



# A recent advancement on hydrothermal carbonization of biomass to produce hydrochar for pollution control

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## Abstract

A thermochemical conversion method known as hydrothermal carbonization (HTC) is appealing, because it may convert wet biomass directly into energy and chemicals without the need for pre-drying. The hydrochar solid product's capacity to prepare precursors of activated carbon has attracted attention. HTC has been utilized to solve practical issues and produce desired carbonaceous products on a variety of generated wastes, including municipal solid waste, algae, and sludge in addition to the typically lignocellulose biomass used as sustainable feedstock. This study aims to assess the in-depth description of hydrothermal carbonization, highlighting the most recent findings with regard to the technological mechanisms and practical advantages. The process parameters, which include temperature, water content, pH, and retention time, determine the characteristics of the final products. The right setting of parameters is crucial, since it significantly affects the characteristics of hydrothermal products and opens up a range of opportunities for their use in multiple sectors. Findings reveal that the type of precursor, retention time, and temperature at which the reaction is processed were discovered to be the main determinants of the HTC process. Lower solid products are produced at higher temperatures; the carbon concentration rises, while the hydrogen and oxygen content declines. Current knowledge gaps, fresh views, and associated recommendations were offered to fully use the HTC technique's enormous potential and to provide hydrochar with additional useful applications in the future.

**Keywords** Hydrochar · Hydrochar activation · Hydrothermal carbonization (HTC) · Pollutants · Wastewater

## Abbreviations

ECs	Emerging contaminants
HMF	Hydroxy methyl furfural
HTC	Hydrothermal carbonization
HTL	Hydrothermal liquefaction
HW	Hydrothermal wastewater
OFG	Oxygen functional groups
WHO	World Health Organization

## 1 Introduction

3/4 of the planet is comprised of water of which less than 1% of water on earth is exclusively for our use. For example, the total amount of water on earth is equivalent to hundred gallons, of which two gallons are ice and remaining 97 gallons are salt water. Nowadays, there is widespread concern over the depletion of such a valuable resource. A water crisis results when a region's supply of potable water is insufficient to meet demand [1].

In recent years, high population rate and rapid industrialization have significantly polluted the environment. One of the most vital sources necessary for human survival is water, which is becoming more contaminated by organic pollutants like dyes and heavy metal ions. Even toxic pollutants in water bodies with low concentrations can possess serious risk to the health of people and the environment [2]. The World Health Organization (WHO) establishes the international guidelines for the quality of drinking water that serve as a guide for various regulatory organizations in setting standards. The primary goal of this recommendation is to

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safeguard public's health in terms of security of drinking water [3].

The recent rise in water contamination is mostly the result of advanced technology being used in numerous industrial sectors that produce a diverse range of products. Living systems on Earth require the existence of freshwater bodies. Despite the fact that 70% of the globe is filled with water, just 3% of it is clean water that is fit for human use. In addition, the release of toxic pollutants, such as pesticides, herbicides, pharmaceuticals, phenols, organic dyes, and heavy metals, threatens this small amount of freshwater that is still in existence [4].

The public has always been concerned about environmental pollution, particularly water pollution. Wastewater that is contaminated with metal and comes from a variety of sectors, like agriculture, industries like tannery, textile dyes, nuclear, battery, mining, etc. The environment and human health have always been at risk from contaminants like domestic sewage. The most immediate effects on the environment are the destruction of aquatic habitat, the degradation of soil, which reduces crop yields, and the likelihood that heavy metals existing in contaminated water are absorbed by plants, where they enter food chains and harm animals and humans [5]. The spread of water-borne infections is one of the main consequences of water pollution. The impact of drinking untreated water will have catastrophic impact. The degradation of the dynamic ecosystems is another risky outcome. The food chain is further affected by water pollution. Untreated wastewater releases pollutants into the environment and poses health hazards when ingested. As a result, wastewater treatment is now essential. If the treated water is released, it will improve the water bodies' quality rather than pollute them. Reclaimed water could be used in number ways to enhance its productivity [1].

In recent years, the need for clean water for domestic use has also been accelerated by factors, such as rapid urbanization, rising global population, and climatic change. As a result, water treatment facilities are obligated to ensure that treated effluents discharged into the environment meet local water quality standards [6]. As a result, wastewater treatment is required to address issues of global water scarcity, poor water quality, and scarcity of water. Consistently, around 14000 demise are connected to the issue of water contamination. Effective treatment methods like electro-dialysis, precipitation, electro coagulation, ion exchange, adsorption, chemical oxidation, membrane filtration, etc. have emerged as a result of this to get rid of pollutants in wastewater that are harmful and toxic [7]. Adsorption has emerged as the technique that has received the greatest recognition as a sustainable technology for treating wastewater on a worldwide scale [8]. The target molecule adheres to the particular surface of the adsorbent, causing adsorption to occur. The effectiveness of the adsorption is determined

by the interfacial contact between the adsorbate and the constitutional species of the adsorbent [9].

Despite many technical advancements and successes, wastewater treatment is still a significant problem on a global scale. Heavy metals in wastewater must be removed, because, if improperly managed, they pose a major risk to human health. For the ecosystem and the welfare of people, heavy metal removal from effluent is crucial [10].

Every technique has its difficulties, whether they relate to the economy or ultimate safe disposal. Because the metal ions cannot be changed into harmful species, it must be reduced to a very small amount for reuse, recovery, or final disposal. To maintain environmental safety, it is required to remove the hazardous substances. The problems with the environment brought on by untreated industrial streams have been addressed in a number of ways [3].

Certainly, the most important step in processing wastewater using the adsorption approach is selecting the right adsorbent. This is done to achieve the best effectiveness of waste removal as well as to choose an adsorbent that is both economical and environmentally safe. Regarding efficiency in large-scale adsorption, hydrochar has shown to be the best-chosen adsorbent [8].

At temperatures within 180 and 260 °C inside a pressure vessel, the thermochemical process known as HTC transforms fresh biomass into rich products, such as the carbon-rich solid hydrochar, liquid bio-oil, and gases. The fundamental benefit of the HTC method versus other thermochemical ones such as gasification and pyrolysis is that since this procedure is carried out in aqueous medium, no expensive pre-drying step is necessary, making it more affordable. High productivity and product quality, simplicity of use, and lower environmental hazards are further benefits associated with this method [11]. Normally 35–80% of the hydrochar produced by the HTC process. The autoclave develops pressure at temperatures between 180 and 250 °C, which causes the water in the system to be in a subcritical condition and have a high H<sup>+</sup> content. This creates an environment that is favorable for the biomass feedstock to dehydrate and decarboxylate into hydrochar [7]. By boosting hydrophobic characteristics, lowering volatile and oxygen contents, and enhancing energy density, HTC appears to be a viable option for improving wet, low-value fuels [12]. Hydrochar has lesser quantity of heavy metals and better thermal value than pyrolytic biochar, and it may be produced without pyrolysis using HTC. While HTC produced hydrochar with more aliphatic structures and lower thermal stability, pyrolysis produced biochar with more aromatic structures and better thermal stability [13].

The term “hydrochar” refers to biochar formed from HTC, and it has a lot of oxygen-containing functional groups on its surfaces, which helps it absorb contaminants. The porous nature of hydrochar is enhanced by raising the

residence time and temperature, which raises the possibility of using hydrochar as an adsorbent [14]. Due to its smaller quantity of oxygen-containing functional groups and mineral components, several investigations have concluded that hydrochar has a poorer adsorption capability for heavy metals than pyrolyzed biochar [15]. Hydrochar quality varies immensely, owing to the wide variety of precursor material, the intricate nature of HTC reactions and thus requires characterization [16]. Regarding the generation of functionalized carbon materials as well as the numerous possible uses of hydrochar in the fields of energy conservation and safeguarding the environment, hydrochar's prospective advantages and applications have attracted a lot of interest in recent years [17].

There are a ton of various words used to describe the solid byproducts of thermochemical conversion processes, since there are no standardized definitions for them. It is crucial to differentiate between words like hydrochar, biochar, and charcoal depending on the raw materials and usage. The term “biochar” is a synonym for “charcoal” whenever utilized for soil applications. Charcoal is a solid, carbon-rich substance formed when natural organic materials are carbonized. It is primarily used to provide energy through burning. The word hydrochar, on the other hand, is comparable to biochar but is created hydrothermally, leading to distinct substance. In dry carbonization methods like pyrolysis, biochar is often generated as a solid product, whereas hydrochar is typically formed as a solid–liquid combination [18].

Utilizing hydrothermal liquefaction, HTC, and pyrolysis methods, waste biomass may be converted into char with significant pore volume and specific surface area that is superior to raw biomass. The use of char-based adsorbents to remove contaminants from wastewater and water has grown in favor in recent years. The feasibility of char-based adsorbents on an industrial scale was predicted and evaluated using a variety of contemporary techniques, such as machine learning. Several techno-economic assessments were carried out for the broad range of waste management solutions on a commercial basis [19].

The generation of activated carbons from hydrothermally treated biomasses, such as sawdust, coconut shells, rice husks, maize cobs, and rice straw, is the subject of several investigations. These precursors are activated to produce extremely porous activated carbons, whose huge surface areas make it easier for them to function as adsorbents. Since it allows for significant mass transfer and adsorbate loading, high porosity is highly desirable for improved adsorbent performance. The textural characteristics of activated carbons are influenced by varied activation conditions, such as temperature and activating agent concentration, making them appropriate for a variety of applications [20].

Three distinct saccharides like kraft pulp,  $\beta$ -cyclodextrin, and glucose were combined in a straightforward HTC

method to create saccharide-based hydrochars with excellent adsorption capabilities. The hydrochars' adsorption behavior was investigated using methylene blue as an ideal contaminant. Because of its highly negative surface charge and macropore, the glucose-based hydrochar had a greater ability to adsorb than the other hydrochar [21]. Because of its limited porosity and surface area, hydrochar formed from rice straw may not be as effective in decontaminating the environment as it could be. Hydrochar is a carbon substance with several functional groups involving oxygen on its surface. Potassium carbonate may be used to activate this hydrochar, and as a result, this substance is referred to as activated carbon. Using a hydrothermal co-precipitation procedure, this activated carbon may be transformed into magnetic carbon material. The hydrochar's porosity and adsorption capacity are boosted as a result of this magnetization and chemical activation. With its quick sorption ability and surface area, this magnetically activated hydrochar helps remove triclosan from effluent. Furthermore, using an external magnetic field, it is simple to recover magnetic hydrochar from effluent [22].

Biomass characteristics and reaction processing variables have a significant impact on the physicochemical and structural characteristics of hydrochar. Yet, a number of trial-and-error experiments are necessary to determine the ideal processing variable for a given biomass feedstock. It is difficult to properly characterize the quality and amount of hydrochar generated from biomass HTC, since such investigations are time-consuming, labor-intensive, and expensive. Moreover, because of the intricate control mechanisms that drive the HTC process, current computational methods cannot accurately anticipate the characteristics of hydrochar. To ensure hydrochar's appropriateness for diverse applications, it is imperative to develop more efficient and effective ways to ascertain its physicochemical and structural features. Using modern data-science techniques like machine learning (ML) technology, which can untangle, measure, and comprehend huge and complex datasets in bioenergy production systems, it is feasible to overcome the aforementioned difficulties [23].

The class of ML techniques known as artificial neural networks (ANNs) is capable of learning mathematical models from empirical information without being aware of the exact mathematical connections between the inputs and outputs. They are categorized as a “black box.” The use of ANNs in the thermochemical field is now attracting a great deal of attention for a variety of applications, including the estimation of product mass yields from HTC of biogas digestate, anticipation of the gasification characteristics of municipal solid wastes, forecasting of gas composition and product yields from biomass gasification, and the assessment of biomass pyrolysis and gasification processes. Support vector regression and random forest techniques were used to

analyze the energy densification, energy recovery, yield, and heating value of hydrochar and pyrochar. Significant results were seen, with an average  $R^2$  of 0.94 for pyrochar and 0.9 for hydrochar [24]. Parthasarathy and co-workers used a model developed using ML to predict the characteristics of fuel hydrochar. Based on 281 data points, the authors chose an ensemble support vector machine (E-SVM) as the classifier in conjunction with the slime mode algorithm (SMA) for optimisation. To create and evaluate the model, three datasets were combined: cow dung, leftovers, and sewage sludge. The average  $R^2$  and RMSE for the suggested ESVM\_SMA model were 0.94 and 2.62, respectively [25].

This review highlights shortages of information and potential future directions for hydrochar research by compiling studies that have already been done on the production and use of hydrochar. The importance of this review is to identify the potential precursors for producing hydrochar using the conventional hydrothermal method in contrast to other methods currently in use, the process variables affecting hydrochar formation, and using the generated hydrochar for a wide range of applications is highlighted. The novelty of it is brought about by highlighting the importance of various kinds of machine learning technique which is used to estimate the product yields resulting from HTC process.

## 2 Hydrochar

Hydrochar is the term for the solid byproduct from HTC [26]. Hydrochar, a black solid remnant with carbon as the primary structure and a larger fraction of oxygen functional groups (OFG), is produced by a hydrothermal reaction using organic wastes or its compounds as the raw material, water as the solvent, and oxygen as the reaction medium [27]. Due to abundance, affordability, and sustainability of its feedstocks, hydrochar has gained a lot of attention [28].

Hydrochar produced from biomasses via HTC is utilized to improve soil fertility, to hold onto water, fuel, and as an adsorbent [26]. Thermochemically converted hydrochars and activated carbons are all pyrogenic materials that contain some organic carbon [29]. The hydrochar is also a good starter for producing activated carbons through chemical or physical activation due to its low aromatization degree and specific oxygen activity [30]. Hydrochar has a high affinity for water due to the presence of OFG on its surface and can be utilized to improve soil's ability to retain water [31]. Due to hydrochar's water-washing effect during HTC and the presence of water-soluble inorganic compounds, the ash percentage of hydrochar was lower than that of biochar [32]. Hydrochar and biochar are both somewhat similar products; however, hydrochar is made under entirely distinct pre-treatment conditions. Biochar is often made as a solid residue material in a dry carbonization process like

pyrolysis, whereas hydrochar is frequently created as slurry—a two-phase mixture of solid and liquid through hydrothermal carbonization [33].

As a new adsorbent for organic contaminants in polluted water, hydrochar appears to have two environmental advantages: first it recycles waste; second, it can be used to remove contaminants. Numerous chemical processes, including aromatization, polymerization, condensation, decarboxylation, dehydration, and hydrolysis, result in the formation of hydrochar. Based on the pore structure, surface area and surface OFG hydrochar is applied in adsorption [34]. Since hydrochar has a high degree of friability and hydrophobicity, it can be easily removed from liquid products. Based on the many types of biomass used, hydrochar has been widely used for soil improvement, wastewater pollution abatement, bioenergy production, and carbon sequestration [17]. However, this substance could potentially be used in other applications such as catalysis [35].

Due to its exceptional qualities as an economical and ecologically acceptable sorbent for the elimination of contaminants from the aqueous phase, hydrochar has grabbed the attention of the scientific community. A range of biomass feedstocks, including agricultural residues, sewage sludge, manure, and microalgae, have been utilized in the production of hydrochar [15]. The performance and characteristics of hydrochar are greatly influenced by the feedstock and thermochemical treatment conditions [36].

Recent studies have shown that hydrochar produced via wet chemical reaction with renewable biomass differs from char produced from pyrolysis. As a result, hydrochar preparation for energy storage, environmental benefit assessment, activation for environmental mediation, and property optimization has received increasing attention [37]. Biochar and hydrochar can both perform the same tasks, but it is still crucial to assess their effectiveness in these applications and compare them to biochar. This is owing to the possibility that the physicochemical properties of biochar and hydrochar are substantially different [38]. The hydrochar method is also environmentally friendly, because unlike dry pyrolysis, it produces no toxic chemical waste or byproducts [39].

Hydrochar is currently recognized as the next developing sustainable carbonaceous adsorbent which may be produced by HTC for any type of feedstock, replacing the conventional activated carbon that was previously used. With little aromatization, low ash content, and high-carbon content, HTC-produced hydrochar has a high OFG level. However, the HTC method resulted in hydrochar with a low porosity and a lower surface area due to pore blockages predominantly caused by the condensation of hydrocarbon on the hydrochar's surface. This drawback requires that hydrochar be modified or activated [40].

HTC allows for the direct conversion of agricultural and forestry waste biomass into hydrochar, a carbon-rich

substance, under benign reaction conditions. Hydrochar's surface is packed with functional group that contains O. As a result, hydrochar can be employed as an efficient adsorbent to extract organic dyes from wastewater; however, due to the lack of phenolic and carboxyl groups and a constrained specific surface area, its adsorbing effectiveness is constrained. Surface modification can boost hydrochar's adsorption capability and number of active surface groups [41].

### 3 Hydrochar production

Hydrochar can be synthesized by adopting the following techniques.

#### 3.1 Hydrothermal carbonization

HTC is a wet thermochemical process that ensures that water stays in the liquid state for a few minutes to many hours while being exposed to little or no oxygen. It takes place at elevated temperatures ranging from 180 °C to 300 °C under autogenous pressures above saturated pressures [42]. The reaction pressure is often autogenic, with the reaction temperature being matched by the saturation vapor pressure of water. The cleavage and hydrolysis of lignocellulosic biomass can be facilitated at elevated temperatures by water with a high ionization constant. Organic materials are hydrolyzed by water, which is further accelerated by acids or bases [37]. This method is advantageous for reducing the ash content too [43]. Waste may be processed via the hydrothermal carbonization procedure, which employs pressure and heat in the presence of water [44]. The utilization of wet feedstock with greater than 50% moisture content distinguishes HTC and eliminates the requirement for energy-intensive drying before or during the procedure [45]. An environmentally friendly technology is the HTC process. It uses heat to turn a wide range of biomass feedstocks into smokeless, high-carbon solid fuels [46]. The requirement of pure deionized water for experiments is one of the main limitations of hydrothermal processes [47]. By applying higher temperatures between 180 and 250 °C at elevated pressure ranging from 2 to 10 MPa for several hours, HTC of biomass and water are studied. Bergius and Specht were the first to introduce the HTC process. They made high-carbon material out of cellulosic material. In a sealed vessel, the cellulose and water mixture was heated to 250–310 °C. The solid with a lower O/C ratio was produced as a result, indicating that HTC was a successful conversion process [46]. Alkali metal concentration in biochar can be decreased using HTC regardless of pre-drying [48].

The aqueous medium's subcritical conditions are significant. It permits water to remain liquid beyond 100 °C and raises the viscosity coefficient when water's viscosity falls.

Additionally, several substances become more soluble than they would normally be, including aldehydes, alcohols, and cellulose. The HTC method is made more favorable by these factors [49].

Water properties can be altered beyond the critical point without causing a phase shift. Water functions as both catalyst and reactant at the critical point. From 25 to 300 °C, the  $K_w$  of water increases, facilitating aromatic heterolytic cleavage and acid–base reactions. Water's dielectric constant decreases as the number of ordered hydrogen bonds decreases. Thus, water is a good solvent for solvating organic molecules, which improves hydrolysis, elimination, and nucleophilic substitution, and leads to high reaction rates in a single phase. High diffusion coefficients and mass transfer are anticipated, since viscosity reduces as temperature rises [50].

One of the most promising technologies is hydrothermal processing, because it can make use of the high moisture content of biomass. The high moisture content must be removed for other processing methods like combustion and pyrolysis, requiring significant energy for drying processes. In contrast, the thermochemical method of hydrothermal conversion of biomass into synthetic solid, liquid, or gaseous fuels and chemicals in hot-compressed water is energy-efficient, scalable, and viable [51]. As a result, it produced process water—a liquid end product, a little quantity of gaseous product, and hydrochar, a solid product with increased energy density. The HTC conditions like type of feedstock, time, and temperature largely determined the degree of conversion. The hydrochar that was created had better energy density, drying performance, and dewaterability [52].

The treated solid residue from several experiments that used the hydrothermal process as a pretreat technique was used for further degradation. Since hydrochar is produced from organic biomass waste, one of its most common properties is the enrichment and recovery of carbon [53].

There are two ways for hydrochar formation: Through solid–solid conversion, which preserves the structural components and morphology of the original biomass, or through aqueous phase degradation of biomass followed by polymerization of organic molecules into a solid phase [54]. Breakdown of hemicellulose, cellulose, and lignin is brought on by these circumstances. The mixture is then restored into a solid substance. There are various steps to the mechanics of the hydrothermal conditioning process. First, the extractive material, hemicellulose, and cellulose are hydrolyzed. Aromatization, polymerization, condensation, decarboxylation, and dehydration come next [55].

At extremely low temperatures (180 to 250 °C), the HTC process uses dehydration and decarboxylation to minimize the amount of oxygen and hydrogen in the feedstock. Hydrothermal parameters that govern this process, such as residence temperature and time, dictate the degree

of coalification of the raw biomass and the intensity of the reaction [17].

Recently, HTC has been considered a different technique for transforming biomass into products with additional value [38]. This technique uses lower temperatures and lighter reactional conditions than other thermal conversion processes to produce a variety of products from diverse types of biomass and has been demonstrating its versatility [56]. HTC can use a variety of feedstocks as precursors, including simple natural biomass like shrub wood, bamboo, fecal sludge, and sweet potato waste as well as pure model components like cellulose, starch, sucrose and glucose [57]. Other types of biomass, such as spent coffee grounds, banana leaves, oil palm biomass, marine plastic debris, sawdust, food waste, cotton and viscose fibers, olive pomace, and algae, can be pretreated with hydrothermal carbonization in addition to sludge [55].

The biomass conversion is accomplished through a series of intricate reactions that are influenced by the water's physical properties. These properties are typically manipulated by varying the time, pressure, and temperature of the biomass and water to produce the desired products. HTC is able to produce liquid products containing inorganic and organic value-added chemicals as well as solid hydrochar, which has superior physicochemical properties to raw biomass feedstocks. When compared to dry torrefaction, HTC hydrochars have lower O/C and H/C ratios and produce more materials of the lignin or coal variety [51].

A significant amount of hydrothermal wastewater (HW), which has a diverse composition and chemical oxygen requirement of up to 10.1–31.1 g/L, is nevertheless produced by the HTC biomass process. To prepare biomass slurry as an HTC feedstock, several researchers have processed HW using it as the water supply. However, the HW's organic content would influence how the HTC reacted and how the char product behaved [58].

When compared to pyrolysis, the HTC is known to offer a number of advantages, including lower emission levels and energy consumption. After drying, feedstocks with high moisture content produce little solid material, making them insufficient sources for pyrolysis. Since HTC does not require the feedstock to be dried, it is possible to process a wider range of feedstocks into hydrochar [38].

The fact that the HTC technique does not require any prior drying or treatment is one of its main advantages. In fact, the existence of moisture is advantageous, since it fully eliminates the need for an energy-intensive drying procedure including an expensive phase change. This process uses less energy than other methods like gasification and pyrolysis, which provide equivalent final products. While leaving behind the more stable carbon particles, HTC enables the biomass structure to emit volatile oxygen-rich molecules, primarily CO<sub>2</sub> [42]. HTC produces more char and consumes less energy than pyrolysis is another advantage. This is in part because HTC operates at lower temperatures than pyrolysis and does not require the feedstock to be dried [38].

Co-hydrothermal carbonization (co-HTC) is a potential thermochemical conversion process that can overcome the limitations of hydrothermal carbonization with a single feedstock. The process of making hydrochar can address the issues of environmental pollution and energy crisis. Co-hydrochar's combustion, and chemical and physical characteristics are influenced by the method of manufacture, the conditions of the process, and the choice of raw materials. Co-hydrochar typically has a > higher heating value (HHV) and a lower H/C and O/C atomic ratio, which enhances combustion efficiency [59].

Hydrochar production by HTC is depicted in Fig. 1.

### 3.2 Hydrothermal liquefaction

The method of hydrothermal liquefaction (HTL) uses water to dissolve or breakdown the biomass's macromolecules

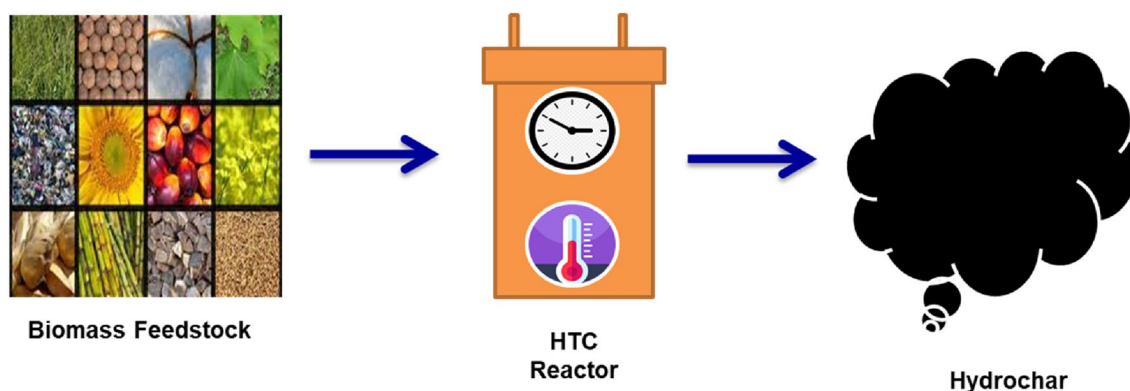


Fig. 1 Hydrothermal carbonization of biomass for hydrochar production

at elevated pressure and standard temperatures [60]. In the thermochemical process known as HTL, biomass is processed at temperatures between 200 and 374 °C while being subjected to high pressures between 5 and 20 MPa. The retention of considerable pressure keeps water as a liquid, because it vaporizes over 100 °C; this situation is referred to as subcritical [61]. HTL is especially suitable for moist feedstocks as the demand for drying is reduced because of the need of a wet reaction environment [62]. Likewise, the HTL process also generates a solid hydrochar, an aqueous phase, and a gas phase. It is crucial to characterize all of these additional products to identify an appropriate marketplace for them as to increase the economic viability of the HTL [63].

Under such conditions, sub-critical water maintains its liquid state and has unique properties like a lower dielectric constant. This property causes water to behave weakly polar and to be more soluble in organic molecules originating from biomass. HTL breaks down extremely reactive molecules, which then swiftly repolymerize to produce greasy compounds. Its liquid form is referred to as bio-oil. In contrast to other hydrothermal processes, HTL uses water as the catalyst and reaction media. HTL is therefore an ideal technique for biomass with high moisture content [60].

Hydrothermal liquefaction wastewater (HTLWW) is a byproduct of the HTL process in which 60–80% of the nutrients and 20–40% of the organic matter from the biomass are transported into the aqueous phase. HTLWW has a complex makeup that includes a variety of polymers, hazardous organics, such as a wide range of nitrogenous heterocyclic compounds, saccharides, benzene, phenols, and alcohols depending on the reaction circumstances [64].

Recent times have seen the emergence of fast HTL technology, which typically operates with an exceptionally high heating rate within a limited amount of time, i.e., 1–20 min. However, the majority of HTL operations were carried out in a micro-reactor without agitation. Alternately, most recent researches employed a novel self-designed external rotating system to guarantee an ample mixture throughout the rapid HTL process [65].

It is widely known that the yield and properties of the compounds greatly depend on the presence of a catalyst affixed in HTL process. For instance, homogeneous catalysts, such as sodium carbonate, were widely used in the catalytic HTL method, because they were more affordable, widely available, and coke-free than heterogeneous catalysts [65].

Pyrolysis and HTL, two different thermochemical processes that generate bio-oil and biochar, are controlled by the reaction temperature. The generation of bio-crude and its composition in HTL of biomass are influenced by the reaction conditions, because the ionic content of water varies

according to the temperature of the reactor, which speeds up various reactions [66].

In the research, little is known about the mechanisms of hydrothermal liquefaction. The three main phases in the HTL process are depolymerization, decomposition, and recombination. In short, biomass is broken down and depolymerized into smaller molecules. These substances might be quite reactive, thus polymerizing and producing bio-based solid, gas, and crude substances [67]. It also releases a minimal amount of gas and C/N/P piled up aqueous phase byproducts in addition to bio-crude [68]. Additionally, significant process variables, including breakup of the components, condensation, repolymerization process, retention time, and temperature, from various steps might change correspondingly. Because biomass is a strange combination of lipids, proteins, lignin, and carbohydrates, the mechanism and reaction chemistry of biomass liquefaction are likewise intricate [67].

To produce biochar, bio-oil, and gaseous materials, biomass is subjected to depolymerization reactions, such as repolymerization, aromatization, deoxygenation, dehydration, hydrolysis, and fragmentation under these conditions. The kind of biomass and HTL operating conditions affect the final products' yield [61]. According to the temperature regime, two competitive reactions like hydrolysis and repolymerization have different dominances over one another. For example, at low reaction temperatures, hydrolysis predominates repolymerization, whereas at high temperatures, repolymerization tends to take over or compete directly with hydrolysis [66].

In the water-driven depolymerization procedure known as HTL, pressurized hot water is employed as a catalyst and reactant. This process converts the biopolymeric structure into byproducts like solid, liquid, and gas phases in a confined, oxygen-free environment. When compared to fast pyrolysis oil, HTL crude bio-oil is often more stable, has lower oxygen and moisture levels, and has a better calorific value and energy density. Carbon dioxide makes up more than 80% of HTL's gaseous products, with smaller amounts of styrene (C<sub>8</sub>H<sub>8</sub>), toluene (C<sub>7</sub>H<sub>8</sub>), benzene (C<sub>6</sub>H<sub>6</sub>), ethylene (C<sub>2</sub>H<sub>4</sub>), ethane (C<sub>2</sub>H<sub>6</sub>), methane (CH<sub>4</sub>), hydrogen (H<sub>2</sub>), and carbon monoxide also present (CO) [69].

Moreover, char produced by HTL has demonstrated significant possibilities for use in heterogeneous catalysts and a variety of industrial uses including nutraceuticals, food, cosmetics, organic fertilizer, livestock feed, pigment, and chemicals. HTL can be used as an economically sound substitute for the traditional thermochemical conversion of biomass to produce liquid biofuels from feedstocks with high water amount of water. HTL has several merits over other thermochemical conversion techniques, but its main benefit is that it skips the costly and time-consuming pre-drying stage [70].

The thermochemical transformation process known as hydrothermal liquefaction of microalgae is a potential technique for the generation of bio-crude oil. Excellent energy efficiency along with reduced processing energy costs as a result of eliminating wet biomass drying stages are two advantages of this technique. When algal biofuels are produced via the HTL method, an adequate amount of remnants are also produced as byproducts, which are referred to as hydro or biochar. The total economics of producing algal biofuel will improve with the proper use of the hydrochar produced by the HTL process [71].

To enhance the process efficacy and reaction conditions, recent research has concentrated on employing co-solvents or reactive organic solvents in place of water in the HTL process. Due to its weaker polarity, organic solvents like ethanol have substantially lower critical pressures and temperatures than water [71].

HTL process is detailed in Fig. 2.

### 3.3 Hydrothermal gasification

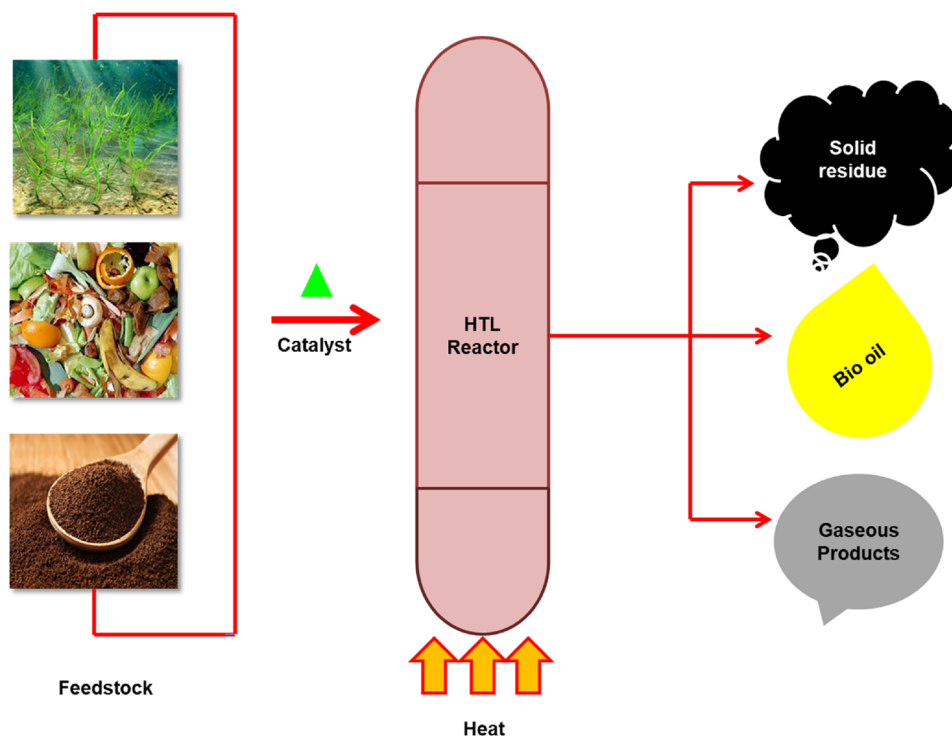
A favorable thermochemical technique called hydrothermal gasification uses pressurized hot water to break down carbon-rich biomass into its primary byproducts, which include trace amount of higher hydrocarbons, carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and hydrogen (H<sub>2</sub>). The generated gas may be utilized as a source of heat or treated more to yield hydrogen-rich gas products. Lesser quantities of hydrochar were produced as a result

of the higher rate of biomass disintegration under supercritical water conditions [28]. Because of its ability to use wet biomass and a comparatively low-temperature hydrothermal gasification is the most promising, since it exhibits energy and cost-efficiency. Both subcritical and supercritical water gasification occur during hydrothermal processes. At supercritical circumstances, water takes on the characteristics of a non-polar solvent, dispersing the biomass particles to overcome the problems caused by inefficient mass and heat transfer as well as viscosity. Additionally, hydrothermal gasification exhibits liquid-like density and gas like viscosity of supercritical water, which results in greater solubility and effective transformation of biomass into gases [72].

### 3.4 Microwave-assisted hydrothermal carbonization

In microwave pyrolysis method, biomass is thermally broken down into its components in a low-oxygen, inert environment. Electromagnetic radiation having a frequency between 300 MHz and 300 GHz and a wavelength between 1 and 1 mm is known as microwave radiation [73]. Due to the resistance between molecules that emerges from the association with electromagnetic field, microwave heating is typically mentioned to as dielectric heating. Therefore, the ability of the material to be scorched by microwave relies on both its capacity to absorb and retain energy as well as its ability to radiate this energy as heat. Substances with strong interactions with microwave due to their dielectric

**Fig. 2** Hydrothermal liquefaction process





characteristics are referred to as absorbers. The more polar and mobile the components of biomass are, the better they will absorb microwave [74].

In contrast to conventional heating systems, microwave-assisted heating systems have gained popularity recently because of their benefits and characteristics. Conventional heating seems to have a number of drawbacks, including heat dissipation, long retention time, and lower yield from unwanted side reactions. Microwave heating results in a higher molecular heating level and can also raise the ambient temperature uniformly. As a result, microwave heating does have an increased processing rate, resulting in a shorter retention time with less energy use. Additionally, compared to traditional heating, the high heating value and calorific value of hydrochar produced by microwave heating is larger [75]. Microwave heating permits quicker and more homogeneous heat transfer via dipole rotation and ionic conduction with a lower energy loss than traditional heating by means of convection and conduction, which considerably shortens the time of reactions and extractions without sacrificing the simplicity of control [76].

In contrast to the traditional hydrothermal technique, microwave irradiation provides both uniform and rapid heating procedure that can drastically save time, cost, and maximize hydrochar yield [77].

The ability of microwave irradiation to heat molecules at the molecular level, results in uniform and rapid thermal reactions, has recently caught the interest of chemists. To ensure complete purity of the char, the thermal conversion of the biomaterial needs to be heated uniformly. To lower production costs, the heating procedure should also be quick. The biomaterials may be heated quickly and uniformly across the bulk using microwave heating [78]. Internal and external surfaces of the reaction vessel can both be heated by microwaves at the same time [79]. Additionally, the carbon could be recycled and used repeatedly thanks to microwave technology. This method does not harm the

carbon; instead, it increases the surface area, which makes it easier for contaminants to adhere and improves the value. The fundamental contrast between conventional heating systems and microwave devices is how heat is produced. In the first method, the carbon bed is heated by convection or conduction, while the heating element is located outside the vertical furnace or rotary kiln where thermal regeneration is typically carried out [78].

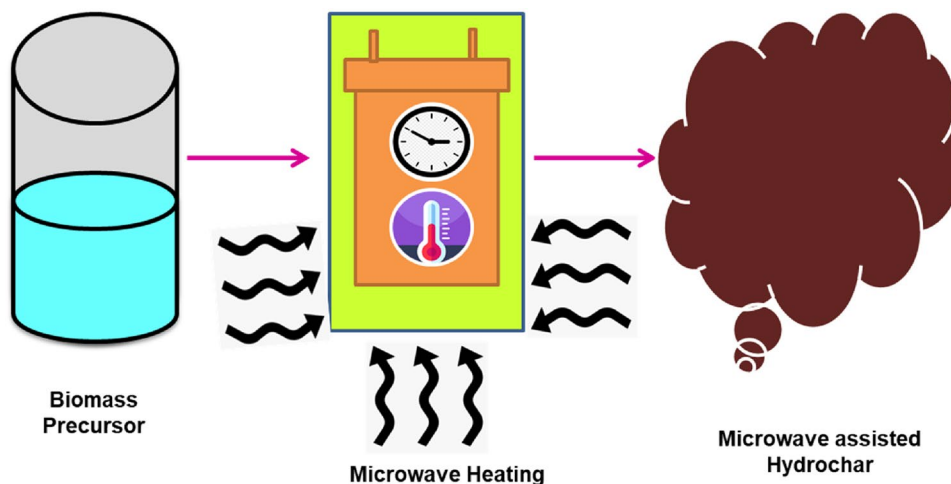
Recent times have seen the application of microwave heating in association with the HTC method to treat diverse biomass, including cow dung, algal biomass, and lignocellulose [80]. HTC in a microwave technique was optimized for the generation of hydrochar from waste seaweed. Utilizing microwave technology to create hydrochar from discarded seaweed may be an energy-efficient way to create hydrochar that meets the same standards as hydrochar created using more traditional heating techniques [81].

Hydrochar production using microwave-assisted technique is depicted in Fig. 3.

#### 4 Reaction mechanism of hydrochar

HTC reaction's first stage is hydrolysis, which involves the reaction of water with cellulose, hemicellulose, or extractives to break ether bonds primarily  $\beta$ -(1–4) glycosidic bonds and ester. As a result, a variety of products are developed, such as soluble oligomers like oligo-saccharides from hemicellulose and cellulose. While cellulose hydrolysis begins at temperatures above 230 °C, hemicellulose begins to hydrolyze at HTC temperatures above 180 °C. It is possible for cellulose to break down into oligomers, which can hydrolyze into fructose and glucose. In hydrothermal media, other elements such as extractives—monomeric sugars mostly fructose and glucose as well as different phenolic glycosides, oligomeric sugars, aliphatic acids, and alditols are highly reactive. At 260 °C, a very

**Fig. 3** Microwave-assisted hydrothermal carbonization



minor amount of lignin reacts and produces phenol and its derivatives. At temperatures between 200 and 260 degrees Celsius, inorganic components are relatively stable and will likely not change; hence, the breakdown of polymeric components could cause inorganics to leak out of the solid mass and into the solution [82].

Hemicellulose breaks down during HTC, resulting in high-molecular-weight oligo-saccharides, pentoses (compounds with five ring members), such as hexoses and xylose (compounds with six ring members), such as fructose and glucose. Hexoses are also produced when cellulose decomposes. Through dehydration, intramolecular cyclization, recombination, C–C-bond cleavage, and ring-opening monosaccharides become hydroxy methyl furfural (HMF) and furfural, which are reactive intermediates. Retro-aldol condensation reactions lead to the formation of ketones. Closed-chain compounds are directly dehydrated to produce acids. Hydrochar microstructures are created when furfural and HMF are polymerized. Through solid–solid conversion, insoluble lignin, a fraction of cellulose and hemicellulose that has not been hydrolyzed, forms the hydrochar network [19].

## 5 Role of water in HTC

For ions to move from one bond to another, water is both a necessary solvent and an effective transition media. Moreover, it randomly connects and disconnects the weak chemical bonds from one substance to another. Water is an essential component of the HTC process, because it reacts with the biomass structure to change its structure. Additionally, water behaves differently under subcritical conditions compared to water under ambient conditions. Organic chemicals are easily miscible with water at a subcritical environment. Due to the polymeric and rigid nature of lignocellulosic materials, there is a greater propensity for the breakdown of lower molecular weight organic compounds, including COOH and OH bonds, which eventually cause these compounds to become miscible with water [83]. Due to its low cost, safety, and inherent presence in wet biomass, water is used as a reactive medium in the HTC process. Water can also be used in place of hazardous solvents and reactive substances [84].

The liquid mixture used in the HTC process is referred to as volatile liquids. The ionization constant is another distinctive feature of subcritical water. The high range of the ionization constant indicates that there are many  $H^+$  and  $OH^-$  ions present under subcritical conditions. In this circumstance, the hydrolysis of lignocellulosic materials can be accelerated by an in-situ acid- or base-catalyzed reaction [83].

## 6 Process parameters/ variables

Various process variables influencing the formation of hydrochar is depicted in Fig. 4.

### 6.1 Temperature

The HTC process relies greatly on temperature, since it supplies energy needed to heat and break down the biomass particles. The efficiency of biomass conversion grows with temperature because of the rise in energy supply by temperature [42].

Temperature is a key factor in the HTC process, since it directly influences the water characteristics that lead to ionic interactions in the subcritical zone. Above the critical point, the reaction mechanism in the supercritical water area changes from ionic to free-radical processes. Anyhow, a rise in temperatures alters the viscosity of the water in HTC processes where ions are the dominant factor, making it easier to permeate porous media and accelerating the decomposition of biomass. Additionally, when the temperature exceeds the activation energy, bond breakage in biomass macromolecular organics begins [17]. Condensation, decarboxylation and dehydration occur when the temperature crosses the activation energy. The process resembles pyrolysis when temperatures are too low. While less oil and gas are produced at higher temperatures, solid hydrochar

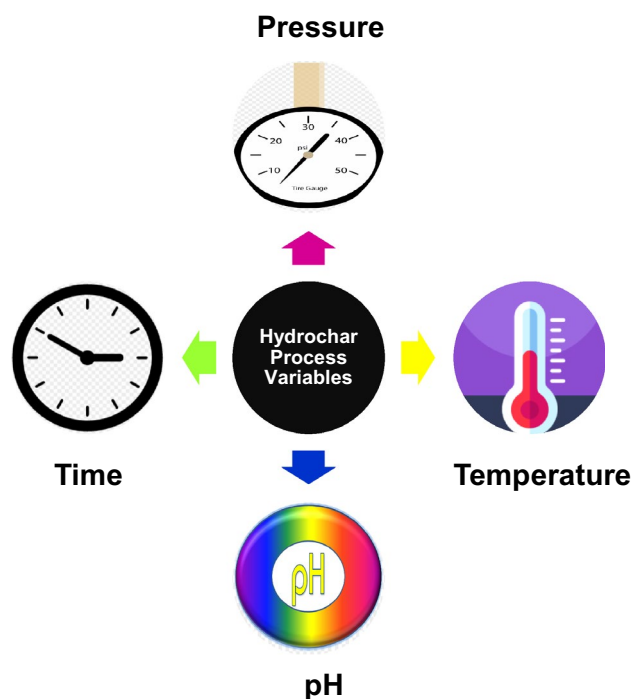


Fig. 4 Process parameters influencing hydrochar formation

yields are primarily increased. The link between temperature and the H/C and O/C ratios of biomass degradation is well shown in the Van Krevelen diagram [33].

Temperature below 250 °C is ideal for the production of char, moderate temperatures until 375 °C is preferred for the production of oil and temperatures beyond 375 °C mostly produce gas. Furthermore, gasification can occur at temperatures higher than 375 °C. Temperature is another factor that affects the quantity of biomass compounds that can be hydrolyzed. At 180 °C, hemicellulose completely hydrolyzes, while cellulose does so at roughly 220 °C. In contrast to the monomers reaction that takes place during the homogeneous reaction when the temperature is inadequate to split apart the biomass's basic constituents, pyrolysis-like processes are more likely to happen at lower temperatures. Contrary to solid–solid conversion, using high temperatures with enough time duration may result in large degree of subsequent conversion and intermediate dissolution by polymerization, generating secondary char, which predominates the process of hydrochar generation [42].

## 6.2 Residence or retention time

Biomass conversion via hydrothermal processes is comparatively a sluggish process [85]. HTC residency period might last anywhere between a few minutes and a few days. However, reaction time only influences the hydrolysis processes to a certain time window, after which it has no discernible effect on the process. In general, it is noted that larger amounts of solid product are produced during longer reaction times. Both the product composition and the total amount of biomass converted are determined by reaction duration. The rate of biomass decomposition and hydrolysis are both relatively quick in supercritical circumstances [46].

The residence duration of the hydrothermal reaction is one of the crucial factors in the formation of carbon-rich materials. Residence time affects the recovery of solid products, but on comparison with temperature, its impact is much less. The amount of solid hydrochar produced depends directly on residence time. Large amounts of solid hydrochar are produced when the retention period is short, while limited portion are created when the retention time is lengthy [83].

## 6.3 Pressure

Another factor in the breakdown of biomass is pressure. Pressure preserves single-phase media for liquefactions that are both sub- and supercritical. This single-phase liquefaction is crucial to avoid the large enthalpy inputs required for the phase transition of solvents. Two-phase systems need a lot of heat to keep the system at the right temperature, which led to the invention of supplementary hydrochar

using polyaromatic structures. Maintaining pressure beyond the critical pressure of the media will control the amount of hydrolysis and biomass dissolution, which might also enhance favorable reaction pathways thermodynamically for the production of liquid fuels or gas. Additionally, pressure raises solvent density. Molecular components of biomass are effectively penetrated by high-density medium, which enhances extraction and decomposition [86].

Isotropically, the pressure inside the reactor rises as the temperature does. Internal gravitational forces and natural convection forces that take place during heating are the two main factors that affect how materials are distributed within the reactor. The pressure within the reactor can be raised by enhancing the temperature or by introducing nitrogen. The Le Chatelier concept is applied inside the reactor. Thus, to retain the equilibrium at mounting pressure, the reaction equilibrium switches among the solid and liquid phases, which have less moles. This can be confirmed, since at increasing reaction pressures, condensation and polymerization reactions are claimed to rise concurrently with a reduction of dehydration and decarboxylation processes. The method generates gases, which are compressed and disintegrated into water to offer a wider access to the fluid stage. Rise in pressure also makes it easier for hydrogen ions to exchange [42].

## 6.4 pH

According to some studies, the pH level has fallen as a result of generation of organic acid in HTC process. To catalyze the breakdown of bio-macromolecules and the production of hydrochar during the hydrothermal reaction, organic acids play a vital transitional role. As a result, pH changes during the HTC process have an impact on the characteristics of hydrochar. During the hydrothermal process, it is commonly considered that the generation of organic acids from the biomass, such as formic acid, levulinic acid, and lactic acid, is auto-catalytic, and causes a pH reduction. The hydrothermal reaction process can be accelerated or changed to produce the desired hydrochars by adding acid or alkali as a catalyst. This causes a surge in protons or hydroxide-ions and a high ionic strength [83].

## 6.5 Feedstock–water ratio

The ratio of feedstock to water in the HTC process is yet another critical element. While a reduced water content during HTC could lead to an uneven distribution of temperature within the reactor, a higher water level during HTC favors biomass breakdown, comparable to the hydrolysis reaction. Additionally, water content and feedstock loading affect the hydrochar's quality. Biomass can be treated with HTC to create energy-dense hydrochar, which can then be pelletized

to create fuel pellets. The fuel pellets can be utilized in coal power plants or for home heating [87].

## 7 Hydrochar composition

With only trace amounts of S and N<sub>2</sub>, hydrochar is mostly composed of C<sup>o</sup> and O<sub>2</sub>. The rate of deoxygenation, condensation, and aromatization increased at extreme temperatures, while the amount of N<sub>2</sub> and S content of the hydrochar was barely altered. It showed that the atomic ratios of H/C and O/C in hydrochars were less compared to those found in the feed due to reactions caused by the production of water and carbon dioxide during HTC. The H/C and O/C atomic ratios of hydrochar often declined with temperature. Low H/C and O/C atomic ratio fuels have the benefits of less energy losses, water vapor, and smoke [88].

## 8 Hydrochar activation methods

Modification of hydrochar can be done, as shown in Fig. 5

### 8.1 Physical activation

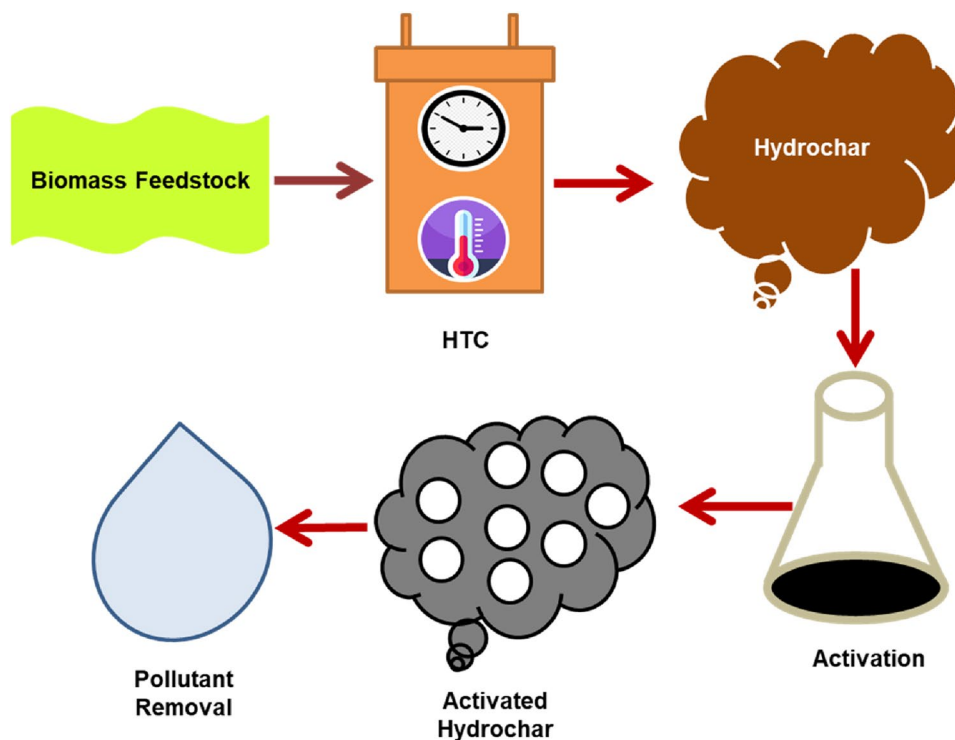
Using a variety of the gas flow type, air, steam, and carbon dioxide or a mixture of the above with further gas varieties like nitrogen or carbon monoxide, physical activation is a high-temperature process that lasts for several hours under

a gas flow. Microwave heating could be used to help in the heating process [89].

### 8.2 Chemical activation

The process of chemically activating biomass or char involves impregnating the material with a chemical activator, charring it for 1–24 h in the absence of O<sub>2</sub> at temperature ranging between 500 and 800 °C, and then washing the calcined material in H<sub>2</sub>O and HCl to eliminate the activator. Various chemical agents, including potassium hydroxide, zinc chloride, orthophosphoric acid, potassium carbonate, sodium hydroxide, ferric chloride, sodium carbonate, and sulphuric acid, have been investigated in papers. The intercalation of ions into the carbon matrix, aromatization, and dehydration are some of the primary processes that are expected to happen during chemical activation. It must be mentioned that hazardous reagents are frequently used in considerable quantities during chemical activation. On contrast with physical activation, chemical activation offers many advantages, including lower operating temperatures, but there are also significant drawbacks, including the need for additional washing [89].

Fig. 5 Hydrochar modification



## 9 Functionalization of hydrochar

One of the simplest methods for altering the features of hydrochar is through hydrochar functionalization, which involves exposing its organic surface to particular functional groups. Adding acid groups like  $-\text{COOH}$  or  $\text{SO}_3\text{OH}$  to hydrochar is a typical modification technique that makes it suitable as a solid acid catalyst for the production of biofuel or cellulose hydrolysis. This approach involves joining acid groups with carbon atoms on the amorphous carbon layer of the hydrochar formed to produce carboxyl, hydroxyl, or phenolic groups on the surface of the solid acidic catalysts [28]. Existence of hydrochar's surface functionalities can be utilized to make it easier to add catalytic species to the carbon-based solid [90].

## 10 Hydrochar vs biochar

The method of producing hydrochar from biomass is called hydrothermal carbonization. Rather than drying conditions, hot-compressed water is used in this procedure to treat the biomass. The HTC technique provides a number of benefits over the conventional dry-thermal pre-treatments that produced the biochar. Both procedures produce char, but the physio-chemical characteristics of the char differ noticeably, and these differences have an impact on the char's ability to be used for common tasks including removing wastewater contaminants, enhancing soil, and producing bioenergy. The HTC processes' reaction mechanisms demonstrated how valuable hydrochar is and how it outperforms biochar. This is due to the lower alkali metals and alkaline earth concentration that it has [8].

## 11 Hydrochar applications in various fields

### 11.1 Heavy metal adsorption

Any metal with an atomic weight between 63.5 and 200.6 with a specific gravity greater than 5.0 is referred to as a heavy metal [91]. The environmental issue is due to the existence of inorganic metal in the environment as a result of industrial processes like Cr and Ni coating, etc. These pollute the groundwater as well as the earth's aqueous system. The hazardous metals include Ni, Mn, Zn, Hg, Cd, Pb, Cu, and Cr. These metals have an adverse effect on humans and can lead to poisoning. Heavy metals are found in a variety of forms both in aqueous and food system [92].

Heavy metals have been produced as a result of many human environmental activities, and because they cannot

degrade, they have accumulated in the environment. The standard concentration limit for Cr, Mn, Fe, Ni, and Cu in water is 0.05, 0.5, 0.2, 0.02, and 2 mg/L, respectively, as determined by the World Health Organization (WHO) [7]. Heavy metal elimination is also important for overall health, because they are carcinogenic, teratogenic and lead to negative medical issues [93]. In comparison to dyes, heavy metal ions are more hazardous, non-degradable, and have good solubility and mobility in aqueous effluents. Furthermore, even at extremely low concentrations, heavy metal ions are very hazardous [94].

Chromium is a metal that can be hazardous and cancer-causing that results from human activities [95]. Lead is frequently found in wastewaters let out from smelting, mining, pesticides, and paint industries [96].

The impact of  $\text{H}_2\text{O}_2$  addition on hydrothermally generated biochar (hydrochar) from peanut shell for eliminating aqueous heavy metals was investigated by Yingwen Xue and co-workers. Characterization tests revealed that the hydrochar surfaces had more oxygen-containing functional groups, notably carboxyl groups, after  $\text{H}_2\text{O}_2$  alteration. The altered hydrochar therefore demonstrated improved lead sorption capability, with a sorption rate of 22.82 mg/g [97].

To examine the responses of zinc and cadmium, *Sedum alfredii* was hydrothermally converted at temperatures between 210 and 300 °C using various solvents such as HCl and water, and the properties and prospective uses of the resulting hydrochars were investigated. The removal of zinc and cadmium from the solid phase was aided by the incorporation of HCl and low temperature. At 210 °C and with HCl present, the greatest removal efficiencies of zinc and cadmium were 89.3% and 95%, respectively [98].

Huijuan Song reported on an effective method for HTC of sunflower straw (*Helianthus annuus* L.) for getting rid of heavy metals. Examined was the impact of various HTC temperatures and HCl additive concentrations on the effectiveness of heavy metal removal. According to the findings, raising the HCl concentration or temperature during HTC facilitated the transfer of heavy metals from hydrochar to liquid products. After hydrothermal conversion at a temperature of 200 °C and 2% HCl, up to 87% of Pb, 94% of Cu, and 99% of Zn and Cd were removed to the liquid products. When the temperature was raised from 160 °C to 280 °C, the species of heavy metals in hydrochars changed from unstable to stable [99]. Table 1 denotes the rejection of heavy metal from aqueous solution by employing hydrochar from biomass as feedstock by employing HTC.

### 11.2 Dye adsorption

Due to their ability to produce color, synthetic dyes are indeed a prerequisite in many important industries, including textile, paper, and leather sectors. An estimated one hundred

**Table 1** Rejection of heavy metals and its adsorption capacity

S no	Feedstock	Location	HTC temperature (°C)	Residence time (h)	Heavy metal evacuated	Initial concentration (mg/L)	Hydrochar dose	Q <sub>max</sub> (mg/g)	Refs
1	Pine Sawdust	Xingtai, Hebei Province, China	180	12	Cu(II) Zn(II)	10–100	25 mg	214.7 227.3	[100]
2	Sawdust Wheat Straw Corn Stalk	Suburb of Tianjin, China	200	20	Cd(II)	20	2 g/L	30.40–40.78	[101]
3	Avacado Seed	–	250	12	Ni <sup>2+</sup>	0.1–8.5 mmol/L	2 g/L	0.12–0.35 mmol/g	[102]
4	Eucalyptus Sawdust Corn Straw Corn Cob	Dalian, China	220	–	Cr(VI)	100	0.1 g	34.07 30.15 29.46	[103]
5	Pine Wood	–	300	4	Pb(II)	75 100 125	50 mg	46.7	[104]
6	Corn Straw (HC) Corn Straw (H <sub>3</sub> PO <sub>4</sub> -HC) Corn Straw (PEI-HC)	Harbin, China	240	2	Pb(II)	20	10 mg	32.67 353.4 214.0	[105]
7	Sawdust	Beijing Suburb	260	2	Pb(II)	10	–	92.80	[106]
8	Corn Cob	Beijing, China	300	0.5	Cr(VI) Ni(II)	20 50	0.05 g	33.663 29.059	[107]
9	Bamboo Powder	Li'an City, Zhejiang Province, China	200	24	Cu(II)	40–220	40 mg	140.65	[108]
10	Pinecone	Harbin, Heilongjiang province, China	200	5	Cd(II) Pb(II)	–	–	62.49 149.33	[109]
11	Corn Straw	China Agriculture University	200	30 min	Zn(II) Cu(II)	50 20	50 mg	207.6 56.1	[110]
12	Phytolacca acinosa Roxb	Xiangtan City, Hunan Province	180	8	Cd	–	–	246.6	[111]
13	Crocus sativus petals	Evar, Khorasan Razavi province	180	11.5	Pb(II)	100	50 mg	89.52	[112]
14	Seaweed	Talty's in Lisycasey, Co. Clare, Ireland	200	60 min	V(V)	25	50 mg	12.3	[113]
15	Mango Peels	Sindh, Pakistan	200	5	Pb(II)	100	30 mg	38.31	[114]

thousand commercially available dyes are used to produce seven hundred thousand tons of varied colors every year. Most dyes are frequently thrown into environmental water bodies after they have served their purpose. More than half of the dyestuffs which are currently found in the environment across the globe is from the textile sector, which discharges the most of them about 54%. Although the precise quantity of dyestuffs released into the environment by each

company is unclear, but it can be estimated that the amount is sufficiently huge to pose a serious environmental concern [115].

Organic dyes are teratogenic, mutagenic, cancerous, and extremely poisonous and their spontaneous discharge inside the habitat can result in major environmental problems along with health risks for people and other living things. Therefore, it is vital to remove colors effectively and economically

before discharging dye effluent. Because of its considerable OFG on the surface, high porosity structure, and well-developed surface area, hydrochar is acknowledged as an effective substitute for the elimination of organic dyes from wastewater [116].

Malachite green (MG) is used as a pollutant to assess the adsorption capability, while pine and peanut shell serve as base materials to make effective sorbents. Sorption tests were conducted with different operational parameters, such as contact duration, interfering ions, and pH. Results indicate that enhancing the surface hydroxyl functional groups of adsorbents by a single-step alteration with ethanol and NaOH is a successful chemical modification. Sorbents developed from HTC with chemical modifications have the best sorption efficiency; the  $q_e$  of altered hydrochar made from pine and peanut shell is as high as 562.2 and 570.34 mg/g. Adsorption kinetics and isothermal studies show that the majority of the sorption activity takes place on the surface of sorbents, and that chemical adsorption is the dominating method for removing MG as a consequence of the augmentation of surface hydroxyl functional groups by chemical modification [117].

Hydrochar as sorbent for the elimination of dye from aqueous systems and their associated parameters are depicted in Table 2.

### 11.3 Emerging contaminants

Emerging contaminants (ECs) are substances that are present in the environment but whose presence and effects have only lately been detected. Engineered nanomaterial's, industrial compound, such as metabolites and degradation products, food additives, veterinary products such as hormones, herbicides, and pharmaceuticals and personal care products, are just a few of the many contaminants that fall under the category of ECs [136]. The usage of pesticides has been recommended because to its high efficacy and quick results. These substances are becoming more and more common for managing and boosting crop yields to attain outstanding results [137].

One of the humanity's biggest scientific advances over the past century has been the development of antibiotics, which have transformed how bacterial infections are treated by either killing or limiting the growth of microbes and saved countless lives. However, in the last few years, a specific health concern has been the increase of antibiotic residues in water bodies [138].

Isothiazolinones have been utilized as antimicrobials in a variety of industries, including paint and sunscreens, cleansing products, household products, and cosmetics. These chemicals are widely used; however, disinfection preservatives may build up in living spaces or even in people, which

can be hazardous to human health. Skin sensitization risks might arise from isothiazolinone at high dosages [139].

Studies have shown that these ECs are commonly and extensively present in effluents and surface water. Particularly, the use of hydrochars in the rejection of contaminants has caught the interest of many scientists because of their affordability and effectiveness [136].

One of the most popular methods used globally to remove water impurities is active carbon adsorption, which is very effective and has a straightforward operational design. However, the materials employed have a significant impact on the efficacy of its usage as a carbon source. Due to the growing need for activated carbons, hydrochars made from HTC of biomass resources, including as crop residues, can be transformed into excellent activated carbons, a higher value-added product, which can be used to clean polluted waters [140]. Activated hydrochars for eliminating ECs from aqueous solutions are portrayed in Table 3.

### 11.4 Electrochemical applications

Fortunately, studies have shown that hydrochar is a valuable material for electrochemical devices like batteries and supercapacitors. Batteries and supercapacitors both provide energy, with batteries offering a high energy density and supercapacitors a high power density [151]. For use as supercapacitor electrode materials, transition metal oxides, carbon materials, and electronically conducting polymers are being closely examined. Pseudocapacitance and electrical double layer capacitance are responsible for the majority of the capacitance in carbon materials and transition metal oxide electrodes, respectively. Hydrothermal carbonization of biomass and carbohydrates yields functional carbonaceous materials. Surface functional groups can be found in varying amounts in hydrothermal carbon [152]. As a result of its stability, aromaticity, porosity, polarity and smaller surface area, hydrochar has drawn interest for these applications [28]. Role of hydrochar for supercapacitor applications is shown in Table 4.

### 11.5 Soil amendments

Hydrochar application in the soil, however, could have a positive or negative impact on crop yield. The hydrochar's greater surface area and porosity increase soil activity by providing the soil organisms with adequate aeration, water, and minerals that guard against contagious diseases. Due to the lack of significant polar functionality on its surface, newly formed hydrochar generally exhibits a hydrophobic character. Moreover, over time, after being incorporated into the soil, the hydrochar oxidizes through interaction with atmospheric oxygen, becoming more hydrophilic and

**Table 2** Hydrochar and its associated parameters for dye removal

S. no	Biomass source	Location	Dye type	pH	Time	Q <sub>max</sub> (mg/g) or % removal	Concentration (mg/L)	Refs
1	Pinewood	–	Methylene Blue	7	3 h	86.7	0–400	[104]
2	Sludge	Japan	Methylene Blue	> 8	–	63.3 (Physical activation) 122.4 (Chemical activation)	100	[118]
3	Rattan Furniture waste	Nibong Tebal, Penang, Malaysia	Methylene Blue	7	8 h	359	25	[119]
4	Bamboo	Lin'an City, China	Methylene Blue	7	24 h	655.76	300	[120]
5	Waste Shrimp Shell	Wenzhou City, Zhejiang Province, China	Methyl Orange	4	300 min	755.08	50	[121]
6	Coffee Husk	Buon Ma Thuot City, Daklak Province, Vietnam	Methylene Blue	7	2 h	415.8	50–500	[122]
7	Quercus coccifera	Akkent	Basic Red 18	10	60 min	–	50–455	[123]
8	Coconut Shell	Nibong Tebal, Penang, Malaysia	Methylene Blue	3–11	24 h	200.01	25–250	[124]
9	Chikpea Stem	Siirt in Turkey	Methylene Blue	2–10	90–180 min	96.15	40–80	[26]
10	Bamboo Shoot Shell	Xiangtan City	Rhodamine B	–	20 min	85.8	2–300	[125]
11	Salix psammophila	–	Malachite Green	7	24 h	476	500	[126]
12	Rice Straw	Nanchong, Sichuan Province, China	Methyl Orange	6.7	24 h	849	200–1000	[127]
13	Bamboo	Zhejiang Province Anji County, China	Congo Red 2-Naphthol	–	–	90.51 72.93	–	[128]
14	Cow Bones	Kupang, Nusa Tenggara Timur, Indonesia	Methyl Red	6	30 min	7.2	60	[129]
15	Tannin-based sludge	Maringa, Parana, Brazil	Methylene Blue	10	240 min	808.83	50–2800	[130]
16	Betel Nut Husk	–	Methylene Blue	6.7	6 h	324.4	25–250	[131]
17	Pomegranate Peels	–	Basic Red 46	–	5 min 60 min	286.90 367.72	–	[132]
18	Laurel Leaves Watermelon Peels	–	Reactive Red 180 Basic Red18	4 6	60 min	99.8% 98.8%	100	[133]
19	Wheat Straw	Vicinity of Sanandaj City, Kurdistan Province, Iran	Rhodamine B	6	90 min	80	5	[134]
20	Arabic coffee ground Olive oil cake	–	Methylene Blue Crystal Violet	7	15 min	76–90% 50–70%	50–200	[135]

developing carboxylic and phenolic functional groups on its surface [28].

Global climate, ecosystem sustainability, and agricultural production are all seriously threatened by increased soil degradation. One of the most vital and practical methods to bring down greenhouse gas emissions, enhance carbon sequestration, boost crop productivity, and enhance soil quality is to add-on soil organic carbon. Current findings have shown that hydrochars can also be useful multipurpose soil additives. Hydrochar utilization for soil amendment is

highly dependent on HTC conditions and feedstock [167]. The use of hydrochar as an organic growth medium for vegetable seedlings in gardening and horticulture, or as a soil amendment, is one of the potential uses for this material that is gaining interest. Using hydrochar in both situations, the potential for arable land to sequester carbon is increased and greenhouse gas emissions may be reduced [20].

Sandy soil's ability to retain water is improved with the addition of hydrochar. Applying hydrochar to the soil decreases its density and enhances the size of its pores,



**Table 3** Activated hydrochars for the evacuation of ECs and its adsorption capacity

S. no	Biomass source	Location	ECs concentrated	Activating agent	Equilibrium time	Kinetic fit	Q <sub>max</sub> (mg/g)	Refs
1	Sludge	PSPD Kovai Uni	Diclofenac	KOH	15 h	Pseudo-Second Order	37.23	[141]
2	Peach Stones	–	Caffeine	H <sub>3</sub> PO <sub>4</sub>	480 min	Pseudo-Second Order	68.39	[142]
3	Sucrose	–	Ibuprofen	–	360 min	Pseudo-Second Order	95.6	[143]
4	Brewers Spent Grain	–	Acetaminophen	KOH	240 min	–	165.94	[144]
5	Argan Nut Shell	Southeast Morocco	Caffeine Diclofenac	H <sub>3</sub> PO <sub>4</sub>	60 min 90 min	Pseudo-Second Order	210 126	[145]
6	Prunus serrulata bark	South of Brazil	Atrazine	H <sub>2</sub> SO <sub>4</sub>	240 min	Elovich model	63.35	[146]
7	Rice Husk	Nan province, Thailand	Atrazine	KOH	20–60 min	Pseudo-Second Order	4.06	[147]
8	Shrimp Shells	Qingdao, China	Tetracycline	HCl	36 h	Pseudo-Second Order	229.98	[148]
9	Flax Shives Oat Hulls	Saskatchewan, Canada	Carbamazepine	H <sub>3</sub> PO <sub>4</sub> NaOH	12 h	Sips model	293.5 162.6	[149]
10	Magonia pubescens–Sapindaceae	Brazil	Bisphenol A	Water Vapor	240 min	Pseudo-First Order	21.26	[56]
11	Banana Peel	–	Ethoprophos Terbufos Diazinon	–	20–240 min	Pseudo-Second Order Intraparticle Diffusion Model	3.19 3.07 3.19	[150]

permitting the soil to hold more water. Hydrochar can be used as a fertilizer for soil; however, its physicochemical properties and resistance to microbial decay rely on HTC working conditions and precursor. The use of hydrochar as a soil supplement, however, has been shown in a number of studies to affect plant growth in both favorable and unfavorable ways, depending on the type of plant and soil [168].

### 11.6 Greenhouse gas emission

Biochar is a well-known resource for carbon sequestration for preventing climate change, since pyrolysis changes biomass into a more durable form. Similar uses may be made with hydrochar if it is found to be similarly recalcitrant. Researchers have examined at the fluxes of greenhouse gases in soil, including nitrous oxide, carbon dioxide, and methane. It has frequently been discovered that hydrochar is less powerful to biochar at reducing climate change, because it is less stable in soils. In contrast to unaltered soil, hydrochar was shown to reduce nitrous oxide emissions while increasing ammonia, carbon dioxide, and methane emissions from soil [38].

### 11.7 Carbon sequestration

The technique of sequestering and trapping carbon is known as carbon sequestration. Hydrochar particles are less likely to self-ignite because of their high surface oxygen content. To solve all of the problems caused by hydrochar's poor soil stability, extensive research in this field is required. Hydrochar is effective at removing carbon dioxide from the air, which lessens the impact of global warming [169].

## 12 Hydrochar benefits

Hydrochar offers various benefits including the presence of metals with reduced concentrations of alkaline and alkali earth metals and heavy metals, high capacity for adsorption of both polar and non-polar functional groups and reduced ash content. Additionally, hydrochar has lower carbon recovery and higher atomic O/C and H/C ratios when created at the same operational process temperature. Additionally, HTC's hydrochar is considered to be environmentally safe, and thus, unlike other char, it does not produce any harmful chemicals or byproducts [169].

**Table 4** Hydrochar for supercapacitor applications

S. no	Hydrochar source	Precursor location	Activating agent	Surface area and pore diameter	Specific capacitance (F/g)	Current density (A/g)	Refs
1	Hemp Straw	Gansu, China	KOH	865 m <sup>2</sup> /g 2.44 nm	279	0.5	[153]
2	Argy wormwood	Harbin	KOH	927 m <sup>2</sup> /g 10.75 nm	344	1	[154]
3	Bamboo	–	KOH	3132 m <sup>2</sup> /g	435.5	0.5	[155]
4	Enteromorpha prolifera	Coasts of China	KOH	1528 m <sup>2</sup> /g 1.71 nm	200	1	[156]
5	Jatropha oilcake	Asian Countries	KOH	746.7 m <sup>2</sup> /g 1.305 nm	174.78	1	[157]
6	Expired Fresh Milk	–	KOH- H <sub>3</sub> PO <sub>4</sub>	465 m <sup>2</sup> /g 11.2 nm	186.3	–	[158]
7	Corn Starch	Changchun, China	H <sub>3</sub> PO <sub>4</sub>	1188- 1239 m <sup>2</sup> /g 2.21–4.70 nm	144	0.625	[159]
8	Salacca peel	–	KOH	2907.31 m <sup>2</sup> /g	15.57	–	[160]
9	Bamboo Shoot Shells	China	KOH	~3300 m <sup>2</sup> /g ~2.8 nm	188	10	[161]
10	Carrageenan	–	KOH	2502 m <sup>2</sup> /g 1.3 nm	230	1	[162]
11	Bamboo	Zhejiang, China	KHCO <sub>3</sub>	1509.5 m <sup>2</sup> /g 2.34 nm	467	0.5	[163]
12	Rice Straw	Zhejiang, China	KHCO <sub>3</sub>	2786.5 m <sup>2</sup> /g 2.68 nm	317	1	[164]
13	Miscellaneous wood fibers	Hengyou Furniture Group Co., Ltd., Daxing'anling, China	KOH	~1807 m <sup>2</sup> /g	345	0.5	[165]
14	Rice Husk	–	NaOH KOH	1355 m <sup>2</sup> /g	179.4	6.25	[166]

### 13 Future scope

Although biomass could be effectively converted to hydrochar using the HTC method, the specific mechanisms by which hydrochar is formed are not completely understood and are limited to the degeneration of pure chemicals. Utilizing hydrochar will assist in lowering the amount of sludge and solid waste released into the environment, minimizing land pollution, and encouraging the circular economy by turning trash into a product with added value. The demand to increase waste into hydrochar conversion is also advantageous to the economy. The mechanisms of hydrochar production from complex biomass must therefore be clarified through additional study. Studying the utilization of green activating agents in the production of activated carbon is necessary. Perhaps, it is possible to conduct additional research to learn how to enhance these hydrochar properties to more effectively eliminate pollutants in water.

More extensive analysis on hydrochars generated using various individual or combined materials needs to be carried out to determine the links between the HTC conditions, their

feedstocks, and physicochemical features of hydrochar. Furthermore, the methods of hydrochar production from various materials at varied HTC settings employing various ingredients must be explained.

Limitations like handling and disposal issues, commercial viability, renewability, and lack of regeneration must be resolved to create improved adsorbents. Discovering how to dispose of used chars through reactivation, burning, landfilling, and recycling is enlightening. The process's effectiveness will be ensured by the used adsorbents' capacity to be reused.

### 14 Conclusion

An effective method for creating hydrochar with a huge capacity for the synthesis of activated carbon is hydrothermal carbonization. It is discussed how variables like temperature, retention time, and pressure affect the characteristics of hydrochar while also being essential for achieving the required porosity in activated carbons. While numerous

approaches have been created to stimulate hydrochar to enhance its physio-chemical characteristics, new syntheses and inventive manufacturing techniques are urgently needed to create designed carbon products with added value from hydrochar. Over time, it has been noted that hydrochar is extensively used in the treatment of wastewater. Due to its capacity for regeneration, high efficacy, surface area, and pore volume, hydrochar is projected to be a desirable alternative for the elimination of a range of contaminants. Hydrochar also finds its application in wide variety of fields like enhancing soil and crop productivity, supercapacitors, carbon sequestration and greenhouse gas emission. Before using hydrochar and its derivatives in actual applications, it is important to investigate and analyze their ecotoxicity and environmental consequences, because they may have negative effects.

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## Declarations

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