[152–154]
7	<i>Portieri</i> ® p. (R)	Phycobiliproteins, Phycoerythrin, Phycocyanin	Antioxidants, anti-inflammatory, Colorants, Radical scavenger	[154]
8	<i>Cladophora glomerata</i> (C)	Chlorophyll	Tissue growth stimulators	[155]
9	<i>Neopyropia y</i> ®ensis (R)	Porphyran	Antioxidant, Anti-inflammatory	[156]
10	<i>U</i> ® lactuca (C)	Carotenoids such as astaxanthin, beta-carotene, fucoxanthin, lutein	Anti-inflammatory, Antiaging, Tyrosinase inhibition, Antioxidants, Photoprotective	[153]
11	Rhodophyta (R)	Lutein	Skin whitening	[157]
12	<i>Paraglossum lancifolium</i> (R)	Lipid soluble pigments such as Xanthophyll and Carotenoids Beta-carotene, Lutein	Antioxidant, Anti-inflammatory, Antiphotoreaging, Photoprotection, Anti-photoaging	[158]
13	<i>Undaria pinnatifida</i> (P)	Fucoxanthin	Photoprotective	[159]
14	<i>Porphyra</i> sp. (P)	Zeaxanthin, Alpha and beta carotene	Anti-inflammatory, Photoprotection, Antioxidant, Antiaging	[160]
15	<i>Gracilaria gracilis</i> (Figure 1k) (R)	Phycobiliproteins (R-phycoerythrin allophycocyanin, Phycocyanin)	Antioxidant	[151]
16	<i>Sargassum siliquastrum</i> (P)	Fucoxanthin	Skin protector, Antiphotoreaging, Antiwrinkle	[161]
17	<i>Ulva lactuca</i> (C)	Zeaxanthin, Neoxanthin, Antheraxanthin, Siphonein, Siphoxanthin,	Photoprotection, Antiphotoreaging, Anti-inflammatory	[162]
18	<i>Himanthalia elongata</i> (P)	Fucoxanthin extract	Antioxidant	[163]
19	<i>Ascophyllum nodosum</i> (P)	Fucoxanthin	Antiaging, Antiwrinkle	[164]
20	<i>Fucus vesiculosus</i> (P)	Fucoxanthin	Antioxidant	[165]
21	Phaeophyta	Fucoxanthin	Antiphotoreaging	[166]
22	<i>Sargassum siliquastrum</i> (P)	Fucoxanthin	Anti-melanogenic (skin whitening effect), Antioxidant, Anti-inflammatory	[167]
23	<i>Gelidium crinale</i> (R)	Carotenoids	Antioxidant	[168]

C, Chlorophyta; R, Rhodophyta; P, Phaeophyceae.

Figure 5. Cont.

Figure 5. Chemical structures of marine macroalgae derived pigments. (a) Chlorophyll A, (b) phycoerythrin, (c) alpha-carotene, (d) xanthophyll, (e) loraxanthin, (f) astaxanthin, (g) fucoxanthin, (h) violaxanthin, (i) lycopene, and (j) zeaxanthin.

6. Phenolic Compounds

Phenolic compounds are one of the secondary metabolites that make an important group of components for skin cosmetic benefits. Due to wide varieties of biological actions, they can be incorporated in various skin cosmetic preparations. They can be categorized into simple phenolic compounds and polyphenols, comprising bromophenols, phlorotannins, flavonoids, terpenoids, etc. [169]. Marine macroalgae derived phenolic compounds and their cosmetic benefits are presented in Table 4. Gómez et al. [170] and Morais et al. [171] reported the presence of a high concentration of phlorotannins in brown algae whereas bromophenol, phenolic acids, terpenoids, and flavonoids are predominant in green and red macroalgae. Different phenolic groups have different cosmeceutical benefits with Phlorotannin acting as a hyaluronidase inhibitor and conferring cosmetic effects (such as antiwrinkle, antiaging, skin whitening, and anti-allergic effects). Marine macroalgae are the producer of these molecules and lead to valuable ingredients in cosmetic formulations. Mateos et al. [172] revealed bioactive potentials of seaweed-derived phenolic compounds with antimicrobial, anticancer, antioxidant, anti-inflammatory properties, etc. which make it very attractive to cosmetic and cosmeceutical products. Phlorotannin has more attention

in cosmetic applications due to multiple benefits in cosmetics such as antioxidant, anti-inflammatory, anti-allergic, hyaluronidase inhibitor, and MMP (matrix metalloproteinase) inhibition [173]. In addition, it shows protection against damaging UV rays, but also gives protection against ionizing radiations [174]. Seaweed-derived Bromophenol reported organoleptic properties (such as flavor) [175]. Sanjeeva et al. [176] reported anti-allergic, anti-wrinkle, and anti-aging activities of phlorotannins due to inhibition of hyaluronidase enzyme. Polyphenol content from the brown alga *Fucus vesiculosus* reported UV protection, skin-soothing benefits as well as skin age spot reduction [177]. The chemical structures of macroalgae derived phenolic compounds are illustrated in Figure 6.

Figure 6. Chemical structures of marine macroalgae derived phenolic compounds. (a) Eckol, (b) dieckol, (c) phenol, (d) phlorofucofuroeckol B, (e) octaphlorethol A, (f) eckstonol, (g) sargachromanol E.

Tyrosinase inhibition and skin whitening effect exhibited by phlorotannin from brown alga *Sargassum fusiforme* (formerly *Hizikia fusiformis*) [178]. Bromophenol from *Laurencia* sp. reported antioxidant and antimicrobial effects which can be concerned for photopro-

tection in the cosmetic formulation [175]. Li et al. [179] and Zou et al. [180] studied the biological activity of phlorotannin from different brown marine macroalgae such as *Ecklonia cava*, *E. cava* subsp. *stolonifera* (formerly *E. stolonifera*), *E. cava* subsp. *kurome* (formerly *Ecklonia kurome*), *Ishige okamurae*, *S. fusiforme*, *Eisenia bicyclis*, *U. pinnatifida* (Figure 1b) and *Sargassum thunbergii* (Phaeophyceae). Phlorotannin is phloroglucinol-based polyphenols, mainly found in brown algae. Phlorotannins have a wide range of beneficial applications such as anti-melanogenesis, antiaging, and antioxidants which are applicable in cosmetic formulations [181–185]. In a dose-dependent manner, Ryu et al. [186] studied that methanol extract of *Corallina pilulifera* which is rich in phenolic content inhibited the matrix metalloproteinase 2,9 expression in UV induced dermal fibroblast cells. Joe et al. [182] and Kong et al. [187] found strong MMP inhibition by *E. bicyclis*, *E. cava*, and *E. cava* subsp. *Stolonifera* derived Phlorotannin.

Table 4. Applications of macroalgae derived phenolic compounds in skin cosmetics.

No.	Name of Macroalgae	Phenolic Compound/s	Characterization or Analysis of Phenolic Compounds	References
1	<i>Macrocystis pyrifera</i> (P)	Phlorotannins, Phloroeckol, Tetrameric phloroglucinol	Antioxidant, Antidiabetic, Antiaging	[188]
2	<i>Ascophyllum nodosum</i> (Figure 1o) (P)	Ascophyllan	MMP inhibition	[189]
3	<i>Cystoseira foeniculacea</i> (P)	Polyphenol	Antioxidant	[190]
4	<i>Stephanocystis hakodatensis</i> (P)	Phenol	Antioxidant	[191]
5	<i>Ecklonia cava</i> subsp. <i>Stolonifera</i> (P)	Fucofuroeckol-A	Protection against UVB radiation	[192]
7	<i>Corallina pilulifera</i> (R)	Phlorotannins	Antiaging, antiinflammatio, antioxidants, antiallergic, UV screens	[193]
8	<i>Ishige foliacea</i> (P)	Phlorotannin	Antimelanogenic, inhibition of tyrosinase and melanin synthesis	[194,195]
10	<i>Laminaria ochroleuca</i> (Figure 4f) (P)	Polyphenol	Antioxidant	[196]
11	<i>Caulerpa racemo</i> ® (C)	Flavonoids, Hydroquinone, Saponins	Tyrosinase inhibitor	[197]
12	<i>Ecklonia cava</i> (P)	Dioxinodehydroeckol	UV B protective	[198]
13	<i>Ecklonia cava</i> subsp. <i>stolonifera</i> (P)	Phlorotannins	Inhibition of Matric metalloproteins (MMPs), Antiwrinkle, Tyrosinase inhibitor, Skin whitener	[199]
14	<i>Saccharina latissima</i> (Figure 4g) (P)	Phenol	Antioxidant	[200]
15	<i>Ecklonia cava</i> (P)	<i>Dieckol</i>	Anti-adipogenesis	[201]
16	<i>Ecklonia cava</i> subsp. <i>kurome</i> (P)	<i>Phlorotannin</i>	Anti-inflammatory, Hyaluronidase inhibition	[202]
17	<i>Caulerp</i> ® p. (C)	Flavonoids, Phenols	Tyrosinase inhibitors	[203]
18	<i>Rhodomela conf</i> ® <i>oides</i> (R)	Polyphenol, Bromophenol	Antioxidant, Antimicrobial, DPPH inhibition	[204]
19	<i>Eisenia bicyclis</i> , <i>Ecklonia Cava</i> subsp. <i>stolonifera</i> (P)	Eckol	Anti-inflammation, Skin whitening activity	[205,206]
20	<i>Schizymenia dubyi</i> (Figure 1c) (R)	Phenol	Anti-melanogenic, Tyrosinase inhibition	[207]

Table 4. Cont.

No.	Name of Macroalgae	Phenolic Compound/s	Characterization or Analysis of Phenolic Compounds	References
21	<i>Cystoseira compressa</i> (Figure 4h) (P)	Fuhalol	Antioxidant	[208]
	<i>Cystoseira compressa</i> (Figure 4h) (P)	Fuhalol	Antioxidant	[208]
22	<i>Ecklonia cava</i> (P)	dieckol	Promotes hair growth	[209]
23	<i>Fucus vesiculosus</i> (Figure 1a), <i>Gongolaria nodicaulis</i> (Figure 4i), <i>Ericaria selaginoides</i> (Figure 4j), <i>Gongolaria usneoides</i> (Figure 4k), <i>Ecklonia cava</i> (P)	Phlorotannins such as Fucophloroethol, Fucodiphloroethol, Fucotriphloroethol, Phlorofucofuroeckol bieckol or dieckol	Skin whitening effect, Antioxidant, Anti-inflammatory, Antihistamine, Photoprotection	[210]
24	<i>Ascophyllum nodosum</i> (Figure 1o) (P)	Phlorotannins, Eckols, Fucols, Phlorethols	Inhibition of tyrosinase, Anti-inflammation, Anti UV, Anti-allergic, Chelators, Antiaging, Hyaluronidase inhibitor	[210]
25	<i>Meristotheca dakarensis</i> (R)	Glucosaminoglycan	Anti-aging, Collagen synthesis	[13]
26	<i>Gongolaria nodicaulis</i> , <i>Ericaria selaginoides</i> , <i>Gongolaria usneoides</i> (Figure 4k) (P)	Phlorotannins such as bioeckol, 7-phloroeckol, phlorofucofuroeckol, fucophloroethol	Anti-inflammation, Antioxidant, Anti-aging, Inhibition of hyaluronidase	[210]
27	<i>Fucus spiralis</i> (Figure 4l) (P)	Phlorotannins	Inhibition of lipid peroxidation, hyaluronidase inhibitor, antiaging, antiwrinkle, Anti-inflammatory, Antiwrinkle	[210]
28	<i>Ecklonia cava</i> , <i>Ecklonia cava</i> subsp. <i>stolonifera</i> (P)	Eckol, 6,6'-bieckol, doeckol, Phlorofucofuroeckol-A, 8,8'-bieckol	Anti-allergic	[211]
29	<i>Eisenia bicyclis</i> , <i>Ecklonia cava</i> subsp. <i>stolonifera</i>	Phlorofucofuroeckol A	Hepatoprotective, Anti-tyrosinase	[212,213]
30	<i>Eisenia arborea</i> , <i>Ecklonia bicyclis</i> (P)	Phlorotannins	Anti-inflammation, Hyaluronidase inhibitor, antiwrinkle	[214]
31	<i>Eisenia arborea</i> (P)	Phlorofucofuroeckol A	Anti-allergic	[215]
32	<i>Ascophyllum nodosum</i> (Figure 1o), <i>Fucus serratus</i> (Figure 4n), <i>Himanthalia elongata</i> (Figure 1h), <i>Sargassum muticum</i> (P)	Phlorotannins	Antioxidant, Antibacterial, antiviral, photoprotection, Anti-inflammatory	[216–218]
33	<i>Ecklonia cava</i> (P)	Eckols, fucols, phlorethols, Fuhalols, fucophlorethol	Anti-aging, Anti-inflammation, Hyaluronidase inhibitor, antiallergic, UV protector	[218]

C, Chlorophyta; R, Rhodophyta; P, Phaeophyceae.

7. Fatty Acids

Seaweeds are well known for various types of fatty acids such as glycolipids, triglycerides, sterols, and phospholipids. The chemical structures of marine algae derived fatty acids are illustrated in Figure 7. These have been reported as being higher in seaweed as compared to terrestrial plants. Different types of fatty acids from different macroalgae and its cosmetic benefits are presented in Table 5. Dawczynski et al. [219] reported antiallergic and antiinflammation activity and skin protector (emollient) of seaweed-derived fatty acids.

Rhimou et al. [220] studied effective bacterial growth inhibition from methanolic extract of *Ceramium virgatum* (formerly *Ceramium rubrum*) (Figure 11) (Rhodophyta) against *Escherichia coli*, *Enterococcus faecalis*, and *Staphylococcus aureus*. Although, macroalgae-derived fatty acids (SFA, MUFA, PUFA) have been characterized for their antioxidant, anti-inflammatory, anti-allergic activities, etc. It may serve as soothing benefit that makes skin safer by maintaining hydration. The presence of polyunsaturated fatty acids (omega-3, omega-6) is responsible for skin nutrition and for maintaining skin health. These fatty acids are important regulators of several cellular processes as well as good health mediators [221]. Pimentel et al. [222] and Kumari et al. [223] suggested a predominant amount of eicosapentaenoic acid (EPA) and arachidonic acid in Phaeophyta and Rhodophyta whereas Chlorophyta have a high amount of docosahexaenoic acid (DHA). Higher quantities of C18-PUFAs presented in Chlorophyta species while C20-PUFAs in Rhodophyta species. Antiaging and antioxidant activity was reported in methanolic extract of *Corallina pilulifera* (Rhodophyta) by reducing the expression of gelatinase and by inhibition of free radical oxidation in human dermal fibroblast and human fibrosarcoma (HT-1080) [186]. A previous study reported that topical applications of medium-chain triglycerides, linoleic acid, soy lecithin, and vitamin A can promote wound healing in mice. It plays its role in the mediation of inflammation, cell proliferation, wound contraction, and tissue remodeling [224]. The fatty acids, mainly mixtures of triglycerides of saturated and unsaturated fatty acids commonly used as an ingredient in cosmetic formulation. Bonnet, [225], Bialek et al. [226], Rabasco and González et al. [227], and Zielinska and Nowak [228] suggested the significant importance of fatty acids in healing effects, which can be used in creams, emulsions, cosmetic masks, lipsticks, bath fluids, nail polishes, etc. Moreover, fatty acids play an important in overcoming excessive dryness of the skin, and their use is beneficial for skin and hair.

Figure 7. Chemical structures of marine macroalgae derived fatty acids. (a) Sterol, (b) fucosterol, (c) campesterol, (d) ergosterol, (e) cholesterol.

Table 5. Applications of macroalgae derived lipids and fatty acids in skin cosmetics.

No.	Name of Macroalgae	Fatty acid	Cosmetic Benefits	References
1	<i>Chondrus crispus</i> (Figure 4b) (R)	EPA, AA, DHA, GLA, LA, Palmitic acid, Oleic acid	Antiallergic, Anti-aging, Anti-inflammation, Antiwrinkle, Antimicrobial, Emollients,	[229]
2	<i>Undaria pinnatifida</i> (Figure 1b) (P)	PUFA	Anti-inflammatory	[229]
3	<i>Ulva lactuca</i> (Figure 1n) (P)	Fatty acid such as C18 and C16 type	In-vitro and in-vivo Nrf2-ARE activation, Cell protective, Antioxidant	[230]
4	Phaeophyceae (Brown algae) (P)	Unsaturated Fatty acids	Antioxidant	[231]
5	<i>Ulva lactuca</i> (Figure 1n) (P)	Lipopeptides	Inhibition of elastase, enhance collagen synthesis	[232]
6	<i>Himanthalia elongata</i> (Figure 1h) (P)	Fatty acids and volatile compounds	Antioxidant, Antimicrobial	[233]
7	<i>Porphyridium purpureum</i> (R)	Eicosapentaenoic acid, Docosahexaenoic acid, Eicosatetraenoic acid, Polyunsaturated omega-3 fatty acids	Antioxidant, Anti-inflammatory, Anti-photoaging	[234]
8	<i>Ulva rigida</i> (Figure 4m) (C), <i>Gracilaria</i> sp. (R), <i>Fucus vesiculosus</i> (Figure 1a), <i>Saccharina latissima</i> (Figure 4g) (P)	Lipidic profile	Antioxidant	[235]
9	<i>Sargassum fusiforme</i> (P)	Fucosterol	Protection against photodamage, UVB protector, MMP inhibition, Enhance procollagen formation, Anti-inflammatory	[236,237]
10	<i>Gracilariopsis longissima</i> (R), <i>Saccharina japonica</i> (P)	(8E)-10-oxo-8-octadecenoic acid, (E)-9-oxo-10-octadecenoic acid, Myristic acid, Palmitic acid	Anti-inflammatory	[238]
11	<i>Silvetia siliquosa</i> (P)	Fucosterol	Antioxidant, Stimulate antioxidant enzymes such as catalase, glutathione peroxidase	[239,240]
14	<i>Sargassum fusiforme</i> (P)	Fucosterol	Anti-aging, MMP inhibition	[241]
15	<i>Codium fragile</i> (C)	Sterol	Anti-inflammatory	[242]

C, Chlorophyta; R, Rhodophyta; P, Phaeophyceae.

8. Minerals

Depending on the environment in which macroalgae inhabit, they are highly diversified in mineral composition (especially with regards to trace elements including zinc, magnesium, aluminum, silica, copper, iodine, selenium, iron, manganese, and micronutrients including calcium, sodium, phosphorus, potassium, and chlorine). Kuda et al. [243] examined the mineral content in concentrates of harvested seaweed *Sargassum coreanum* (formerly *Sargassum ringgoldianum* subsp. *coreanum*) from Japanese beaches. They found the highest concentration of potassium, magnesium, and calcium in these samples. Likewise, *Kappaphycus alvarezii* (Figure 1m) (Rhodophyta) presented high levels of magnesium and calcium ions [244].

Minerals have a very essential vital role as cofactors of different metalloenzymes [245]. Moreover, a combination of calcium and magnesium improves barrier repairs in topical

skincare products [246]. Indeed, acid-induced burns are relieved by gel solution containing calcium gluconate solution [247]. Likewise, magnesium silicate (talc) and magnesium sulphate (i.e., Epsom salts) have reported enhancement of skin benefits. Talc is most frequently useful in baby skin powders to prevent diaper rash. In adults, it can be used as a lubricant and to reduce wetness in the perineal and axillary areas [248]. In addition, Boisseau et al. [249] found improvements in skin softness and exfoliation, relief in muscle tension, and the promotion of relaxation by Epsom salts. They also reported the key regulatory role of Mg^{++} and Ca^{++} in the proliferation and differentiation of keratinocytes. Likewise, magnesium silicate (talc) and magnesium sulphate (Epsom salts) have reported enhancement of skin benefits.

Talc is most frequently useful in baby skin powders to prevent diaper rash as well as in adults to reduce wetness in the perineal and axilla areas (and as a lubricant) [250]. They also reported the key regulatory role of Mg^{++} and Ca^{++} in the proliferation and differentiation of keratinocytes. ZnO-based skin protectants are cost-effective, easily formulated, and stable under aerobic conditions [250,251]. Zinc oxide is superior to zinc sulphate to mitigate inflammation and enhance re-epithelization of partial-thickness porcine skin [252]. Due to low water solubility, it sustains in the skin at the wound site. Newman et al. [253] revealed the importance of skin in sunburned skin and under ultraviolet exposure. Bissett et al. [254] found significantly delayed UV-induced tumors in Guinea pigs and mouse models by topical use of a 2-furildioxime (iron chelator).

Borkow et al. [255] exhibited a significant role of copper oxide in reducing facial wrinkles and an improvement of skin appearance. Besides, selenium is useful to protect the skin by involving antioxidant enzymes, especially glutathione, peroxidase, and thioredoxin reductase [256]. Selenium mitigates the effect of UV exposure as well as inhibits photodamage and may reverse photoaging [257–259]. An application of culture media containing selenium or selenomethionine significantly reduced UV-induced death of keratinocytes and melanocytes [260].

9. Challenges and Opportunities

There are more than 1000 substances derived from natural sources enlisted in the INCI (International Nomenclature of Cosmetic Ingredients), of which approx. 300 substances were considered harmful to the skin and the environment and about 50 considered to have carcinogenic properties. No formulations to be utilized in skin care is 100% harmless [261]. However, users have changed their choice and become highly dependent on green products to overcome the effects of synthetic cosmetic ingredients. Macroalgae have received much attentiveness in investigating sustainable bioactive ingredients that are secure, effective, and natural [262]. A variety of marine macroalgae-derived biological active components has been given more significant values in preparing formulation due to their huge benefits on the skin [263,264]. Macroalgae are found to be safer as they have very insignificant cytotoxicity when analysed on human cell lines and can be used to extract bioactive components by using novel extraction techniques [265,266]. Marine algae are widely utilized in biofuel production, wastewater treatment, food, and agriculture sector (as well as the pharmaceutical sector) [267]. By product of these industries could also be a promising compound for skin applications in an effectual and cost-efficient alternative to synthetic ones [268]. There are many challenges in the application of macroalgae as a cosmeceutical component such as culturing, harvesting, extraction, characterization, etc. Cultivation of macroalgae on large scale requires optimum conditions such as the light of a particular wavelength, pH, sterilization, nutrients availability, amount of CO_2 , temperature, salinity, carbon source, and nutrients [269]. According to the species of macroalgae and its application, the type and design of biological reactor used for cultivation. Mainly macroalgae collected from the sea or by cultivating in the sea environment in a specific season. Compared to that, culturing in a lab-based bioreactor is expensive and it gets contamination easily. Macroalgae are easily cultivated by using seawater instead of freshwater, which supplies nutrients, reduces cost, and improves the production of

seaweed-based bioactive ingredients such as lipids carbohydrates, proteins, amino acids, and phenolic compounds [269]. Nevertheless, sea cultivation could be a challenge as well as needs large amount of seawater, and the cost of construction, well-functioning, and up keeping of the space are substantial. Sometimes, open culturing may affect algae culture and low quality of yield which was affected by the biotic and abiotic factors [270].

The extraction procedure of bioactive ingredients can be classified into conventional and novel techniques. Some are routinely used methods such as Soxhlet, soaking, boiling, saponification, classical solvent-based procedures, and maceration, whereas others are novel methods including extraction using enzymes, microwave digestion, ultrasound, or supercritical fluid-based methods. The novel extraction procedure is preferred as it offers several benefits including high yield, high quality, minimum usage of solvents, and low time requirement. The enzyme-based method is a safe and environment-friendly approach for macroalgae-derived metabolites. By using various enzymes, different types of algae-based metabolites can be extracted. This procedure can also reduce the problem of water dissolution, immiscibility of biologically active components, and maintain the efficacy and high catalytic efficiency of phycocompounds [266,271]. Microwave-assisted extraction in the open vessel is safe, effective, and useful for bigger samples. It also reduces the extraction time and minimizes solvent utilization [272,273]. Sometimes, high power, high temperature, and high amount of pressure may degrade the yield and reduce its amount. Moreover, low pressure exhibited its effect on the product of polysaccharides from the cells. Additionally, an increase in time can directly increase the product but increasing time also causes degradation of polysaccharides [274]. Due to its non-toxicity and low cost, carbon dioxide is often used in supercritical fluid-based extraction methods. It is beneficial to extract non-polar compounds such as fatty acids, phenolic, sterols, phenolic compounds, and some pigments [274]. Ethanol solvent has been applicable as a cosolvent to improve the efficacy of phenolic components and carotenoids in this method [275]. Likewise, ultrasound-based extraction is used to extract phenolic ingredients, but this may be influenced by time, temperature, power, and the intensity of the ultrasound. Sometimes, the optimum extraction time is also required to stop the metabolites degradation. It is mainly useful in the extraction of phenolic compounds and laminarin. Increasing the efficiency and yield of phycobiliproteins from *Gelidium pusillum* can be achieved by a combination of ultrasound with maceration [276].

The safety of cosmetic products can be ensured by maintaining quality control and standardization. Some macroalgae species have high cosmetic value due to their highly diversified molecules and are required to evaluate the presence and concentration of heavy metals and pesticides. The sterilization level must be high, as set by the WHO and US FDA (Food and Drug Administration) [266]. One of the precautions to be reported in preparing cosmetic formulations is the harmful effect of toxicity which arises due to the presence of phototoxic compounds or photo allergens. These compounds may become activated by coming in contact with the skin and light exposure. Many of these compounds are oxidants and produce ROS [277]. People are not aware that these natural cosmetic products are a combination of many natural raw materials and chemical components that might develop unfavourable effects. Thus, after in vitro and in vivo experiments of prepared formulation, a clinical investigation has to be performed to determine the well-being and effectiveness of the product on human health. It is believed that the cosmeceutical sectors would become significantly enhanced in forthcoming years [278]. Therefore, a deeper level of investigation is required to formulate better cosmetic products.

10. Conclusions

Marine macroalgae-derived bioactive constituents have been applicable in cosmeceuticals applications due to their potential skin benefits. This wide variety of applicability and skin benefits enhances interest in and potentiality for use of seaweed-based constituents in cosmetic products. However, it is well demonstrated that cosmetic companies have become more interested in use of marine macroalgae by extracting active compounds and

their applications in cosmetic preparations. Macroalgae are a valuable resource of bioactive components, with scientific evidence revealing their benefits for safer use in humans and wellbeing. Marine algae-derived molecules showed biological effects on the skin, such as skin whitening, antiaging, antiwrinkle, photoprotection, moisturizing, and collagen-boosting, anti-inflammatory, antimicrobial, anticellulite, antiviral, and anticancer activities. Moreover, many cosmeceutical companies already use marine algae extracts and have derived compounds from these extracts in their formulations. However, the biochemical profile monitoring of macroalgae presents a problem that industries need to overcome. The development of its cultivation and sustainable methods of extraction procedures shows the significant key for this confined, which is being analyzed with noteworthy benefits. However, more detail analysis requires to understand the exact mechanism of some compounds since some compounds have not been fully explored. Therefore, the further analysis and evaluation are essential to improve the quality of cosmetic formulations which will be useful to enhance consumers safety.

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