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# Microwave assisted and conventional hydrothermal treatment of waste seaweed: Comparison of hydrochar properties and energy efficiency



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#### HIGHLIGHTS

- Comparison of microwave-assisted and conventional hydrothermal carbonization of waste seaweed
- 1 h of MHC yields hydrochar with equal adsorption of HC produced under standard heating for 4 h.
- Microwave heating is 70 % more energy efficient for producing hydrochar from waste seaweed.
- Formation of oxygen-containing functional groups boosts adsorption capacity

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## GRAPHICAL ABSTRACT



#### ABSTRACT

Waste seaweed is a valuable source for converting into value-added carbon materials. In this study, the production of hydrochar from waste seaweed was optimized for hydrothermal carbonization in a microwave process. The produced hydrochar was compared with hydrochar synthesized by the regular process using a conventional heating oven. The results show that hydrochar produced with a holding time of 1 h by microwave heating has similar properties to the hydrochar produced in a conventionally heated oven for 4 h (200 °C and water/biomass ratio 5): carbon mass fraction (52.4  $\pm$  3.9 %), methylene blue adsorption capacity (40.2  $\pm$  0.2 mg g<sup>-1</sup>) and similar observations on surface functional groups and thermal stability were made between hydrochars produced by both methods. The analysis of energy consumption showed microwave assisted carbonization consume higher energy in compare to conventional oven.

The present results suggest that hydrochar made from waste seaweed and using the microwave technique could be an energy-saving technology for producing hydrochar with similar specifications to hydrochar produced by conventional heating methods.

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# List of symbols

Roman	svm	hol

Roman sy	mbols
a <sub>T</sub>	Toth constant, $L g^{-1}$
as	Sips constant, $L mg^{-1}$
b	Redlich-Petersen constant, L $^{\beta}$ mg $^{-\beta}$
С	concentration, mg $L^{-1}$
Cp	specific heat, J kg $^{-1}$ K $^{-1}$
D <sub>h</sub>	hydraulic diameter, m
Η	convective heat transfer coefficient, W $m^{-2} K^{-1}$
k	thermal conductivity, W m <sup><math>-1</math></sup> K <sup><math>-1</math></sup>
K <sub>L</sub>	Langmuir equation coefficient, $L mg^{-1}$
K <sub>F</sub>	Freundlich equation coefficient, $mg^{1-1/n}L^{1/n}g^{-1}$
K <sub>R</sub>	Redlich-Petersen equation coefficient, $L g^{-1}$
K <sub>T</sub>	Toth equation coefficient, mg $g^{-1}$
Ks	Sips equation coefficient, L $g^{-1}$
m	hydrochar dosage, g
n	Freundlich adsorption intensity
Nu <sub>D</sub>	Nusselt number
Pr	Prandtl number
$pH_{PZC}$	pH for the point of zero charge
Q	applied energy, J
Q <sub>0</sub>	Langmuir maximal adsorption capacity, mg $g^{-1}$
Re	Reynolds number
n <sub>t</sub>	Toth constant
T <sub>HTC</sub>	hydrothermal carbonization temperature, °C
Ts	surface temperature, °C
T∞	fluid temperature, °C
$T_{\rm f}$	film temperature, °C
V	volume, L
V	Fluid velocity, m s <sup><math>-1</math></sup>

# Greek symbols

β Redlich-Petersen coefficient	see Eq.	(5)
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- Sips coefficient, see Eq. (7) βs
- removal efficiency, % η
- difference Δ
- density, kg m $^{-3}$ ρ
- dynamic viscosity, kg m  $^{-1}$  s  $^{-1}$ μ

## Superscripts

0	initial
0	minutui

equilibrium e

# Abbreviations and acronyms

BET	Brunauer-Emmett-Teller
DTG	Differential thermogravimetric
FTIR	Fourier-transform infrared
HC	hydrochar
HTC	hydrothermal carbonization
MB	methylene blue
MHC	microwave hydrochar
MHTC	microwave assisted hydrothermal carbonization
RSSQ	residual sum of squares
TGA	thermogravimetric analysis
TOC	total organic carbon

## 1. Introduction

Nowadays, waste biomass is either dumped or burnt in uncontrolled conditions, and therefore, it becomes another source of environmental pollution. One of the most abundant biomasses in the world is macroalgae, which are observed every year in bloom in many coastal areas, of the world (Rybak, 2018). The green tide phenomenon occurs regularly in coastal areas when large amounts of green algae bloom. One of the largest blooms was recorded in 2008 on Qingdao island, where >1 million tons of Ulva were removed from the area, an operation that cost >100 million US dollars (Hiraoka et al., 2011). In South Korea, there have been several cases of Ulva outbreaks, mostly on Jeju Island with an estimated about 10,000 tons of waste seaweed per year (Chang et al., 2011; Kim et al., 2011; Nizamuddin et al., 2018).

Hydrothermal carbonization (HTC) is an energy-efficient thermochemical conversion process that converts biowaste into value-added products like biochar/hydrochar in the solid phase, bio-oil, methanol, ethanol in the liquid phase, and gaseous (Mannarino et al., 2022; Stobernack et al., 2021; Wang et al., 2019). Carbonization under hydrothermal conditions is a suitable technology for biomass with high moisture content, (Seyedsadr et al., 2018; Steinbruch et al., 2020; Stemann et al., 2013) as the biomass does not need to be dried beforehand. This reduces overall process costs and energy requirements. Due to the aqueous reaction medium, biomass with high moisture content such as algae, sewage sludge, industrial effluents are suitable feedstocks for hydrothermal processes (Kang et al., 2019; Okolie et al., 2019; Śliz et al., 2022; Wang et al., 2018). In conventional heating methods, heat is generated by an external (electrical) oven and then transferred by convection, conduction, and radiation from the external to the internal part of the autoclave and then the reactants. The development of alternative, sustainable technologies for converting biomass to hydrochar is getting attention. The need for innovative approaches to energy conservation cannot be overemphasized (Dai et al., 2017; Nizamuddin et al., 2018). The disadvantages of conventional heating methods, include extensive heat losses, unselective heating, uncontrolled side reactions leading to higher energy consumption, and longer residence times. Heating oil and high pressure steam are commonly used for heat transfer in HTC production on large scale. The microwave-assisted HTC (MHTC) process uses microwave energy to generate heat directly in the reaction mixture, eliminating the need for an external heat source. The choice between heating oil, high pressure steam, and the MHTC process depends on factors such as the specific HTC reaction, desired reaction rate, and available resources. MHTC was developed, which is more energy-efficient than conventional heating methods because of homogenous (i.e. volumetric) heating, and it provides selective, fast, and significantly reduces processing time and costs (Nizamuddin et al., 2018). In HTC of biomass, microwaves can be used to selectively heat the biomass, which can influence the selectivity of the products. The HTC process involves the conversion of biomass into a solid form of carbon called hydrochar, through a series of chemical reactions, including hydrolysis, decarboxylation and polymerization, that occur at high temperatures and pressures in the presence of water.

Microwaves can selectively heat biomass through its dielectric properties. This can lead to faster and more efficient conversion of biomass into hydrochar and it can influence the selectivity of the products. The latter can be controlled by specific reaction conditions, such as temperature, pressure, and reaction time.

Additionally, the use of microwaves can also lead to local heating and rapid heating/cooling cycles, which can further influence reaction kinetics and product selectivity. This can enable the conversion of specific components of biomass into desired products, such as the selective conversion of cellulose into hydrochar or the selective conversion of lignin into biocrude.

In summary, the use of microwaves in the hydrothermal carbonization of biomass can lead to an enhancement in the selectivity of the products by influencing the reaction kinetics and enabling the selective conversion of specific components of the biomass into desired products (Yu et al., 2020a; Yu et al., 2020b; Zhang et al., 2022).

More generally, microwave technology is used as a heating method to promote chemical reactions, and offers high energy efficiency and fast operation. For instance, 16 % energy saving has been demonstrated in the calcination of limestone (Fall et al., 2011), and also in drying processes using microwave technology compared to conventional ones showed energy saving of 20 % (Sabarez et al., 2012) and 11 % (Szadzińska et al., 2016).

In conventional heating, heat is transferred from the surface of the reacting medium mostly by convection and conduction and then by radiation from the surface of the material, which is considered an indirect process (Guiotoku et al., 2014; Nizamuddin et al., 2018; Nobre et al., 2021). A temperature gradient is created from the outside to the inner core of the reacting medium and the heat is transferred to a steady state (Nizamuddin et al., 2018). In MHTC, heat is introduced directly into the bulk of the material through direct molecular interactions initiated by electromagnetic waves (Guiotoku et al., 2014). The advantages of microwave heating are fast reaction rates and homogeneous heat distribution, which significantly reduces reaction time, energy consumption, and costs (Dai et al., 2017; Nüchter et al., 2004).

The size of the feedstock can significantly impact the heat transfer efficiency and reaction kinetics during thermochemical processing. Smaller particle sizes result in higher surface area to volume ratios, leading to faster heat and mass transfer, faster reaction times, and higher yields. In contrast, larger particle sizes have the lower surface area to volume ratios and result in slower heat transfer and longer reaction times. However, microwave heating, which is a volume-heating process, is not affected by the particle size of the feedstock. Using larger biomass materials can result in rapid thermochemical reactions without the need for particle size reduction, leading to substantial energy savings. To ensure consistency and to eliminate any potential variability in the results, the authors crushed the dried biomass into particles smaller than 500  $\mu$ m in each experiment. The use of a sieve helped eliminate large particles that could affect the heat transfer efficiency and standardize the particle size, allowing for reliable and reproducible results (Lei et al., 2009; Septien et al., 2012).

The hydrothermal carbonization process involves several key stages such as pretreatment, where the seaweed is typically chopped to a suitable size and dried to remove excess water; hydrolysis, where the seaweed is heated in the presence of water, breaking down into simpler sugars and organic acids, dissolved in the water; dehydration, decarboxylation, where the organic acids in the liquid begin to lose their carboxyl groups, forming volatile gases such as  $CO_2$ ,  $CH_4$ , eventually condensation, (re)polymerization, and aromatization which is called carbonization, where the remaining liquid and solid materials begin to undergo thermal decomposition, releasing more gases and forming a solid, carbon-rich material known as hydrochar; and cooling and recovery, where the hydrochar is cooled and separated from the gases, which can be captured and used as a source of energy. The hydrochar can then be used as a soil amendment or fuel (Jin, 2014; Zhang et al., 2018).

In the thermal degradation process, one reaction path occurs in the solid phase, resulting in the production of a solid product known as primary char. The primary char is composed mainly of carbon, but may also contain other elements such as hydrogen, oxygen, and nitrogen (Cao et al., 2021; Dutta et al., 2022; Zhang et al., 2019).

The second path leads to char by repolymerization of soluble intermediates in the aqueous phase, and the residue is called secondary char, which is deposited on the surface of the primary char and has a sphere-like geometry (Anca-Couce et al., 2014; Castello et al., 2014; Titirici and Antonietti, 2010; Volpe and Fiori, 2017).

Specifically, the aqueous phase in HTC consists of intermediates mainly derived from cellulose and hemicellulose. Some of the cellulose in the aqueous phase decomposes to monomers and oligomers such as 5hydroxymethylfurfural and phenolic derivatives, which are highly reactive and can lead to the formation of a solid substance called 'secondary char' through polymerization and condensation. There is also undissolved cellulose that undergoes dehydration and decarboxylation reactions leading to the formation of 'primary char'. At the same time, decarboxylation reactions take place and the gas phase is formed, which mainly consists of carbon dioxide and carbon monoxide (Babatabar et al., 2022; Williams and Khodier, 2020).

The produced hydrochar can be used in various fields, e.g. as fuel, for soil amendment, for enhancing soil fertility, and, for the adsorption of pollutants (Fang et al., 2018).

The improvement in soil quality and fertility that results from using Hydrochar leads to higher crop yields, reduced soil erosion, and improved soil structure, all of which contribute to sustainable development (He et al., 2022).

One of the most important environmental applications is the usage of hydrochar as cheap adsorbent for wastewater treatment to remove inorganic substances (especially heavy metals) and organic compounds (dyes, pesticides, pharmaceuticals) (Jellali et al., 2019; Shi et al., 2020). Hydrochar, with its carbon-negative characteristics, plays a crucial role in promoting sustainability. Its ability to effectively remove pollutants such as heavy metals, pesticides, and toxic organic compounds from the water makes it a valuable tool in controlling water pollution. Among all types of pollution, wastewater-containing dyes not only cause direct harm to human health, but also affects the whole ecosystem (Chen et al., 2021; Liu et al., 2021; Tu et al., 2019). Currently, there are a variety of methods to treat dye wastewater, such as physical adsorption, biodegradation, oxidation, photocatalysis, etc. (Liu et al., 2020). Hydrochar has a relatively large adsorption capacity without the disadvantages of sludge production and/or exorbitant costs, which makes this material suitable for the removal of pollutants from water (Jellali et al., 2019).

There is much research regarding the hydrothermal carbonization process with the conventional method and microwave technique, Deng et al. investigated the conversion of seaweed into hydrochar via microwave assisted technique (Deng et al., 2022), Steinbruch et al. studied the direct hydrothermal processing of whole green seaweed Ulva sp. biomass via microwave assisted heating (Steinbruch et al., 2020), Cao et al. valorized red seaweed food waste into levulinic acid and algae hydrochar through a microwave-assisted process (Cao et al., 2019), Polikovsky et al. applied subcritical water hydrolysis to green seaweed Ulva sp. biomass to co-produce food, energy, and chemicals, resulting in high heating value hydrochar, via a batch reactor (Polikovsky et al., 2020), Smith examined the potential of three species of kelp as a biofuel feedstock by processing them through hydrothermal carbonization via a batch reactor (Smith and Ross, 2016). Despite these studies, there is limited research on the energy requirements for these methods (Dai et al., 2017; Nizamuddin et al., 2018; Nüchter et al., 2004). There is much research regarding the hydrothermal carbonization process with the conventional method and microwave technique: Deng et al. investigated the conversion of seaweed into hydrochar via microwave assisted technique (Deng et al., 2022); Steinbruch et al. studied the direct hydrothermal processing of whole green seaweed Ulva sp. biomass via microwave assisted heating (Steinbruch et al., 2020); Cao et al. valorized red seaweed food waste into levulinic acid and algae hydrochar through a microwave-assisted process (Cao et al., 2019); Polikovsky et al. applied subcritical water hydrolysis to green seaweed Ulva sp. biomass to co-produce food, energy, and chemicals, resulting in high heating value hydrochar, via a batch reactor (Polikovsky et al., 2020); and Smith examined the potential of three species of kelp as a biofuel feedstock by processing them through hydrothermal carbonization via a batch reactor (Smith and Ross, 2016). Despite these studies, there is limited research on the energy requirements for these methods (Dai et al., 2017; Nizamuddin et al., 2018; Nüchter et al., 2004).

In the traditional hydrothermal carbonization process, the biomass undergoes a series of complex chemical and physical transformations in the presence of high temperature and pressure. The biomass is partially decomposed into volatile matter and intermediate products, and further converted into hydrochar. However, in the microwave-assisted hydrothermal carbonization process, the use of microwaves can accelerate the heating of the biomass, which can significantly reduce the processing time and improve the overall efficiency of the process.

Furthermore, the microwave-assisted hydrothermal carbonization method can also lead to changes in the structure and properties of the resulting hydrochar. For example, it has been reported that microwave heating can promote the formation of mesoporous structures in hydrochar (Cao et al., 2009), which can enhance its adsorption capacity for organic pollutants. On the other hand, the traditional hydrothermal carbonization method tends to produce hydrochar with more micropores size pores, which may result in a lower adsorption capacity.

The primary purpose of this study is to synthesize hydrochar that can serve as an affordable absorbent material. Additionally, the study aims to establish hydrochar production using a microwave-assisted technique with similar properties compared to hydrochar produced using a conventional oven.

Deng et al. focused on optimizing the operating conditions for the MHTC of seaweed. Their goal was to assess the product distribution and yield and to estimate the potential economic benefits that could drive the development of the MHTC process (Deng et al., 2022). Meanwhile, Cao et al. examined the effects of various parameters on the production of hydrochar from red seaweed (*Gracilaria lemaneiformis*). Their study demonstrated that the proposed process had good energy efficiency and carbon recovery (Cao et al., 2019).

In this research, the hydrothermal carbonization of waste seaweed was used to compare the energy consumption of microwave heating and heated by conventional oven in producing similar hydrochar product. The optimal conditions to obtain hydrochar via conventional heating, as previously reported (Soroush et al., 2022), were used as a baseline for comparison with the hydrochar produced using microwave-assisted heating. Both hydrochar products were used in an adsorption study using methylene blue to evaluate the properties as future adsorbent material.

#### 2. Material and methods

This section contains information on the materials used in this study, the experimental procedures, and characterization of the produced materials and it describes the details of the heat calculation for the HTC and MHTC process.

#### 2.1. Material

The material used in this research is Ulva pertusa, a green alga (Chlorophyceae) (Pandey et al., 2014) (Supplementary information section S.1). Ulva pertusa was collected in April 2019 from the coastal area of Busan city, South Korea (representing the waste seaweed, as mentioned in Section 1). The moisture content of waste seaweed was 83.9  $\pm$  0.1 %. After collection, it was washed twice with tap water and once with distilled water to remove other species or debris. The washed seaweed was dried at room temperature for 72 h and then in a drying oven (brand JSR, JSOF series) at 105 °C for 4 h. The drying step has two purposes: firstly, it is done to stabilize the material to preserve it for long-term use and, secondly, it is done to control the water to biomass ratio, which is otherwise difficult to regulate. The dried seaweed was then crushed and screened (500 µm sieve) to obtain a uniform particle size. This was done to ensure that the particle size of the feedstock was consistent and standardized for each experiment. 500 µm sieve, to effectively screen out particles that were larger than the desired size.

#### 2.2. Experimental

The crushed seaweed was mixed with distilled water for MHTC. The MHTC experiment was carried out in a CEM Discover SP microwave reactor (with a volume of 35 mL). Hydrothermal carbonization via conventional oven (with volume of 50 mL for autoclave, Fig. S-1, Supplementary information, section S.2) has been done in previous work (Soroush et al., 2022), which was investigated in detail by using the same biomasses and optimizing the produced HC by using different reaction times of 1, 2, 4, and 6 h and different water to biomass ratios of between 1 and 10 under 3 different reaction temperatures of 180, 200 and 250 °C. The optimal experimental conditions for using a conventional oven were established as a

temperature of 200 °C, water to biomass ratio of 5, and a residence time of 4 h, and this hydrochar was taken as a reference to performing microwave assist hydrothermal carbonization at the same condition (apart from the residence time) to eventually ensure that they are of the same quality. Since microwave-assisted heating is a fast heating process, the influence of the reaction time should be investigated and the rest of the process conditions were kept similar to previous work for sake of comparison. In this context, a reaction time between 5 and 150 min was considered in order to obtain hydrochar (all experiments were conducted three times and the resulting hydrochar from each condition was blended to ensure homogeneity and readiness for further examination) with comparable properties to conventionally heated HTC. The water to biomass ratio in hydrothermal carbonization may have an impact on the heating process by microwaves. While water serves as a heat transfer medium by absorbing microwave energy and transferring it to the biomass, it also requires more energy to raise its temperature. Therefore, it is not straightforward to state that a higher water to biomass ratio will directly result in faster heating. The high water content also increases the thermal conductivity of the reaction mixture, allowing heat to be more evenly distributed throughout the mixture (Oktaviananda et al., 2017; Yang and Zhang, 2022).

When the water to biomass ratio is low, the reaction mixture will contain less water, which can reduce the heat transfer efficiency. The low water content can cause uneven heating of the biomass, resulting in a lower carbonization yield. The low water content also reduces the thermal conductivity of the reaction mixture, which can lead to less consistent heating of the biomass (Gao et al., 2021). This research focuses on comparing the hydrochar produced through conventional oven methods with hydrochar produced through microwave heating methods using the same characterization methods. The produced hydrochar's energy consumption from standard oven heating is evaluated and compared to the energy consumption in the production of hydrochar by microwave-assisted heating. For MHTC, around 1 g of waste seaweed was loaded into the glass vial and 5 mL of distilled water was added, corresponding to the water to biomass ratio same as the amount found in previous work (Soroush et al., 2022). The optimization of reaction conditions was based on the type of raw biomass used. The use of seaweed rich in cellulose necessitated the optimization of conditions to enhance cellulose conversion to hydrochar. Cellulose is a complex carbohydrate that is difficult to break down. Therefore, high temperatures and high pressures are typically required to effectively convert cellulose to hydrochar and longer reaction times are also needed to ensure complete conversion (Lucian et al., 2018).

The sealed glass vial was put into the microwave, stirring started and the reactor was heated up to the set temperature of 200 °C, corresponding to the temperature as found in previous work (Soroush et al., 2022) within 20 min. Thereafter, the HTC process was maintained at the reaction temperature for a certain reaction time. During the process, the pressure has been measured and recorded by the machine. After the reaction, the reactor was cooled down to 60 °C, and then the liquid and solid products were separated by vacuum filtration with F1001 grade filter paper, size 125 mm. The liquid products were stored in the refrigerator at 4 °C for further analysis, and the solid char was dried in a conventional heating oven at 105 °C for 3 h and stored at room temperature.

The hydrochar produced by microwave hydrothermal treatment was designated as MHC, and hydrochar produced by conventional heating (with a reaction time of 4 h) was designated as HC. The procedures for conventional heating can be found in previous work (Soroush et al., 2022).

The mass yield of hydrochar was calculated according to Eq. (1):

$$Mass \ yield = \frac{Mass \ of \ produced \ char}{Mass \ of \ raw \ feeds tock} \times 100\%$$
(1)

#### 2.3. Characterization

The compositional analysis of the feedstock and hydrochars was carried out in an elemental analyzer (model Vario MACRO cube, Germany). Calibration was performed using sulfanilic acid ( $C_6H_7NO_3S$ ) to quantify carbon, hydrogen, nitrogen, and sulfur.

A thermogravimetric analyzer (TGA) (TA Instrument Q600, USA) was used to study the thermal stability and decomposition behavior of char and seaweed. A heating rate of 10 °C min<sup>-1</sup> to 800 °C with a nitrogen flow of 100 mL min<sup>-1</sup> was applied. The ash content is obtained by changing the gas from nitrogen to air at 800 °C, with the remaining residue corresponding to the ash.

Fourier-transforms infrared spectra (FTIR) were obtained by using a Nicolet FTIR spectrometer model VERTEX 70 (wave number range 500–4000 cm<sup>-1</sup>), by mixing the sample with KBr powder in a batch process, to investigate the surface functional groups of hydrochar and biomass.

The pH value of hydrochar was obtained by adding hydrochar to distilled water at a ratio of 1:10 and stirring at a constant speed of 150 rpm for 2 h. Then, the pH of the slurry was measured using a pH electrode with a pH meter S220 from METTLER TOLEDO.

The adsorption experiments were performed with methylene blue (MB). This compound is widely used in the textile industry (Hameed et al., 2007), next to other applications in various industries, such as in the dyeing of paper, leather, and food products, which makes it a relevant compound to study in the context of industrial waste management. Furthermore, MB is a widely used indicator for water pollution, which makes it an ideal choice for testing the effectiveness of new adsorbents for water treatment (Ferrentino et al., 2020; Li et al., 2019b; Qian et al., 2018).

An amount of 0.01 g of hydrochar was added to 5 mL of MB dye solution (based on previous work (Soroush et al., 2022)) with different concentrations of 5, 30, 50, and 100 mg  $L^{-1}$  during an equilibrium time of 2 h at room temperature. In all tests, the stirring rate was 800 rpm and the pH was fixed to 4, 7, and 9 using buffer solutions to study the effect of pH on adsorption. All experiments were performed in triplicate.

The pH for the point of zero charge (pH<sub>PZC</sub>) was used to characterize the electrical state of the adsorbent surfaces in dispersions. For the determination of the pH<sub>PZC</sub> of the produced hydrochar, 5 mL of NaCl solution  $(0.1 \text{ mol } \text{L}^{-1})$  was poured into separate test tubes and the solutions were adjusted to different pH values (2-12). Hydrochloric acid  $(1 \text{ mol } \text{L}^{-1})$  and sodium hydroxide  $(1 \text{ mol } \text{L}^{-1})$  were used to adjust the pH. After preparing the indicated buffer solutions, 0.01 g of hydrochar was added to each solution, and the samples were shaken at 150 rpm. After 24 h and when the pH stopped changing, the adsorbents were separated from the solution and the pH of the solution was measured to determine the pH<sub>PZC</sub>.

After the adsorption experiment, the solid and liquid phases were separated using a PES membrane with a pore size of  $0.2 \mu m$ . The MB concentration in the filtrate was determined by UV–Vis spectrometry (K LAB CO., LTD) at a wave length of 665 nm.

The liquid product after carbonization was measured by subtracting the mass of the final liquid product from the initial mass of distilled water. Total organic carbon (TOC) was analyzed using a HUMAS TOC3300L analyzer, in South Korea, which measures organic carbon using the UV-West oxidation NPOC method.

The adsorption capacity of hydrochar was calculated by Eq. (2), where  $q_e$  is the adsorbed MB amount (mg g<sup>-1</sup>),  $C_0$  is the initial concentration (mg L<sup>-1</sup>),  $C_e$  is the equilibrium concentration (mg L<sup>-1</sup>), V is the volume of MB solution (L), and m is the hydrochar dosage (g):

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

The equilibrium adsorption data are fitted with the Langmuir (Eq. (3)), Freundlich (Eq. (4)), Redlich-Petersen (Eq. (5)), Toth (Eq. (6)) and Sips (Eq. (7)). isotherms, given in Eqs. (3) to (7), where  $q_e (mg g^{-1})$  is the amount of MB, adsorbed on the hydrochar at equilibrium, in these equations,  $K_L (L mg^{-1})$ ,  $K_F (mg^{1-1/n}L^{1/n} g^{-1})$ ,  $K_R (L g^{-1})$ ,  $K_T (mg g^{-1})$  and  $K_s$ (L g<sup>-1</sup>) are the equilibrium coefficients of the Langmuir, Freundlich, Redlich-Petersen, Toth, and Sips isotherm, respectively.  $Q_0$  is the maximal MB adsorption capacity (mg g<sup>-1</sup>), b (L<sup> $\beta$ </sup> mg<sup>- $\beta$ </sup>) and  $\beta$  are Redlich-Petersen constants, where  $\beta$  ranges from 0 to 1.  $a_T$  (L g<sup>-1</sup>) is the isotherm constant of Toth, while  $a_s$  (L mg<sup>-1</sup>) and  $\beta_s$  are isotherm constants in the Sips model.

$$q_{e} = \frac{Q_{0}K_{L}C_{e}}{1 + K_{L}C_{e}}$$
(3)

$$q_e = K_F C_e^{1/n} \tag{4}$$

$$q_e = \frac{K_R C_e}{1 + b C_e^{\beta}} \tag{5}$$

$$q_{e} = \frac{K_{T} a_{T} C_{e}}{\left(1 + \left(K_{T} C_{e}\right)^{n_{t}}\right)^{\frac{1}{n_{t}}}}$$
(6)

$$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}} \tag{7}$$

For modeling purposes, it can be added that the Langmuir isotherm (2-parameter model) is a nested model of the Redlich-Petersen, Toth, and Sips isotherms (3-parameter model) when  $\beta = 1$ ,  $n_t = 1$ , and  $\beta_s = 1$ , respectively. The second observation is that the Freundlich isotherm is a nested form of the Sips model for the case when  $a_s = 0$ . The third observation is that the Toth model represents the Langmuir model for  $n_t = 1$ .

For all adsorption models, the goal is to minimize the difference between the experimental data and predicted responses and to evaluate the statistics in terms of significance for the obtained parameter values. In this context, the residual sum of squares (RSSQ), calculated according to Eq. (8), measures the difference between the predicted values and the experimental data set for the optimized set of parameters and the smaller the value for the RSSQ is, the better the model fits the experimental data:

$$RSSQ = \sum_{i=1}^{n} (q_i - f(x_i))^2$$
(8)

Where  $q_i$  is the experimentally measured MB concentration and  $f(x_i)$  is the predicted value of  $q_i$ , using the adsorption models (Eq. (3)to (7)). Adsorption models and RSSQ have been fitted using the least squares method in the Scipy library in Python (Supplementary information, section S.3).

For comparing these different adsorption models, the RSSQ and F-value have been calculated, F-distribution test was used to compare the fits of the two nested models by considering a number of parameters, Supplementary information, section S.4.

## 2.4. Heat calculation

The heat input in the laboratory scale conventional heating oven to reach the HTC set temperature was calculated by Eq. (9), where Q, m,  $C_{p_1}$  and  $\Delta T$  represent the applied energy (J), the mass of substance (kg), the specific heat capacity (J kg<sup>-1</sup> K<sup>-1</sup>), and the temperature difference, respectively:

$$Q = m \cdot C_p \cdot \Delta T \tag{9}$$

The energy required to maintain a set temperature in a conventional heating oven was calculated by evaluating the heat loss due to the flow of heat from the autoclave with air movement at a velocity inside the oven of 0.1 to  $1 \text{ m s}^{-1}$ . This type of heat transfer is known as forced convection, where the movement of air within the oven is caused by a fan or other means of mechanical ventilation. The properties of the surrounding air are also evaluated at the so-called film temperature, which approximates the temperature of the fluid inside the convection boundary layer. This allows for a more accurate calculation of the heat loss from the oven.

The energy required to maintain a constant temperature in a conventional autoclave was calculated by determining the heat loss from this autoclave. Information about heat flow and air velocity was used to estimate the heat loss, which was then set equal to the energy required to maintain the initial set temperature. The heat loss represents the heat transferred from the autoclave to the surroundings through convection.

In convective heat transfer, the Churchill-Bernstein relation, Eq. (12) is used to estimate the dimensionless Nusselt number for cross flow over a cylinder (corresponding to the shape of the autoclave reactor). The dimensionless Reynolds number was calculated by Eq. (11):

$$Re_{D} = \frac{\rho V_{\infty} D_{h}}{\mu} \tag{10}$$

Where  $\rho$  is the density of the fluid, (kg m<sup>-3</sup>), V\_{\infty} is the bulk flow velocity, (m s<sup>-1</sup>), D<sub>h</sub> is the hydraulic diameter (m), (Supplementary information, section S.4), and  $\mu$ , the dynamic viscosity of the fluid, (kg m<sup>-1</sup> s<sup>-1</sup>).

$$Nu_D = \frac{hD_h}{k} = 0.3 + \frac{0.62 \cdot Re_D^{1/2} \cdot Pr^{1/3}}{\left[1 + \left(\frac{0.4}{Pr}\right)^{2/3}\right]^{1/4}} \left[1 + \left(\frac{Re_D}{282,000}\right)^{5/8}\right]^{4/5}$$
(11)

Where  $Nu_D$  is the surface averaged Nusselt number calculated for a characteristic length equal to the hydraulic diameter of the autoclave, h is the convective heat transfer coefficient, (W m<sup>-2</sup> K<sup>-1</sup>), k is the thermal conductivity of the fluid (W m<sup>-1</sup> K<sup>-1</sup>), Re<sub>D</sub> is Reynolds number using the cylinder diameter as its characteristic length (Eq. (11)), and *Pr* is the Prandtl number. Eq. (12) is valid for a wide range of Reynolds numbers and Prandtl numbers, as long as the product *Pr*Re<sub>D</sub> is greater than or equal to 0.2 (Churchill and Bernstein, 1977).

The rate of heat transfer by convection, is determined from Newton's law of cooling, expressed as Eq. (12).

$$Q = hA\Delta T \tag{12}$$

Where Q is energy (W), h is convective heat transfer coefficient (W m<sup>-2</sup> K<sup>-1</sup>), A is heat transfer area (m<sup>2</sup>) (Suplementary information, section S.2) and  $\Delta T$  is temperature difference.

For the microwave technique, the energy requirement has been provided by the microwave machine itself, see Section 2.2.

## 3. Results and discussion

#### 3.1. Effect of process conditions on hydrothermal carbonization product

As mentioned in Section 2.2, the hydrothermal carbonization via conventional oven has been optimized and all presented results refer to the hydrochar produced at 200 °C and a water/biomass ratio of 5 as experimental conditions that have been evaluated in previous work (Soroush et al., 2022).

In this research, the main difference between MHTC and HTC is the use of microwave energy in MHTC. The microwave energy can potentially accelerate the carbonization process, leading to a shorter reaction time. Additionally, the microwave energy may help to break down the lignocellulosic structure of the biomass, leading to a more porous hydrochar. It was also suggested that the use of microwave energy can reduce the amount of water required for the carbonization process, which may help to improve the energy efficiency of the process (Güleç et al., 2021; Holliday et al., 2022).

The effect of reaction time on yield, which quantitatively shows how much waste seaweed was converted into hydrochar during MHTC, is given in Fig. 1. With increasing reaction time, an increase in solid yield was observed that could be linked to secondary charring progress, which occurs during the production of hydrochar and is characterized by the further breakdown of organic matter through heat and pressure, leading to the formation of more hydrochar, corresponding to the results found by Knežević et al. (Knežević et al., 2010) and Guiotoku et al. (Guiotoku et al., 2009) for hydrochar derived from woody biomass and pine sawdust, respectively.

After a reaction time of 60 min, the MHC yield did not increase significantly ( $\pm$  4 %) and it could be concluded that 60 min reaction time is a

sufficient residence time for the MHC. The yield of MHTC (after a reaction time of 1 h) was found to be 6 wt% lower compared to the optimal yield of HC obtained from a conventional heating oven (44.0  $\pm$  0.5 wt%) under similar process conditions (temperature 200 °C, water/biomass ratio of 5), with the exception of a longer reaction time of 4 h in the previous work (Soroush et al., 2022).

The HTC products are solids as the main product, liquid, which may contain small quantities of bio-oil mixed with water, and gas, which can be considered to consist mainly of CO2 (Wang et al., 2018). Fig. 1b, shows the total yields of solids, liquids, and gases, with the latter yield calculated by mass balancing. The graph demonstrates that as the solid yield increases, the liquid yield decreases, which could indicate secondary charring. By promoting the polymerization reactions in the aqueous phase (for longer reaction time), more compounds interact with each other and the aqueous yield decreases over reaction time (by 50 % by increasing the reaction time, see Fig. 1b). As a consequence, the secondary char condenses on the surface of the primary char, so that the overall solid yield increases over reaction time (by 25 % by increasing the reaction time, see Fig. 1b). Fig. 2 shows the total pressure in the gas phase during hydrothermal carbonization as a function of reaction time. The total pressure can be considered as a measure of the number of molecules in the headspace using the ideal gas law,  $p_{tot} \sim n$  (the ideal gas law is still considered valid since the reaction conditions are below 100 bar and 1000 K). Inspection of the experimental results, as presented in Fig. 2, confirmed that, after 90 min, of reaction time, the gas pressure and consequently the gas yield decreased and after 90 min slightly increased. The same result was observed in Fig. 1b. This result can be explained by the fact that the gas phase product is mainly CO<sub>2</sub>, methane, and hydrogen. By increasing the reaction time, CO<sub>2</sub> being the major gas compound that appears to evolve more at the beginning of the HTC reaction (<90 min), is easily soluble in water at high pressure (Liu et al., 2011), so other evolved gases like methane and hydrogen keep contributing to additional headspace pressure so the overall gas pressure still increased at longer reaction times.

Fig. 3a compares the elemental analysis of the raw biomass with that of the hydrochar at different reaction times as information on the chemical composition of the hydrochar and biomass. After hydrothermal carbonization, the carbon mass fraction of hydrochar increases by 41 % compared to raw waste seaweed. The higher carbon mass fraction in hydrochar is one of the reasons that makes it a more suitable carbon-based material for applications such as soil amendment (Lei et al., 2021). The increase in carbon mass fraction from 33.0  $\pm$  0.5 % to a maximum of 56.1  $\pm$  0.3 % and the decrease in oxygen mass fraction from 43.8  $\pm$  0.9 % to 26.6  $\pm$  0.3 % (Fig. 3b) are due to carbonization, degradation of surface chemical functions (Guiotoku et al., 2009). The carbon mass fraction of the hydrochar produced by the conventional HTC method, using the same optimized process conditions, was 54.6  $\pm$  0.3 %, which was close to the carbon mass fraction of MHTC after 60 min (52.4  $\pm$  0.2 %).

According to the van Krevelen diagram (Fig. 4) where the atomic O/C and H/C ratios have been plotted, the dehydration and decarboxylation lines during the process have been plotted as well and the results show these reactions continue by increasing the reaction time.

A possible explanation is that the dehydration process can be a chemical or a physical process. In the latter, water molecules are removed from the biomass due to the increased hydrophobicity of the hydrochar. Chemical dehydration in biomass carbonization occurs through the elimination of hydroxyl groups, resulting in a decrease in the H/C and O/C ratios (Jin, 2014). Alongside this dehydration, decarboxylation takes place the time that there is enough water in the system. The carboxyl group starts to degrade at around 150 °C resulting in the production of CO<sub>2</sub> (Funke and Ziegler, 2010). These results have been described in the van Krevelen diagram of the decarboxylation and dehydration progressing during hydrothermal carbonization as evidenced by a simultaneous decrease in the H/C and O/C ratio (Lei et al., 2021).

It is noticeable that by increasing the reaction time after 40 min, MHCs do not show a significant difference in their extent of decarboxylation and dehydration in the van Krevelen diagram (Fig. 4). In comparison to

hydrochar produced by the conventional heating method at similar conditions, MHC shows a similar evolution in dehydration and decarboxylation reactions.

The carbon yield in the solid, liquid, and gaseous phases has been measured. The amount of carbon in the gas phase was calculated using the carbon balance (Fig. S-3, Supplementary information, Section S.6). The highest carbon content was found in the solid phase after 40 min. Erses Yay et al. (Erses Yay et al., 2021), and Taufer et al. (Taufer et al., 2021) have shown that higher residence times lead to slightly lower carbon yields (Erses Yay et al., 2021; Taufer et al., 2021), while in this study the carbon yield in the solid product increased, which could be explained by the promotion the formation of secondary char (Anca-Couce et al., 2014; Remón et al., 2018).

Thermogravimetric (TGA) and differential thermogravimetric (DTG) analysis were used to determine the thermal stability of the material and the thermal mass loss of the material. As shown in Fig. 5, three stages of thermal decomposition were observed. From Fig. 5a, it can be observed that the highest total mass loss, up to 800 °C is related to the hydrochar produced after 5 min and that as the reaction time increases, the final mass loss of different hydrochar decreases by increasing the reaction time. This observation confirms that the thermal stability of those hydrochar produced at longer residence times is higher (Kang et al., 2019). After 40 min, the mass loss difference between hydrochar produced through microwave heating (MHC) and conventional heating (HC) was within 4 wt%. This suggests that MHC shows comparable thermal stability as HC produced under similar conditions. This is also supported by the fact that the chemical composition of the hydrochar remains similar, even as the reaction time increases past 60 min (Fig. S-4, Supplementary information, Section S.7).

To explain Fig. 5b, the mass loss peak below 105 °C is proposed to be related to dehydration. The first decomposition peak of MHC occurs at around 190 °C, which is related to the decomposition of hemicellulose (Román et al., 2012; Ross et al., 2008). The second step of the degradation occurs at around 320 °C and represents the decomposition of cellulose.



**Fig. 1.** a) Effect of reaction time on MHC yield and comparison with optimized HC (Soroush et al., 2022), b) MHTC product yield, solid (—), liquid (—), and gas (—) yield. Dashed line is added to guide the eye.

With increasing reaction time in MHTC, the decomposition of cellulose in those hydrochars increased and the corresponding peak intensity in TG decreased significantly. A slightly positive shift in peak temperature, corresponding to cellulose decomposition in the DTG result, with increasing reaction time is due to the fact that more cellulose can be converted into more stable material by cross-linking with a longer reaction time.

A remarkable peak at 510 °C was observed, which might indicate the decomposition of inorganic materials within hydrochar (Chen et al., 2012; Islam et al., 2015; Leng et al., 2020; Ross et al., 2008; Xu et al., 2020). On the other hand, the TGA result of MHC compared to HC at similar operating conditions showed that the MHC after 40 min of reaction time has similar behavior.

FTIR spectra (Fig. 6) show that further aromatization reactions take place with increasing reaction time. The peak around 2360 cm<sup>-1</sup> is due to a C=C bond that increases with increasing reaction time.

The transmittance peak around  $3500 \text{ cm}^{-1}$  (Fig. 6) represents the hydroxyl group in carboxylic acids and hydroxyl functional groups. With increasing reaction time, this peak becomes weaker and it slightly shifts, describing dehydration and decarboxylation due to the elimination of hydroxyl and carboxyl groups during hydrothermal carbonization. All the potential bonds that could be related to the carboxylic acid groups has been represented in Fig. 6, which are one of the main groups on the surface of hydrochars and play an important role in the adsorption mechanism.

The abundance of functional groups, O- and H-containing functional groups (e.g.  $CH_x$ , O—H, C=O, etc) has been specified and the area underneath the FTIR spectra correlates with the amount of a given bond shows decreased (Fig. S-5, Supplementary information, Section S.8). O- and H-containing functional groups which mainly are the carboxylic acid groups, dropped with increasing reaction times which corroborates with what has been observed in the van Krevelen diagram that by increasing the reaction time, the O/C and H/C atomic ratios decreased. This result is consistent with the adsorption experiments.

#### 3.2. Dye adsorption

The adsorption experiments were carried out with methylene blue (MB) as the model compound for adsorption. The experiments were carried out in batch mode to study the effect of the reaction time on adsorption capacity.

The adsorption mechanism of the dye on the hydrochar depends mainly on the properties of the dye, including its ionic charge, and also on the properties of the hydrochar (Phuong et al., 2019). The FTIR results can explain the adsorption mechanism: The spectra demonstrate the presence of oxygen-containing acidic functional groups, such as carboxylic acid groups on the surface of hydrochar, and this functional group can interact with the cationic MB molecule. There is a slight difference among the adsorption isotherms of different MHC produced at different reaction times, and they showed that the adsorption capacity hardly decreased with increasing reaction time due to the elimination of acidic functional groups from the hydrochar surface that also has been demonstrated in the FTIR results and van Krevelen diagram (Fig. 4). On the other hand, the results show that the hydrochars produced by the two different methods behave almost the same and HC has a slightly higher adsorption capacity than MHC.

The MB molecule is majorly cationic at pH values higher than its pK<sub>a</sub> value (= 3.85) and it is majorly neutral below its pK<sub>a</sub> (Peres et al., 2018). The pH value of solid hydrochar that has been measured in this research and the result shown increased from  $6.1 \pm 0.1$  to  $6.6 \pm 0.1$  (Fig. S-6, Supplementary information, Section S.9) by increasing the reaction time, which means lower proton concentration on the surface of hydrochar, so the adsorption capacity decreases consequently. In comparison to HC, the pH of MHC (5.8  $\pm$  0.11, is higher, so it is concluded that HC is a better absorbent for MB which translates in the adsorption experiments into an adsorption capacity of HC being slightly higher than that of MHC (Iturbe-Ek et al., 2015; Jellali et al., 2019).



Fig. 2. Headspace total pressure versus reaction time for hydrothermal carbonization in a microwaved assisted set-up. Reaction time is(-) 5 min, (-) 20 min, (-) 40 min, (-) 60 min, (-) 90 min, (-) 120 min, and (-) 150 min.



Fig. 3. Elemental composition of raw seaweed and hydrochar produced by microwave under different reaction times, and hydrochar produced with conventional heating for comparison. Dashed line is added to guide the eye. Elements C, H, N and S were measured by elemental analysis, and the oxygen content was obtained by difference, O = 100 - C - N - H - S - Ash all expressed in wt% d.b.

 $pH_{PZC}$  is the point at which the adsorbent surface charge is neutral. At a pH above this point, the adsorbent surface has a negative charge, and at a lower pH, the surface charges become positive. As shown, the  $pH_{pzc}$  of



Fig. 4. van Krevelen diagram for comparing HC and MHC for different reaction times, at reaction temperature 200  $^\circ C$  and water to biomass ratio 5.

MHC has been measured and the result is 4.3 (Fig. S-7, Supplementary information, Section S.10) and this value verifies that the MHC surface is acidic, which has previously been confirmed by FTIR results, as there are plenty of O-containing functional groups on the surface. At pH lower than  $pH_{pzc}$  the surface of MHC is positively charged and has a lower interaction with the cationic MB molecule. Along this line, the adsorption experiment indicated (Fig. 7) that the adsorption of MHC at pH 4 has the lowest adsorption capacity (Nguyen et al., 2021).

The adsorption mechanism of dye on hydrochar can be explained by the physical and chemical interactions between the dye molecules and the surface of the hydrochar.

The adsorption of the dye MB onto hydrochar is due to a combination of hydrogen bond interactions, electrostatic interactions,  $\pi$ - $\pi$  interaction, and weak Van der Waals forces, as shown by several studies (Li et al., 2019a; Li et al., 2021; Lv et al., 2022; Xu et al., 2021). The presence of hydroxyl groups on the hydrochar surface and shifts in the O—H and C—N stretching vibrations of the dye and hydrochar confirm hydrogen bond interactions, while shifts in the C—N stretching vibration of the dye suggest electrostatic interactions also play a role. The adsorption of MB onto hydrochar is considered to be dominated by chemisorption (Li et al., 2019a).

Physical adsorption, also known as physisorption, occurs when the dye molecules are held on the hydrochar surface by weak Van der Waals forces.

(a)

100 90 Hydrochar via conventional oven 80 70 Weight, (%) 60 50 40 30 20 0 100 200 300 400 500 600 700 800 Temperature, (°C) (b) 0.6 5 (min) 20 (min) 40 (min) 60 (min) 90 (min) 0.5 Hydrochar via conventional ov 120 (min Deriv. Weight, (%/°C) 150 (min 0.4 0.3 0.2 0.1 0.0 0 100 200 300 400 500 600 700 800 Temperature, (°C)

**Fig. 5.** (a)Thermogravimetric and (b) differential thermogravimetric curve of MHC at 150 min (—), 120 min (—), 90 min (—), 60 min (—), 40 min (—) and comparison to HC (—), at reaction temperature 200 °C and water to biomass ratio 5.

This type of adsorption is generally reversible, and the adsorbate (dye) can be easily removed from the adsorbent (hydrochar) by washing or heating.

Chemical adsorption, also known as chemisorption, occurs when the dye molecules form chemical bonds with functional groups on the hydrochar surface. This type of adsorption is generally irreversible and the adsorbate is tightly bound to the adsorbent (Cheng et al., 2021). Li et al. and Tran et al. have shown that the MB adsorption mechanism on the hydrochar is controlled by chemisorption (Li et al., 2019a; Tran et al., 2020) and Ferrentino et al. confirmed the complex mechanism (Ferrentino et al., 2020).

To describe the adsorption mechanism, the models of Langmuir, Freundlich, Redlich-Petersen, Toth, and Sips have been fitted and the results are shown in Table 1 for the MHC derived at a reaction time of 60 min, which was considered to produce the optimal hydrochar. The related parameters and coefficients, estimated for the above models, are listed in Table 1. The maximal adsorption capacity of the hydrochar produced from waste seaweed is 57.4 mg g<sup>-1</sup> for MHC and 40 min reaction time. Compared to other hydrochar reports, shows better adsorption behavior. For example, Islam et al. and Neolaka et al. report that hydrochar from Bali cow bones and corn stover has maximal adsorption capacity of 23.6 and 7.7 mg g<sup>-1</sup>, respectively (Islam et al., 2022; Neolaka et al., 2022).

A comparison of the mentioned models (Table 1) shows that the Toth isotherm model has the lowest RSSQ value, which indicates a closer fit to the actual data and the highest F-distribution test value, which indicates a better overall fit of the model, so it can be concluded that the Toth isotherm



**Fig. 6.** FTIR spectra of MHC at 150 min (—), 120 min (—), 90 min (—), 60 min (—), 40 min (—), and HC (—), at reaction temperature 200 °C and water to biomass ratio 5. The value 3500 cm<sup>-1</sup> is related to hydroxyl group in carboxylic acids and hydroxyl functional groups, 3000 cm<sup>-1</sup> is related to aliphatic C—H bonds, and small scale higher than 3000 cm<sup>-1</sup> represents sp<sup>2</sup> C—H, and lower than 3000 cm<sup>-1</sup> represents the sp<sup>3</sup> C—H bond. The value 1650 cm<sup>-1</sup> is related to C=O bond, and 1020 cm<sup>-1</sup> is related to C—O bonds.

is the best model in comparison to the others (Supplementary information, section S.2).

The Toth isotherm model is a type of adsorption isotherm that describes the relationship between the amount of a substance adsorbed on a solid surface and the equilibrium concentration of that substance in the surrounding solution.

The Toth isotherm model is an equation that predicts the adsorption of a substance onto a surface. It is based on the concept of Langmuir adsorption and it considers adsorption as a two-step process, involving adsorption onto active sites and desorption from the surface. The Toth model takes into account the effects of surface heterogeneity and adsorbate-adsorbate interactions.

In the case of adsorption of dye onto hydrochar, the Toth model accounts for the presence of functional groups such as –OH, –COOH on the hydrochar surface that can participate in chemical reactions with the dye molecules and lead to strong dye adsorption.

The Toth isotherm is particularly useful for describing adsorption on hydrochar because of its porous and heterogeneous surface, which can accommodate both physisorption and chemisorption mechanisms (Cheng et al., 2021; Terzyk et al., 2003; Tran et al., 2017).

The maximal adsorption amount based on the adsorption experiment was 41.4  $\pm$  0.3 mg g $^{-1}$  for the hydrochar produced after 40 min. From



**Fig. 7.** Toth adsorption isotherm for MHC at pH: (—) 7, (—) 9, (—) 4, at reaction temperature 200 °C and water to biomass ratio 5 and reaction temperature 1 h.

#### Table 1

Adsorption isotherm parameters of MB adsorption onto different hydrochar.

			La	ngmuir		
HC type	Time (min)	q <sub>e</sub> (mg g <sup>-1</sup> )	Qa	(mg g <sup>-1</sup> )	$K_L (L mg^{-1})$	RSSQ ((mg $g^{-1})^2$ )
MHC	40	41.35 ± 0.3	2 57	.42 ± 2.09	$0.16 \pm 0.01$	4.91
	60	$40.16 \pm 0.1$	7 50	$.54 \pm 1.06$	$0.29 \pm 0.02$	2.48
	90	$39.48 \pm 0.0$	3 51	.93 ± 2.27	$0.21 \pm 0.02$	8.14
	120	$39.36 \pm 0.8$	5 48	.62 + 2.38	$0.24 \pm 0.03$	13.56
	150	$39.37 \pm 0.3$	9 47	.92 + 2.15	$0.26 \pm 0.03$	11.32
HC	4 h	$36.96 \pm 0.0$	18 46	$.48 \pm 3.03$	$0.39 \pm 0.09$	8.55
			Freund	lich		
HC type	Time (min)	$q_{e}$ (mg g <sup>-1</sup> )		$1-1/n L^{1/n} g^{-1}$	n	RSSO $((mg g^{-1})^2)$
мнс	40	41.25 + 0.22	0.70 +	0.70	1.02 + 0.11	1254
WITC	40 60	$41.33 \pm 0.32$	9.79 <u>-</u> 19.41	+ 1 10	$1.52 \pm 0.11$ 2.17 + 0.18	20.76
	00	$40.10 \pm 0.17$	12.41	± 1.10	$2.17 \pm 0.18$ $2.11 \pm 0.00$	29.70
	120	39.46 ± 0.03	11.17	± 0.55	$2.11 \pm 0.09$	22.90
	120	39.30 ± 0.83	11.30	+ 0.71	$2.25 \pm 0.21$	11.26
110	150	39.37 ± 0.39	12.18	± 0.71	$2.35 \pm 0.13$	11.30
HC	4 n	$36.96 \pm 0.08$	14.04	± 1.4/	$2.25 \pm 0.27$	15.8
			Redlich-Petersen			
HC type	Time (min)	$q_{e} (mg g^{-1})$	$\overline{K_{R} (L g^{-1})}$	b (L mg <sup><math>-1</math></sup> ) <sup><math>\beta</math></sup>	β(-)	RSSQ((mg $g^{-1})^{2}$ )
MHC	40	$41.35 \pm 0.32$	$14.29 \pm 3.07$	$0.61 \pm 0.28$	$0.72 \pm 0.07$	1.756
	60	$40.16 \pm 0.17$	$18.08 \pm 2.12$	$0.53 \pm 0.14$	$0.87 \pm 0.05$	1.192
	90	$39.48 \pm 0.03$	30.20 + 3.02	$1.78 \pm 0.25$	$0.65 \pm 0.01$	0.176
	120	$39.36 \pm 0.85$	17.69 + 7.29	$0.67 \pm 0.56$	$0.81 \pm 0.13$	10.65
	150	$39.37 \pm 0.39$	$3648 \pm 7.70$	$2.03 \pm 0.59$	$0.69 \pm 0.03$	1 031
HC	4 h	$36.96 \pm 0.08$	$39.01 \pm 7.85$	$1.61 \pm 7.85$	$0.76 \pm 0.04$	1.319
			Toth			
HC type	Time (min)	$q_{e} (mg g^{-1})$	$K_{\rm T}$ (mg g <sup>-1</sup> )	$a_{T} (mg g^{-1})$	$n_{T}(-)$	RSSO ( $(mg g^{-1})^2$ )
21	40	41.05 + 0.00	105.00 + 00.01	0.57 + 0.65	0.51 + 0.14	0.05
MHC	40	$41.35 \pm 0.32$	$105.20 \pm 30.91$	2.57 ± 0.65	$0.51 \pm 0.14$	0.05
	60	$40.16 \pm 0.17$	$59.62 \pm 0.37$	$2.35 \pm 0.42$	$0.74 \pm 0.12$	0.33
	90	$39.48 \pm 0.03$	$1/8.38 \pm 30.96$	$1.45 \pm 0.07$	$0.32 \pm 0.03$	0.01
	120	$39.36 \pm 0.85$	$66.87 \pm 26.13$	$2.01 \pm 0.95$	$0.60 \pm 0.27$	0.96
	150	$39.37 \pm 0.39$	$124.63 \pm 31.24$	$1.20 \pm 0.11$	$0.33 \pm 0.05$	0.01
HC	4 h	$36.96 \pm 0.08$	$181.43 \pm 23.37$	$3.53 \pm 0.28$	$0.31 \pm 0.01$	0.32
			Sips			
HC type	Time (min)	$q_{e} (mg g^{-1})$	$K_{\rm s} \ ({\rm mg} \ {\rm g}^{-1})$	$a_{s} (mg g^{-1})$	β <sub>s</sub> (-)	RSSQ ((mg $g^{-1})^2$ )
MHC	40	$41.4 \pm 0.30$	9.89 ± 0.44	0.690 ± 0.113	$0.81 \pm 0.07$	2.11
	60	$40.2 \pm 0.20$	$14.81 \pm 0.49$	$0.906 \pm 0.059$	$0.91 \pm 0.06$	1.64
	90	$39.48 \pm 0.03$	$12.14 \pm 0.18$	$0.557 \pm 0.084$	$0.69 \pm 0.03$	0.34
	120	$39.36 \pm 0.85$	$12.73 \pm 1.10$	$0.615 \pm 0.193$	$0.82 \pm 0.14$	10.21
	150	$39.37 \pm 0.39$	$13.93 \pm 0.33$	$0.383 \pm 0.148$	$0.67 \pm 0.04$	0.92
HC	4 h	$36.96 \pm 0.08$	$18.75 \pm 1.21$	$0.74 \pm 0.06$	$0.31 \pm 0.05$	1.43

the FTIR results, the MHC produced at a reaction time of 40 min had a higher concentration of acidic functional groups, which consequently led to a stronger electrostatic interaction with the MB dye molecule and finally to a higher adsorption capacity.

Summarizing, the characterization of MHC in different reaction times and comparison with HC, showed that MHC produced at 40 min and 60 min have very similar properties regarding carbon content, surface functional groups, thermal stability, and adsorption behavior compared to HC produced in conventionally heated oven at the same operating condition of 200 °C and water to biomass ratio of 5 which was synthesized after 4 h.

### 3.3. Energy considerations

Microwave ovens use electromagnetic energy and generate electromagnetic waves that heat the reactant inside the vessel. Unlike conventional heating, they do not heat the entire reactor plus its contents but use the waves only to heat the reactant (i.e. water plus biomass) inside, making them more electricity efficient than traditional ovens. MHC has been produced in a microwave oven and consumed 676 kJ/g<sub>char</sub>.

The energy consumption using the autoclave in conventional heating oven was calculated by considering the heat energy required to reach the set temperature, in addition to the heat loss of the autoclave. The mass of the autoclave reactor used in this work was 2.2 kg, the material of this reactor is stainless steel with a specific heat capacity of 502 J kg<sup>-1</sup> K<sup>-1</sup>. Inside the reactor, 30 mL of water was used for the reaction, and the specific heat capacity of water is 4200 J kg<sup>-1</sup> K<sup>-1</sup>. The autoclave with mentioned characteristics was heated from room temperature (25 °C) to reaction temperature at 200 °C and was kept at this temperature for 4 h. According to Eq. (9), the energy required to heat the autoclave in a conventional heating oven was calculated to be 197 kJ/g<sub>char</sub> of which only 3.7 kJ/g<sub>char</sub> is allocated to heat up the water and feedstock.

In order to obtain an acceptable estimate of the heat loss during the holding time (during HTC reaction at the set temperature), the average of the film temperature as if the reactor was placed in a room at 25 °C (112.5 °C) and the actual surrounding temperature of 200 °C was chosen. Using this film temperature of 156.25 °C, and taking an acceptable air velocity in the oven of 0.2 m s<sup>-1</sup>, the heat loss for the used autoclave amounts up to 972 kJ/g<sub>char</sub>. In order to check the variability of the assumptions made, the heat loss was also calculated for a ± 20 °C range and this gave rise to heat loss values between 760 and 1283 kJ/g<sub>char</sub>. Fig. S-2 in Supplementary information demonstrates that the total energy demand for the hydrothermal reaction when using conventional heating is consistently greater than the energy consumption in a microwave-heated reactor, across all film temperatures. The autoclave will stay at 200 °C for the further reaction, and during the reaction, a mixture of steam and gas is produced in the headspace of the autoclave at 14.53 bar. To produce this amount of steam at the mentioned pressure in a sealed autoclave, 0.97 kJ of energy is required, assuming that steam is an ideal gas. Overall, this contribution can be neglected, compared to the calculated value.

In conclusion, the total energy required for the hydrothermal reaction with conventional heating for all possible film temperature values will be higher than the energy consumption in a microwave-heated reactor. In our best effort approach, an intermediate film temperature was assumed and the obtained results are comparable to (or even lower than) other literature reports (Afolabi et al., 2020; González-Arias et al., 2022; Kang et al., 2021; Shao et al., 2020; Śliz and Wilk, 2020).

## 4. Conclusion

This research compared the production of hydrochar from waste seaweed using microwave assisted hydrothermal carbonization (MHTC) and conventionally heated hydrothermal carbonization (HTC). The results showed that MHTC can potentially lead to a shorter reaction time and a more porous and reactive hydrochar in comparison to conventionally obtained HC at the same reaction temperature and same water to biomass ratio. The yield of MHC produced was 6 % lower than the yield of conventional HC and the carbon mass fraction was a maximum of 17 % higher than the carbon mass fraction of hydrochar from conventional heating. Overall, the study suggests the potential benefits of using microwave heating in the hydrothermal carbonization process.

In our best effort to calculate the heat losses in the conventional set-up, it was shown that the energy consumption of the microwave set-up was somewhat lower than the conventional heating oven. For future work, the authors suggest scaling up the microwave technique by focusing on optimizing process parameters such as temperature and pressure for improved efficiency and cost-effectiveness. In addition, it is advisable that the consumed heat can be directly measured to give a more objective comparison that relies on experimental values, rather than calculations where certain assumptions are required.

## CRediT authorship contribution statement

Sepideh Soroush: Writing Original Draft, Investigation, Methodology, Formal analysis, Data curation;

Frederik Ronsse: Methodology, Review & Editing, Supervision;

Jihae Park: Resources, Review & Editing;

Stef Ghysels: Review & Editing;

Di Wu: Review & Editing;

Kyoung-Woong Kim: Review & Editing;

Philippe M. Heynderickx: Conceptualization, Methodology, Validation, Formal analysis, Data Curation, Writing - Review & Editing, Supervision, Project administration, Funding acquisition

#### Data availability

Data will be made available on request.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.163193.

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