Hydrochars from industrial macroalgae "*Gelidium Sesquipedale*" biomass wastes

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Abstract

Macroalgae wastes from the Agar–Agar industry were used as a feedstock to obtain hydrochars by means of hydrothermal carbonization. The effect of temperature (200°C and 230°C) and time (2h and 6h) on the yield, higher heating value (HHV) and chemical-morphological-textural properties of the hydrochars was studied. The carbon content and the higher heating value were observed to increase with the hydrothermal carbonization. The hydrochars yields (up to 60%) were much higher than yields obtained using conventional char (27.5-33.5%). The hydrochar obtained at 230°C and after 6h showed a HHV of 23.25 MJ/kg, which is similar to that of lignite HHV. The H/C and O/C atomic ratios decreased as a consequence of the dehydration and decarboxilation reactions. Hydrothermal carbonization barely changed the vegetal structure of the macroalgae waste. The hydrochars were found to be essentially meso-macroporous with average pore sizes of up to 110.5 nm.

Keywords: *Gelidium Sesquipedale* biomass, Industrial macroalgae waste, Hydrothermal carbonization, Pyrolysis, Sustainable hydrochars.

1. Introduction

The increase in population and quality of life since the Industrial Revolution has been accompanied by a growing demand for energy worldwide and by the generation of large amounts of different types of waste. This demand for energy has been met largely by the exploitation of conventional fossil fuels.

Organic solid wastes are one of the largest groups of wastes produced worldwide and the rate at which they are being generated is constantly increasing. Traditionally, organic solid wastes have been eliminated by incineration or landfill, but recently

implemented stricter environmental regulations require new strategies to ensure a more sustainable and profitable waste management. Indeed, good waste management must be given top priority if this waste is to be transformed into valuable resources, such as fuels (Ferrera-Lorenzo et al. 2014a, 2014b, Stephen and Periyasamy 2018), adsorbents (Ferrera-Lorenzo et al. 2014c, 2014c, Gil et al. 2014) and other valuable chemicals (Saqib et al. 2018).

Thermochemical conversion by pyrolysis or hydrothermal carbonization (HTC) could be used to manage wastes, such as organic municipal solids, agricultural wastes, food wastes, forest wastes, etc., by turning them into high value products. It is well known that in pyrolysis, a thermochemical process that takes place in an inert atmosphere and at atmospheric pressure, the thermally treated material is transformed into three fractions: solid (char), gas and liquid (condensable liquids or oils). In the process of pyrolysis up to high temperatures (more than 600°C), organic matter is thermochemically transformed with a high energy consumption. Furthermore, biomass wastes have high moisture content, so they must be pre-dried prior to heat treatment at high temperature. Hydrothermal carbonization (HTC) at low temperature is an alternative procedure to thermal treatment at high temperature, like pyrolysis, both by conventional and microwaves heating. HTC at low temperature is a more sustainable procedure due to the energy saved as a direct consequence of working at lower temperatures (less than 300°C).

In general, HTC is performed by applying moderate temperatures (180-250°C) to biomass in the presence of water under autogenous pressure and during several hours to obtain a sustainable carbon material referred to as hydrochar. The composition, structure and potential uses of hydrochars vary significantly depending on the

composition of the feedstock and process conditions (temperature, reaction time, pressure and solid/water ratio). Although HTC is a scientifically well-known technology, it has not yet been commercialized (Kumar et al., 2018) and remains on a laboratory or demonstration scale (under TRL) (Tajammal Munir et al., 2018). For a long time, HTC has been applied to explain the mechanism of coal coalification and to produce fuels but little attention has been paid to the production of hydrochars (Kruse and Dahmen, 2018). However, in recent years HTC has received great deal of attention as a method for obtaining sustainable carbon products and/or as a residual biomass management process (Gascó et al. 2018; Lucian et al. 2018). There is a clear need therefore for further research on the characteristics of hydrochars obtained from different types of biomass in order to find a high-value uses for them.

In this research study, new alternative treatments are investigated with the aim of finding a more efficient and sustainable management of industrial macroalgae "Gelidium Sesquipedale" biomass wastes. The biomass waste is subjected to HTC treatment and the effect of the temperature and duration of the thermal process on the yield, higher heating value (HHV) and chemical-morphological-textural properties of the obtained hydrochars is studied. Furthermore, since this industrial biomass waste has been used by the research group in previous works, including studies on the use of the energy produced by pyrolysis of this waste, by conventional and microwave heating, it will be possible to compare the results obtained previously with those of the present research work.

2. Materials and Methods

2.1. Industrial macroalgae waste selection and hydrochar preparation

An industrial macroalgae waste, algae meal (AM), from the Agar–Agar industry “ROKO-AGAR” from Spain is used as a precursor for the production of hydrochars. ROKO-AGAR is the largest European producer of Agar-Agar and who provides the macroalgae industrial waste to carry out this work. The macroalgae waste was sampled for a period of one month by the personnel of the industrial plant in order to ensure their representativeness during the sampling period and following standard procedures. The total sample (80 kg) was quartered by division cone until a representative sample of about 2 kg was obtained.

Four hydrochars were prepared as follows: 1.0 L of wet AM solution with 30% solids content was introduced into a Teflon recipient inside a Hastelloy autoclave supplied by Demede S.L. The autoclave is equipped with two thermocouples, one of which is inserted into the Teflon recipient and brought into contact with the sample, while the other is in contact with the outer part of the Hastelloy wall. The temperature difference between the two thermocouples is around 20°C. The samples were heated up to 200 and 230°C and the final temperature was maintained during 2 or 6 hours under autogenous pressures to produce the hydrochars labelled HAM200-2, HAM200-6, HAM230-2 and HAM230-6, respectively. After being cooled down to room temperature, the aqueous solutions were filtered and the hydrochars were dried at 80°C during 24 hours and sieved to below 2 mm.

2.2. Materials characterization

The samples were characterized as follows:

The ultimate analysis (of the carbon, hydrogen, nitrogen and sulphur contents) was carried out on LECO CHN-2000 and S-144-DR automatic instruments. The Oxygen content was obtained by difference as: $100\% - (\%C + \%H + \%N + \%S + \%Ash)$. The atomic ratios (H/C) and (O/C) were also determined. The Higher heating value (HHV) was estimated according to the formula proposed by [Channiwala and Parikh \(2002\)](#).

$$HHV \text{ (MJ/kg)} = 0.3491 * C + 1.1783 * H + 0.1005 * S - 0.1034 * O - 0.015 * N - 0.021 * Ash$$

where C, H, S, N and ash represent the carbon, hydrogen, sulphur, nitrogen and ash content (wt %, dry basis), respectively.

The electrical conductivity (EC) and pH of AM and the four hydrochars were determined in a 4 g L^{-1} aqueous sample solution, after 1 hour of agitation, using a Crison micro-pH 2000 and a Crison 222 conductivimeter. The organic carbon (C_{oxi}) content was determined by the Walkley Black method based on the oxidation of the organic carbon with dichromate ([Nelson and Sommers, 1996](#)). The cation exchange capacity (CEC) was determined using the method proposed by [Ciesielski and Sterckeman \(1997\)](#) employing a Cohex extractant solution and a Perkin Elmer Analyst 400 Atomic Absorption Spectrophotometer. The exchangeable K content was measured in the Cohex extractant solution using a Perkin Elmer Analyst 400 Atomic Absorption Spectrophotometer. In addition, the extractable phosphorus (P_{olsen}) content was determined by the Olsen method using a Shimadzu UV-1203 spectrophotometer at a wavelength of 430 nm ([Watanabe and Olsen, 1965](#)).

Fourier-transform infrared spectroscopy (FTIR) was applied in order to determine the main functional groups on the surface of the materials. For this purpose, a Nicolet 8700 Fourier Transform Infrared Spectrometer was employed. The FTIR analysis was carried

out using diffuse reflectance (DRIFT) and a MCTA detector. Before the analysis, the materials were dried at 120°C during 18 h to eliminate any water (to avoid interferences between 3200 and 3600 cm⁻¹) and/or any possibly adsorbed environmental compounds.

The hydrophysical characterization was performed as follows: the field capacity (FieldC) and wilting point (WP) were determined as the sample moisture content at 33 kPa (FieldC) and 1500 kPa (WP) (Richards, 1954). FieldC represents the water contained in the sample after all excess water has been drained away and WP represents the minimal moisture content required by the plant to avoid wilting. The available water (AW) was calculated from the difference between FieldC and WP.

Thermogravimetric analyses were carried out in a Thermogravimetric Analyzer TGA Labsys Setaram (Setaram Instruments). 20 mg of sample was heated at 15°C min⁻¹ up to 850 °C in an air atmosphere at a flow rate of 30 mL min⁻¹.

The morphological analysis of the hydrochars was performed using a scanning electron microscope Zeiss (Model DMS-942) at a 20.00kV accelerating voltage and beam. The microscope is equipped with a dispersive energy X-ray analysis system (Link-Isis II). The samples were coated with iridium for examination by SEM-EDX and images were taken at different magnifications.

The textural characterization of the materials was carried out as follows. The real density was determined by means of helium pycnometry. The specific surface area and pore size distribution (PSD) were ascertained from the nitrogen adsorption/desorption isotherm at 77 K and the Hg density and the meso-macroporosity were determined by means of mercury injection porosimetry.

The true densities or helium densities were measured by means of helium pycnometry on a Micromeritics AccuPyc 1330 pycnometer. Before the analysis, the samples were outgassed for 18 h at 120°C.

The specific surface areas and pore size distributions (PSD) of the materials were measured by nitrogen adsorption/desorption at 77 K on Micromeritics ASAP 2420 volumetric adsorption analyzer. Nitrogen adsorption isotherms were used to calculate the BET surface areas (S_{BET}) of the samples in accordance with the Brunauer-Emmett-Teller (BET) theory (Brunauer et al. 1938, 1940 and Brunauer, 1970) and the total pore volume (V_{TOT}) at a relative pressure of 0.99. The pore size distributions were analyzed by applying Barret-Joyner-Halenda (BJH) method to the N_2 adsorption analysis data (Barret et al., 1951); the Harkins and Jura model was employed for the thickness curve and the Standard model for the BJH correction. Before the analysis, the samples were outgassed for 18 h at 120°C.

The bulk and skeletal densities, the total meso-macropore volume, porosity and the average pore diameter were obtained by Mercury porosimetry on a Micromeritics AutoPore IV 9500 Series apparatus, which provided a maximum operating pressure of 228 MPa. The contact angle and surface tension of the mercury were set at 130° and 485 dym/cm, respectively. Before the analysis, the samples were outgassed for 2h at 120°C.

3. Results and discussion

3.1. Chemical characterization of the materials

Table 1 shows ultimate analysis of the feedstock and derived hydrochars. The elemental composition of AM was altered significantly due to the HTC. During the HTC process,

the carbon content tended to concentrate in the hydrochar as a result of the increasing migration of oxygen and hydrogen present in the different compounds into the liquid and gaseous phases. [Table 1](#) shows that the carbon content of AM increased after HTC, especially at the highest temperatures and reaction times, while the hydrogen, nitrogen and especially oxygen contents decreased. These variations resulted from a reduction in the O/C and H/C ratios, suggesting that decarboxylation and dehydration reactions occurred during the HTC treatment. At 200°C, the increase in the reaction time from 2 to 6 hours caused a slight decrease in the H/C ratio but did not affect the O/C ratio. However, an increase in the reaction temperature from 200 to 230°C significantly reduced the H/C and O/C ratios. These results suggest that during the HTC of AM, dehydration and decarboxylation reactions took place at the highest temperatures, as can be seen from the Van Krevelen diagram ([Supplementary Information](#)). The hydrochar HAM230-6 shows a similar elemental composition to those of low-rank coals. However significant differences are brought to light by the ultimate analysis of these hydrochars and the chars obtained by pyrolysis under various experimental conditions (temperatures between 600 and 900 ° C, different heating rates, etc.) of a previous research work carried out using this residue ([Ferrera-Lorenzo 2014a](#)). First of all the carbon content of the hydrochars (< 55%) is lower than that of the chars obtained by pyrolysis (>65%). Another important difference is their ash content with the hydrochars exhibiting a lower ash content than the chars (10-14% compared to 19-26% in the chars). Taking into account the chemical composition of the hydrochars obtained (high carbon content and moderate ash content) these materials could be used as precursors of activated carbons ([Lopez-Anton et al. 2015](#), [Ruiz et al. 2015](#), [2017](#)).

Table 1 shows that the elemental carbon content had a significant influence on the hydrochar energy content. The estimated higher heating value (HHV) of the feedstock (18.35 MJ/kg) increased significantly with the application of HTC (up to 23.25 MJ/kg). The hydrochar HAM230-6 showed a HHV of 23.25 MJ/kg which is similar to the HHV of lignite. It follows that under these conditions, AM could be used to obtain fuels. The calculation model used to determine the HHV of the hydrochars was also applied to the results previously published ([Ferrera-Lorenzo 2014a](#)) for the char obtained by pyrolysis at 750°C where the HHV determined experimentally (25.49 MJ/kg) is very similar to the calculated value (25.07 MJ/kg). These values are around 10% higher than the maximum value of HHV shown by the hydrochars.

[Table 2](#) shows the hydrochar yields after the HTC treatment of AM. They range from 52.3 to 60.6 wt%. These values were similar to those obtained previously by different authors using other biomasses as feedstock ([Gascó et al., 2018](#)). It can be seen that the yields decreased with increasing temperature and reaction time due to the decomposition of cellulose and hemicellulose and the formation of liquid and gaseous by-products ([Kambo and Dutta, 2015](#)). The values of the yields ([Table 2](#)) were higher than the yields obtained for this biomass waste in conventional pyrolysis (yields of up to 33.5 wt%) ([Ferrera-Lorenzo 2014a](#)).

Four hydrochars had a pH lower than the original feedstock but their pH increased with temperature or duration of the HTC. Other authors have obtained similar results ([Liu et al., 2017](#); [Lucian et al., 2018](#)). It should be pointed out that the hydrochars prepared in this work were not washed with water so that some organic acid compounds produced during the HTC process could have been adsorbed onto the hydrochar surface and influenced their pH. Alkaline components may also have dissolved in the liquid phase

(Kambo and Dutta, 2015). Reza et al. (2015) reported that hydrochars produced at 200°C had a lower pH than those produced at 260°C. A possible reason for this is that at low temperatures, simple sugars and hemicellulose tend to degrade into organic acids and are then polymerized, while at high temperatures lignin starts to degrade, producing phenolic substances with only a slightly acidic pH.

In the present study, the EC of the AM feedstock increased slightly with the HTC process. In general, the hydrochar EC are lower than that of the feedstock probably because the ashes dissolve (Reza et al, 2013). However, Chen et al. (2017) observed that hydrochars produced by HTC at 190°C from watermelon peel had more soluble salts than the feedstock probably due to the adsorption of the salts dissociated from the biomass during the HTC.

It is well known that cation exchange capacity (CEC) is related to the ability of samples to adsorb nutrients, and is one of the most important properties for the agronomic use of hydrochars in soil amendment, growth stimulation media and as green roof components. In this study CEC decreased slightly with increasing HTC temperature due to the removal of functional groups and increasing aromatization, as can be seen from the O/C and H/C ratios (Table 1). The value of the soil CEC depends on content and type of clay and organic matter and soil pH. Typical values of soil CEC ranges from 5 cmol_c/kg (sandy soils) to >30 cmol_c/kg (clay soils) (Sonon et al., 2014). The addition of organic matter is an usual way to increase soil CEC due to pure organic matter can have a CEC from 250 to 400 cmol_c/kg (Moore, 1998). The AM CEC was 146 cmol_c/kg while hydrochar CEC ranged from 114.79 to 122.18 cmol_c/kg being adequate materials for their use as organic amendment for agronomic applications. Indeed, Álvarez et al. (2017) observed increments in ryegrass production after peat replacement with biosolids

hydrochars with CEC between 35 and 51 cmol_c/kg. Also, the CEC values were very similar to the values obtained by [Gascó et al. \(2018\)](#) for pig manure hydrochar prepared at the same temperature.

The P_{Olsen} content of the four hydrochars was higher than that of the AM. This result was similar to that obtained previously after the HTC of pig manure and watermelon peel ([Chen et al., 2017](#); [Gascó et al., 2018](#)). It is well known that P in biomass is bound to organic matter (proteins and phospholipids). During HTC, the P is dissociated from organic compounds due to the cleavage of organic structures. It is then adsorbed onto the hydrochar increasing the soluble P and P_{Olsen} content. [Chen et al. \(2017\)](#) had previously observed that with the increasing severity of the HTC reaction, more P became insoluble. This is due to the fact that the P_{Olsen} content of hydrochars derived from AM decreases with increasing temperature or reaction time.

[Calvelo-Pereira et al. \(2011\)](#) observed that organic carbon oxidised with potassium dichromate (Coxi) could be used to estimate the labile fraction of carbon in biochars and therefore serve as an indicator of the degree of biomass carbonisation. The four hydrochars employed in this study showed higher Coxi values than the feedstock, indicating that more labile carbon structures were produced during HTC. [Gascó et al. \(2018\)](#) obtained the same result for hydrochar prepared from pig manure. Instead of low H/C ratios indicating higher aromatic hydrochars content compared to AM, the four hydrochars derived from AM showed a low chemical resistance to dichromate oxidation. Only, in the case of the two hydrochars prepared at 230°C, did the Coxi content decrease with increasing reaction time from 2 to 6 hours.

The FTIR spectra of AM and the four derived hydrochars are in the [Supplementary Information](#). The four hydrochars show a large number of peaks which is indicative of

the presence of numerous functional groups on the surface of the hydrochar. Peak identification has been determined through previous research's ([Gascó et al., 2018](#); [Sevilla et al., 2011](#)).

The broad band centred at 3400 cm^{-1} can be attributed to O-H stretching in the hydroxyl and carboxyl groups. This peak becomes less intense as the temperature or reaction time of the HTC increases and moves towards the lowest wavelengths. This result is related to the reduction of the H/C and O/C ratios resulting from dehydration and decarboxylation reactions. The peaks between 2940 and 2800 cm^{-1} are a result of C-H stretching in aliphatic and aromatic groups. The peak at 1660 cm^{-1} is attributed to C=O in ketone, amide and carboxylic groups whereas the peak at 1620 cm^{-1} is associated to C=C in aromatic structures. As the temperature or reaction time in the HTC process increases, the intensity of the peak at 1660 cm^{-1} decreases whereas the intensity of peak at 1620 cm^{-1} increases. Similar results were previously obtained by [Sevilla et al. \(2011\)](#). This result is indicative of progressive aromatization, evidenced by the reduction of the H/C and decarboxylation with the reduction in the O/C atomic ratio ([Table 1](#)). The increase in aromaticity is corroborated by the increase in intensity at 1460 cm^{-1} and 770 cm^{-1} ([Sevilla et al., 2011](#)). Finally, the peaks between 1000 and 1280 cm^{-1} are associated to aliphatic ether (C-O-C) and alcohol (C-O) stretching. The intensity of the peaks increased with HTC at 200°C but decreased significantly with the HTC of MA at 230°C in association with a significant reduction in the O/C atomic ratio.

[Fig. 1](#) shows combustion characteristics of samples recorded by thermogravimetric (TG) and derivative thermogravimetric analysis (dTG). Thermal analysis has been used for decades to characterize carbonaceous materials as it provides information about the chemical characteristics of samples without requiring any extraction step and

differences observed in the combustion behaviour of hydrochars can indicate differences in their composition (Dell'Abate et al., 2000; Méndez et al., 2011; Pietro and Paola, 2014).

Four stages were differentiated during the combustion of the samples. The initial mass loss from room temperature to 150°C was attributed to the loss of moisture and the volatilization of very light volatile materials (Stage I). However, the main differences between the feedstock and hydrochars were observed between 200 and 650°C during the combustion of the organic matter (Kumpiene et al., 2011). According to previous studies carried out by Dell'Abate et al., 2000 or Prieto and Paola, 2014 two regions could be clearly differentiated (Dell'Abate et al., 2000; Prieto and Paola, 2014). The first one from 200 to 375°C was attributed to the decomposition/combustion of light compounds and carbohydrates, such as cellulose or hemicellulose (Stage II). The second one from 375 to 650-730°C (Stage III) was ascribed to the combustion of more stable structures of high molecular weight like lignine (Pietro and Paola, 2014) and the combustion of refractory carbon. Finally, at the highest temperatures, weight loss was associated to the decomposition of carbonates. Comparison of the dTG curves in Fig. 1 shows that the combustion peak with its maximum at 320°C for MA became thinner when the temperature and residence time of HTC increased, indicating that light compounds like hemicellulose and a fraction of the cellulose decomposed or were transformed during the polymerization/condensation reactions. Reza et al. (2014) reported that, although pure cellulose did not degrade during HTC at temperatures lower than 200°C, hydrolysis products from the degradation of the hemicellulose could catalyse the degradation of the cellulose at these temperatures. Fig. 1 shows that the greatest reduction in cellulose content was obtained with HTC at 230°C, especially with

reaction times of 6 hours. At the same time, the second combustion band related to the combustion of larger polymerized carbon structures increased and moved towards the lowest temperatures. This indicates that HTC instead of promoting the carbonization of organic matter is producing more homogeneous polymerized structures. Finally, the weight loss associated with the decomposition of carbonates became less intense in the hydrochars which indicates that during the HTC process some carbonates were dissolved in the aqueous phase (Gascó et al., 2018).

Table 3 summarises the weight loss in Stages II and III from 150 to 370°C and 370 to 620-730°C, respectively. The ratio between the weight losses (WL_{StII}/WL_{StIII}) of the two stages was also calculated. As the temperature or reaction time of the HTC increased, hydrochars became thermally more stable. With HTC at 200°C, the weight loss in Stage II decreased, while the increase in the weight loss in Stage III indicates the degradation of cellulose and hemicellulose as well as polymerization reactions. However, at 230°C, the weight loss in Stage II decreased but the increase in reaction time from 2 to 6 hours, also caused a decrease in weight loss in Stage III indicating the degradation of lignin.

The DTA combustion profiles of the AM feedstock and the derived hydrochars are included in [Supplementary Information](#).

It can be observed that thermal properties of AM changed significantly after the HTC treatments. The two exothermic peaks of AM that became one broad band during the combustion of the hydrochars shifted to lower temperatures as the temperature or reaction time increased, indicating that during the HTC, not only did decomposition of cellulose, hemicellulose and lignin take place but also that new structures with high HHV formed and that then they decomposed at low temperatures. Petrovic et al. (2013)

previously obtained similar results in the combustion of hydrochars prepared by the HTC of grape pomace solutions (20% solid content) at 180, 200 and 220°C. In addition, Wang et al. (2016) found that the greater the degree of carbonization of hydrochar achieved by the HTC of sludges, the easier it was for the combustion of volatiles and char to take place. However, other authors obtained different results. For example, Mihajlović et al. (2018) prepared hydrochars by the HTC of biomass solutions (10% solid content) at 180, 200 and 220°C and found that the second combustion peak shifted to higher temperatures as the temperature of the HTC increased. Finally, the endothermic peak associated with the decomposition of carbonates decreased with increasing temperature or reaction time, suggesting either that they dissolved in the liquid phase or that the carbonate compounds decomposed during the HTC of AM.

Table 4 shows the hydrophysical properties of AM and the derived hydrochars. The field capacity (FC), wilting point (WP) and available water (AW) content could have a great importance when hydrochars will use for horticultural application. FC represents the sample water content after excess water has drained away, WP is the minimal water content required by the plant to avoid wilting and AW is the available water for plants. Indeed, the increment of hydrochar available water content can be related with the increment of crop yields when hydrochar is used as growing media (Álvarez et al., 2017). HTC treatment significantly reduced their field capacity and wilting point with respect to feedstock but hydrochars had higher available water content than raw material. Indeed, the production the hydrochar obtained at 230°C during 6 hours (HAM230-6) had a AW content a 260% higher than raw material (AM) according with Gascó et al. (2018) who observed the same trend for pig manure hydrochars. Therefore, hydrochars obtained from algae meal wastes may be suitable as means of amendment

for soils in arid regions or as components of growth media. Previous works carried out by [Álvarez et al. \(2017\)](#) have shown that mixtures of peat and hydrochars from biosolids or urban waste have hydrophysical properties suitable for their use as growth media or top soils. Hydrophysical properties are related to porosity and pore size distribution. Water is easily available to plant when it was in larger pores ([Rowell, 1994](#)) but with decreasing pore diameter, the plant needs to consume progressively more energy to take up more water. These properties are related to the pore size distribution mentioned in section 3.3.3 (mercury porosimetry).

3.2 Morphological characterisation by SEM microscopy

SEM images were taken in order to observe morphological changes caused by the HTC process in the hydrochars with respect to the macroalgae waste. Selected SEM images are shown in [Supplementary Information](#). These SEM images of the hydrochars were taken at different magnifications (x500, x1000 and x5000). All of them correspond to the parts of the macroalga biomass wastes from which they are derived. On the basis of our previous knowledge of these macroalgae wastes ([Ferrera-Lorenzo 2014a, 2014c, 2014d](#)), the SEM images show that the hydrochars conserved, to a large degree, the original structures of the industrial macroalgae wastes.

The presence of mineral matter in the hydrochars was observed using SEM-EDX. This information is presented in [Supplementary Information](#). Worthy of note is the absence of heavy metals and presence of alkalis, alkaline-earths, sulphur and silicon, as might be expected of a material of vegetal origin.

3.3. Textural characterisation of the materials

3.3.1. Helium picnometry

[Table 5](#) shows the results of the textural properties of the materials. The hydrochars show helium or real densities ranging between 1.51 and 1.76 g cm⁻³. These values are within the normal limits of the real densities of char materials derived from biomass wastes ([Gil et al. 2014b](#), [Gao et al. 2017](#)). The chars obtained by [Fu et al. \(2011\)](#) in their research on the effect of temperature, in the 600°C and 900°C range, on the structural features of chars from pyrolyzed agricultural wastes display helium densities between 1.50 and 1.74 g cm⁻³.

3.3.2. Nitrogen adsorption/desorption at -196°C

The N₂ adsorption/desorption isotherms obtained for the hydrochars are of type IV according to the BDDT classification ([Sing et al., 1985](#)). This information is present in [Supplementary Information](#). For comparison purposes, the nitrogen isotherm of the char obtained from the same biomass waste and obtained by pyrolysis with conventional heating in a horizontal electric furnace at 750°C, using an annealing time of 60 min and a heating rate of 5 °C/min ([Ferrera-Lorenzo et al. 2014a](#)), has also been represented. The hydrochars and conventional char have negligible microporosity and so at low relative pressure they show insignificant N₂ adsorption. However, at high relative pressure (0.98-1.00) the hydrochars exhibit an considerable N₂ adsorption indicating the presence of mesopores (2-50 nm) and macropores (>50 nm). The presence in the isotherms of a cycle of hysteresis, which does not show a plateau at high relative pressures, confirms the existence of mesopores. Hydrochars show a higher volume of nitrogen adsorption than conventional char, so HTC would be more effective for in the development of mesopores than pyrolysis. The hydrochars show a higher level of adsorbed N₂ volume at $p/p^0 = 0.99$ than the conventional char, with values of between 0.036 and 0.068 cm³/g, [Table 5](#) and [Supplementary Information](#). The BET surface area

for the hydrochars ranges between 5.9 and 12.7 m²/g, which is consistently higher than the BET area value (3.9 m²/g) of conventional char (Ferrera-Lorenzo et al. 2014c).

Fig. 2 shows the porosity distribution of the hydrochars studied using the BJH model and applied to the adsorption branch of the N₂ isotherms.

As illustrated in Fig. 2a), the graph of dV/dW pore volume versus pore width shows that the hydrochars have pores between 5 and 100 nm with a maximum located at a pore size of 20 nm, although this distribution is displaced to higher values with a maximum value of 30 nm for the hydrochar obtained at higher temperature and time duration (HAM230-6). Fig. 2b) shows that it is the larger pores that contribute most to the total pore volume of the hydrochars. This is because one large pore can have a volume that equals that of many small pores.

3.3.3 Mercury porosimetry

An examination of the hydrochars by nitrogen adsorption at -196 °C showed that they have negligible microporosity but some mesoporosity in their structure. In view of this, the study of the texture of hydrochars was expanded to include mercury porosimetry, since this technique is suitable for the study and characterization of mesopores and macropores..

The cumulative pore volume and the pore volume size distribution results obtained by mercury porosimetry for the hydrochars are presented in Fig. 3 while the results related to the total pore volume, porosity and average pore size are given in Table 5. As can be seen in Fig. 3a) as the HTC treatment increases in severity (i.e. a higher temperature and/or longer time), the greater the volume of mercury accumulated by the materials, indicating the development of more meso and macroporosity. Fig. 3b) shows that the

temperature of the HTC treatment seems to have a significant effect on macroporosity development since the materials obtained by HTC at 230°C, and especially the hydrochar obtained after 6 hours of treatment, HAM230-6, reflect a strong contribution by macroporosity with maxima between 500-1000 nm. The total pore volume increases from 0.320 cm³g⁻¹ for HAM200-2 up to 0.605 cm³g⁻¹ for HAM230-6, materials obtained with a midler and a stronger HTC treatment, respectively (Table 5). The porosity, with pore sizes ranging from 5.5 to 12000 nm, follows the same trend and increases from 28.9% for HAM200-2 up to 44.8% for HAM230-6, Table 5. Similarly, the average pore size, 62.8 nm for HAM200-2, also increases with HTC treatment. Especially worth noting is the value that HAM230-6 presents (110.5 nm) since it is much higher than those of the other materials. It can be inferred that HTC at 230°C and a time of 6 h, favours larger average pore sizes. This fact is related to the availability of greater amount of water for HAM230-6, Table 4.

4. Conclusions

HTC technology was used to obtain different hydrochars for the upgrading and sustainable management of macroalgae industrial wastes. HTC at 230°C during 6 hours produced hydrochars with a HHV of 23.25 MJ/kg, similar to low-rank coals. In addition, it was found that a higher degree of carbonization, facilitated the combustion of the hydrochars. The available water and phosphorous content present in the algae meal increased with HTC, making the resulting hydrochars suitable for use as growth media components. The hydrochars retained to a large extent the vegetal structure of the wastes and displayed a meso and macroporous nature.

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FIGURE CAPTIONS

Fig. 1. TG and dTG curves of samples: a) AM, b) HAM200-2, c) HAM200-6, d) HAM230-2 and e) HAM230-6

Fig. 2. Pore size distribution derived from the N₂ adsorption branch isotherms using the BJH model. a) dV/dW versus pore width b) dV/dlog(W)) versus pore width.

Fig. 3. Mercury porosimetry of hydrochars: a) Cumulative mercury intrusion vs. pore size of the hydrochars and b) Modal pore throat diameter for samples of the hydrochars.

Table 1. Ultimate analysis, ash content and estimated heating value of AM and hydrochars

HYDROCHAR	Ultimate analysis (wt%, dry basis)					Ash (wt%)	Atomic ratio		HHV (MJ/kg)
	C	H	N	S	O		H/C	O/C	
AM	43.99	5.95	5.21	1.02	36.13	7.70	1.62	0.62	18.49
HAM200-2	50.73	5.47	4.86	0.95	27.58	10.41	1.29	0.41	21.11
HAM200-6	50.06	5.35	4.43	1.02	27.19	11.95	1.28	0.41	20.75
HAM230-2	49.93	5.24	4.35	1.09	25.32	14.07	1.26	0.38	20.74
HAM230-6	55.08	5.39	4.39	1.22	20.33	13.59	1.17	0.28	23.25

Table 2. Main characteristics of AM and derived hydrochars and yield of HTC

SAMPLE	Yield (wt%)	pH	EC (dS/m)	Coxi (wt%)	CEC (meq/Kg)	K (mmolc/kg)	P _{Olsen} (mg/kg)
AM		7.37d±0.02	0.10±0.01	26.78±1.02	146.21±1.49	3.79±0.79	1076.20±56.57
HAM200-2	60.0	6.04±0.11	0.35±0.02	32.68±2.63	122.18±0.83	3.98±0.37	3485.15±234.69
HAM200-6	55.5	6.11±0.01	0.37±0.02	34.75±0.37	118.44±1.08	3.68±0.19	2969.20±117.24
HAM230-2	58.2	6.30±0.03	0.37±0.01	36.29±0.78	119.49±2.06	3.26±0.23	2533.40±183.71
HAM230-6	52.3	6.58±0.01	0.38±0.04	33.89±1.48	114.79±4.17	2.94±0.11	1794.75±279.59

Table 3. Thermal analysis of the materials: weight loss in the Stages II (150 to 370°C) and III (370 to 620-730°C).

SAMPLE	$WL_{StageII}$ (wt%)	$WL_{StageIII}$ (wt%)	WL_{StII}/ WL_{StIII}
AM	37.33	42.24	0.88
HAM200-2	34.92	45.69	0.76
HAM200-6	34.74	44.67	0.78
HAM230-2	34.03	43.85	0.78
HAM230-6	27.35	39.14	0.88

Table 4. Field capacity (FC), wilting point (WP), available water (AW) of AM and derived hydrochars

SAMPLE	FC (%)	WP (%)	AW (%)
AM	241d±1	227.9d±2.2	13.2a±1.2
HAM200-2	116.6b±0.7	90.0c±0.3	26.6b±0.4
HAM200-6	107.7a±2.0	80.7b±1.5	27.0b±0.5
HAM230-2	108.8a±0.7	76.6ab±1.7	32.2c±0.9
HAM230-6	121.9c±1.1	74.4a±3.1	47.5d±4.2

Table 5. Textural parameters of the hydrochars

Sample	Helium Density (g/cm ³)	N ₂ adsorption		Mercury Porosimetry		
		S _{BET} (m ² g ⁻¹)	V _{TOT} at p/p ⁰ = 0.99 (cm ³ g ⁻¹)	5.5-12000 nm Total Pore Volume Hg (cm ³ g ⁻¹)	5.5-12000 nm Porosity (%)	Average pore diameter (4V/A) (nm)
HAM-200-2	1.572	5.9	0.0359	0.320	28.9	62.8
HAM-200-6	1.761	10.3	0.0549	0.393	40.2	65.8
HAM-230-2	1.537	12.7	0.0680	0.493	39.2	71.9
HAM-230-6	1.512	10.1	0.0651	0.605	44.8	110.5

Fig. 1. TG and dTG curves of samples: a) AM, b) HAM200-2, c) HAM200-6, d) HAM230-2 and e) HAM230-6.

Figure 2. Pore size distribution derived from the N_2 adsorption branch isotherms using the BJH model. a) dV/dW versus pore width b) $dV/d\log(W)$ versus pore width.

Fig. 3. Mercury porosimetry: a) Cumulative mercury intrusion vs. pore size of the hydrochars and b) Modal pore throat diameter for samples of the hydrochars.

Supplementary data for:

Hydrochars from industrial macroalgae "Gelidium
Sesquipedale" biomass wastes

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Fig. 1S. Van-Krevelen diagram

Fig. 2S. FTIR spectra of AM and derived hydrochars

Fig. 3S. DTA of AM feedstock and derived hydrochars

Fig. 4S. SEM images of the hydrochars at different magnifications (x500, x1000, x5000).

Fig. 5S. SEM-EDX images of the hydrochars from macroalgae biomass wastes, with special relevance in the mineral matter present.

Figure 6S. N₂ adsorption isotherms of hidrochars and conventional char (Ferrera-Lorenzo 2014c) obtained from the algae meal.