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# Production of Algae-Derived Biochar and Its Application in Pollutants Adsorption—A Mini Review

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**Abstract:** Developing algae cultivation for food, chemicals, and bio-energy generates a significant amount of algal waste/residue after utilization. Meanwhile, harmful algal blooms caused by abnormal proliferation of various algae produce a large amount of algal biomass, posing serious harm to human health, the environment and the economy. Converting algae body to biochar is a crucial method with which to take advantage of this resource. Biochar usually has a large specific surface area, developed pore structure, high cation exchange capacity and rich surface functional groups. With the advantage of stable physical/chemical properties and easy modification techniques, biochar posited as an ideal adsorption material. From the perspective of algal biomass utilization, this paper reviews the preparation and modification methods, structural characteristics, physicochemical properties and environmental implications of algal biochar. The adsorption effect and mechanisms of algal biochar on nutrients, heavy metals, and organic matter in water are introduced. In light of the current research status, the challenges faced in practical application of algae-derived biochar adsorption materials are pointed out, and a research direction for preparation and application is also developed, with a view to providing a reference for the further utilization of algae-derived biochar.

**Keywords:** algae; biomass; biochar; adsorption; water pollution



Received: 31 December 2024
Revised: 20 January 2025
Accepted: 26 January 2025
Published: 27 January 2025

**Citation:** Li, L.; Wang, J.; Sun, W.; Peng, X.; Qi, X. Production of Algae-Derived Biochar and Its Application in Pollutants Adsorption—A Mini Review. *Separations* **2025**, *12*, 32. https://doi.org/10.3390/separations12020032



## 1. Introduction

Algae, simple aquatic photosynthetic organisms, play an important role in the global ecosystem as a primary producer forming the basis of food chain. They are globally distributed owing to their high adaptation to environmental conditions and can be easily seen in the waters of seas, lakes, rivers, estuaries and coasts [1]. In addition to the ecological function of $CO_2$ fixation and climate regulation, algae are also extensively cultivated as food or raw materials in the energy, chemistry engineering and pharmaceuticals industries [2,3]. Compared to terrestrial lignocellulosic biomass, algae have a faster growth rate, larger yield, and no requirements for arable land and potable water [4]. These advantages have contributed to the rapid growth of algae-based industries, while systematic studies are still relatively few on the reutilization and harmless disposal of the large amounts of algal residue/waste [5]. Waste algal biomass remains after wastewater treatment and algal

residue obtained after product extraction poses potential environmental risks and reduces the economic value of algae biomass.

On the other hand, production of wild algae is also considerable. Influenced by climate change and deterioration of water quality, harmful algal blooms (HABs) occur frequently globally [6]. HABs caused by various species of algae are observed in almost all coastal waters, with a large range, a vast amount, and recurrent and continuous occurrence [7–9]. HABs damage the ecological balance of coastal waters and pose a great threat to human health, seafood, and tourism [10]. At present, the prevention and effective treatment of HABs are lacking. Huge numbers of algae bodies are treated as garbage after being salvaged and transported, which results in a waste of this biomass resource. Unreasonable treatment and disposal will also breed mosquitoes and harmful bacteria, causing further harm to the environment and human health. Obviously, algae biomass has a wide range of sources and is abundant in mass and amount. The utilization of algae biomass is of great significance.

Algae are also currently applied as water treatment technology. The cell wall of algae can absorb nutrients, heavy metals and organics by the process called biosorption and most pollutants can be metabolized. The advantages of the algae biosorption technique are economic viability and low-energy consumption, but the supply and identification of effective algae species limits its application [11]. Furthermore, if algae are used in environmental pollution mitigation, a mass of algal biomass is produced in this process and finding a better disposal method should be carefully considered.

Biochar is the carbon-rich solid product obtained from the thermochemical treatment of any organic substance. Many waste organic materials have been used to produce biochar, like tires, plastics, and textile fibers [12–14]. In addition, sewage sludge, municipal solid waste and feces of livestock and poultry are also selected as precursors for biochar production [15,16]. Nevertheless, waste biomass is still the most widely considered and available feedstock of biochar due to its abundance and cost-effectiveness. Research on biochar preparation from forest/agriculture residues, fruit/seed peels, and shellfish suggest potentials for these feedstocks, and the as-prepared biochar has versatile applications [17–19]. Biochar is thought to be a sustainable solution to issues regarding the environment, climate and energy, owing to its unique physicochemical properties and strong stability, as well as its “green” origination [20]. The environmental application of biochar can be found in water treatment, soil remediation, flue gas cleaning, etc. [21–23]. Studies have shown good removal efficiency for diverse pollutants, regardless of the environmental medium [15]. Biochar is considered as a negative emission technology, which can reduce greenhouse gas emission and store biogenic C in soil [24]. This is very important for climate regulation. Biochar has also been applied for various energy-related uses, such as in solid fuel, supercapacitors, fuel cells, and electrocatalysts [25].

The conversion of algae into biochar materials provides a crucial idea for algal biomass resource utilization. Biomass can be converted into biochar by (hydro-) pyrolysis under oxygen-limited or oxygen-free conditions [26]. Carbon content of the product after (hydro-) pyrolysis is increased, and the physical and chemical properties are changed. The process usually produces carbon-based materials with larger specific surface area, more developed pore structure, higher cation exchange capacity, richer surface functional groups, and stable physical and chemical properties [27–29]. By adjusting the (hydro-) pyrolysis conditions, like temperature, time, catalyst, and co-(hydro-) pyrolysis raw materials, the physical structure and chemical character of as-prepared biochar can be tuned [30–32]. Modification can be conducted easily before, during or after the preparation process, aiming to highlight the physical and chemical properties of the product for specific needs. Thus, functionalized biochar has been prepared for diverse utilization in soil remediation, water treatment and

electrochemical application [33–36]. As a green, environment-friendly and sustainable material, biochar has attracted wide interest in its application in the field of adsorption. Researchers have investigated the preparation and modification of biochar derived from agricultural and forestry waste, livestock manure, and household waste, and analyzed the adsorption characteristics of different types of biochar for common pollutants, proving that biochar materials have good adsorption capacity and great application potential [37–40]. Unlike terrestrial biomass, which is mainly composed of cellulose, hemicellulose, and lignin, the main components of algae biomass are lipids, sugars and proteins. Algae biomass also has more moisture and inorganic elements (K, Na, Ca, Mg, Fe, Zn, etc.) [41]. It is worth noting that the inherent differences in structure and components between algal and lignocellulosic biomass lead to differences in preparation conditions and in the biochar properties of the final products. Thus, technical development and process optimization, in particular for algae biomass, are needed.

Based on the resource utilization of waste algal biomass, the preparation, modification, structure characteristics, physical/chemical properties and environmental implications of algal biochar are reviewed in this paper. The adsorption effect and mechanism of algal biochar on nutrients, heavy metals, and organic pollutants in water are introduced. In light of current research, the challenges faced in the practical utilization of algae-derived biochar adsorption materials are pointed out, and a research direction of its preparation and application is also suggested, with a view to providing references for further utilization of algal biochar.

## 2. Algae Biomasses

### *2.1. Classification of Algae*

Algae are simple chlorophyll containing organisms that can photosynthesize chemicals with water, $CO_2$ and sunlight in algal biomass [42]. As shown in Figure 1, they are rich in a variety of species and can be broadly classified as macroalgae and microalgae according to cell structure and size [43]. Macroalgae are multicellular lower plants with a leaf-like thallus which can grow as large as 60 m in length. Green algae (*Chlorophyta*), red algae (*Rhodophyta*) and brown algae (*Phaeophyta*) are the major groups of macroalgae identified by their photosynthetic pigments [44]. Microalgae are unicellular or simple-multicellular photosynthetic microorganisms with a size of <400 μm in diameter and are mainly distinguished by their pigmentation. The most general categories are diatoms (*Bacillariophyceae*), green algae (*Chlorophyceae*), blue–green algae (*Cyanophyceae*), yellow–green algae (*Xanthophyceae*), and golden algae (*Chrysophyceae*) [1].

Despite the abundance of algae species, only a few types of algae are commercially cultivated or used practically [45]. The feedstock for algal biochar is inclined to select waste/residue algae from product extraction and algae bodies collected from HABs in terms of reutilization of biomass [46,47]. For example, Dastidar et al. [48] used *Spirulina platensis* algae residue from the biodiesel industry to prepare biochar and examined its adsorption capacity for Congo red. Results show that algae-based biochar had comparable removal efficiency to commercial activated carbon, and was an effective method for production of biochar adsorbents in a sustainable manner for the algae biodiesel industry. Ai et al. converted golden tide stranding, *Sargassum horneri*, to biochar by pyrolyzation with potassium ferrate for $CO_2$ capture [49]. The porous material had a high specific surface area and $CO_2$ adsorption capacity with excellent cycling stability and easy regeneration. Thus, a simple and cost-effective route was proposed to synthesize biochar on a large scale and make good use of waste algae.

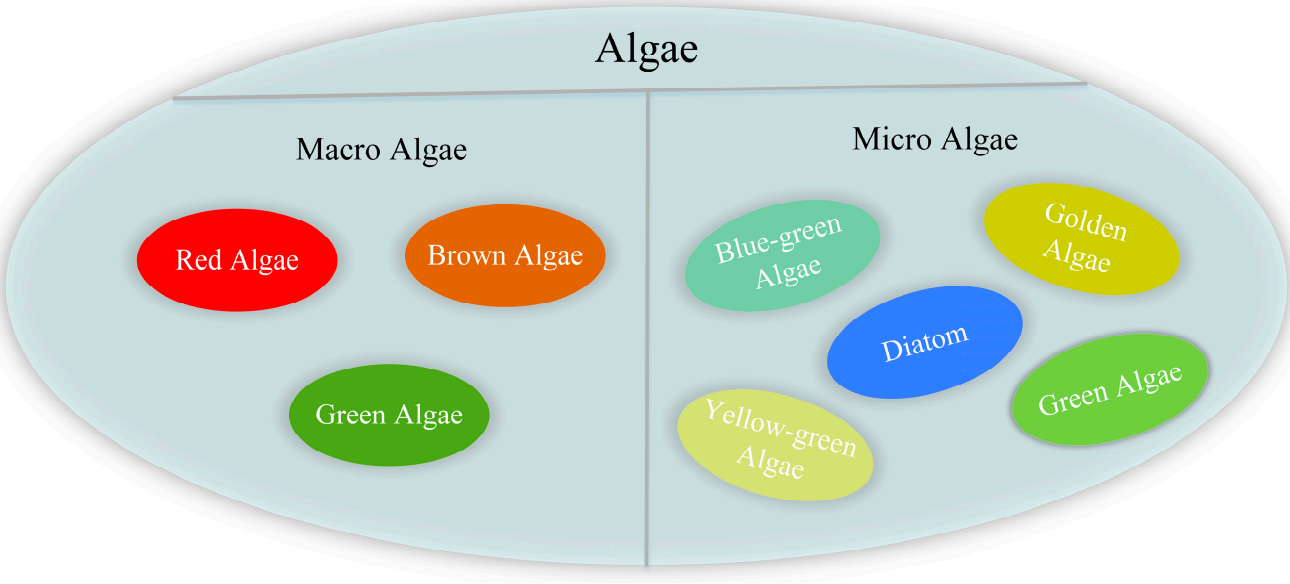



**Figure 1.** Broad classification of algae according to cellular structure and pigments.

### *2.2. Components of Algae*

The morphology structure and chemical components of feedstock are important factors in the preparation of biochar, which significantly affect its physicochemical properties [50]. It has been confirmed that variation in raw materials can lead to change in pore characteristics, surface area and functional groups in the final biochar product [18]. Algae biomass is more tender than terrestrial biomass because of the lack of lignocellulosic structure, and this contributes to a worse thermal stability of the feedstock and less porosity in algae-derived biochar [51]. Chemical components of algae biomass vary dramatically based on algae species, cultivation method, collection location and season while, in general, the main components are lipids, proteins and carbohydrates [46,52]. Comparatively, terrestrial biomass is composed of cellulose, hemi-cellulose and lignin, with little mineral content [29]. Thus, biochar prepared from algae typically has higher cation exchange capacity, pH and N doping content, but lower C content and yield compared to terrestrial biomass-derived biochar [5,41].

Lipids are target compounds extracted from algae to form biodiesel [53]. Their content ranges from 0.9% to 77.0% depending on algae species and cultivation conditions [44]. It can be seen from Table 1 that microalgae contain higher concentration of lipids in comparison with macroalgae. Thus, microalgae are mainly cultivated and selected as feedstock for biofuel production. The extracted residual algae biomass, as well as the macroalgae, can be converted to biochar materials instead of disposed as waste [46]. Proteins are polypeptide chains composed of amino acids, and can be used to produce pyrroles and indoles applied in pharmaceuticals, adhesives, and herbicides [54]. Normally, microalgae are more enriched in proteins than macroalgae, as indicated in Table 1. Proteins are the main source of N-doped function groups in algae-derived biochar, and are beneficial to applications in soil amendment, catalysis and adsorption [41]. Carbohydrates are sugar monomers or polysaccharides produced from the photosynthesis process of algae biomass and can be used as food and pharmaceutically [55]. Although different algae species can generate different carbohydrates, mannitol is usually regarded as the main photosynthetic product of algae biomass [46]. Macroalgae possess higher carbohydrate content than microalgae for extracellular protection and cell adhesion [55].

**Table 1.** List of chemical components and proximate analysis of common macro- and microalgae.

| Algae | Chemical Components (wt%) | | | Proximate Analysis (wt%) | | | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | Lipid | Carbohydrate | Protein | Moisture | Volatile Matter | Fixed Carbon | Ash | |
| Macroalgae | | | | | | | | |
| *Ulva fasciata* | 2.37 | 40.91 | 11.42 | 10.29 | - | - | 20.89 | |
| *Crassiphycus corneus* | 1.93 | 23.55 | 21.27 | 4.3 | - | - | 34.16 | [56] |
| *Sargassum vulgare* | 4.02 | 39.07 | 10.32 | 4.53 | - | - | 30.09 | |
| *S. thunbergii* GEEL-15 | 7.88 | 37.0 | 7.14 | 9.89 | - | - | 20.84 | |
| *M. stellatus* GEEL-16 | 4.63 | 35.08 | 9.14 | 9.23 | - | - | 28.17 | [57] |
| *Ulva* sp. GEEL-17 | 6.67 | 55.4 | 4.24 | 11.28 | - | - | 21.23 | |
| *Ulva lactuca* | 1.45 | 32.61 | 12.17 | - | - | - | 20.94 | |
| *Dictyopteris australis* | 1.34 | 33.12 | 9.7 | - | -- | | 28.11 | [52] |
| *Halymenia venusta* | 1.43 | 34.81 | 14.13 | - | - | - | 17.12 | |
| *Gracilaria gracilis* | 1.7 | 28.6 | 13.7 | 5.88 | 53.1 | 10.9 | 36 | [58] |
| *Cladophora glomerata* | 2.4 | 34.7 | 26.3 | 4.4 | 44.8 | 29.1 | 26.1 | |
| *porphyra* | 1.5 | 47.7 | 35.7 | 9.3 | 70.8 | 16.9 | 3.0 | [59] |
| *Enteromorpha prolifera* | 4.31 | 20.21 | 42.06 | 4.86 | 55.9 | 10.69 | 28.56 | [60] |
| *Laminaria digitata* | 1.0 | 46.6 | 12.9 | 8.0 | 79.9 | 13.1 | 9.9 | [61] |
| *Caulerpa sertularioidis* | 1.88 | 44.7 | 9.44 | 10.42 | - | - | 31.24 | |
| *Acanthophora spicifera* | 1.4 | 48.51 | 6.55 | 8.12 | - | - | 47.04 | [62] |
| *Cystoseira trinodis* | 1.3 | 33.18 | 12.59 | 10.14 | - | - | 35.29 | |
| Microalgae | | | | | | | | |
| *Nannochloropsis* sp. | 30.0 | 18.64 | 40.8 | 4.23 | 79.21 | 10.26 | 6.3 | [63] |
| *Chlorella vulgaris* | 24.57 | 22.18 | 45.45 | 5.6 | 70.4 | 16.2 | 7.8 | [64] |
| *Scenedesmus almeriensis* | 24.6 | 25.2 | 44.2 | 2.9 | 67.9 | 9.7 | 19.4 | [65] |
| *Nannochloropsis gaditana* | 26.3 | 25.1 | 40.5 | 3.5 | 79.8 | 10.2 | 6.4 | |
| *Isochrysis* | 39.3 | 13.9 | 32.9 | 3.67 | - | - | 10.23 | [66] |
| *Scenedesmus* sp. | 19.5 | 29.3 | 36.4 | 4.59 | 75.33 | 12.78 | 7.3 | [67] |
| *Spirulina platensis* | 27.17 | 7.2 | 65.64 | - | - | - | - | [68] |
| *N. granulata* | 28.5 | 14.9 | 35.4 | - | - | - | - | [69] |
| *Nannochloropsis* sp. | 30 | 35 | 43 | - | - | - | - | |
| *Schizochytrium limacinum* | 51 | 24 | 14 | - | 89.4 | 1.7 | 8.9 | [70] |
| *C. debaryana* | 19.9 | 10.1 | 59.4 | 2.7 | - | - | 7.9 | [71] |

The proximate analysis of moisture, volatile matter, fixed carbon and ash in raw algae materials is also important in the preparation progress and the product properties. As these algae are aquatic and photosynthetic organisms, algae biomass has higher moisture content than terrestrial examples. Moisture can dissolve many ions and molecules, which increases the mineralization of algae [72]. The high content of moisture in algae biomass needs dewater pretreatment, resulting in energy consumption in the biochar preparation process. Volatile matter and fixed carbon are parameters used to evaluate the quality of pyrolysis feedstock. They refer to components which are thermally-vaporizable and non-vaporizable after high temperature heating [31]. The ratio of volatile matter/fixed carbon is an indicator to predict biochar yield, with a lower ratio leading to higher productivity [41]. Ash content consists of the inorganic elements (K, Ca, Na, Mg, Zn, Fe, et al.) assimilated from aqueous environments by algae biomass [46]. De-ash options are necessary in some circumstances, especially in the production of biofuel [73] while, in other aspects, the high mineral content in algae-derived biochar provides an advantage for its application in soil amendment and electrochemistry [41].

## 3. Preparation and Modification of Algal Biochar

### *3.1. Preparation of Algal Biochar*

Thermochemical conversion is the main method to produce biochar from biomass. The carbonization of biomass is completed through the process of dehydration, organic structure disintegration and residual solid decomposition [74]. Compared with traditional biotechnologies, such as fermentation and anaerobic digestion, thermochemical conversion has higher efficiency, higher yield and produces a better quality of biochar [75]. Physical and chemical properties of the product can be tuned by changing the parameters, such as temperature, time and heating rate, in the thermochemical conversion process [76]. Torrefaction, pyrolysis and hydrothermal carbonization (HTC) are the most promising thermochemical techniques (Figure 2). They are generally distinguished by pyrolysis temperature, heating rate and reaction medium in the preparation process, and thus cause differences in biochar properties and product distribution [77].

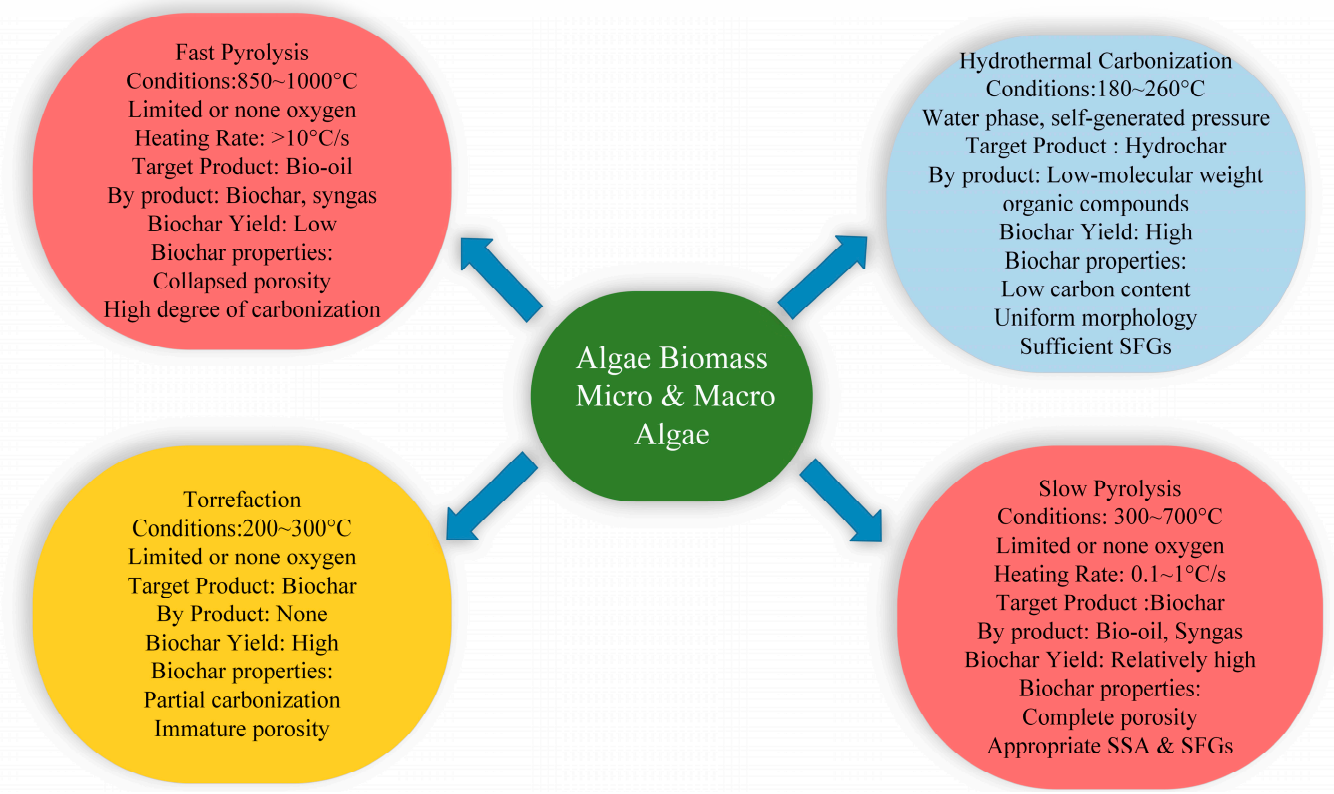



**Figure 2.** Differences in thermal conversion methods for algal biochar.

Torrefaction is a thermochemical process under ordinary pressure and oxygen-limited conditions at a temperature between 200 and 300 °C [78]. In this process, moisture and volatile matter in the feedstock are removed, and the raw biomass is partially decomposed. The torrefied biomass has more C content, higher calorific value and energy density. Thus, torrefaction is often used to upgrade biomass to solid fuel or as a pretreatment for pyrolysis [79,80]. Abundant and fast-growing waste biomass, such as algae, is suitable feedstock in torrefaction for large-scale or practical utilization [81]. Phusunti et al. studied the torrefaction of *Chlorella vulgaris* microalgae at different temperatures (150–300 °C), times (15–60 min) and atmospheres ($N_2$/Air) [82]. Torrefaction loosened the compact structure of raw biomass and broke it into smaller particles. Temperature was the most influential factor on solid yield and on biochar properties. An increase in carbon content, ash content, and fixed carbon content, but a decrease in oxygen content, hydrogen content, and volatile

matter, was obtained with increased temperature and time. It is notable that, at higher temperatures over 200 °C and longer times than 30 min, the calorific value decreased. The results of this research are representative and instructive for the preparation of algae-derived biochar by torrefaction. Similar conclusions have been drawn in other studies of algae torrefaction processes [83,84].

Pyrolysis is the most popular and powerful technique used in the field of biomass thermochemical conversion. It operates at a higher temperature (300–700 °C) and a stricter oxygen-free atmosphere compared to torrefaction [35]. The main components of biomass are rearranged, depolymerized and cracked under pyrolysis conditions, forming a more thermally stable polycyclic aromatic structure. Part of the volatile organic compounds is transformed to bio-oil and bio-gas [85,86]. Pyrolysis can be generally defined as either slow pyrolysis or fast pyrolysis depending on operating conditions. Slow pyrolysis is the most conventional thermochemical process in biomass conversion. In this process, slow heating rate (<1 °C/min) and long residence time (>5 min) at moderate temperature (300~700 °C) are the notable features that contribute to maximum biochar yield and fewer liquid and gas products [18,87]. Fast pyrolysis is a more severe process with extremely high heating rate (>10 °C/s), shorter residence time (0.5~10 s) and higher temperature (850~1000 °C) [87]. Bio-oil is the main target for this process, and biochar is obtained as a by-product [34]. In recent years, advanced pyrolysis, like catalytic pyrolysis and microwave-assisted pyrolysis, are gaining more and more attention. These processes bring advantages for both biochar and bio-oil production and are promising techniques for practical applications [88,89].

Pyrolysis of algae biomass is an uneven decomposition process for its primary components, i.e., lipids, proteins and carbohydrates. Operating parameters, including temperature, heating rate and residence time, greatly affect the degree of decomposition of biomass components [31]. The diverse and complex product distribution in algae biomass pyrolysis indicate an intricate pathway for decomposition (Figure 3). In general, carbohydrates are the first components decomposed below 300 °C, followed by proteins and lipids [90]. Monosaccharides and polysaccharides encompassing glucose, pectin, agar, mannose, alginate, laminarin, fucoidan, etc.,. are the main carbohydrates synthesized in diverse algae species [55]. Carbohydrates are first pyrolyzed to anhydro-sugars and furfurals and then produce oxygenated compounds, such as alcohols, ketones, aldehydes and acids, by a series of reactions [91]. Some of the intermediate pyrolytic products can subsequently undergo cyclization to form aromatic hydrocarbons [92]. Proteins are biological macromolecules assembled from polypeptide chains, and are dehydration and condensation products of amino acids [91]. Pyrolysis of proteins in algae generally refers to the irregular cleavage of the main chain, cleavage of lateral groups, and carbonation reactions [93]. The irregular breaks in the main chains form different fragments in length, as well as N-containing heterocycles. Lateral groups are not stable in pyrolytic conditions and tend to break into small molecule compounds. The other main chains can form polyolefins or benzene derivatives [94]. Cross-linking, cyclization, and dehydro-aromatization reactions of the reactive side chains generate N-doped char [91]. Lipids are small molecules produced from esterification of fatty acids and alcohols. The pyrolysis of lipids starts from decomposition into fatty acids and further reactions, such as cracking, decarbonylation, and aromatization. Isomerization of the intermediates generates aldehydes, ketones, alcohols and acids. Finally, hydrocarbons, CO, and $H_2O$ are formed through cracking, β-scission and elimination reactions [5,95].

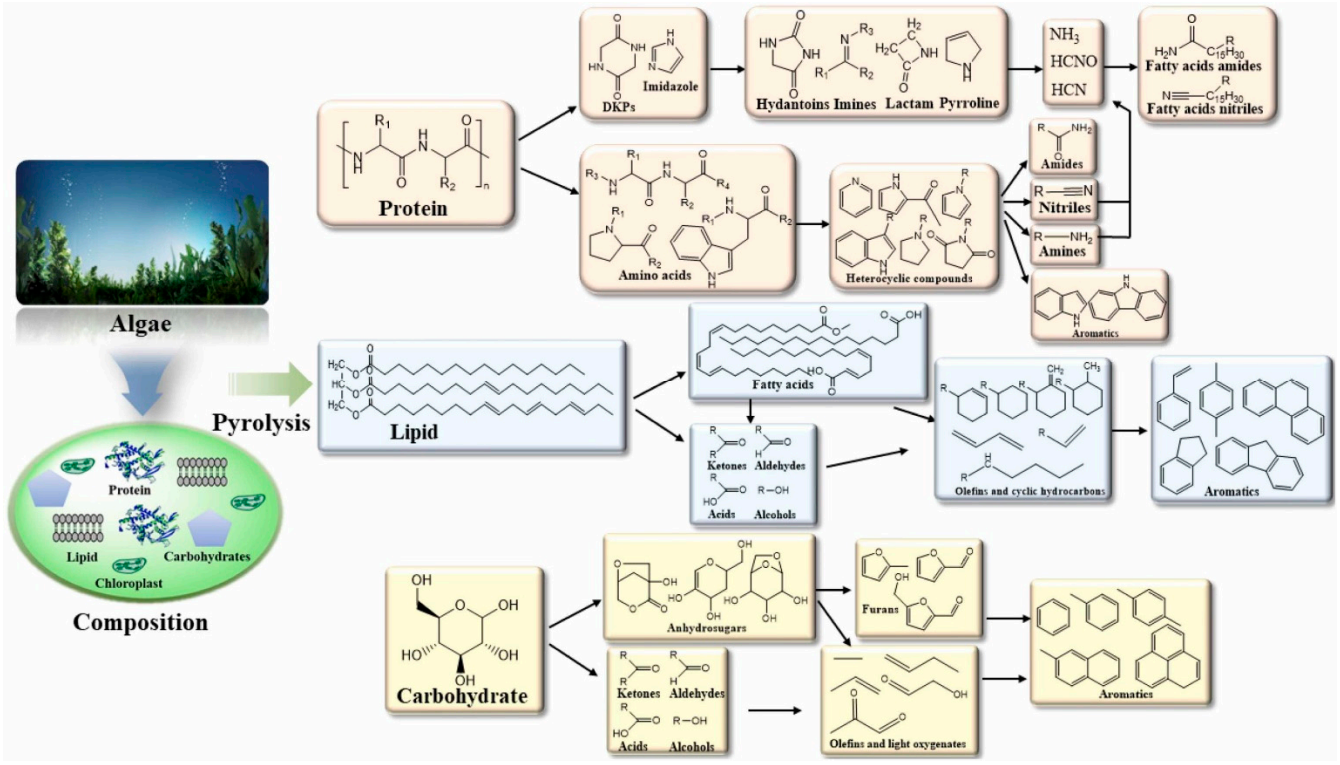



**Figure 3.** Algae decomposition mechanism during the pyrolysis process. Reprinted with permission from Ref. [91]. © 2024 Elsevier B.V.

Hydrothermal carbonization (HTC) is an eco-friendly and cost-effective thermochemical conversion technique. The process is normally carried out at 180~250 °C in water and self-generated pressure of 2~10 MPa [96]. Under these conditions, hot compressed water acts as solvent and activator in a self-catalyzed system, leading to lower reaction temperature and higher biochar yield [97]. Biochar prepared from HTC is usually called hydro-char, and has properties of a high-quality morphology, sufficient functional groups and extensive utilization potential [98]. Algae biomass is an appropriate feedstock for the HTC process as hydrous raw materials, in which energy-intensive dehydration is omitted. Hydrothermal carbonization of algae has higher biochar yields than other thermochemical conversion methods, and product distribution can also be altered by changing parameters like temperature and time [99]. Solid products, such as hydro-char, have high energy density and wide application, liquid products are important value-added chemicals, like aliphatic acid and N-containing compounds, and $CO_2$ is the main gas product of HTC [100,101]. It is worth considering that HTC is a promising biomass conversion technique, other than pyrolysis, in practical utilization, and hydro-char is innately different from pyrolytic biochar in its morphology and chemical properties, as well as its applications [102,103].

### *3.2. Modification of Algae Biochar*

Although thermochemical converted algal biochar has many advantages, the raw biochar products are still restricted by problems of pore blockage, narrow pore size range, limited specific surface area, incomplete development of surface functional groups and impurity of ash or polymers, owing to the complex thermochemical process and diverse product distribution [104]. In order to meet the specific needs of different application fields and stimulate the efficacy of biochar, the activation and modification of the raw biochar product is of great significance. Modified biochar shows improvements in pore structure, specific surface area, surface functional groups content and functionalization

of physical/chemical properties, upgrading its application ability [26,29]. Modification can be carried out before, during or after the preparation process, involving raw material pretreatment, pyrolysis parameter control, impurity removal and product modification. The designed or engineered algal biochar thus created is in a highly developed state.

The modification of biochar mainly includes physical activation and chemical modification. Effects of different modification methods on the properties of biochar are shown in Figure 4.

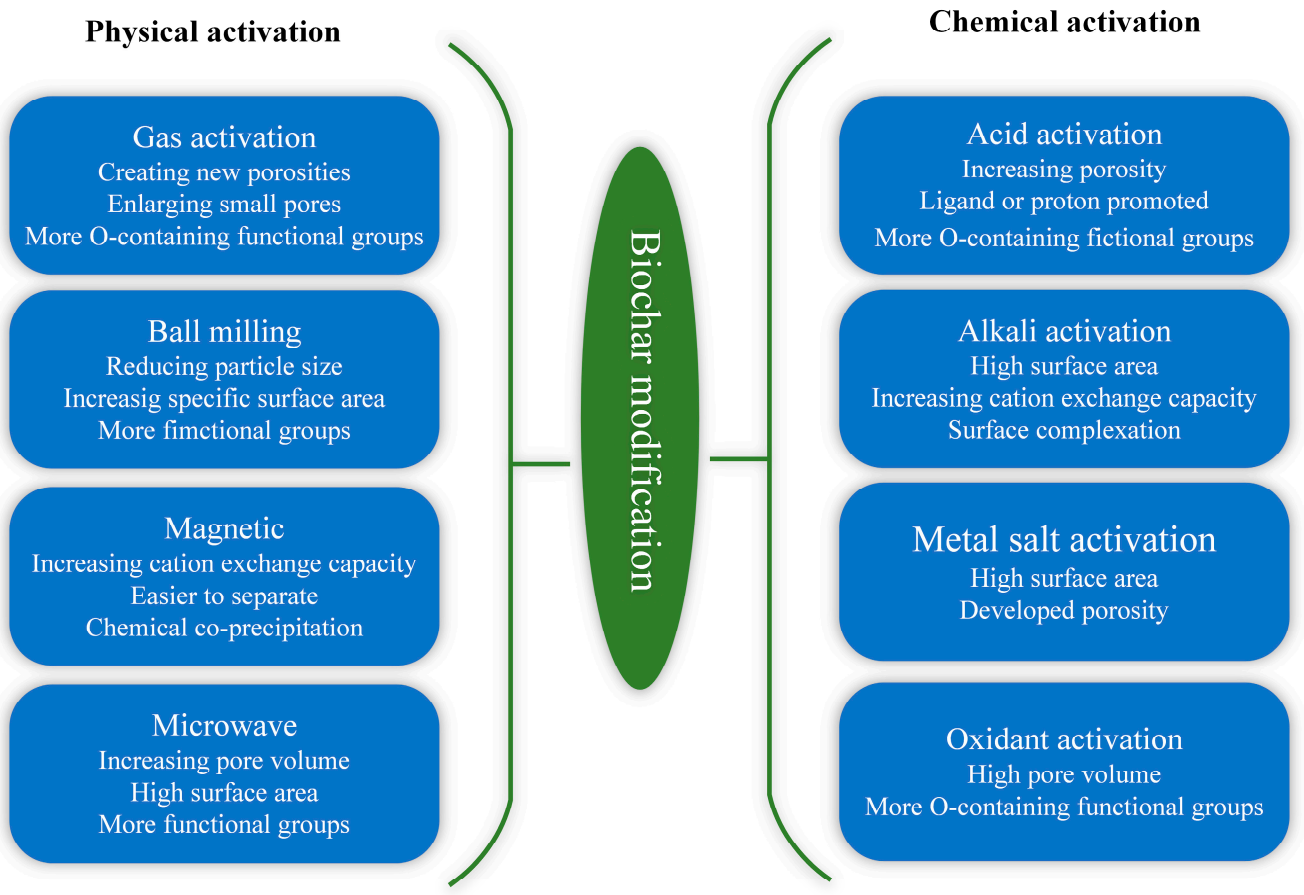



**Figure 4.** Different modification methods and their effect on properties of biochar.

Physical activation is thought to be an in situ or post-procedure in the process of thermochemical conversion. Biomass is firstly carbonized via any thermochemical process and then subjected to physical activation by an oxidizing agent at high temperature, forming an enhanced porous structure [51]. Improvements in porosity, specific surface area and surface chemical properties are achieved after physical activation without the use of chemical additives, representing a green and sustainable method compared to chemical modification [105]. Gas activation, microwave assisted activation, ball milling and magnetic modification are typical techniques of physical activation [106]. Gas activation generally refers to the pyrolysis process of introducing steam or $CO_2$ at a higher temperature (>700 °C), both of which can react with active carbon atoms in biochar [107]. The active carbon atoms are oxidized to produce new pores, expand the existing pores and form more oxygen-containing functional groups. Gas activation can also enhance the aromatic structure of biochar and reduce its polarity [104]. Steam activation can produce both macropores and micropores with a wide pore size distribution, while $CO_2$ mainly forms micropores [106]. Microwave assisted activation is fast and energy-efficient due to the interaction induced by the microwave with molecules in the biomass. Biochar products

have a higher surface area and higher number of surface functional groups [51]. The addition of chemical reactants can engineer the biochar for selected applications, especially in the improvement in surface properties [108,109]. Magnetic modification is the process of attaching magnetic particles to biomass while retaining the properties of biochar through heat treatment or physicochemical reaction [110]. The most commonly used methods are impregnation-pyrolysis, chemical co-precipitation, solvothermal, and reductive co-precipitation with transition metal salts, natural iron ores, and iron oxides as magnetic precursors [51,111]. Magnetically modified biochar generally shows a decrease in porosity and specific surface area but enables separation and recycling, or an enhanced adsorption capacity for pollutants [112,113]. Ball milling is a new mechano-chemical process to prompt chemical and structural modifications of biochar. The kinetic energy produced by constantly crushing and fracturing the moving balls diminishes the particle size of biochar to a nanoscale and enriches oxygen-containing functional groups [114]. Thus, the capacity for adsorption or catalysis of ball milled biochar is greatly strengthened [115].

Chemical modification usually refers to the mixing or impregnation of biomass with chemical reagents during or before the thermochemical conversion. Raw biochar treatment of chemical reagents is also considered as chemical modification [51]. Chemically modified biochar surmounts the obstacles existing in raw biochar in diverse applications, harboring a developed pore structure and surface chemical properties [116]. The primary chemical modification method for biochar involves acid/base modification, metal salt modification, and oxidizer modification [117]. Acid modification can remove the ash and impurities in carbon precursors or the resulting biochar and increase the content of acidic functional groups, together with the polarity of the final products [33]. Hydrochloric acid (HCl), nitric acid ($HNO_3$), sulfuric acid ($H_2SO_4$), phosphoric acid ($H_3PO_4$), oxalic acid and citric acid are widely used [34]. It is notable that utilization of strong acid will cause degradation of the pore structure and decrease the total surface area, while $H_3PO_4$ seems to be more reliable and environmentally friendly [33]. Base modification is an efficient method to promote the development of pore structure and enlarge the specific surface area, and simultaneously to increase aromaticity for better adsorption of organic pollutants and negatively charged ions [51]. KOH and NaOH are the most commonly used bases. The base additive amount is very important to achieve optimal physicochemical status for the biochar product and should be controlled carefully to avoid the corrosion of the reactor and excessive activation leading to the collapse of the biochar structure. Metal salt modification typically refers to the co-pyrolysis of biomass and different metal chlorides through pre-impregnation [33]. Many kinds of metal chlorides, such as $ZnCl_2$, $MgCl_2$, $MnCl_2$, $AlCl_3$, $FeCl_3$, can be the activator in this process [118]. $ZnCl_2$ is generally used as pore forming agent because of its gasification under pyrolytic conditions, which improves the pore structure of biochar [119]. Other metal chlorides are preferred for transformation into metallic oxides, endowing the biochar with outstanding performance in adsorption, catalysis, electrochemistry, and separation [33,120]. Oxidizer modification is a method to refine the surface chemical properties by increasing the number of functional groups. $H_2O_2$ is the most recommendable agent to generate more carbonyl groups which are clean and harmless to the environment [121].

## 4. Physical and Chemical Characteristics of Algal Biochar

An adequate decipherment of structural characteristics and physicochemical properties is beneficial in evaluating the preparation, modification and potential application of biochar. Biochar characterization is necessary for the conversion process and has become a more professional research field of increasing interest [122]. To obtain a precise and holistic characterization, multiple analysis techniques are used in combination [123]. The most commonly adopted techniques are summarized in Figure 5. These techniques reveal the

features of biochar which are commonly defined as physical and chemical properties. The physical properties of biochar primarily involve surface and pore structure, like specific surface area (SSA), porosity, pore volume and pore size distribution, etc. Furthermore, biochar yield, electrical conductivity, higher heating value, hydrophobicity and water holding capacity are also defined as physical properties in many cases [29]. Chemical properties of biochar include ultimate analysis (elemental composition), proximate analysis (fixed carbon content, volatile matter content, ash content), cation exchange capacity (CEC), pH-value and surface functional groups [1]. Both types of property are related to feedstock, preparation condition and modification method, and can influence the effect and the application field of biochar.

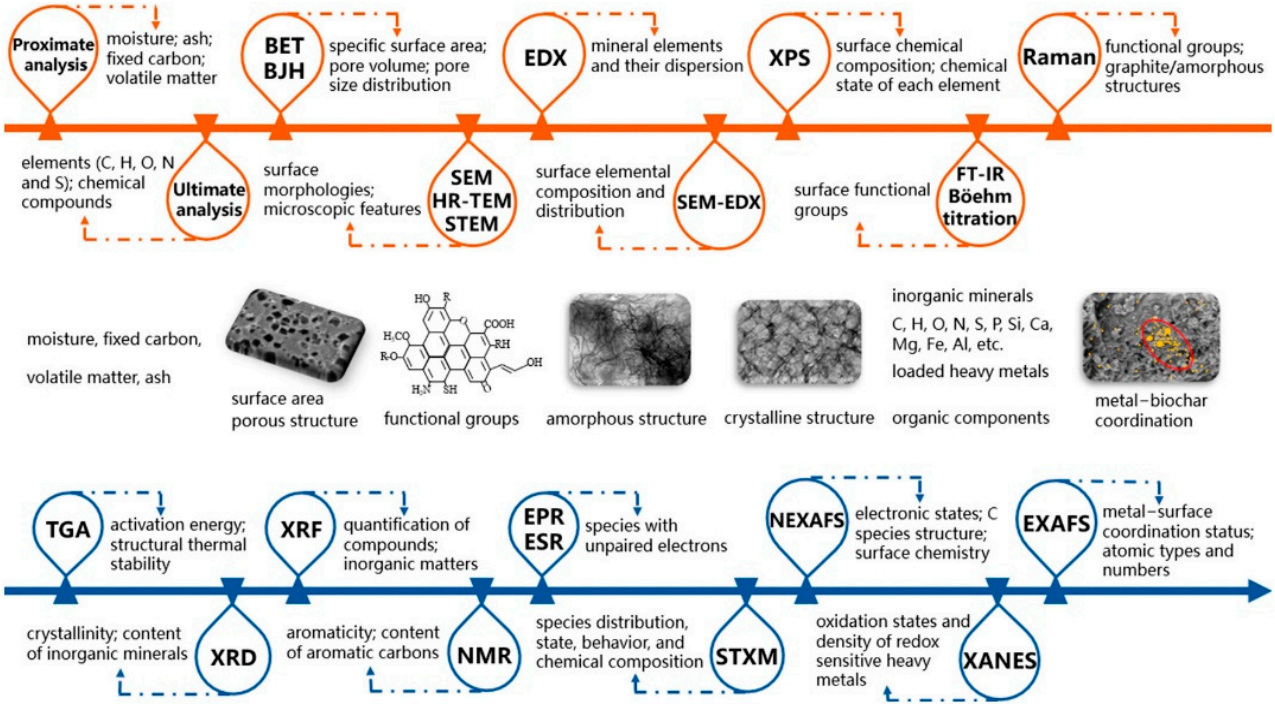



**Figure 5.** Characterization techniques of biochar. Reprinted with permission from Ref. [123]. © 2021 Elsevier B.V.

### *4.1. Physical Properties of Algal Biochar*

A higher content of moisture and ash together with the absence of lignocellulose in algae biomass result in a lower heating value for algal biochar than for terrestrial biomass-derived biochar. This indicates an inadequacy of algal biochar as solid fuel for direct combustion [44]. Biochar yield is another important parameter in biomass conversion, especially for large scale production and practical utilization. Biochar yield from algae biomass greatly depends on algae type and preparation conditions [46,124]. As shown in Figure 2, torrefaction and hydrothermal carbonization provide a higher solid yield than pyrolysis, which produces biochar as the main product. Increasing reaction temperature and time clearly reduce biochar yield, as seen in Table 2.

**Table 2.** Preparation and physical/chemical properties of algal biochar.

| Algae | Preparation | Physical Properties | | | Chemical Properties | | | | | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Yield% | Specific Surface Area $m^2/g$ | Total Pore Volume $cm^3/g$ | C% | H% | O% | N% | H/C | O/C | N/C | pH | Ash% | Volatiles% | Fixed Carbon% | |
| Macroalgae | | | | | | | | | | | | | | | | |
| *Undaria pinnatifida* root | Pyrolysis, $N_2$, 5 °C/min, 2 h, 200 °C | 83.95 | 1.909 | 0.038 | 30.58 | 3.82 | 27.14 | 3.40 | 0.125 | 0.888 | 0.111 | 7.37 | 32.83 | - | - | [125] |
| | ~, 400 °C | 67.70 | 70.29 | 0.112 | 31.92 | 1.74 | 13.56 | 2.35 | 0.055 | 0.425 | 0.074 | 8.38 | 41.85 | - | - | |
| | ~, 600 °C | 47.75 | 61.809 | 0.078 | 36.64 | 0.99 | 11.76 | 2.31 | 0.027 | 0.321 | 0.063 | 10.36 | 48.71 | - | - | |
| | ~, 800 °C | 39.29 | 44.491 | 0.057 | 40.51 | 0.70 | 10.02 | 2.00 | 0.017 | 0.247 | 0.049 | 11.09 | 50.41 | - | - | |
| *Saccharina japonica* | Pyrolysis, $N_2$, 10 °C/min, 1 h 600 °C, bentonite impregnation and co-pyrolysis B:K = 0% | 31.7 | 203 | 0.0904 | 24.5 | 0.47 | 11.7 | 1.21 | 0.019 | 0.478 | 0.049 | 10.2 | 66.7 | 18.9 | 14.4 | [126] |
| | ~, B:K = 5% | 33.6 | 29.2 | 0.0195 | 26.2 | 0.42 | 8.37 | 1.54 | 0.016 | 0.319 | 0.059 | 10.1 | 66.2 | 15.5 | 18.3 | |
| | ~, B:K = 10% | 35.8 | 2.30 | 0.0043 | 23.3 | 0.25 | 5.40 | 1.33 | 0.011 | 0.232 | 0.057 | 10.1 | 70.8 | 11.6 | 17.7 | |
| | ~, B:K = 20% | 36.0 | 6.62 | 0.0211 | 20.2 | 0.21 | 3.03 | 0.68 | 0.010 | 0.150 | 0.033 | 10.3 | 75.4 | 11.1 | 13.5 | |
| Mixture of *Ulva rigida, Fucus spiralis, Pelvetia canaliculate, Himanthalia elongate, Ulva rigida, Fucus spiralis* | Pyrolysis, 3 °C/min, 300 °C,1 h | - | 0.9569 | 0.52 | 49.19 | 4.07 | 18.04 | 2.88 | 0.99 | 0.28 | 0.059 | 7.67 | 25.03 | 47.3 | 27.67 | [127] |
| | ~, 300 °C, 3 h | - | 0.9886 | 0.51 | 51.37 | 4.10 | 18.08 | 3.03 | 0.96 | 0.26 | 0.059 | 8.35 | 22.66 | 45.1 | 32.24 | |
| | ~, 600 °C, 1 h | - | 2.0444 | 0.62 | 55.31 | 1.56 | 12.16 | 2.46 | 0.34 | 0.16 | 0.044 | 9.36 | 27.98 | 18.9 | 53.12 | |
| | ~, 600 °C, 3 h | - | 2.1869 | 0.47 | 57.44 | 1.50 | 8.74 | 2.50 | 0.31 | 0.11 | 0.044 | 9.56 | 29.3 | 16.5 | 54.12 | |
| *Enteromorpha prolifera* | Pyrolysis, $N_2$, 5 °C/min, 4 h, 500 °C | 39.0 | 12.02 | 0.0049 | 28.56 | 1.91 | 26.03 | 2.04 | 0.07 | 0.91 | 0.071 | - | 33.64 | - | - | [128] |
| | ~, 600 °C | 9.5 | 38.49 | 0.0090 | 32.28 | 1.25 | 19.54 | 1.98 | 0.04 | 0.61 | 0.061 | - | 37.78 | - | - | |
| | ~, 700 °C | 8.4 | 99.34 | 0.0208 | 29.35 | 1.23 | 18.56 | 1.59 | 0.04 | 0.63 | 0.054 | - | 43.96 | - | - | |
| | ~, 800 °C | 7.5 | 134.19 | 0.0299 | 20.75 | 1.24 | 19.55 | 1.54 | 0.06 | 0.94 | 0.074 | - | 52.71 | - | - | |
| *Undaria pinnatifida* | Pyrolysis, $N_2$, 10 °C/min, 2 h, 800 °C | - | 69.7 | 0.04 | 63.13 | 2.83 | 14.87 | 2.80 | 0.537 | 0.176 | 0.044 | - | - | - | - | [129] |
| | ~, KOH activation (1:1) | - | 1156.25 | 0.67 | 52.58 | 1.75 | 15.29 | 0.64 | 0.499 | 0.218 | 0.012 | - | - | - | - | |
| Microalgae | | | | | | | | | | | | | | | | |

**Table 2.** *Cont.*

| Algae | Preparation | Physical Properties | | | Chemical Properties | | | | | | | | | | | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Yield% | Specific Surface Area $m^2/g$ | Total Pore Volume $cm^3/g$ | C% | H% | O% | N% | H/C | O/C | N/C | pH | Ash% | Volatiles% | Fixed Carbon% | |
| *chlorella* | Pyrolysis, $N_2$, 800 °C, 20 min | - | 5.00 | 0.01 | 45.03 | 6.89 | 26.37 | 8.43 | 0.15 | 0.59 | 0.19 | 8.7 | - | - | - | [130] |
| | ~KOH activation, microwave, 700 W, $N_2$, 15 min | - | 747.22 | 0.44 | 45.30 | 1.46 | 22.66 | 3.49 | 0.03 | 0.50 | 0.08 | 9.8 | - | - | - | |
| *spirulina* | Pyrolysis, $N_2$, 800 °C, 20 min | - | 5.65 | 0.01 | 44.76 | 6.80 | 24.25 | 10.10 | 0.15 | 0.54 | 0.23 | 8.5 | - | - | - | |
| | KOH activation, microwave, 700 W, $N_2$, 15 min | - | 568.3 | 0.40 | 34.47 | 1.74 | 28.93 | 1.98 | 0.05 | 0.84 | 0.06 | 9.6 | - | - | - | |
| *Chlorella* sp. | Pyrolysis, $N_2$, 2 h, 200 °C | 57.45 | 5.08 | 0.05 | 48.41 | 5.71 | 9.10 | 8.22 | 0.12 | 0.19 | 0.17 | 9.94 | 11.24 | -- | - | [131] |
| | ~, 400 °C | 43.42 | 5.40 | 0.08 | 57.88 | 5.61 | 8.79 | 4.33 | 0.09 | 0.15 | 0.07 | 10.12 | 16.78 | - | - | |
| | ~, 600 °C | 30.45 | 4.05 | 0.07 | 61.57 | 2.71 | 6.81 | 2.93 | 0.04 | 0.11 | 0.05 | 10.39 | 33.56 | - | - | |
| *Spirulina* sp. | Pyrolysis, $N_2$, 2 h, 200 °C | 53.42 | 6.57 | 0.07 | 49.50 | 5.04 | 10.29 | 9.40 | 0.10 | 0.21 | 0.19 | 10.63 | 14.43 | - | - | |
| | ~, 400 °C | 37.79 | 6.46 | 0.07 | 58.57 | 5.01 | 9.63 | 8.30 | 0.08 | 0.16 | 0.14 | 10.88 | 29.45 | - | - | |
| | ~, 600 °C | 27.82 | 7.89 | 0.07 | 64.96 | 2.73 | 6.91 | 5.12 | 0.04 | 0.11 | 0.08 | 11.22 | 36.23 | - | | |
| *Spirulina* sp. | Pyrolysis, $N_2$, 2 h, 350 °C | - | 0.31 | - | 61.63 | 6.62 | 18.71 | 11.77 | 1.289 | 0.228 | 0.191 | - | 1.27 | 56.47 | 42.26 | [132] |
| | ~, 550 °C | - | 1.55 | - | 65.43 | 3.73 | 14.22 | 11.09 | 0.684 | 0.163 | 0.169 | - | 5.53 | 29.55 | 64.92 | |
| | ~, 750 °C | - | 2.63 | - | 66.60 | 1.30 | 12.25 | 9.42 | 0.138 | 0.138 | 0.141 | - | 10.43 | 19.59 | 69.98 | |
| *Nannochloropsis* sp. | Hydrothermal carbonization, Ar, 1 h, 210 °C | 28.6 | 1.38 | 0.01 | 54.89 | 6.42 | 32.19 | 5.98 | 0.12 | 0.59 | 0.11 | - | 11.2 | 66.0 | 19.3 | [133] |
| | ~, 250 °C | 22.7 | 12.56 | 0.01 | 27.33 | 3.29 | 66.40 | 2.67 | 0.12 | 2.43 | 0.19 | - | 53.7 | 33.0 | 11.5 | |
| *Chlorella vulgaris* | Hydrothermal carbonization, 1 h, 260 °C | - | 5.23 | 0.027 | 61.22 | 4.38 | - | 7.25 | 0.61 | - | 0.12 | 7.34 | - | - | - | [134] |
| | ~, citric acid activation | - | 5.89 | 0.014 | 60.46 | 3.78 | - | 7.76 | 0.64 | - | 0.13 | 6.88 | - | - | - | |
| *Spirulina platensis* | Pyrolysis, $N_2$, 5 °C/min, 1 h, $NaHCO_3$ activation 600 °C | - | 279 | 0.24 | 63.5 | 2.5 | - | 10.2 | 0.039 | - | 0.161 | - | - | - | - | [135] |
| | ~, 700 °C | - | 865 | 0.50 | 65.7 | 2.7 | - | 7.5 | 0.041 | - | 0.114 | - | - | - | - | |
| | ~, 800 °C | - | 1511 | 0.93 | 85.7 | 1.2 | - | 1.9 | 0.014 | - | 0.022 | - | - | - | - | |

~ means the same conditions, - means unavailable.

The most significative physical properties of algal biochar are specific surface area (SSA) and pore structure, including porosity, pore volume and pore size distribution. These are created in the thermochemical conversion process and play important roles in many applications, particularly in adsorption [29]. Raw algal biochar usually has disadvantages of less SSA, less developed porosity and blocked pores, owing to its high ash content and fewer lignocellulosic components in algae biomass. Algal biochar's physical properties can be improved by increasing pyrolysis temperature and time as well as by the addition of chemical reactants to achieve an enlarged SSA and a developed pore structure for better application [77]. Chen et al. synthesized *Spirulina* residue-derived N-doped graphitic biochar at different temperatures as catalyst for sulfamethoxazole (SMX) oxidation [136]. Prepared biochar at high temperature (SDBC-900) exhibited larger SSAs, higher content of graphitic N, and better conductivity compared to low temperature (SDBC-400, SDBC-700). It also achieved excellent SMX oxidation efficiency and good disinfection in the oxidation system. Cheng et al. prepared *Enteromorpha prolifera*-derived biochar with self-activation of citrate [137]. The presence of the citrate catalyst greatly enlarged the SSA of biochar and created a more developed pore structure, showing high specific surface areas (up to 1415 $m^2/g$) and pore volumes (up to 1.08 $cm^3/g$). As-prepared biochar composites displayed excellent SMX sorption capacity of 844 mg/g. The high SSA and pore volume were crucial parameters in determining adsorption application.

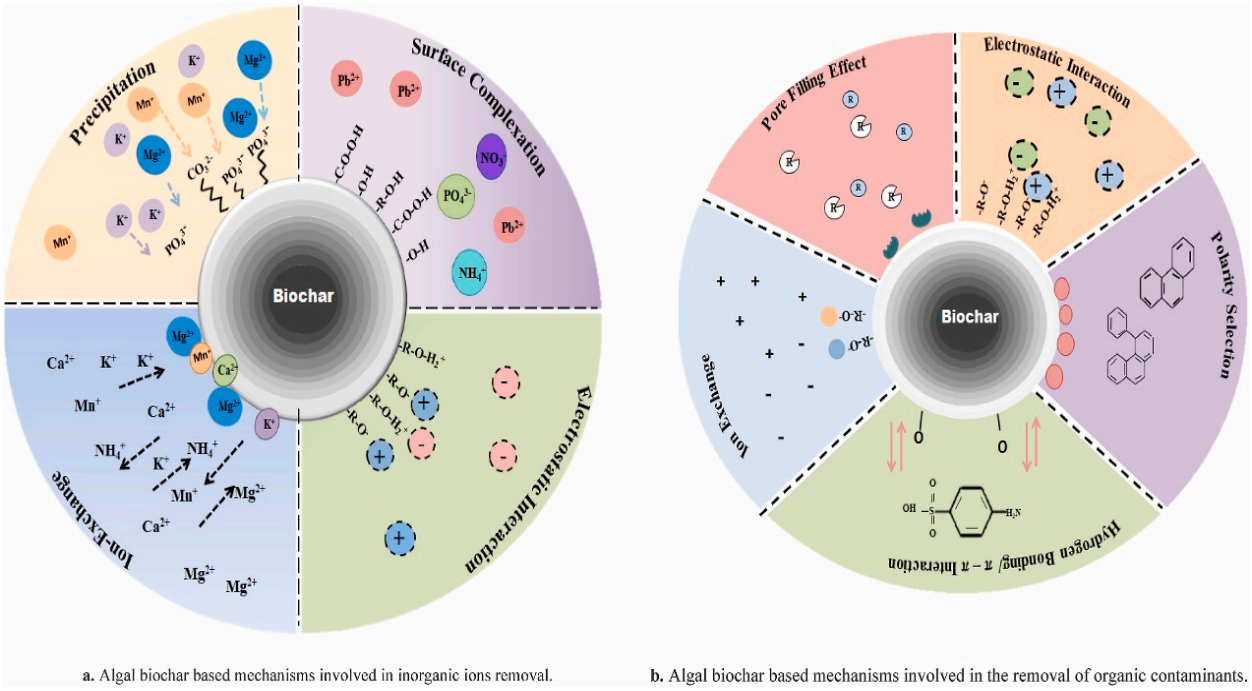
### *4.2. Chemical Properties of Algal Biochar*

As shown in Figure 5, chemical analysis of its elements, composition and surface groups via diverse techniques depicts the characteristics of biochar. The specific chemical properties lead to specialization in utilization. Different chemical properties of algal biochar contribute to different applications. For example, content of inorganic elements (K, Ca, Mg, N, P etc.), pH and CEC are typical indicators of algal biochar as potential additive in soil amelioration and crop production [138]. The addition of biochar can improve soil physical structure, regulate soil pH, increase soil carbon content and fertility, and stabilize heavy metals and other pollutants, thus affecting the soil microenvironment and microbial flora, improving soil quality, and increasing the yield of various crops [139–141]. Ultimate analysis and surface functional groups are key parameters in assessing the adsorption application of algal biochar. In ultimate analysis, chemical elements like C, H, N, O, S are measured to estimate the degree of carbonization. Ratio of H/C and O/C are valuable in judging the stability and aromaticity of biochar [142]. Low H/C or O/C indicates high aromaticity and hydrophobicity, with better adsorption for non-polar organic pollutants [1]. Yang et al. examined the adsorption of tetracycline on *Spirulina*-derived biochar, and a maximum adsorption capacity of 132.8 mg/g was obtained for SPAL-BC750, with lowest H/C and O/C and highest hydrophobicity and SSA [132]. Contrastingly, high O/C suggests more oxygen functional groups with good hydrophilicity and better adsorption for heavy metals [142]. Lee et al. used *spirulina*-derived biochar to adsorb different heavy metals, namely $Cd^{2+}$, $Cu^{2+}$, and $Pb^{2+}$ [143]. Results show that SPBC-200 with the highest O/C of 0.38 contained more oxygen groups, such as O–H, C=O, C–OH, and C–OH, than other biochar pyrolyzed at higher temperatures. It exhibited good adsorption capacity for all heavy metals and was demonstrated as the optimal adsorbent. Surface functional groups are focal point in the preparation and modification process of algal biochar. Their types and contents affect the hydrophilicity/hydrophobicity and surface electrical properties of biochar, and then determine the appropriate application [77]. The most involved surface functional groups in engineering of algal biochar are oxygen-containing (-OH, -COOH, etc.), sulfur-containing (-$SO_3H$, -SH, etc.) and nitrogen-containing (-$NH_2$, pyridinic N, pyrrolic N, etc.) functional groups [144–146]. The formation of functional groups can be based on the

intrinsic elements of feedstock or the extrinsic source of additives. Chemical modification is a very powerful method to generate surface functional groups in algal biochar.

## 5. Adsorption Applications of Algal Biochar in Water Treatment

Water pollution induced by various emission sources is an urgent concern in modern society. Waste water released from farming, breeding, municipalities and industries containing nutrients, heavy metals, dyes, antibiotics, etc., brings harm to the environment and to human health [142]. The desire for sustainable and high efficiency water treatment provides an opportunity for the adsorption application of algal biochar. Thanks to its suitable physical/chemical properties, (engineered) algal biochar shows good adsorption capacity for many pollutants, regardless of their category [34,147]. Both inorganic and organic pollutants can be adsorbed onto algal biochar because of the large SSA, abundant surface functional groups and highly developed porosity, via diverse mechanisms like pore-filling, ion exchange, electrostatic interaction, H-bonding effect, surface complexation, precipitation, etc. [51], as shown in Figure 6.




**a.** Algal biochar based mechanisms involved in inorganic ions removal. **b.** Algal biochar based mechanisms involved in the removal of organic contaminants.

**Figure 6.** Main mechanisms of inorganic (**a**) and organic (**b**) pollutants adsorbed onto algal biochar. Reprinted with permission from Ref. [51]. © 2024 Elsevier Inc.

### *5.1. Adsorption of Nutrients (Nitrogen, Phosphorus)*

Nitrogen (N) and phosphorus (P) are elements that cause water eutrophication. They come from effluents from domestic activities, industrial production and agricultural fertilization, and do harm to the aqueous ecosystem, human health and the economy [148]. Ammonium ($NH_4^+$), nitrate ($NO_3^-$), and phosphate ($PO_4^{3-}$) are the main forms of inorganic N and P in the aqueous phase [149].

Chemical adsorption is dominant in the adsorption process of N and P into (engineered) biochar, involving the mechanisms of ion exchange, ligand exchange and coprecipitation. At the same time, physical adsorption related to SSA and porosity is also concerned as a mechanism in this process [150]. Wang et al. suggested mechanisms for the adsorption of ammonium and phosphate onto red mud modified biochar [151]. The results indicated that surface functional groups and pH were crucial factors for N and P adsorption, while

an increase in SSA and pore structure was also favorable to the adsorption. Oxides or hydroxides of Ca, Mg, Fe, Al, La can greatly improve the adsorption capacity of biochar for N and P. By combining the above metals with biochar, metal ligands can be formed on the biochar surface. N and P are stably coprecipitated with metal compounds and efficiently removed [152–154]. Algal biochar usually requires modification to obtain a better N/P adsorption capacity. Ahn's group reported a series study on adsorption of P by Ca, Mg, Al modified *Laminaria japonica*-derived biochar [155–157]. Biochar prepared via different methods shows good removal efficiency, with the existence of metal oxides. After the adsorption of nutrients, biochar with high content of N/P can be sequentially used as fertilizer or as soil amendment, being beneficial to crop growth and the soil ecosystem [150,158]. Yang et al. compared the phosphate removal rate of algal biochar and $SiO_2$-modified algal biochar and found that the presences of $SiO_2$ particles on the surface of biochar enhanced phosphate sorption. Maximum adsorption capacity of this material is 159.4 mg/g [159].

### 5.2. Adsorption of Heavy Metals

Heavy metals (HMs) in an aqueous environment pose a serious threat to human and other living beings, with high toxicity, carcinogenicity and bioaccumulation. These are anthropogenic pollutants produced from industries like electroplating, mining, smelting and petrochemicals, etc. [123]. Hg, Pb, Cr, Cd, As, Cu, Ni, Co are the most commonly involved and hazardous HMs appearing in the environment [160]. Biochar and its composite materials are considered as efficient, practical and safe adsorbents to remove HMs in water [161]. In the process of adsorption of heavy metal ions in the aqueous phase, the surface electrical and chemical properties of biochar play a decisive role, and the adsorption mechanism includes electrostatic attraction, ion exchange, precipitation, complexation, and pore filling [162,163]. Precipitation, complexation and ion exchange are thought to be the most predominant mechanisms [164]. Therefore, the surface functional groups, cation exchange capacity and surface electrical properties of biochar are very important for the adsorption of heavy metal ions.

The intrinsic characteristics of algal biochar meet the adsorption requirements of HMs, such as high cation exchange capacity (containing more $Na^+$, $K^+$, etc.), and rich surface functional groups (high O/C, facile preparation and modification). Much work has been conducted on the study of HM adsorption onto different kinds of algae-derived biochar, as summarized in Table 3.

**Table 3.** Adsorption effect of algal biochar for different heavy metals.

| Algae | Heavy Metal | Preparation Conditions | pH | Maximal Adsorption Capacity (mg/g) | Adsorption Isotherms | Adsorption Kinetics | Ref. |
|---|---|---|---|---|---|---|---|
| Macroalgae | | | | | | | |
| *Macrocystis pyrifera* | $Cu^{2+}$ | Pyrolysis, $N_2$, 450 °C, 1 h | - | 119.9 | Langmuir | Intra-particle diffusion- | [165] |
| Red macroalgae | $As^{3+}$ | Hydrothermal carbonization, 200 °C, 2 h, $FeCl_3$ impregnation, 24 h | 6 | 3.8314 | Langmuir | Pseudo-Second-Order | [166] |
| *Enteromorpha prolifera* | $Cd^{2+}$ | Pyrolysis, $N_2$, 500 °C, 2 h, KOH activation, 700 °C, 1 h | 7 | 5.84 | Langmuir | Pseudo-Second-Order | [167] |
| *Enteromorpha prolifera* | $Cd^{2+}$ | $H_3PO_4$ impregnation, 12 h, Pyrolysis, $N_2$, 500 °C, 1 h | 7 | 423 | Langmuir | Intra-particle diffusion | [168] |
| *Ascophyllum nodosum* | $Cu^{2+}$ | Pyrolysis, $N_2$, 700 °C, 2 h, coprecipitation with $FeCl_3$ and $FeCl_2$ | 5 | 53.19 | Langmuir | Pseudo-Second-Order | [169] |

**Table 3.** *Cont.*

| Algae | Heavy Metal | Preparation Conditions | pH | Maximal Adsorption Capacity (mg/g) | Adsorption Isotherms | Adsorption Kinetics | Ref. |
|---|---|---|---|---|---|---|---|
| *Kappaphycus alvarezii* | $Cr^{6+}$ | Microwave torrefaction, $N_2$, 560 W, 0.5 h, $H_2O_2$ activation | 3 | 6.009 | Langmuir | Pseudo-Second-Order | [170] |
| *Saccharina japonica*<br>*Sargassum fusiforme* | $Zn^{2+}$ | Pyrolysis, $N_2$, 700 °C, 2 h | - | 84.3<br>43 | - | - | [171] |
| Microalgae *Chlorella Pyrenoidosa* | $Ni^{2+}$ | Pyrolysis, $N_2$, 600 °C, 2 h, KOH activation | 9.19 | 201.18 | Langmuir | Pseudo-Second-Order | [172] |
| *Scenedesmus dimorphus* | $Co^{2+}$ | Fast pyrolysis, $N_2$, 500 °C, 40 °C/min | - | 0.672 | Freundlich | Pseudo-Second-Order | [173] |
| *Spirulina* sp. | $Cu^{2+}$ | Pyrolysis, $N_2$, 200 °C, 2 h | 5 | - | Redlich-Peterson | Pseudo-Second-Order | [143] |
| *Chlorella* sp.<br>*Spirulina* sp. | $Pb^{2+}$ | Pyrolysis, $N_2$, 600 °C, 2 h | 6 | 131.41<br>154.51 | Langmuir | Pseudo-Second-Order | [131] |
| *Chlorella* sp. | $Cr^{6+}$ | Pyrolysis, $N_2$, 450 °C, 1 h | 2 | 15.94 | Langmuir | Pseudo-Second-Order | [174] |

It can be seen that algal biochar prepared from both macro- and micro-algae has good adsorption capacity and removal efficiency for HMs, and engineered algae-derived biochar benefits from diversity of modification. The optimal pH condition for adsorption varies with biochar and HMs species, while it is common to see the best adsorption result at acidic or neutral pH. Most studies concluded that the adsorption of HMs onto algal biochar fit the Langmuir isotherm better than other models. This implies a monolayer sorption on heterogenous surface [144]. The pseudo-second-order curve gave a better prediction of the adsorption kinetics, irrespective of biochar and HM species. It is reasonable to say that the adsorption of HMs onto algal biochar is a chemical action-regulated process with monolayer adsorption onto the functional surface. An improvement in surface area and functional groups can increase the active sites for better HM adsorption capacity.

### *5.3. Adsorption of Organic Pollutants*

Organic pollutants in water are a series of organic compounds that have negative impacts on the environment and on human health, including pharmaceuticals, personal care products, pesticides, dyes, endocrine disruptors, surfactants and plastics [175]. The adsorption performance of organic pollutants is related to the preparation and modification process of biochar (selection of biochar precursors, preparation and modification techniques) and the chemical properties of organic matter. As larger molecules than HMs, the adsorption of organic pollutants onto biochar is considered to be a three-step pathway which contain a successive process of approach and adsorption on the biochar surface, precipitation to form multilayer adsorbates, and penetration into pores [51]. The involved mechanisms are electrostatic interaction, π–π interaction, H-bonding, complex adsorption, hydrophobic interaction, and pore filling [176].

The adsorption of organic pollutants by algal biochar has been widely studied. Research is mainly focused on dyes, antibiotics and other toxic chemicals, as summarized in Table 4. The data show that most adsorption processes can be predicted by the pseudo-second-order kinetic curve, which indicates a chemosorption process. The Langmuir and Freundlich models can both fit adsorption isotherms with different algal biochar and organics. The preparation and modification methods affect the physical and chemical properties of algal biochar, resulting in different adsorption isotherms. More surface functional groups and a suitable pore structure are desired advantages for engineered algae-derived biochar in the adsorption of organic pollutants.

**Table 4.** The adsorption of various organic pollutants by different types of algal biochar.

| Organic Pollutant | Algae | Preparation | pH | Maximal Adsorption Capacity mg/g | Adsorption Isotherms | Adsorption Kinetics | Ref. |
|---|---|---|---|---|---|---|---|
| Dyes | | | | | | | |
| Reactive Yellow -145 | *Chlorella* sp. | Pyrolysis, $N_2$, 550 °C, 1 h | 2 | 48.33 | Freundlich | pseudo-second-order | [177] |
| Methylene Blue | Seaweed | Hydrothermal carbonization with $H_3PO_4$, 200 °C,5 h, KOH impregnation 6 h | 7 | 162.5 | Langmuir | pseudo-second-order | [178] |
| malachite green | Cystoseira Fucales | $H_3PO_4$ impregnation, microwave, 700 W, 18 min | 7 | 86.44 | Freundlich | pseudo-second-order | [179] |
| crystal violet | *Enteromorpha flexuosa* | Pyrolysis, $N_2$, 600 °C, 1 h, ball milled with kaolin, coprecipitation with $FeCl_3$ | 6 | 53.98 | Freundlich | pseudo-second-order | [180] |
| Congo red | *Chlorella* sp. | Microwave wet torrefaction, 800 W, 10 min | 7 | 164.35 | Langmuir | pseudo-second-order | [181] |
| Rhodamine B | *Spirulina* | Pyrolysis, $N_2$, 700 °C, 1.5 h | 6 | 421.93 | Freundlich | - | [182] |
| Methyl orange | *Spirulina* | Pyrolysis, 500 °C, 5 h | 2 | 10.04 | Langmuir | pseudo-second-order | [183] |
| Basic blue 41 | *Saccharina japonica* | α-FeOOH impregnation, Pyrolysis, $N_2$, 600 °C, 1 h | 8 | 1216 | Langmuir | pseudo-second-order | [184] |
| Antibiotics | | | | | | | |
| Ciprofloxacin | *Ulva Ohnoi*<br>*Agardhiella subulata*<br>*Sargassum hemiphyllum* | $ZnCl_2$ impregnation, Pyrolysis, $N_2$, 700 °C, 2 h | 7 | 161<br>227<br>250 | Langmuir | pseudo-second-order | [185] |
| Sulfamethoxazole | *Enteromorpha prolifera* | Pyrolysis, $N_2$, 500 °C, 5 h, KOH activation, 800 °C, 2 h | - | 744.32 | Langmuir | pseudo-second-order | [186] |
| Tetracycline | *Chlorella* | Pyrolysis, $N_2$, 500 °C, 1 h, NaOH activation, 800 °C, 1.5 h | 9 | 310.696 | Freundlich | pseudo-second-order | [187] |
| sulphathiazole | *Spirulina* | Pyrolysis, $N_2$, 400 °C, 2 h, $KHCO_3$ activation, 800 °C, 2 h | - | 218.4 | Langmuir | pseudo-second-order | [188] |
| ofloxacin | *Ulva prolifera* | Pyrolysis, $N_2$, 500 °C, 2 h | 7 | 60.98 | Freundlich | two-compartment first-order | [189] |
| Other organics<br>naphthalene<br>acenaphthene<br>phenanthrene | *Enteromorpha prolifera* | $ZnCl_2$, $FeCl_3$ impregnation, Pyrolysis, $N_2$, 800 °C, 1 h | - | 90<br>51<br>86 | Freundlich | Elovich | [190] |
| p-nitrophenol | *Chlorella* sp. Cha-01 | Pyrolysis, 600 °C, 0.5 h | 7 | 204.8 | Freundlich | pseudo-second-order | [191] |
| Tetrabromobisphenol A | *Ulva prolifera* | Co-hydrothermal carbonization with $FeSO_4$, $Na_2S_2O_4$, 180 °C, 4 h | 4 | 1.47 | Freundlich | pseudo-second-order | [192] |

## 6. Environmental Implications of Algal Biochar

Biochar has gained much attention over recent years, focused on its benefits in multitudinous applications, while the potential risks related to its use are often overlooked. The discharged biochar may interact with environmental media and release associated pollutants, and have a negative influence on organisms including animals, plants, microorganisms, and humans during its transportation [193]. It is of great significance to assess and mitigate the risk of biochar for sustainable development.

Pollutants from biochar can be defined as endogenous and exogenous pollutants according to their origin. Endogenous pollutants originate from the raw parent materials

of biochar and the content of these pollutants varies with preparation conditions [194,195]. Polycyclic aromatic hydrocarbons, heavy metals, and environmentally persistent free radicals are the main endogenous pollutants released by biochar. These pollutants tend to be generated from cellulosic biomass at high temperature [196], and algal biochar seems to avoid the defect related to the absence of cellulosic components in raw materials. In addition, algae may have less heavy metal content, due to a cleaner habitat, than other biomasses. Exogenous pollutants refer to the pollutants adsorbed on spent biochar, or during its migration [193]. These kinds of pollutants are not detoxified but remain toxic, with limited mobility. As time goes on, the aging process will change the properties of biochar and reduce the retention ability of pollutants [197]. Enhancing the reusability/separation of biochar and pollutant recovery may be helpful in conquering this problem. Biochar is separated by filtration, centrifugation or magnetism in laboratory conditions [198,199] and most research reported an acceptable capacity decline at around 5~7 cycles of use [200–202]. The recycling of algal biochar experiences a similar situation. For example, Hu [203] et al. fabricated δ-$MnO_2$-modified algal biochar to remove U(VI) in water, and the sorption amount could remain at 94.8% after 5 cycles. Liu [204] et al. studied the removal of tetracycline with algal biochar pyrolyzed from a mixture of Enteromorpha and Chlorella vulgaris, and the removal rate still remained at over 80% after 5 cycles. Another method for biochar reuse is to turn the used biochar into valuable material in other application fields. The most common case is the use of spent biochar after nutrient adsorption as fertilizer or soil amendment [205]. Algal biochar is inherently rich in inorganic elements and is a better candidate for soil application compared with other forms of biochar.

In summary, detailed and long-term research is needed to evaluate the environmental risk of biochar. Algal biochar may cause less pollution and is more reusable than terrestrial biomass-derived biochar under some circumstances.

## 7. Conclusions and Prospects

Converting algal biomass into biochar is of great significance both in basic research and practical application for resource utilization. Thermochemical conversion is the most commonly used method, and mainly includes torrefaction, pyrolysis and HTC. These techniques are generally distinguished by pyrolysis temperature, heating rate and reaction medium, leading to variations in biochar properties and product distribution. Raw algal biochar usually has limited performance and applications due to the poor development of its physical structure and chemical properties, thus modification is needed. Modification can be carried out before, during or after the preparation process, involving physical activation and chemical modification. Both methods can improve the quality of biochar by upgrading its physical and chemical properties. Vital physical and chemical properties of biochar are SSA, pore structure, pH, CEC and surface functional groups. These are key factors in determining the effect and application field of biochar, and their characterization is an important feature of biochar production. Algae-derived biochar materials have been proved to be promising adsorbents in water treatment. Nutrients, heavy metals and organic chemicals can be efficiently removed from contaminated water. The adsorption processes benefits from the large SSA, abundant surface functional groups and highly developed porosity. Diverse mechanisms, like pore-filling, ion exchange, electrostatic interaction, H-bonding effect, surface complexation and precipitation, are involved for both inorganic and organic pollutants.

Current research shows that algal biomass is a suitable raw material for practical production of biochar, which can be a promising adsorbent used in water treatment. The advantages are as follows:

(1) Very large amount of biomass. Algal biomass mainly comes from two sources: artificial cultivation and wild growth. The purpose of artificial cultivation is to produce food, bio-oil and other useful chemicals. Huge amounts of algal residues will be generated after different forms of processing. Wild algae often appear in the form of HABs, which show a wide influence range, long duration and high biomass yield. Thus, there is sufficient material basis for the production of algal biochar.

(2) Very fast growth rate. The growth rate of algae biomass is much faster than that of land-based biomass, and large amounts of algae can be accumulated in a short period of time. This feature provides a guarantee for the continuous production of algal biochar materials. In addition, the cultivation of algae can absorb a large amount of $CO_2$, which could reduce the emission of $CO_2$ to the atmosphere, thus contributing to the relief of global warming.

(3) Abundant preparation and modification techniques. The preparation process and modification methods for algae-derived biochar are diverse and powerful. Various parameters can be regulated according to need to prepare a variety of functional biochar materials, which improve the application of algal biochar.

(4) Wide adsorption application and good adsorption effect. Algae-derived biochar can adsorb most pollutants in a water environment, such as nutrients, heavy metals and organic pollutants. Generally, by adjusting the preparation parameters and optimizing the physicochemical properties of biochar, the adsorption effect of algal biochar on different pollutants can be improved.

However, it should also be noted that the practical application examples for algae-derived biochar are still very limited, and most of the research is at the laboratory simulation stage, for the following reasons:

(1) In the practical water treatment process, the environment is complex, and there are many kinds of pollutants and various interference factors which may affect the adsorption performance, resulting in limited practical application.

(2) Due to its micro-(nano) particles, the environmental toxicity of algal biochar should be studied thoroughly before large-scale applications. There may be potential negative effects to living beings during the migration and accumulation of biochar in a natural environment.

(3) The recycling and disposal of biochar after adsorption of heavy metals and organic chemicals needs to avoid secondary pollution. These post-treatments increase cost and difficulty in algal biochar applications.

(4) An efficient and systematic industrialized production method for algal biochar is still lacking. There are few commercially available algal biochar products.

In order to make better use of algal biomass resources, and enhance the practical application ability of algae-derived biochar adsorbents in water treatment, in-depth exploration can be carried out regarding the following aspects in the future:

(1) The effects of different preparation/modification methods on the physical and chemical characteristics of algal biochar should be summarized and clarified in detail so that suitable biochar adsorbents can be produced according to different target pollutants to improve removal efficiency.

(2) Research on biochar recycling and pollutant recovery should be strengthened. Development of magnetic materials, soil amendment and technologies for pollutant enrichment/desorption/recovery are promising in increasing the value of used biochar and adsorbed chemicals.

(3) The mechanism of migration and transformation of algal biochar in the environment and organism should be studied to estimate its environmental toxicity.

(4) Further research on the actual application of algal biochar in real water environments should be carried out, enhancing the adsorption effect of algal biochar in complex conditions.

(5) Low cost and feasible industrialized preparation techniques for algal biochar should be developed to narrow the gap between the theory and practice of biomass utilization.

**Author Contributions:** L.L. and X.Q. had the idea for the article, L.L., J.W. and W.S. performed the literature search, L.L. and X.P. performed the data analysis, L.L. drafted the original manuscript, X.Q. critically revised the manuscript. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was financially supported by the Doctor Foundation of Hebei Normal University of Science and Technology (No. 2023YB017 and 2024YB034) and Hebei Agriculture Research System HBCT 2024040203.

**Data Availability Statement:** No new data were generated in this study, and data sharing is not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

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