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Review

Macroalgae and Microalgae Biomass as Feedstock for Products Applied to Bioenergy and Food Industry: A Brief Review

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Abstract: This article is a brief and critical review of the state of the art in algae production in the food and energy industries. Review and experimental articles from the last five years were selected to recapitulate the reasons for interest in algae cultivation, for which we highlight the most valuable phytochemicals passing through their niches in the food market, their bioenergetic potential and the possible uses of algal waste biomass. In addition, we punctuate the advent of algae biorefineries. The objectives of this study were to list the main points related to interest in cultivation, drawing a parallel between the establishment of algae in the food market and its potential to establish itself in the energy market. It was concluded that the use of algae biorefineries has been used as a solution for the food, chemical and energy markets, despite the need for the development of broader research on industrial scale.

Keywords: algae; macroalgae; microalgae; waste; biomass; food; bioenergy; biorefinery; phytochemicals; biotechnology

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1. Introduction

Since the 1970s, different energy crises have occurred, and, together with the depletion of non-renewable energy sources, this has generated great concern worldwide. Research for new energy sources is focusing on renewable raw materials (or feedstocks) for bioenergy production, and it is estimated that 50% of the world's energy will come from these sources in the following years [1]. Within this context, the production of bioenergy from algal biomass is promising; however, further studies are needed because the efficiency of bioenergy production is influenced by many variables. Two of the main variables are the following: the alga species—as it is estimated that there are 150,000 identified species—and the optimization of parameters to produce bioenergy on a large scale in a commercially competitive way [1,2].

Algae are organisms that can be found in all aquatic habitats, including oceans, rivers, ponds and wastewater. These organisms are produced on an industrial scale for food and nutritional supplements, and their extracts are used in cosmetics and pharmaceuticals and can also be used for biofuel production. Microalgae are single-celled organisms, whereas macroalgae are multicellular. Several bioproducts are produced by microalgae, such as polysaccharides, pigments, lipids, proteins, vitamins and other bioactive compounds. Like microalgae, macroalgae are considered appropriate substrates for biofuel production because they are also rich sources of biopolymers, such as agar, carrageenans and fatty acids, including eicosapentaenoic (EPA), docosahexaenoic (DHA) and alpha-linolenic (ALA), among other molecules [3,4].

From a macro perspective, this study aims to determine the following: Why is there an interest in algae exploitation in the energy and food markets, and what are the bottlenecks in these areas? This central question led to five minor leading questions: (1) What are the most valuable algae phytochemicals already described? (2) What are the uses for algae in the food market, and what are their future prospects? (3) What is missing regarding the implementation of algae in the bioenergy market? (4) What is the state of the art of the use of waste biomass from algae? (5) Can biorefineries cultivate algae and reach the food and energy markets? These questions guided our research on different sources, using selected keywords to build an article database and resulting in 56 papers from the last five years focused on these subjects. The information extracted from the papers was summarized in five topics directed by the leading questions, as follows: (1) The most valuable algae phytochemicals; (2) The nutraceutical consolidation of algae in the bioenergy market; (3) The algal potential for bioenergy; (4) Algae waste biomass utilization; and (5) Cultivating for food and energy: algae biorefineries allow both and beyond (Figure 1).

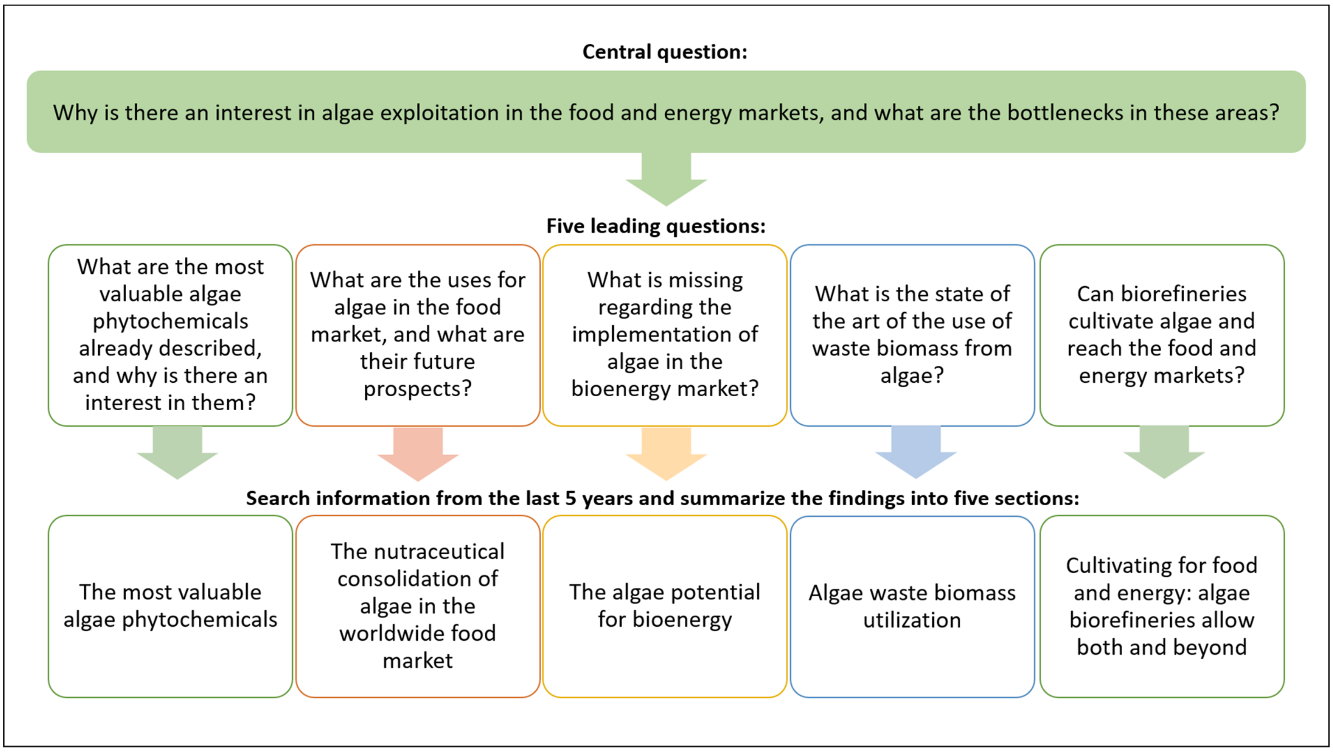

Figure 1. Summary flowchart of the research method. The flowchart of the research method was designed using the starting question of discovering the motives for interest in algae exploitation in the energy and food markets and the bottlenecks in these areas. This central question led to five minor leading questions, which guided the research in the databases, and the information extracted from the papers was summarized into five topics directed by the leading questions.

The inclusion criteria for building our scientific articles database were: (1) the inclusion of one of the following search terms: algae, waste, biomass, food, bioenergy, biorefinery, phytochemicals and biotechnology; and (2) confirmation of the adequacy of the central themes (focusing on the use of algae for the food and energy markets) after going through the analysis and manual selection. The studies were organized in an online database and distributed into groups according to the five topics structured by the leading questions. The sources that were used for searching for the articles were Google Scholar, PubMed, CAPES periodical portal, Elsevier and ScienceDirect, which are selected materials that are open-access and available online. We worked independently, and afterward, we all worked together to build the database and analyze the articles' information. No automation tools were used in the process. In the following sections, we answer the leading questions and present the results found in our search.

Finally, this review is a compilation of the newest information from the last five years in algae biomass research in the food and energy fields, in which we bring to the reader, in a clear and summarized way, answers to specific questions regarding our five section topics. Our intention with this mini-review was to identify the main concepts and bottlenecks in these areas, interrelating them and casting a critical eye to project a panorama of future applications. This panorama of algae fields and products can be seen in Figure 2.

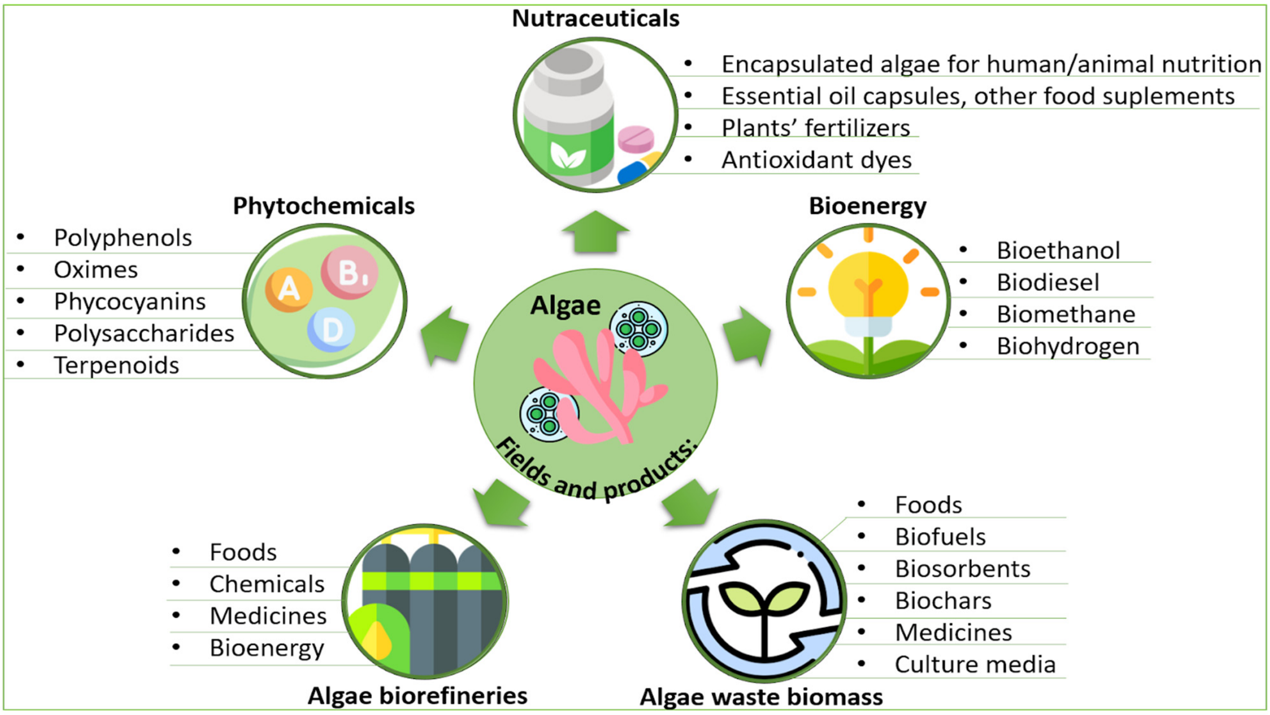

Figure 2. Algae fields and products. This schematic outlines the five directions taken from algae cultivation, or the five major areas of algae interest we identified and its by-products. This figure and the graphical abstract were designed using icons provided by http://flaticon.com (access on 4 January 2023).

2. The Most Valuable Algae Phytochemicals

A wide range of bioactive properties exist in algae due to the presence of some compounds, which promote antibacterial, anticancer, antioxidant, antifungal and antiviral properties [5,6]. Much research has been developed focusing on the main phytochemicals found in seaweed, aiming to study their bioactive potential [5–8]. In this context, some of the most studied marine algae with bioactive potentials—the macroalga *Chaetomorpha* sp. and microalga *Porphyridium purpureum*, *Chlorella vulgaris*, *Arthrospira platensis*, *Nannochloropsis oculata*, *Hypnea musciformis*, *Padina gymnospora* and *Spirulina platensis*, as well as their biological actions—are described in this section.

Marine macroalgae, also known as seaweeds, are natural inhibitors of α-glucosidase and α-amylase, and they can be used as hypoglycemic agents in food products [9]. In microalgae, their enzymatic inhibitory effect and antioxidant activity, along with their phytochemical profiles, were studied by Vieira et al. [8] for *Porphyridium purpureum*, *Chlorella vulgaris*, *Arthrospira platensis* and *Nannochloropsis oculata*. These authors reported that all studied species have bioactive potential, with the antioxidant activity reaching 0.81 to 11.70 mmol TE/100 g of biomass and an enzymatic inhibitory effect for the following enzymes: acetylcholinesterase (8.66 to 40.89% inhibition), butyrylcholinesterase (6.85 to

31.68% inhibition), α-amylase (IC50 ranging from 7.50 to 31.04 mg/mL) and pancreatic lipase (IC50 from 3.26 to 24 mg/mL). Among the investigated species, *P. purpureum* followed by *N. oculata* showed the greatest results in the evaluation of enzyme inhibitory activities in Alzheimer's disease, with emphasis on *P. purpureum*, which showed a 50% reduction in the enzyme α-amylase, demonstrating a promising result for type 2 diabetes treatment as well.

In a review focused on investigating the microalga *N. oculata* carried out by Zanella and Vianello [10], it was possible to highlight the high content of carotenoids, proteins and lipids, which give this species good nutritional value and bioavailability when ingested. In another study [5], the marine alga of the genus *Chaetomorpha* sp. was considered therapeutically promising due to its high antioxidant and anticancer activities. Ethanolic extracts of *Chaetomorpha* showed high IC_{50} antioxidant activity (9.41 $\pm$ 0.54 mg/mL). The same extracts showed inhibition of the MDA-MB-231 breast cancer cells of IC_{50} = 225.18 $\pm$ 0.61 µg/mL, attributed to the dichloroacetic acid present in the extract.

In addition to the bioactive compounds with antioxidant effects, most algae show some kind of cancer cell inhibition due to the presence of antineoplastic compounds. Saadaoui et al. [7] mentioned in their review the use of ethanolic extracts of *H. musciformis* and *P. gymnospora* against NCL-H292 lung cancer cells, showing promising results (IC_{50} = 22.0 $\pm$ 3.5 µg/mL and 15.9 $\pm$ 2.8 µg/mL, respectively); in contrast, ethanol and chloroform extracts from *Dictyota dichotoma* showed antineoplastic action of IC_{50} = 25.2 $\pm$ 1.1 µg/mL and 22.0 $\pm$ 3.5 µg/mL, respectively. These effects were attributed to the presence of polysaccharides, terpenoids and peptides. In another study, Hao et al. [11] evaluated the inhibitory effect of phycocyanins extracted from *Spirulina platensis* against A549 lung cancer cells, reporting effective results in inhibiting cancer cells by increasing the apoptotic rate.

In general, algae have a great established potential for the extraction of bioactive compounds with different biological effects, but more in vivo and cytotoxicity studies must be carried out to validate their use for medical treatments and food supplementation [12]. In the following section, we demonstrate how algae biomass can be used as a functional ingredient for food enhancement with its bioactive diversity.

3. The Nutraceutical Consolidation of Algae in the Worldwide Food Market

Algae represent a relatively unexplored source of bioactive compounds, such as polyphenols, alkaloids, tannins, flavonoids and sterols. Beyond the algal proteins and bioactive peptides, lipids and carbohydrates enable its use in functional foods—also called nutraceuticals- and its market holds greater value compared with the original biomass [13]. Seaweed has been used for a long time in foods due to the presence of bioactive compounds such as pigments, vitamins and antioxidants, which are mainly used as plant fertilizers and as human and animal nutrition [14,15].

In the 1950s, microalgae were considered a source of protein for human consumption, and by the 1960s-1970s the alga genera *Chlorella* and *Spirulina* were grown commercially for protein supply. The cultivation of *Dunaliella* and *Haematococcus* was used for pigment production in the 1980s (especially beta-carotene and astaxanthin). The production of polyunsaturated fatty acids began in the early 1990s with a focus on omega-3. Globally, the demand for edible algae has increased because of its high nutritional value and growing consumption by Asians, beyond cultural habits, mainly due to its functional benefits, which are being better described at this time [13,14].

Regarding the applications of algae in the food industry, dyes such as β-carotene, astaxanthin, fucoxanthin and phycocyanin are of great interest due to their antioxidant action. The pigments present in algae can become substitutes for synthetic sources that, depending on the dye and the concentration used, are harmful to health. However, there is still a lack of research on algal food dyes, its stability against temperature and time, its properties, health safety and the development of efficient extraction processes. Besides that, the advantages of producing algae rely on the fact that they are environmentally sustainable, they do not need arable lands for cultivation, and they present fast growth and high productivity [14].

Macroalgae and microalgae are gaining increasing attention also because of their high protein levels (up to 70% in several species of microalgae) and essential amino acid profile content. In microalgae, amino acid levels such as isoleucine, valine, lysine, tryptophan, methionine, threonine and histidine are similar or higher than those found in foods such as eggs and soy [16]. Seaweeds are rich in amino acids responsible for the umami taste (glutamic acid, aspartic acid, glycine and alanine). The index of essential amino acids that comprise the protein's nutritional properties is higher for red algae than that for brown and green algae. However, when compared to other protein-rich food sources, seaweed is limited by its low levels of lysine, threonine, tryptophan, cysteine and methionine [17].

The high protein content associated with antioxidant pigments and other compounds present in algae make them promising for direct incorporation in food products or in extract forms. In the extract of *Gigartina* sp., Echers et al. [18] found proteins containing new peptides with amphiphilic properties that stabilize the oil/water interface, suggesting a high probability of utilization as emulsifiers. The stabilization property is what causes stabilization in a suspension phase, making solutions stable without separation processes. As an example of stabilizers, there are carrageenans (red algae's polysaccharides), which are already used as milk protein stabilizers [17,19].

The presence of polyunsaturated fatty acids (PUFAs) is another reason why algae have received attention, which include the ω-3 (alpha linolenic acid, eicosapentaenoic acid and docosahexaenoic acid) and ω-6 family (γ-linolenic acid and arachidonic acid) [20]. Currently, research demonstrating the dietary effects of these PUFAs are linked to commercially available fish oil supplements containing mixtures of ω-3 acids, for which there is a significant growing global market [21].

In addition to proteins and lipids, algae also have polysaccharides in their composition, another class of complex macronutrients that have antioxidant, hypolipidemic and hypoglycemic activities [22]. One of the most interesting applications of microalgal polysaccharides is for the encapsulation technique used in coating nanomaterials [17,18]. Seaweed's sulfated polysaccharides have also attracted researchers' attention, being obtained from various algae, such as the microalga *Porphyridium cruentum* or the macroalga *Gigartina skottsbergii* [19]. In food, algae are desirable for their texturizing, stabilizing, emulsifying and thickening properties, although its applications are not restricted here; in the biotechnology area, for example, they can be used as expression vectors for vaccine production [23].

Foods with added algae have been investigated and several works have evaluated its potential as a food ingredient to improve the nutritional quality of food products. In general, the *Spirulina* and *Chlorella* genera are used the most in studies with food applications, and other genera such as *Haematococcus*, *Nannochloropsis* and *Aurantiochytrium* are also gaining attention due to their nutritional value. Considering the studies, the concentration of algae in the tested products ranges from 2% to 6% (*w/w*). Among the foods in which algae is added, the most common are baked goods, such as breads and cookies. The addition of flour, sugar and eggs in these bakery products is advantageous and can hide and moderate the flavor and color of incorporated algae. In contrast, dairy products such as yogurt and ice cream are more challenging to enrich with algae [17,18,23].

Besides all the benefits of using algae in foods, some problems, such as sensory issues (such as a greenish color and/or a strong fishy taste), are noticeable in these products. The high costs of microalgal processing, collection and processing make large-scale production difficult. Another obstacle is the legislative issue regarding the incorporation of algae in food, as only some algae are considered "generally recognized as safe" (GRAS) by the Food and Drug Administration (FDA), including *Spirulina* sp., *Chlorella* sp., *Haematococcus* sp., *Dunaliella* sp. and *Chlamydomonas reinhardtii*, and new species require studies of toxicity, concentration and chemical composition [17,18,23].

Ultimately, trends in the food industry—like the energy industries and others—are driven by the consumers, and it has been noticed that, today, they crave healthier, more nutritious and ecological products. In this sense, the use of vegetable ingredients to replace animal products is one of the strong trends in the food market today. The incorporation of algal biomass is seen as healthy by consumers, in addition to its production being sustainable, which is also well regarded [13]. Another significant industrial sector where algae could be included is the energy sector, and this is discussed in the next section.

4. Algae Potential for Bioenergy

Algal fuels are environmentally friendly for reducing global carbon dioxide emissions. Plant-based biodiesel production requires the cultivation of oil-producing crops (palm soybean, oilseed rape, etc.) on cultivable land, and to avoid competition on these lands with food production, most governments limit these feedstock supplies for biofuels. Algal biomass has a low percentage of lignin compared to plants, so this is one of the advantages that makes them suitable substrates for biofuels [24,25]. Algae can be converted into different biofuels, making it possible to convert their lipids into biodiesel and carbohydrates into bioethanol [1,2]. The acid hydrolysis of *Palmaria palmata* releases glucose and galactose, which can be fermented into bioethanol [26], and *Eucheuma cottonii* serves as a sugar feedstock for bioethanol production [27].

What determines the biodiesel generation potential in algae is the algal lipid content, and a great challenge in extraction is removing all the aqueous fractions of the biomass (dehydrate) and retaining the lipid fraction, which represents a smaller percentage. For the algal lipids to be converted into biodiesel, it is necessary to perform a transesterification or hydrogenolysis reaction. The viability of commercializing algal biodiesel is critically questioned and, without the advent of biorefineries with co-products, producing the fuel alone may, in fact, not become profitable [28].

Some microalgae and cyanobacteria can have a high concentration of lipids, which can be extracted via different techniques. Moretto et al. [29] observed that strains of *Chlorella* sp., *Arthrospira* sp. and *Sphaerospermopsis torques-reginae* show good fatty acid profiles with potential for biodiesel production. Mamo et al. [30] extracted oil from *Scenedesmus*, yielding 20.8% biodiesel of its dry weight via a microwave-digester-assisted chemical method. For the transesterification process, a nano-catalyst made from goat bone waste was used. The results obtained from this research suggest the potential use of *Scenedesmus* microalga as a feedstock for biodiesel together with the usage of goat bone waste as a nano-catalyst.

Among the macroalgae with potential for biofuel production, brown algae are the largest ones, with filamentous characteristics. According to literature data, almost all global brown algae biomass is produced from the algae orders Fucales and Laminariales, and in terms of productivity, brown algae outperform green and red algae. With this, there is an interest in the sustainable production of biofuels from brown algae, as they are valuable sources of compounds (carbohydrates and oils) that can be used for biochemical and thermochemical conversions [31]. According to Kouhgardi et al. [31], brown algae have already been used to produce drop-in biofuel, a fuel that can be used in existing engines and be produced on an industrial scale at a low cultivation cost.

Related to other biofuels such as biogas and biohydrogen, Chen et al. [32] applied microwave gamma irradiation to pretreat *Laminaria japonica* and obtained a biohydrogen yield of 15.8 mL/g, and Kumar et al. [33] employed a surfactant-assisted disperser to pretreat *Ulva reticulata* and obtained 45.5 mL of biohydrogen. The production of biogas from algal biomass occurs via anaerobic digestion, and the hydrolysis and microbial fermentation of sugars result in biomethane. In the case of hydrogen, the algal cells already generate and store it during photosynthesis [28].

The main barrier of utilizing algal biomass for biofuel production is breaking the rigid cell wall that confines the soluble organics. The cell wall components of algal biomass vary depending on the species; thus, obtaining a common pretreatment technique is quite impossible. Literature reports have suggested that microalgal biomasses, such as *Chlorella* spp.

and *Nanochlorum* spp., have trilaminar layers that provide high resistance to the cell wall [24]. Kavitha et al. [24] described the existing pretreatments employed to disintegrate algal biomass, with emphasis on enhancing biofuel yield for pilot-scale implementation. These pretreatments help break the cell walls and release the intracellular organics into the aqueous phase, a process known as liquefaction. There are many pretreatment methods that achieve the liquefaction of algal biomass: individual (e.g., ultrasonic, dispersion, thermal, biological, chemical), combined (e.g., thermo-chemical, chemo-mechanic) or phase-separated (e.g., chemical induced mechanical, nanoparticle induced biological) methods. Phase-separated or combined pretreatments are recommended to increase liquefaction, biodegradation and, finally, biofuel production [24].

In the case of biological pretreatments for algal biomass, such as enzyme-mediated pretreatment, the enzyme cost is a major drawback. Additionally, using live microbes for pretreatment can lead to the generation of by-products, such as formates, propionates and butyrates, which hamper the downstream process. In some cases, the generated by-products can be utilized by the inoculated bacteria; in others, the bacteria "kidnap" the released soluble organics, leading to decreased biofuel production. Biotechnology has the solution; creating genetically modified microbes for algae pretreatment may solve some fermentation and by-product issues [24].

Regarding the pre-treatments, thermal and acid strategies generate toxic by-products, which can negatively affect biofuel production, such as that of furfural compounds and acids, including levulinic, formic, tannic and terpenic. Several detoxification methods can be employed in order to remove inhibitors generated on algal biomass pretreatments, which include distillation, organic solvent extraction, lime precipitation, ion-exchange chromatography and activated carbon absorption [24]. Hong et al. [34] employed microwaves to pretreat the microalga biomass of *Scenedesmus obliquus* and noted the formation of furfural compounds, in which activated charcoal was used to detoxify the inhibitors via adsorption. Nguyen et al. [35] also detected furfural compounds after employing physicochemical pretreatment on *Gelidium amansii* biomass and used polyethylene-amine to detoxify the inhibitors via ion exchange.

It is true that the generation of biofuel from algal biomass has been a topic of interest in recent years, but apart from the advantage of having greater yield efficiency, the complex and rigid algal cell walls make it biofuel production difficult. Despite the progress in algae biofuel production, it is still in the infant stage because of its need for energy- and cost-intensive pretreatments. Today, phase-separated and synergistic pretreatments are the best liquefaction methods with lower energy and cost inputs for algal biofuel production [24].

Recent trends on algal biomass pretreatment methods are addressing problems related to mechanical, thermal, chemical and biological processes besides introducing different emerging pretreatment techniques, such as microfluidizers, pulsed arc technology and coated membranes [28]. Future work should focus on developing novel economic biomass disintegration methods. The use of residual algae biomass, both for bioenergy and for different purposes, is also a crucial point of interest in the algae research area, as we discuss in the next session.

5. Algae Waste Biomass Utilization

The algal bloom process is a natural activity that occurs in aquatic environments and has a negative impact on water treatment, the industrial field and the environment as a whole. This phenomenon occurs due to the excess of nutrients present in the water, mainly from anthropogenic sources. Excess biomass can serve several applications, adding value to an initially problematic material [36]. Another concern is algal biomass residues from industrial activity, which also require guidance and applicability. Given this scenario, algae biomass residues can be used in the areas of bioenergy, biofuels and biosorbents, among other biotechnological applications [37–39].

The residual algae biomass, whether from industrial processing or blooms, can be converted into culture media for growing different microorganisms, bringing to light a biotechnological application in the microbiology field. In the work carried out by Yuan et al. [40], the species *Laminaria japonica* and *Enteromorpha prolifera* were used for the production of a culture medium due to their rich composition of mono/polysaccharides and other nutrients. Another application of residual algae biomass is in the pharmaceutical industry. Harb et al. [41] studied 15 marine macroalgae species with the potential to produce compounds with anti-HIV activity. In the study, the authors evaluated methanolic and aqueous extracts via in vitro tests, obtaining results above 90% antiviral inhibition.

Bloom processes can be problematic, because they can contain cyanobacteria that produce cyanotoxins. Passos et al. [42] investigated the *Microcystis aeruginosa* strain collected from a bloom material from the banks of the Salto Grande reservoir, São Paulo. In this study, it was possible to determine that the biomass had a low calorific value; however, the samples did not demonstrate toxicity and could be used as a source of bioenergy and in the production of animal breeds.

As already mentioned in the previous section, algae are a promising alternative for replacing fossil fuels, being considered excellent raw materials for the so-called third generation of biofuels (derived from algae). From the industrial extraction of carrageenan (a macroalgae residue), for example, bioethanol can be produced [37]. For this work, the biomass of the species *Eucheuma denticulatum* (Spinosum) presented a conversion efficiency of 75% in bioethanol after a process of acid hydrolysis followed by fermentation. Zhong et al. [39] evaluated the possibility of producing bioenergy from the residual algal biomass of the species *Enteromorpha clathrata* provenient of a green tide phenomenon on a thermogravimetric capacity study. The same alga from previous research, *Enteromorpha*, could also be used for biogas production via anaerobic digestion, as described by Zaidi et al. [43].

For biogas production, Ayala-Parra et al. [44] developed a study for fuel production together with nutrient recovery with a strain of the microalga *Chlorella sorokiniana*. This alga demonstrated a high biodiesel production capacity, generating a residue that can be reused for methane and other soluble nutrients via conversion processes. Chen et al. [38] demonstrated the need for acquiring more knowledge about algae biomass combustion residues (slag) for applications in the bioenergy field. In this study, the authors used the species *Chlorella vulgaris*, which showed a high dross tendency due to the high concentration of phosphorus. The slag generated in combustion can cause a reduction in the melting temperature of the ashes, leading to the formation of melting crystals and causing the corrosion of equipment. Given these studies, it is possible to observe the importance of research in the area of bioenergy production with residual biomass, as well as the optimization of processes on an industrial scale.

Residual algal biomass can also serve as a raw material for the production of biosorbents—sorbents produced from plants or organic waste—which can help in the removal of different contaminants from environments or in their pre-concentration. An example of an application for these materials is the removal of excess fluoride in industrial wastewaters and groundwaters contaminated with fluoride, which is caused by low concentrations of calcium and high-alkalinity water. Water defluorination can be performed using biosorbents from algal biomass from effluent treatment stations, as presented by Biswas et al. [36]. For the experiments, a consortium of *Chlorococcum infusionum* and *Leptolyngbya foveolaurum* was used, and it showed good fluoride adsorption capacity, generating a non-toxic waste that could be safely discarded.

In the study by Pennesi et al. [45], the residual biomass of the brown seaweed *Ascophyllum nodosum* (Linnaeus) was used for indium adsorption, which has a high economic value due to its low availability. In this work, a comparison was made between an adsorbent material from natural biomass and another from industrial waste biomass, resulting in adsorption capacities estimated at 63 and 46 mg/g, respectively. The authors indicated its potential for industrial applications as an algal residual biomass biosorbent due to the high adsorption capacity of indium. Studies of biosorbents are necessary in order to find better adsorbent materials that can interact with different compounds, thus presenting wide applicability.

A problem in the algae-based biodiesel industry is the generated biomass residue, which, however, can be converted into biochar, a charcoal of vegetable origin or organic residues produced from thermal treatments (e.g., pyrolysis) under limited conditions of oxygen. Biochar can be applied for soil correction or as biosorbents. Biosorbents present great advantages due to the different active sites present in these molecules, which allow the adsorption of different compounds. Biochar's adsorption efficiency can be determined through chemical or physical methods [46,47].

Gumus et al. [46] used the residue of the algal species *Gongolaria barbata* (Stackhouse) for the removal of green aniline. In this study, 99% biochar efficiency was found in the aniline removal, and it showed a reusing capacity above 71.6%. In the work by Lucaci et al. [47], the residual algal biomass was used as a biochar for copper removal. The biomass received a thermal treatment for the production of biochar, and this was compared with the biochar produced from the residual biomass of soy and mustard, in which the three presented excellent adsorption results [47]. Another application of biochar is presented in the work by Zhu et al. [48], who used it to remove methyl orange, showing good adsorption results. This biochar was prepared from the residual biomass of microalga from the genus *Spirulina* from a phycocyanin processing plant.

Seaweed waste also has great potential as a raw material for the food industry due to its functional and nutritional properties. In the work by Harb et al. [49], the authors evaluated 12 species of seaweed from the Brazilian coast, which presented good levels of fiber, proteins and carbohydrates, as well as expressive concentrations of minerals, free amino acids and fatty acids, adding value to this biomass considered as waste. However, the authors reported that there is a need for toxicity studies.

As is known, in addition to the increase in the world demand for food, there is also an increase in energy demand, which society and researchers need to be aware of. Through algae biorefineries, it is possible to combine the production of valuable products, such as functional foods, therapeutic molecules and bioenergy together, as shown in the following section.

6. Cultivating for Food and Energy: Algae Biorefineries Allow Both and Beyond

It is known that the massive growth of the world population has caused an increase in the demand for food and energy, in addition to an increase in waste and environmental pollution. Petroleum is still our main source of energy, and its by-products are the elements of most of the materials used in our society, even though it is a non-renewable source and its industry is the main emitter of greenhouse gasses. The efficient use of natural resources and the correct management of waste are processes that need to be studied, improved and completely incorporated into our daily lives so that we can guarantee sustainable development [28].

Among the promising alternatives to gasoline and the use of petroleum, lignocellulosic and algal biomass have shown remarkable progress and are ecologically correct. The sustainable transformation of biomass into biofuels, along with high-value products, minimizing waste and increasing profit, is the ultimate goal of a biorefinery [50]. Microalgal biomass is a source for various industrially valuable products obtained from either thermochemical or biochemical processes. The thermochemical route employs gasification, pyrolysis, direct combustion or liquefaction to transform algal biomass into diverse bioenergy commodities; the biochemical route utilizes alcoholic fermentation, anaerobic digestion or photobiological hydrogen production in order to obtain biofuels [28].

Biorefineries can be classified into three types according to feedstock: crop grains or juice (first generation), lignocellulosic biomass (second generation) and algal biomass (third generation). Food crops should not be chosen as biofuel feedstocks for replacing fossil fuels, as conventional biorefineries (food-based) do not considerably reduce CO2 emissions. Advanced biorefineries aim to explore the utilization of lignocellulosic or algal biomass to produce energy, fuels, value-added chemicals and nutraceuticals. Lignocellulosic biorefineries contribute to curtailing greenhouse gas emissions, although their land

and water usage causes pollution that can lead to eutrophication. Finally, the production of algae-derived biofuels significantly cuts down greenhouse gas emissions and has a lower carbon footprint [28].

Third-generation biorefineries offer a wide range of high-value products, such as pharmaceuticals, nutraceuticals, energy and other industrial commodities, although they are not yet commercially competitive due to technical challenges and production cost issues. For microalgae, one of the main technical issues is harvesting, which includes several techniques such as sedimentation, flocculation, centrifugation and filtration, among others. Thus, research is exploring the most efficient processes for microalgae harvesting for the production of metabolites at the industrial level [51].

Other additional sources for algae biorefineries that can accelerate the commercial development of algae-based products are lipid-extracted algal biomass, which aims to produce novel technological bio-materials such as hydrochar and biochar; electrodes in microbial fuel cells; supercapacitors; biocomposites; activated carbon; and biosorbents [52]. Bhowmich et al. [53] analyzed the global trends in the areas of biofuel and the bio-products of microalgae and proposed strategies to produce biofuels, biochars and bio-products utilizing wastewater in biorefineries. The strategies include the "zero waste discharge" concept with process integration, wherein microalgae are grown in wastewater. This system has the potential to enable biodiesel production from microalgae, bypassing the technological and economic challenges around large-scale cultivation and the downstream processing of algae.

The execution of the integrated algal biorefinery concept has the possibility to reduce the demand for energy and costs in algae-based biorefineries, making a green economy viable. Kannah et al. [54] provided information regarding the development of cost-effective integrated biorefineries of algal-based bioproducts, discussing life cycle assessment and the techno-economic aspects of integrated algal biorefineries. An economy in which the raw materials for chemical and energy are obtained from natural renewable biological sources is known as a bio-economy. The cost of biofuels such as biodiesel and bioethanol from algae is comparatively higher than that of conventional fuels, in spite of third-generation biofuels being less-studied in the literature. Nevertheless, an integrated biorefinery of algae-based biodiesel, poly (hydroxybutyrate) (PHB) and astaxanthin is able to decrease the biodiesel price to USD 0.48/kg due to revenue from astaxanthin [28,55].

An example of a well-succeeded integrated algae biorefinery was designed by Wu et al. [56] to produce biofuels, biopower and by-products together. For that, the algal biomass is dried and submitted to pyrolysis, producing biocrude oil and syngas, and a part of the wet biomass passes through hydrothermal liquefaction, producing biocrude oil, aqueous residue and syngas. The remnant biomass flows into a series of cell disruption and lipid extractions; then, the lipids flow into chemical conversion to produce biodiesel and glycerol. The liquid residue goes through anaerobic digestion to produce hydrogen and methane, and the solid residue goes through hydrolysis and fermentation to produce bioalcohols. It is a multi-product algae biorefinery, with the nutrients and the generated CO_2-rich flue gas being completely recycled and fed into microalgae cultivation.

Bhatia et al. [28] reunited valuable information regarding the worldwide algae market. They reported that, in recent years, a large number of industries, government organizations and research institutes have been actively working to make algal technologies cheap and sustainable, and there are already a good number of firms in the business of algae-based products, such as Sapphire Energy Inc. (San Diego, CA, USA), Algenol (Fort Myers, FL, USA), BioReal (Luštěnice, Czech Republic), Solazyme Inc. (South San Francisco, CA, USA), Alga technologies (Eilot, Israel), Mera Pharmaceuticals Inc. (Kailua-Kona, HI, USA), Muradel Pvt. Ltd. (Whyalla, Australia), Biorizon Biotech (Almería, Spain) and Solix Algadrients (Fort Collins, CO, USA). The estimated world market demand for microalgae is about USD 6.5 billion, of which 2.5 billion goes toward dietary supplements, USD 1.5 billion accounts for medicinal- and nutritional-based microalgal products, and USD 700 million accounts for aquaculture and animal feed products [57].

Among the different biorefineries, algae-based ones represent the greatest potential for producing biofuels together with bio-based products in connected chains, offering these products at affordable prices rather than being stand-alone. Taking into consideration global demands, such as those regarding feed, climate change and nature-limited feedstocks, the potential of third-generation biorefineries is evident, and researchers must develop technologies for the large-scale production of bio-products to reduce dependency on petroleum, thus contributing to the establishment of a more sustainable society [28].

7. Conclusions and Future Perspectives

It is possible to verify that algae, both micro and macro, have a range of valuable phytochemicals (polyphenols, polysaccharides, oils and peptides) with different bioactivities (antimicrobial, antiviral, antineoplastic, antioxidant and hypoglycemic) and diverse applications; however, these phytochemicals mainly need more toxicity and in vivo studies to correlate chemical structures with biological activities, leveraging their commercialization. In the food industry, we believe that a projection for the coming years is an increase in demand for algae production for several purposes, which should drive improvements in the cultivation and large-scale production of algae, with a search for optimizing the parameters that affect its production.

The main barrier to utilizing algal biomass for biofuel production is breaking their rigid cell wall, and to overcome that, employing some pretreatments is necessary. Phase-separated or combined pretreatments are recommended to increase liquefaction, biodegradation and, finally, biofuel production. Future works should focus on developing novel economic biomass disintegration methods. The use of algae waste biomass is another algal niche that is growing, as it is an excellent alternative for the production of energy and biomaterials, leading to the possibility of adding value to biomass from blooms or industry wastes that were previously problematic residues. However, knowledge concerning biomass composition and the by-products generated in the productive processes is still needed.

It is also important to emphasize the need for more research with algae on an industrial scale. Although there are companies working with algae biomass, there are still few of them, and this can be attributed to difficulties in processing biomass, low yields and, consequently, low profit margins for products. By analyzing data from the literature, we believe that, with the improvement of production processes—which arise from large-scale research—products derived from algae can become more profitable and interesting to consumers, and by increasing their demand, more entrepreneurs will be able to establish companies in this field, resulting in the full consolidation and expansion of the algae-based market.

Finally, third-generation biorefineries can offer a wide range of high-value products, such as pharmaceuticals, nutraceuticals, energy and other industrial commodities, and it can be noticed that the development of integrated biorefineries capable of producing multiple products is crucial for the commercialization of algal fuels. The potential of third-generation biorefineries stands out, and there is a need to develop technologies for their large-scale production to reduce dependency on petroleum and to contribute to the establishment of a more sustainable society.

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