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A bibliographic study of biochar and hydrochar: Differences and similarities

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ABSTRACT

Biomass conversion by thermochemical processes has gained increasing interest due to its carbon-neutral and/or carbon-negative effect. The most common thermochemical approach is pyrolysis, which results in the production of biochar, a well-known carbon-rich material with properties comparable to those of materials derived from fossil sources. In the last decade, hydrothermal carbonization of biomass has attracted attention due to its simple requirements, low cost and lower temperatures, producing a carbon-rich material called hydrochar. This bibliographical study, based on the Scopus database and focused on the last 5 years, without forgetting earlier articles, aims to define the main differences between the two processes and the physico-chemical properties of each char, to summarise the main techniques for their characterisation and to highlight the areas of application according to their properties. This review suggests that it would be strategic to distinguish between the terms hydrochar and biochar to ensure efficient characterisation and appropriate application.

1. Introduction

Since the first industrial revolution, the intensification of human activities has led to an increase in Greenhouse Gases (GHGs) responsible for climate change, a phenomenon of global concern.

Based on the goals set out in the Paris Climate Agreement signed at the UN Climate Change Conference (COP21) in 2015 to hold "the increase in global average temperature well below 2 °C above pre-industrial levels" and to pursue efforts "to limit the temperature increase to 1.5 °C above pre-industrial levels", the recent United Nations Conference on Climate Change (COP28) proposed measures to ratcheting up ambition for near-term climate action [1]. Among the GHGs, carbon dioxide plays a significant role, as it is one of the main by-products of fossil fuels, as evidenced by the increase in its atmospheric concentration level, which is around 420 ppm. For this reason, it is necessary to switch from fossil fuel-based technologies to more environmentally friendly ones [2,3].

In this context, biomass has emerged as a viable and renewable alternative carbon source that is inexpensive, readily available and abundant. It can be converted into biofuels resulting in a carbon neutral process, whereas the conversion of biomass into chemicals or functional carbon materials has a carbon negative effect [4–7].

Carbon-neutral technologies aim to balance CO_2 emissions by removing the same amount of carbon dioxide produced during the process. On the other hand, carbon-negative policy aims to actively remove more CO_2 from the atmosphere than is emitted. This recent concept has evolved over time with the development of new technologies and materials able to exhibit "carbon sequestration" behaviour and has become a crucial goal for several global strategies to mitigate the climate change [8].

Several conversion technologies have been developed and can be broadly categorised as follows:

- Thermo-chemical conversion;
- Bio-chemical conversion;
- Physico-chemical conversion;

Depending on the production process, the bio-product obtained can be used in different areas such as energy production, water treatment and in agriculture for soil improvement and biofertilizer [5,6,9,10].

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In recent years, there has been a growing interest in the thermochemical approach, which, compared to other technologies, is faster, less raw material-specific and capable of producing high value-added products. Depending on the treatment and severity of the conditions, the resulting compounds can be mainly solid (biochar, hydrochar), liquid (bio-oil, bio-crude) and gaseous (syngas, biogas). Among them, biochar and hydrochar, obtained from the most common thermochemical processes, have shown remarkable properties such as porous structure with a high surface area and functional groups, pH buffering capacity and cation exchange capacity, presence of minerals and trace metals, and serve as a reservoir of electron donors and acceptors, making them ideal to replace carbon-based materials derived from fossil fuels [11–16].

A literature analysis with data mining from the bibliographic database SCOPUS using the free software VOSviewer, version 1.6.20 (created by Nees Jan van Eck and Ludo Waltman, van Eck & Waltman, 2010) [17] was carried out with the aim of providing an overview of the impact of char related studies. As a first step, a search was performed using the keywords "biochar" and "hydrochar", separately. The results, shown in Fig. 1, indicate the exponential trend highlighting the relevance of these two materials starting from the year 2010, just before the Paris Climate Agreement signed in 2015.

Another consideration is the total number of documents, 40,088 for biochar and 3,450 for hydrochar. This difference is due to a general interpretation of the word biochar, which is used in some studies to define hydrochar. In this paper the two chars are considered separately and their main characteristics are defined, emphasizing their effective differences [18–21].

During biomass conversion, the possible presence of toxic elements in feedstock leads to their accumulation in the final char; in addition, during their production complex reactions occur that may lead to the formation of substances of some concern such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-dioxins and furans (PCDDs and PCDFs), phenols and phenol derivatives or other as yet unknown toxic chemicals from biogenic material [22–25]. With this in mind and considering that hydrothermal carbonization research is relatively new compared to pyrolysis, the focus has been on characterization techniques in terms of potential applications, attempting to provide a comprehensive overview of the end product.

The use of the co-occurrence analysis has the potential to reveal upcoming research efforts in a given field. In our case, this approach was useful to evidence the relationship between the keywords found in the SCOPUS database. The counting method implemented was frequency, which allowed us to determine the most recurrent keywords and the strength of their associations. We required a minimum of 20 occurrences for each keyword to ensure a meaningful and clean graph.

The co-occurrence network contains several elements:

- Node size indicates the frequency of occurrence of the keyword (number of times it appears);
- Link between nodes indicates the co-occurrence of the keywords where they appear together;
- Link thickness indicate the frequency of co-occurrence (number of times the keywords appear together);
- Colours indicate thematic clusters.

The co-occurrence diagram in Fig. 2 was generated by the VOSviewer software using a SCOPUS dataset of 244 documents from 2012 to 2024 collected using the keywords "hydrochar" AND "hydrothermal carbonization" AND "characterization". It shows the close relationship between the hydrothermal carbonization process and hydrochar/end product or biomass/resource [17]. The keyword hydrochar is associated with characterization and absorption, indicating the main property of this type of char to be investigated. The co-occurrence of the terms "hydrochar" + "biochar" or "hydrochar" + "char properties" is weak, justifying our research in these two directions of use of the two terms and of the identification of specific properties set. Thus, focusing on these features of co-occurrence, the objectives of this study can be listed as: (i) clarify the different chemical, physical, morphological and microstructural properties hydrochar and biochar; (ii) summarise the characterization methods adopted in the scientific literature and standardized practices for determining the properties of hydrochar and biochar; (iii) illustrate the most appropriate applications for each type of char.

2. Process and definition of biochar and hydrochar

The high variability of biomass variability in terms of form, composition and water content combined with the large quantities of produced have made the development of conversion processes essential. Thermal processes such as pyrolysis and hydrothermal carbonization have gained increasing interest due to the production of materials with high carbon content and remarkable versatility for various applications [26–29]. Biotechnology for biomass degradation/digestion seems to have longer times and is unsuitable for small production plants [30,31].

These two conversion processes take place under different

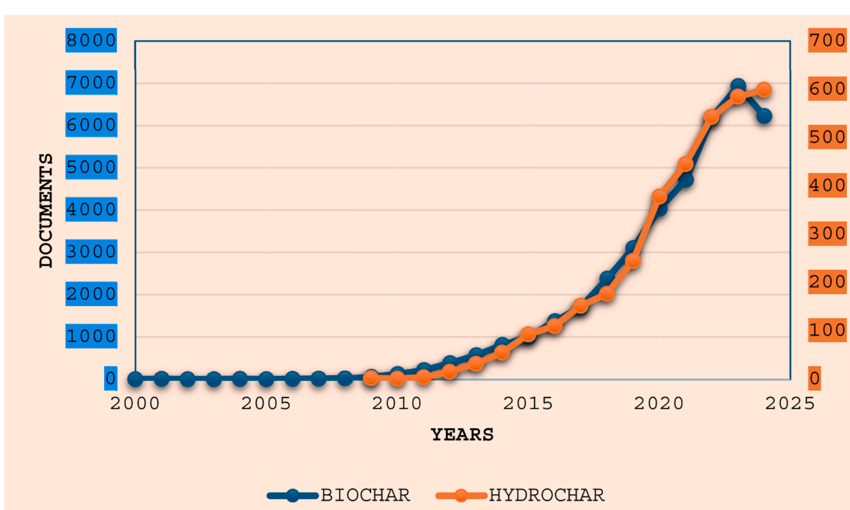

Fig. 1. Documents by year of Biochar and Hydrochar as from data mining on the SCOPUS bibliometric database (set of keyword used: "Hydrochar" and "Biochar", 6 June 2024). Blue, left y-axis, is related to biochar; orange, right y-axis, is related to hydrochar.

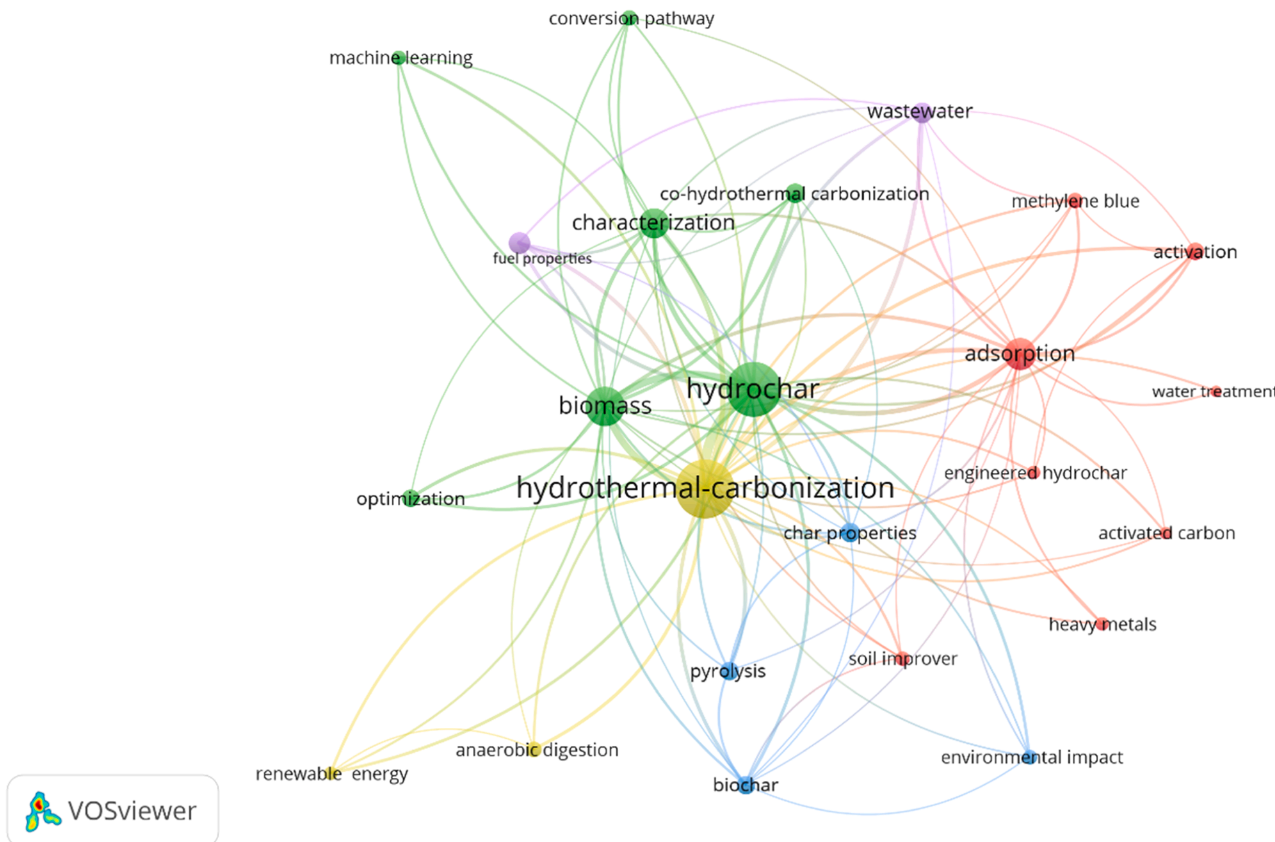

Fig. 2. Keywords network based on co-occurrence data collected from SCOPUS reference data bank in May 2024 and elaborated by VOSViewer.

conditions:

- *Pyrolysis,* the thermal decomposition of dry biomass take place at temperatures between 400 and 700 °C in the absence or in an oxygen-deficient atmosphere. According to different residence times and heating rates we can distinguish: slow pyrolysis (low heating rate, 5–7 °C/min, long vapor residence time >1 h); fast pyrolysis (high heating rate >200 °C/min and short vapor residence time <10 s). The solid end product is a carbonaceous material called "biochar", defined by the "World Biochar Certificate (WBC) & Carbon Standards International" as a "porous, carbonaceous material produced by pyrolysis of biomass and is applied so that the contained carbon remains stored as a carbon sink or replaces fossil carbon in industrial manufacturing. It is not made to be burnt for energy generation" [32,33].

  Other end products are in the gaseous phase (e.g. CO_2, CO, CH_4) and liquid phases (e.g. bio-oil, tar, water) with the proportion of solid:liquid:gas strongly influenced by process conditions [34,35]
- In *hydrothermal carbonization* (HTC), biomass conversion takes place in an aqueous environment and in closed reactors at temperatures between 180 and 250 °C. In these conditions an autogenous pressure is generated (2–6 MPa), moreover subcritical water is able to maximize the ionic product and solubilize organic compounds. The process produces a solid-liquid mixture and a small amount of gases with a negligible contribution to the greenhouses effect [32]. The solid end product is a carbon rich material called "hydrochar" and defined as "solid, porous carbon-like material with a C-content up to 60 wt %" [36,37].

The selection of treatment methods, i.e. pyrolysis or HTC conversion, is primarily determined by the biomass type and its composition. In order to reduce conversion costs, it is important to select the most appropriate process according to the amount of moisture and, in some cases, to the fat content [38,39]. Indeed, the requirement for moisture content in pyrolysis is typically below 30 % in weight, thus limiting the biomass types that can be processed and necessitating the costly drying pretreatment. Conversely, HTC conversion has gained prominence in waste treatment, particularly for wet biomass, due to its simple requirements, low costs and lower temperatures. This process simulates the natural humification process and produces a material, hydrochar (HC), which is more degradable and versatile than biochar due to the presence of oxygenated functional groups, labile carbon and fewer aromatic structures [32,36,40–43].

3. Physicochemical properties

Although chars are produced by different processes, they are generated by the same complex reactions: degradation, dehydration, decarboxylation, demethanation and repolymerization. However, the diversity of biomass and process conditions defines specific and unique reaction pathways, resulting in chars with different physicochemical properties that significantly affect their potential applications [43–45].

The final product properties and yield are strongly influenced by parameters such as temperature, residence time and biomass type. Among these, temperature plays a key role in the physicochemical properties of chars as it is the driving force that influences the dominant reaction mechanism.

In the case of hydrothermal carbonization, due to the lower temperatures compared to the pyrolysis, the kinetics of the process can be modulated by setting acidic conditions, catalysing the reactions in the system [46,47]. In addition, both the concentration and the type of acid have an impact on the final properties of hydrochar, affecting its:

- carbon content, the addition of acids, particularly inorganic acids such as sulfuric acid (H_2SO_4), can significantly increase the carbon content of hydrochar. This is due to the increased effectiveness of the acid as a catalyst during the HTC process. Increased carbon content is often associated with increased aromaticity of the hydrochar [46–48];
- process yield, acidic conditions tend to reduce the yield of hydrochar. This is due to the degradation of macromolecules present in the starting biomass and the formation of liquid or gaseous products. In other words, acid promotes the conversion of the feedstock into a variety of products, not just hydrochar [47,48];
- acid functional group, the addition of acids, particularly strong acids such as H_2SO_4, increases the amount of acid functional groups, such as carboxylic and sulfonic, on the hydrochar surface. These groups can act as active sites for adsorption and other catalytic applications. Note that excessive carbonization time is detrimental to the formation of surface acid groups [48,49];
- surface area and pore volume, the addition of hydrochloric acid (HCl) has been shown to increase the specific surface area (SSA) and total pore volume of hydrochar. This effect is probably due to the acid promoting hydrolysis of the biomass [46];
- nutrient content, acid catalysis can promote the extraction of nutrients such as phosphorus and nitrogen from biomass. For example, HTC with hydrochloric acid (HCl) can extract almost 100 % of the phosphorus and a significant amount of nitrogen from manure. Sulfuric acid increases the release of nitrogen in the form of ammonia. Most of the extracted phosphorus is in the form of phosphate (PO_4-P). It should be noted that these solubilized nutrients are found in liquid by-products [46–48];
- pH, both the hydrochar and the process liquids resulting from HTC are acidic, regardless of the starting pH. However, at lower starting pHs, the acidity of the process liquids is higher. In addition, the pH of the process liquids can be lower than the pH of the hydrochar [50, 51].

Generally, the discussion between biochar and hydrochar is conducted by taking into consideration the proximate analysis (moisture content, fixed carbon, volatile matter and ash content), ultimate analysis (carbon, hydrogen, nitrogen, sulphur and oxygen composition), porosity, and functional group. Moreover carbon, hydrogen and oxygen content are used to build the Van Krevelen diagram, which is obtained by plotting the H/C and O/C revealing the main features of chars in relation to those of natural materials such as peat, coal, anthracite and others (Fig. 3) [26,28,40,52–57].

Table 1 shows the main properties of biochar and hydrochar produced from the same biomass, allowing a char-centred comparison that highlights the main differences between the two materials.

The ultimate analysis is used to check the evolution of the carbon content and to understand, through the H/C and O/C ratios, the reaction path and thus the degree of aromaticity and polarity. A low H/C indicates a higher degree of aromaticity, while a high O/C indicates a higher polarity [64]. Table 1 shows how the degree of aromaticity follows the trend biochar> hydrochar> biomass trend, while the polarity goes in the opposite direction. This pattern can be explained by considering the temperature of the processes; the higher temperature in pyrolysis produces a material with higher carbon content and fewer functional groups, as oxygen and nitrogen are released as gaseous by-product. Proximate analysis is used to define the stability of chars, in particular volatile organic matter and fixed carbon are the extremes that determine stability or lability. High levels of volatiles are characteristic of hydrochar and result from incomplete carbonization due to lower process temperatures. Higher levels of fixed carbon are observed in biochar, due to better stability than hydrochar. The lower ash content of hydrochar can be explained by the presence of a reaction medium in the HTC process, which allows the dissolution of inorganic species, reducing the contribution to the ash content. Differences in pH value can be explained either by the dissolution of inorganic and organic compounds in the aqueous medium, corresponding to an acidic pH for hydrochar, or by the easy rearrangement of functional group, through dehydrogenation, decarboxylation and aromatization reactions, favoured by high pyrolysis temperatures that increase the pH value of biochar [55,57,65].

Biochar and hydrochar show different chemical (acids and bases) and thermal stability. The study of these characteristics can be predicted from proximate and ultimate analysis; in particular, biochar has been found to be more stable than hydrochar due to a higher degree of aromaticity, which confers high thermal resistance, and the lower content of functional groups lowers its reactivity toward acids and bases as well as to oxidation [66–71]. It can be concluded that the complexity of the properties of the two chars', which are strongly dependent on the biomass source (Table 1), and their best exploitation can find benefits in different application areas to address the most important environmental issues [72]. Thus, as a complex substrate, char requires an approach

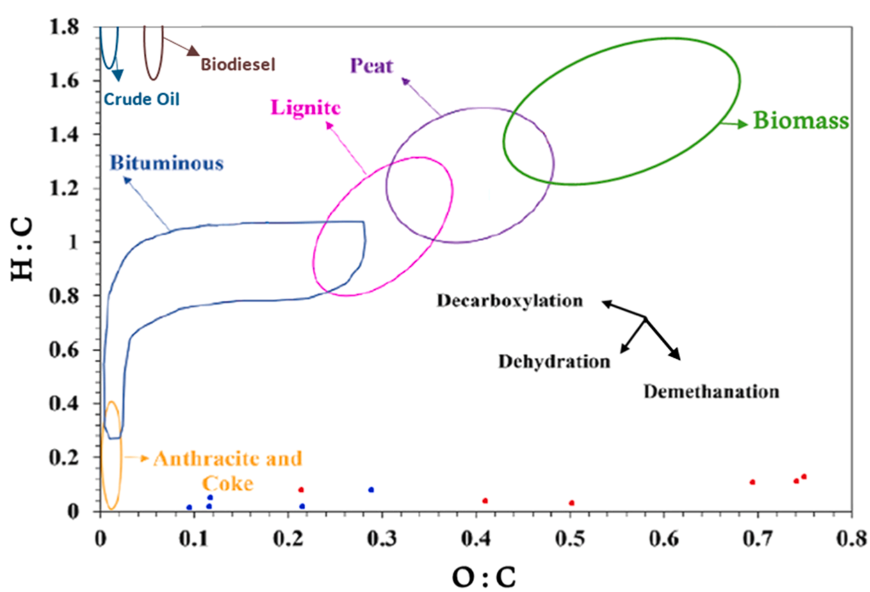

Fig. 3. Van Krevelen diagram: biomass (green), peat (violet), lignite (magenta), bituminous (blue), anthracite and coke (orange). Blue dots are biochars example and red dots are hydrochars example reported in Table 1.

Table 1
Literature note on the comparison of the main physicochemical properties of biochar and hydrochar obtained from the same raw material; T (°C) Temperature; C, H, N, S, O (%): content of carbon, hydrogen, nitrogen, sulphur and oxygen respectively: VM: volatile matter; FC: fixed carbon; MC: moisture content;.

Biomass	T (°C)	C (%)	H (%)	N (%)	S (%)	O (%)	O/C	H/C	VM **(%)**	FC **(%)**	MC **(%)**	Ash **(%)**	pH	BET (m^2/g)	Ref.
Hickery wood (HW)	-	45.51	6.17	0.15	-	47.83	1.05	0.14	-	-	-	-	5.8	0.1	[58]
Biochar-HW	600	81.81	2.17	0.73	-	14.03	0.17	0.03	-	-	-	-	8.4	401.0	[58]
Hydrochar-HW	200	53.52	6.13	0.25	-	39.84	0.74	0.11	-	-	-	-	6.0	2.5	[58]
Bagasse (BG)	-	45.82	6.25	0.36	-	47.18	1.03	0.14	-	-	-	-	6.0	0.4	[58]
Biochar-BG	600	76.45	2.93	0.79	-	18.33	0.24	0.04	-	-	-	-	7.5	388.3	[58]
Hydrochar-BG	200	53.32	6.23	0.44	-	39.93	0.75	0.12	-	-	-	-	5.7	3.8	[58]
Bamboo (BB)	-	46.52	6.11	0.2	-	46.89	1.01	0.13	-	-	-	-	6.6	> 0.1	[58]
Biochar-BB	600	80.89	2.43	0.15	-	14.87	0.18	0.03	-	-	-	-	9.2	375.5	[58]
Hydrochar-BB	200	55.27	6.18	0.21	-	38.27	0.69	0.11	-	-	-	-	6.3	1.3	[58]
Fresh water (FS)	-	12.46	4.63	1.77	3.33	39.75	3.19	0.37	61	1.38	-	38.1	6.6	96.5	[42]
Biochar-FS	700	11.47	0	1.04	1.01	5.19	0.45	0	14	4.57	-	81.3	7.8	108.9	[42]
Hydrochar-FS	200	8.63	0.82	0.73	1.4	25.66	2.97	0.1	35	1.75	-	62.8	4.3	197.6	[42]
Microalagae (MA)	-	44.21	6.54	6.95	0.36	26.13	0.44	1.77	70	13.7	-	15.8	-	-	[59]
Biochar-MA	700	80.64	2.29	9.31	0.52	7.23	0.09	0.03	15	38.7		46.3	9.9	-	[60]
Hydrochar-MA	210	68.82	8.93	6.42	0.01	15.81	0.23	0.13	54	16.7		29.1	5.5	-	[60]
Feedstock	-	47.9	5.7	0.12	0.19	44.5	0.7	1.4	-	-	-	1.6	-	-	[61]
Biochar	600	75.7	0.8	0.43	0.19	26.7	0	0.1	-	-	-	18.5	-	-	[61]
Hydrochar	240	66.4	4.4	0.24	0.25	4.5	0.5	0.8	-	-	-	2.1	-	-	[61]
Microalgal	-	49.1	7.64	9.85	-	21.1	0.43	0.15	-	-	-	12.3	6.17	0.221	[62]
Biochar-MA	500	67.3	2.62	10.9	-	0.16	0	0.039	-	-	-	19	5.87	0.313	[62]
Hydrochar-MA	200	65.6	8.75	6.6	-	11.7	0.18	0.13	-	-	-	7.35	4.46	0.191	[62]
Spent coffee ground		48	7.58	2.29	-	42.1	0.8	0.15	85	13.97	7.53	1.45	5.4	-	[63]
Biochar-SCG	400	69.8	5.78	4.25	-	20.2	0.29	0.082	39	57.21	2.53	3.72	8.4	-	[63]
Hydrochar-SCG	200	62.6	7.62	2.47	-	27.3	0.43	0.12	73	26.02	3.46	0.54	3.9	-	[63]

with multiple characterisation techniques, which will be detailed in the next section.

4. Characterization techniques

Physico-chemical characterization is essential to assess both the conversion efficiency and the final application of chars. In this regard, a wide range of analytical techniques are currently used for the in-depth determination of char properties [53,55,73–75].

This section summarizes the main analytical techniques and methodologies used for char characterization.

4.1. Proximate and ultimate composition

4.1.1. Proximate analysis

Proximate analysis focuses on the chemical composition of a material in terms of moisture content, fixed carbon, volatile matter, and ash content. It is a simple and inexpensive approach that is commonly used to assess the macro-composition and calorific capacity [76–80]. As mentioned in the previous section, fixed carbon and volatile matter are an indicators of char stability, which affects their potential applications. In fact, in some industries, particularly metallurgy, high fixed carbon contents (90/95 %) are required to replace fossil carbon sources [81].

To the best of our knowledge, no standardized ad hoc methods have been established for biochar and hydrochar, so in several studies the proximate analysis is performed following standard procedures for coal/coke characterization [77,82–89].

The determination is carried out by a thermal program under specific conditions, and can be performed using a muffle or instrument, through thermogravimetric analyser (TGA) [90,91]. The most commonly used standard methods are those provided by the International Standard Organization (ISO-562–2024; ISO-687; ISO-1171–2024 [92–94]) and by American Society for Testing and Materials International (ASTM D-3173; ASTM D-3174; ASTM D-3175 [95–97]), although only in the latter includes specifications for the instrumental determination (ASTM D-5142 [98])(Table 2).

4.1.2. Elemental analysis

Ultimate analysis, also known as elemental analysis, is carried out to determine the carbon, hydrogen, nitrogen and sulphur content by using an elemental analyser (Table 2). The oxygen content is calculated by subtracting the C, N, H, S and ash contents from the total mass of char [86,102,103]. The oxygen to carbon and hydrogen to carbon ratios can be used to construct the Van Krevelen diagram, based on the main reactions that occur during thermo-conversion, and to monitor the degree of carbonization by comparing the values obtained with those of known materials (Fig. 3). In addition, the carbon to nitrogen ratio can be used as an indicator of nutrient retention and nutrients availability to the plant [28,42,104–111].

Table 2
Standard methods used for biochar and hydrochar characterization.

Standard	**Title**	**Ref.**
ISO−562−2024	Coke and Coal Determination of Ash	[92]
ISO−687	Hard Coal and Coke Determination of Volatile Matter	[93]
ISO−1171−2024	Coke Determination of Moisture in the General Analysis Test Sample	[94]
ASTM D−3173	Standard Test Method for Volatile Matter in Analysis Sample of Coal and Coke	[95]
ASTM D−3174	Standard Test Method for Moisture in the Analysis Sample of Coal and Coke	[96]
ASTM D−3175	Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal	[97]
ASTM D−5142	Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by instrumental Procedures	[98]
ASTM D−5373	Standard Test Methods for Instrumental Determination of Carbon, Hydrogen and Nitrogen in Laboratory samples of Coal and Coke	[99]
IBI-STD−2.1	International Biochar Initiative – Biochar Standards-	[100]
EPA-Method 6020B	Inductively Coupled Plasma – Mass Spectrometry	[101]

Very recently, energy dispersive X-ray spectroscopy (EDX), and X-ray photoelectron spectroscopy (XPS) has been reported to fit with ultimate analysis [112,113]. Although not detected by EDX, nitrogen concentration was determined by XPS methods, as were carbon and oxygen by both spectroscopies.

4.2. Thermogravimetric analysis (TGA)

Thermogravimetric analysis is of fundamental importance to the characterization of hydrochar and biochar, providing essential information on their thermal and combustion properties and composition. TGA makes it possible to study the behavior of materials during heating resulting in:

- combustion profiles: the TGA generates a combustion profile showing the rate of weight loss as a function of temperature. This profile is different for biomass, biochar and hydrochar. Biomass typically generates two peaks due to the different reactivity between the volatile matter and the resulting char. In contrast, biochar and hydrochar show a single peak at elevated temperatures due to of their reduced volatile matter content [114];
- effect of production temperature: TGA is useful to investigate how process temperature affects the properties of hydrochar and biochar, allowing production conditions to be optimized in order to obtain materials with specific properties [114,115];
- material characterization: in addition to its use in proximate analysis (**paragraph 4.4.1**) and in the study of thermal stability, TGA can be coupled with Fourier transform infrared (FT-IR) spectrometry to analyse the gases produced during combustion, allowing identification and quantification of main gaseous products, such as CO_2, CO, H_2O, NO, HCl, and HCN providing information on environmental impact [114–116].

4.3. Surface functional groups

In the biomass conversion, many reactions take place leading to the development of different surface functionalities such as hydroxyl (-OH), amino (-NH_2), carboxyl (-(C=O)OH), nitro(-NO_2), ester(-(C=O)OR), ketone (-OR), aldehyde(-(C=O)H) which occur mainly on the external surface rather than on the pore surfaces [117]. Therefore, the study of functional groups plays a significant role, both in providing a clearer understanding of reaction pathways and in identifying the optimal application based on material affinity (hydrophilic/hydrophobic) and its behaviour in environments (acidic/alkaline).

4.3.1. Boehm titration

Boehm titration is a method of quantifying the oxygen-containing acid functional groups present on the surface of a material. This technique takes advantage of the principles of acid-base titrations and is based on the use of 3 different bases NaOH, $NaHCO_3$ and Na_2CO_3. Assuming that NaOH neutralizes the acid groups (carboxylic, lactonic and phenolic), Na_2CO_3 neutralizes the carboxylic and lactonic groups and $NaHCO_3$ only the carboxylic groups, the specific amount of functional groups can be determined by calculating the difference in volume between the 3 bases [51,118–120].

4.3.2. Fourier transform infrared spectroscopy (FT-IR)

In many studies functional groups are analysed by infrared spectroscopy (FT-IR) and in some cases Attenuated Total Reflectance (ATR-FT-IR) is also used due to its easy operability and time efficiency compared to FT-IR analysis. Other techniques such as Raman spectroscopy and X-ray Photoelectronic Spectroscopy (XPS) can assist in determining the composition of surface functional groups and understanding how elements bind on the surface of materials, useful information to comprehend reactivity and adsorption capacity [12,55,73,75,88,89,117,118,121–129].

4.4. pH

The change in char pH is strongly related to the functional group rearrangement and to the ash content. Thermally degraded materials generally have high pH value due to the degradation of acidic functional groups and the accumulation of ash (e.g. alkali salts) [55,84]. However, as mentioned above, in the hydrothermal process, the abundant dissolved organic acids produced from the hydrolysis of organic matters along with leaching of inorganic components, results in a lower pH value of hydrochar [57,130].

The pH is an important parameter that affect the chemical species in char material, the physico-chemical properties of the adsorbate-adsorbent mechanism and determines the mobility of heavy metals [131–133]. Generally, pH studies are performed dissolving chars in water with a solid to liquid (w/v) ratio that varies between studies [28,63,84,102,130,134] However, the International Biochar Initiative (IBI-STD-2.1) provides a standardized method with a solid to deionized water ratio of 1:20 (w/v) (Table 2) [100]. The suspension is first shaken and equilibrated for 1.5 h, then measured using a pH meter [42,58–60,100,135,136].

4.5. Surface charge analysis

Surface charge analysis is a technique used to study the electrical properties of material surfaces, including biochar and hydrochar. This analysis is critical to understanding how materials interact with their environment, particularly in aqueous solutions [113,137–139]. Surface charge analysis is conducted using the following approaches and is closely related to pH:

- point of zero charge (PZC): the PZC is the pH value at which the net surface charge of a material is zero. In other words, at this pH, the number of positive and negative charges on the surface is equal. Char with high PZCs are often better suited for anion adsorption, while those with lower PZCs are better for cation adsorption [137,139];
- Zeta potential (ζ): it measures the difference in electrical potential between the surface of a particle and the surrounding medium. it is a key indicator of the stability of a colloidal suspension of biochar and hydrochar. A high absolute value of zeta potential indicates strong repulsion between particles preventing agglomeration and sedimentation. Conversely, zeta potential values close to zero can lead to particle aggregation, reducing the effectiveness of chars efficacy as adsorbents or soil conditioners [138];
- ion exchange capacity: Cation Exchange Capacity (CEC) and Anion Exchange Capacity (AEC) measure the amount of negative or positive charges that a material can exchange with its surroundings. Ionic exchange capacity is related to the presence of functional groups, acidic or basic, on the surface of the material. Char produced at low temperatures has a higher CEC while those produced at high temperatures have higher AEC, these parameters are important in assessing the effectiveness of biochar and hydrochar in adsorbing cations or anions in a given environment [139].

4.6. Electrical conductivity

Electrical conductivity (EC) can be used to investigate plant uptake, phytotoxicity, adsorption behavior and electron transfer capacity (DIET) by determining the inorganic ion concentrations in aqueous solution [75,105,140]. It is directly related to pH and can be assessed using a conductivity meter according to the procedure proposed by International Biochar Initiative (IBI-STD-2.1) [55,60,100].

4.7. Structural and morphological texture

The structural and morphological textures of biochar and hydrochar are some of the most attractive and versatile features of these materials [75,141].

XRD (X-ray Diffraction) pattern, obtained using powder diffractometer, provides information on the crystalline/amorphous phase of chars.

SEM (Scanning Electron Microscopy) is used to determine the morphology of the surface and is usually coupled with Energy Dispersive X-ray analysis (EDX) in order to examine the chemical composition of the surface, proving particularly useful in screening for the presence of minerals, metals and other elements such as phosphorus in biochar or hydrochar [42,82,102,117,142].

4.7.1. Specific surface area (SSA) and pore volume

The specific surface area, total pore volume and mean pore size of hydrochar and biochar are measured using the Brunauer-Emmett-Teller (BET) surface area analysis via the N_2 adsorption/desorption isotherm at 77 K [42,67,73].

These analyses make it possible to assess the conversion process through a comprehensive comparison between char and biomass, confirming what was hypothesized with the Van Krevelen diagram. In addition, they are fundamental in understanding the ways in which hydrochar and biochar interact, directly and indirectly, with and affect the environment, thus defining their best area of application [55,57,88, 143,144].

4.8. Heavy metals

Thermochemical processes lead to accumulation of heavy metals in the final product. In the case of the hydrothermal carbonization process, it has been observed that bioavailable heavy metals are transferred to the liquid phase, together with some alkaline metals (K^+,Na^+), while the stable fraction accumulates in the hydrochar.

4.8.1. Inductively coupled plasma (ICP) analysis

The determination of elements of concern such as Pb, Cd, Hg, Cr, Cu, Zn, Fe, Mn, and As, among the most important, is generally performed by Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) or Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) according to the standard method provided by the Environmental Protection Agency (EPA), where digestion and analysis conditions are defined (Table 2) [101,145]. Unless otherwise specified by the analytical standard procedure, ICP-OES is normally used for higher metal concentrations. Other analytical techniques can be used, for example, Taskin et al. performed heavy metal analysis by total reflection X-ray fluorescence (TXRF) spectrometry [55].

In addition, the Tessier sequential extraction procedure can be carried out to study the speciation of heavy metal [84,121,129,131,140, 141,146].

4.9. Concern organic molecules

During pyrolysis and hydrothermal carbonization processes, harmful organic molecules can be produced which limit the range of application of chars. Although complicated reaction pathways make it difficult to predict the types of organic substances of concern the focus is on the determination of aromatic hydrocarbons (AHs), polycyclic aromatic hydrocarbons (PAHs) and in general on volatile organic compounds (VOCs) by gas chromatography (GC) combined with various approaches such as solvent extraction or pyrolysis [41,55,147–152].

Other analytical methods are reported to provide advanced characterization tailored to the application area: total organic carbon, ^{1}H and ^{13}C nuclear magnetic resonance and solid state ^{13}C nuclear magnetic resonance [61,82,117,135,140,141,153,154–157].

5. Areas of application

The superior physico-chemical properties along with their sustainable processes make biochar and hydrochar ideal substitutes to replace carbon-based material derived from fossil carbon sources. Distinguishing between the properties of biochar and hydrochar is a challenging task due to their significant reliance on the biomass of origin and the process conditions. The detailed data presented in Table 1, categorised according to biomass type, can be succinctly summarised in a direct comparison table (Table 3) that encompasses several of the properties discussed in Section 4.

Discussing Table 3 row by row from top to bottom, we can say that, as outlined in the preceding sections, biochar necessitates a greater energy expenditure due to the elevated temperatures at which it is processed in comparison to hydrochar. Graphite-like monolayers may be more easily present in biochar, given the higher process temperatures. Such structures lead to a higher electrical conductivity of biochar compared to hydrochar [45]. The presence of aromatic carbon, electron donor or p electron rich functional groups at the temperatures at which biochar is formed has been demonstrated to facilitate its absorption capacity in comparison to hydrochar [158,159]. The removal of volatile matter during pyrolysis has been shown to promote higher porosity in biochar, while the presence of water has been demonstrated to inhibit pore collapse and enhance interconnectivity in hydrochar [160]. The process of cleavage of H and O bonds occurs at elevated temperatures during the pyrolysis stage of the production process. This results in the biochar being more alkaline in nature than the hydrochar [158]. High temperatures also remove or strongly alter hydrophobic and hydrophilic surface functional groups, making biochar more hydrophobic than hydrochar. This makes hydrochar more likely to be affected by hygroscopicity when it is stored [161,162]. The higher grindability of hydrochar is dependant also from its lower crystallinity with respect to biochar [163].

Table 3
Summary of data shown in Table 1.

	Biochar	Hydrochar
process energy	high	low
electrical conductivity	high	low
absorption capacity	high	low
porosity	high	low
surface area	low	high
acidity	low	high
hydrophobicity	low	high
grindability	low	high

Aiming to compare and depict their application areas, another data mining was conducted from bibliographic database SCOPUS and elaborated with the free software VOSviewer, version 1.6.20 [17]. The keywords used are “biochar-application” (Fig. 4) and “hydrochar-application” (Fig. 5), from the two datasets obtained the analysis was focused on review studies: 1771 documents ranging from 2012 till October 2024 for the former and 131 for the latter ranging from 2015 till October 2024.

Co-occurrence networks facilitated the identification of the main application fields and highlight that the two materials are broadly used in: waste management, environmental remediation and soil improver (Figs. 4–5). In both cases “waste management” refers to all applications where char have been used to treat and purify waste (e.g. wastewater treatment), while “environmental remediation” refers to the removal of contaminants from soil, water and the atmosphere.

5.1. Soil improver

The beneficial effects of biochar and hydrochar on soils are well known, as shown by the strong co-occurrence reported in Fig. 4 and Fig. 5. The choice of one char over the other depends on the specific requirements of the soil and crop. In addition, as the two chars have different chemical and physical properties, they have different purposes as well as different mechanisms that lead to soil improvement [22,104, 164–167]. The main effects of these materials are on soil structure, nutrients, pH, cation exchange capacity (CEC), carbon sequestration, and microbial biomass.

Both types of two char improve soil structure due to their porosity, which can increase water retention, and lower soil density increasing aeration [22,53,168,169]. Biochar generally has a greater surface area and porosity than hydrochar, making this material more effective in nutrient adsorption. Hydrochar has a higher content of functional groups and may have a higher cation exchange capacity, and can also

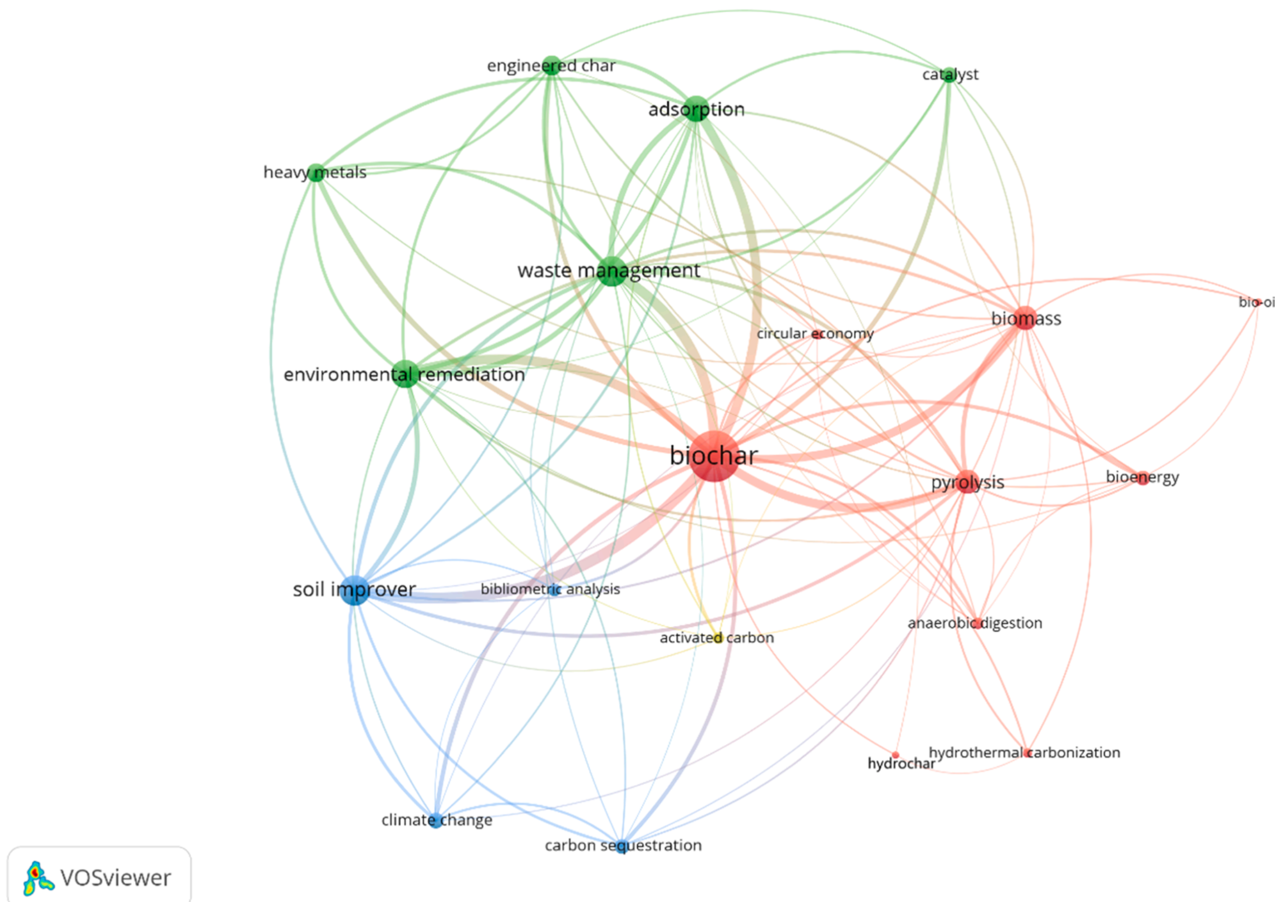

Fig. 4. Keywords network based on co-occurrence data collected from SCOPUS reference data bank in October 2024 and elaborated by VOSViewer.

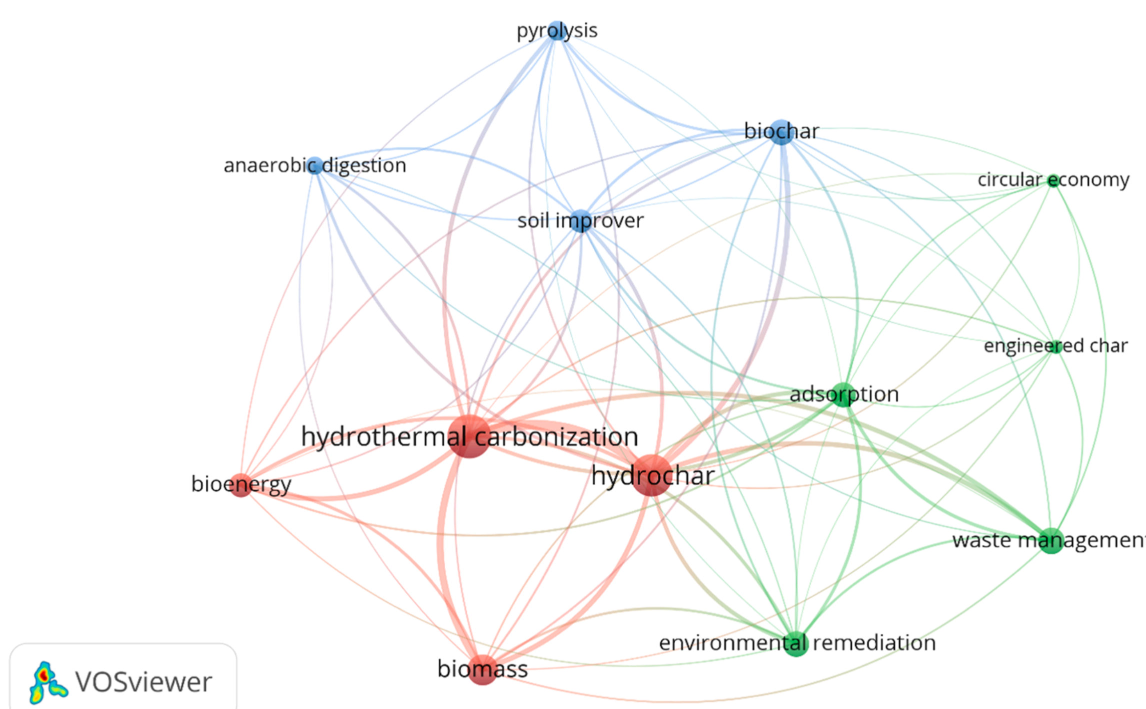

Fig. 5. Keywords network based on co-occurrence data collected from SCOPUS reference data bank in October 2024 and elaborated by VOSViewer.

hold more nutrients and act as a slow-release fertilizer [105,164,169–173]. Biochar is considered to be more effective for long-term carbon sequestration due to its greater stability and resistance to microbial degradation. Hydrochar, despite its lower stability, can still contribute to the adsorption of atmospheric CO_2 due to the presence of functional groups on the surface [22,53,174,175].

In summary, the higher porosity and higher pH makes the biochar a better candidate to reduce both bulk density and acidity in the soil, thus improving quality and fertility. Meanwhile, hydrochar has a higher content of macro- and micro-nutrients along with lower pH values resulting in a better fertilizing effect, while the higher stability (lower labile C content) along with lower DOM content of biochar provides a better reduction of greenhouse gas emissions [55,176–180].

5.2. Removal of contaminants and pollutants

The two networks (Figs. 4 and 5) show how applications in waste management and environmental remediation are a more closely related to adsorption, grouped in the same cluster, outlining the main interaction mechanism of biochar and hydrochar in the removal of contaminants or pollutants and focusing the attention on the related properties such as surface functional groups, structure, specific surface area and pore volume [181,182]. These properties can be improved or tailored by activation methods (physical, chemical and biochemical), doping with heteroatoms or oxygen-containing functional groups, or by combining chars into composites resulting in "engineered chars" [165,169,183–190].

In addition to the influence of the properties just mentioned and discussed in Section 3, a significant role is played by dissolved organic matter (DOM), defined as the continuum of organic molecules of different size and structure passing through a filter with a pore size of 0.45 μm, including dissolved organic carbon (DOC), dissolved organic nitrogen and dissolved organic phosphorus. The potential applications of chars are also dependent on DOM as it controls the fate and transport of organic and inorganic contaminants, microbial activity and plant growth. The dissolved organic matter is conditioned by biomass type and process temperature, for this reason Song et al. studied DOMs of biochar and hydrochar obtained from the same biomass and show that the hydrochar-DOM had a better performance than the biochar DOM for higher content, lower aromaticity and more different type of organic functional groups [141,167,191-193]. Dickson et al. demonstrated the importance of DOM in enhancing the adsorption capacity of biochar towards mercury by separately studying the material with and without dissolved organic matter and observed an increase in adsorption capacity when it was present, confirming its importance also in environmental remediation and contaminant removal applications [194].

In terms of environmental remediation and waste management applications, both chars show interesting sorption capacity, in particular biochar is able to provide both chemisorption and physisorption thanks to its structural properties combined with alkaline nature and high mineral content [195]. On the other hand, hydrochar exhibits mainly chemisorption due to the well-preserved surface functional groups and lower porosity [173,196]. However, due to the lower process temperature, hydrochar may contain a higher number of toxic contaminants, so its application, especially in environmental remediation, requires a careful evaluation [197].

Handling and disposal of the two char are closely related to the chemical and physical properties of the materials, the specific application and the country in which they are used.

6. Conclusion

This paper aims to advance the knowledge on biochar and hydrochar, the main conclusions are: (i) among the different thermochemical routes for biomass reduction and valorisation, pyrolysis and hydrothermal carbonisation appear to be more sustainable and economical, resulting in high yields of biochar and hydrochar production, respectively; (ii) the two chars differ significantly in their chemical composition, morphological characteristics and functionalities, making them versatile tools not only for wastewater remediation but also for other applications, including fertilisers and bioenergy; (iii) the multiple applications of biochar and hydrochar, due to their enhanced surface physicochemical properties, include efficient metal biosorption, soil fertility improvement and carbon sequestration. As a result, research into the production and use of biochar and hydrochar from different types of biomass has increased significantly in the last 5 years. According to the published data, the term "hydrochar" has been introduced only recently, in the last 14–15 years, to describe different characteristics compared to biochar. Both terms begin to individualise differences in the preparation process as well as in the properties of the final char, suggesting a more diffuse, conscious use of the terms "biochar" and "hydrochar".

In the future, the use of HTC technology will become more widespread where the biomass has a fraction that is too wet or too fatty for effective pyrolysis. At this point, it will become increasingly important to tracking the most of the unique properties of hydrochar, while maintaining the qualities that distinguish it from biochar.

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Berrettoni Mario: Writing – review & editing, Supervision. **Leonelli Cristina:** Writing – review & editing, Conceptualization. **Cognigni Paolo:** Writing – original draft, Methodology, Data curation.

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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Author contributions

CL had the idea for the article, PC performed the literature search, data analysis, and drafted the manuscript, CL and MB critically revised the work, MB supervised the bibliometric activity.

Data availability

Data will be made available on request.

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