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Characteristics of biochar from algae of the sea of Japan

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Abstract

The paper presents a comparative analysis of biochars produced from seaweed collected from the Sea of Japan, including Ahnfeltia tobuchiensis, a mixture of algae (Neorhodomela sp.), Zostera marina, Phyllospadix iwatensis, and Saccharina japonica, and Zostera marina. Medium-temperature pyrolysis (500 °C) was used to produce the biochars, with a carbonation time of 1 hour. These biochars have an alkaline reaction and can be used as soil ameliorants for acid soils. The yield of biochar produced after medium-temperature pyrolysis ranges from 39% to 57%, with the highest yield coming from Ahnfeltia tobuchiensis and the lowest from Saccharina japonica. All of the biochars contain essential nutrients, including nitrogen (N), phosphorus (P), and potassium (K). Biochar obtained from the algal mixture appears to be the most promising raw material for producing biochar due to its high content of these elements and good yield. In general, all biochar derived from marine macroalgae can be considered a promising organic fertilizer. Not only the extracted algae, but also the storm emissions from them, can be used as raw materials. This makes the production of biochar from these sources a potentially promising product for the fertilizer market.

Keywords: Biochar, Marine macrophytes, Plant nutrition elements, Pyrolysis, Seaweed, The Sea of Japan.

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1. Introduction

Obtaining new products from organic waste has become an increasingly important topic in modern society, and one of the main areas of research relates to the use of biochar. Biochar is a highly porous and high-carbon product that is produced thermochemically under oxygen-limited conditions [1]. The use of this material can help solve several significant problems, such as ensuring the rational use of biomass, developing renewable energy sources, increasing the yield and quality of agricultural products, and minimizing the negative effects of climate change [2].

Biochar has a wide range of properties and has been shown to be effective in many applications. It is used in agriculture, animal husbandry, water purification, cosmetology, dermatology and pharmaceuticals [3-5]. The use of biochar in agroecology is a traditional practice and there is growing interest in research in this field. According to an analysis by Meena et al., from 2010 to 2021, the number of studies on biochar in the field of agriculture increased from 42 to 882 [2]. The growing interest in studying biochar for use in soils is justified by the multitude of positive effects it has. Biochar positively affects the formation of soil aggregates and increases the pore space in the soil, which in turn leads to improved water retention, enhanced aeration, and reduced soil density [6-8]. Since the pore space in the soil is a habitat for soil microorganisms, increasing the number of pores through the use of biochar increases biological activity in the soil [9, 10]. Biochar has proven its effectiveness as a meliorant, as it is able to increase the pH of acidic soils [7] improve the ion balance of saline soils [11] increase the content of total organic carbon [12] and the content of available phosphorus [13]. Biochar is able to reduce greenhouse gas emissions from the soil [10, 14, 15]. Biochar is an effective sorbent [7, 16].

However, despite the existence of reliable data on the positive effect of biochar on soil properties, the degree of influence is very diverse and depends on the initial properties of the raw material, the method of production, and the external parameters of the experiment [2].

The composition and properties of biochar vary depending on the properties of the raw materials used and the conditions for producing biochar [3-5, 17]. Factors such as time, temperature and pressure directly affect the yield and characteristics of biochar. The biochar obtained from different raw materials has different parameters. Currently, biochar is obtained from waste products from agriculture, paper production, poultry farms, animal husbandry, and the food industry [18, 19]. Biochar obtained from wood is considered to be the most promising due to its characteristics. It has a high carbon content and a higher C/N ratio compared to other types of biochar [20].

Biochar can be produced from any biological material [21]. Plant residues and aquatic plants provide a rich, inexpensive, and environmentally friendly source of biomass with significant energy potential. This makes them a promising area for energy production [22].

Seaweed differs from land-based crops in its higher growth rate, increased productivity, and carbon dioxide (CO_2) capture rate [22]. In this regard, algae is a promising raw material resource for sustainable renewable energy production [23].

Biochar obtained from marine and freshwater algae is gaining popularity, and like biochar from more traditional biomass sources, it is being tested in various fields of application. Biochar produced from seaweed serves as an environmentally friendly method for improving soil fertility and addressing environmental challenges in the agricultural sector [24]. Algal biochar differs from lignocellulosic biochar in a higher cation exchange capacity, higher content of heteroatoms and more developed porous structure [23]. Biochar obtained from algae typically has a high content of phosphorus and potassium due to the specific composition of raw materials used [25, 26]. It stands out that the special characteristics of algal biochar make it possible to use it in agriculture to optimize soil structure: it improves moisture-retention properties of soil, increases air permeability, and promotes gradual release of nutrients [23]. Algal biochar stands out as an affordable absorbent material characterized by high absorbency, a developed porous structure, and a unique surface chemical composition that guarantees excellent thermal stability [21]. Algal biochar is effective against many pollutants, regardless of their category [27]. It has been found that biochar prepared from Chlorella sp. algae purifies wastewater from p-nitrophenols more effectively than conventional powdered activated carbon [21]. In addition, biochar from biomass residues of Spirulina platensis can remove about 82.6% of Congo red dye. Biochar obtained from macroalgae also demonstrates a high level of purification, removing about 90% of dye from polluted waters [21].

Despite some existing literature on the properties and applications of algal biochars, information is limited, and there are difficulties in developing algal biochar as a promising material for environmental restoration [23].

The purpose of this study is to investigate the characteristics of biochar produced from various types of seaweeds in the Sea of Japan, with a focus on their potential use as fertilizers.

2. Materials and Methods

The object of the study is biochar, which is obtained by medium-temperature pyrolysis of algae. Algae, which are released from the coasts of the Primorsky Territory in the Sea of Japan, were selected as the plant material for pyrolysis. The most common algae species that are released into the bays of Primorsky *Region include Ahnfeltia tobuchiensis, a mixture of Neorhodomela sp. and Zostera marina, Phyllospadix iwatensis, and Saccharina japonica* [26, 28]. The pyrolysis conditions are presented in the table (Table 1). As a result of pyrolysis, the raw material has a different appearance Figure 1 depending on the initial plant material.

Table 1.
Pyrolysis conditions.

Types of marine macrophytes for biochar production	Pyrolysis temperature, °C	Pyrolysis time, h
Ahnfeltia tobuchiensis	500	1
Algae mixture: Neorhodomela sp., Zostera marina., *Phyllospadix iwatensis*	500	1
Saccharina japonica	500	1
Zostera marina	500	1

After collection, the algae were air-dried for a week. The algae were pyrolyzed in a SAFTherm STZ 1214 furnace (Henan sante furnace technology co., ltd, China) in a nitrogen flow at a temperature of 500°C for 30 minutes, the heating rate was 8.3 deg/min, and the nitrogen flow rate was 3 l/min. The yield of biochar from the pyrolysis of air-dried was calculated using the equation 1[29].

$$Biochar\ yield, \% = \frac{W_{biochar}}{W_{seaweed}} \times 100\% \quad (1)$$

where, Wbiochar is the weight of the biochar (g), Wbiochar is the weight of the initial seaweed (g).

The pH value of the aqueous extract was determined using the standard methods described by Rajkovich, et al. [30]. To measure the pH, biochar was first crushed and a fraction with a particle size less than 1 micrometer was selected. This fraction was then mixed with 25 milliliters of distilled water and stirred for 60 minutes. After mixing, the pH was measured using a combination electrode and a Mettler Toledo conductivity sensor (USA).

The total nitrogen content in biochar was determined using the Kjeldahl method [31]. Available forms of phosphorus and potassium in biochar were determined using the spectrophotometric method [32]. The content of heavy metals was determined according to Methods for the Examination of Composting and Compost [33].

The carbon content of biochar was determined according to the methodology presented in the International Biochar Initiative (IBI) recommendations [32].

Saccharina japonica | *Algae mixture: Neorhodomela sp., Zostera marina., Phyllospadix iwatensis* | *Zostera marina* | *Ahnfeltia tobuchiensis*

Figure 1.
External biochar obtained from seaweed.

3. Results and Discussion

For any producer of biochar from organic raw materials, it is essential to understand the yield of the finished products after pyrolysis. The yield of biochar obtained from algae during pyrolysis at 500 °C ranged from 39% to 57%. Specifically, the yields were: Ahnfeltia tobuchiensis at 55% to 57%, a mixture of algae (Neorhodomela sp., Zostera marina, and Phyllospadix iwatensis) at 44% to 46%, Saccharina japonica at 39% to 41%, and Zostera marina at 49% to 50%. (Table 2).

Table 2.
Parameters of biochar obtained from various types of marine macrophytes

Types of marine macrophytes for biochar production	***Biochar output (W). %***	**pH**	**N %**	**P_2O_5. mg/g**	**K_2O. mg/g.**	**Corg.. %**
Ahnfeltia tobuchiensis	55-57	8.48	8.2-10.6	3.6	16.8	49.7
Algae mixture: Neorhodomela sp., Zostera marina., *Phyllospadix iwatensis*	44-46	8.65	3.2	11.0	13.9	41.5
Saccharina japonica	39-41	10.38	5.8	4.3	19.9	31.8
Zostera marina	49-50	8.91	1.8-3.2	4.6	19.5	46.7

Acid-base properties are an important parameter that affects the movement and availability of nutrients. The most efficient conversion of macro- and micronutrients into their usable forms occurs at a pH between 6.0 and 7.5.

Studies of the acid-base properties of biochar have shown that the pH of the biochar medium ranges from 8.48 to 10.38, indicating an alkaline reaction. In general, the entire biochar produced has a pH between slightly alkaline and highly alkaline. This type of biochar can have a positive impact on acidic soils and may be a useful ameliorant [34].

The main factors that affect soil fertility are carbon, nitrogen, phosphorus, and potassium. These elements are absorbed by plants in large quantities from the soil. Most of these elements leach out with precipitation, but some, such as carbon and nitrogen, escape into the atmosphere through a small biological cycle. Therefore, when using biochar as fertilizer on agricultural soil, it is important to replenish the nutrients that have been removed, which means adding more of these elements to the biochar.

If we talk about the carbon content of biochars, the most promising one is obtained from Anthelzia, with a content of 49.7%. The least organic carbon can be found in Saccharina japonica, with 31.8% content. Zostera marina and a mixture of algae (Neorhodomela sp., Zostera marina, Phyllospadix iwatensis) have 46.7% and 41.5% organic carbon, respectively. According to the IBI standard, all biochars should have a carbon content between 30% and 60% to be considered promising, which makes them class II [32].

Nitrogen is present in biochar as organic compounds, and its concentration varies depending on the elemental composition of the starting material. The use of biochar can increase nitrogen availability for plants and affect soil microorganisms, ultimately leading to improved crop yields.

Nitrogen and carbon are closely related, as carbon affects the amount of organic matter in the soil. When applied to soil, nitrogen affects the degree of mineralization, or C/N ratio.

The total nitrogen content in different types of biochar varies greatly. Biochar from anthelia has the highest nitrogen content, ranging from 8.2% to 10.6%, while biochar from kelp has almost twice as much, at 5.8%. A mixture of algae and zostera yields biochar with nitrogen concentrations between 1.8% and 3.2% (Table 2).

During plant growth and development, agricultural plants absorb nitrogen from the soil or nutrient solution. However, during the vegetative growth phase, they also actively consume potassium and phosphorus. Therefore, biochar, which is used as a fertilizer, must contain accessible forms of these essential elements in its composition.

Phosphorus is a biogenic element that does not have a natural replenishment process in nature, unlike nitrogen. However, there are exceptions, such as the soils of areas formed on rocks containing apatite and phosphorite deposits. Due to this, the areas of Primorsky Krai designated for agricultural production are deficient in this element. To compensate for this deficiency, they use mineral (superphosphate) and organic fertilizers (siderates) to replenish phosphorus.

In the studied material, the majority of available phosphates were found in biochar derived from a mixture of algae (Neorhodomela sp., Zostera marina, and Phyllospadix iwatensis), with a concentration of 11.0 mg/g. The remaining material (Ahnfeltia tobuchiensis, Saccharina japonica, and Zostera marina) had available phosphorus levels ranging from 3.6 to 4.6 mg/g. Average values for soil availability of available phosphates ranged from 15.0 to 20 mg/100 g, which is believed to be sufficient to provide plants with the element during the growing season. Therefore, it can be concluded that biochar derived from algae when applied to soil can provide plants with P_2O_5.

After the water-soluble form of potassium, the exchangeable form is the closest source of potassium nutrition for plants. This form is represented by potassium ions that are adsorbed on soil colloids. The ease of accessibility of this form for plants is due to the fact that some of the potassium that is adsorbed by the colloids can pass into the soil solution when it is exchanged for other cations. Biochar itself contains potassium in a mineralized form, such as part of potassium carbonate that is formed during the combustion of plant materials. However, the amount of potassium in biochar depends on the type of raw materials used to produce it.

According to the content of exchangeable potassium, the values indicated that in the studied biochar, this element had a relatively high concentration, ranging from 13.9 to 19.9 mg/g. This suggests that this raw material could be used as a fertilizer in soils to supplement this nutrient during the growth of cultivated plants.

4. Conclusion

The analysis of biochar obtained from macrophytes in the Sea of Japan has revealed its unique properties that make it a promising material for agriculture. These marine macrophytes contain a high level of organic substances, making it possible to produce biochar with excellent nutritional characteristics. The resulting biochar has an alkaline pH, which makes it particularly valuable for acidic soil. The addition of biochar can help neutralize acidity and improve soil structure, increasing its water retention capacity, which is especially important in regions with acidic soil, where conventional soil improvement methods may not be effective or affordable. In addition, biochar contains substantial amounts of nitrogen, phosphorus, and potassium, providing a natural source of nutrients for plants. Nitrogen is essential for protein synthesis and other vital compounds, while phosphorus plays a crucial role in root development and fruit formation.

Nevertheless, when planning the use of biochar from marine macrophytes, it is necessary to assess the economic benefits. To reduce the cost of producing biochar from marine macrophytes, their source should be located directly in the region of use. Thus, biochar produced from the Sea of Japan's marine macrophytes could become an effective organic fertilizer. However, considering the alkaline reaction of the biochar and the raw materials used for producing biochar, using biochar derived from these marine plants will be most effective in areas near coastal areas where there are frequent releases beach wrack and acidic agricultural soil.

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