

Review

Hydrothermal Carbonization of Waste Biomass: A Review of Hydrochar Preparation and Environmental Application

Jelena Petrović ^{1,*} , Marija Ercegović ¹ , Marija Simić ¹ , Marija Koprivica ¹ , Jelena Dimitrijević ¹ , Aleksandar Jovanović ¹  and Jovana Janković Pantić ² 

¹ Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franchet d'Esperey St., 11000 Belgrade, Serbia; m.ercegovic@itnms.ac.rs (M.E.); m.petrovic@itnms.ac.rs (M.S.); m.koprivica@itnms.ac.rs (M.K.); j.dimitrijevic@itnms.ac.rs (J.D.); a.jovanovic@itnms.ac.rs (A.J.)

² Faculty of Mining and Geology, University of Belgrade, 7 Đušina, 11000 Belgrade, Serbia; jovana.jankovic@rgf.bg.ac.rs

* Correspondence: j.petrovic@itnms.ac.rs

Abstract: The concept of a bio-based economy has been adopted by many advanced countries around the world, and thermochemical conversion of waste biomass is recognized as the most effective approach to achieve this objective. Recent studies indicate that hydrothermal carbonization (HTC) is a promising method for the conversion of waste biomass towards novel carbonaceous materials known as hydrochars. This cost-effective and eco-friendly process operates at moderate temperatures (180–280 °C) and uses water as a reaction medium. HTC has been successfully applied to a wide range of waste materials, including lignocellulose biomass, sewage sludge, algae, and municipal solid waste, generating desirable carbonaceous products. This review provides an overview of the key HTC process parameters, as well as the physical and chemical properties of the obtained hydrochar. It also explores potential applications of produced materials and highlights the modification and functionalization techniques that can transform these materials into game-changing solutions for a sustainable future.

Keywords: hydrothermal carbonization; waste biomass; carbon materials; biofuel; adsorbents



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1. Introduction

Over the years, human activities have generated an increasing amount of waste biomass. The traditional management of waste biomass via composting or disposal in open landfills causes environmental pollution, economic losses, and health problems. Despite being considered as a waste, biomass is a valuable renewable resource and energy source [1–3]. Currently, different methods and technologies are being researched globally to reduce the use of fossil fuels and mitigate environmental risks such as global warming. Some methods aim to improve crude oil extraction and reservoir reconstruction, while others focus on utilizing CO₂ emissions for energy purposes [4,5]. In addition, the use of waste biomass as a sustainable resource has gained recognition due to its potential to decrease greenhouse gas emissions [6]. However, low energetic potential and stability, high ash content, hygroscopic nature, storage issues, and volatiles released during combustion impair the motivation for its utilization [7]. Significant strides have been made in the adoption of thermochemical conversion processes that can convert biomass into multifunctional products [1,7]. These highly effective processes utilize heat to transform biomass into desirable biofuels, adsorbents, or valuable chemicals (bio-oil, aldehydes, phenols, ketones, acids, and furan derivatives) [1,2,8]. Different techniques have been developed for the carbonization of biomass, including combustion, torrefaction, pyrolysis, gasification, and hydrothermal carbonization [2,8–10].

The last mentioned, HTC, is a highly effective technology for biomass utilization, making it an essential player in waste treatment and solid biofuel production. It is a cost-

effective and environmentally friendly process that operates at moderate temperatures (180–280 °C) and uses water as a reaction medium (Figure 1). The HTC process offers significant advantages, including the carbonization of wet biomass without the need for drying and the absence of gas emissions due to the dissolution of oxides in process water [2,7]. During the HTC process, the raw material undergoes several reactions that include hydrolysis, dehydration, decarboxylation, aromatization, and condensation [11,12]. Temperature and residence time are the main parameters that control the HTC process and affect the structure and characteristics of obtained products [13–15]. Functionalized hydrochars suitable as pollutant adsorbents are produced at lower HTC temperatures, whereas higher temperatures promote hydrochars with enhanced fuel properties [12,14,16,17]. Reaction time shows a similar but milder influence than HTC temperature. During hydrochar formation, a longer reaction time causes yield reduction but results in a more aromatic structure [2]. Furthermore, under HTC conditions, subcritical water behaves as a non-polar solvent and facilitates the hydrolysis of organic compounds of biomass, leading to rapid depolymerization into water-soluble products [14]. Not only is water, as a solvent, an inexpensive option and biomass constituent, but it is also an environmentally friendly and non-toxic one. Moreover, carbonizing in an aqueous medium generates oxygenated functional groups on a solid hydrochar surface [18].

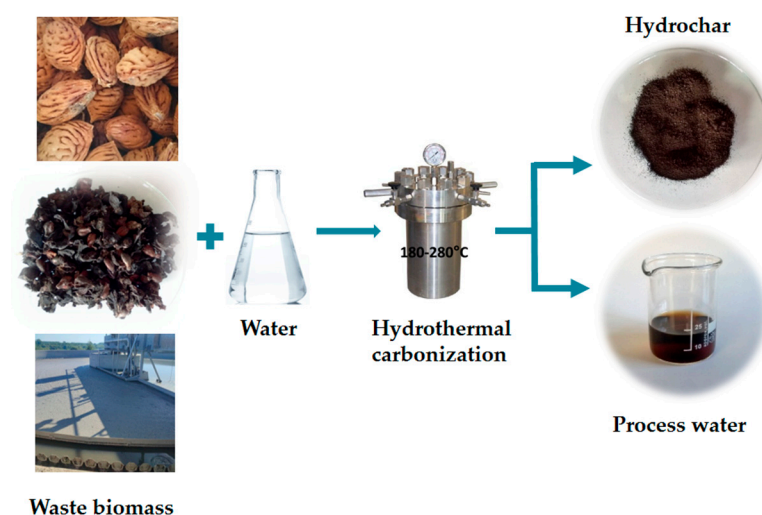


Figure 1. Schematic representation of the HTC process.

The process produces energy-dense, coal-like hydrochar without gas emissions or the need for feedstock drying. These features are particularly significant; they reduce the process's cost and energy consumption and increase application versatility, placing HTC ahead of conventional thermal treatments [11,15]. Derived solid residue exhibits highly hydrophobic and friable properties, which facilitate its separation from the liquid phase. It outperforms raw biomass with higher mass and energy density, better dewaterability, and improved combustion performance as a solid fuel [2,3,19,20]. Due to its characteristics, hydrochar is used for carbon sequestration, soil improvement, bioenergy production, and wastewater pollution remediation. Aside from solid hydrochar, a certain amount of process water (PW) is also created [1,2,11,15,19]. The PW can contain various polluting, organic compounds in considerable amounts and can show potential ecotoxicity [19]. Generation of these dissolved organic fragments in PW can impede clean production of hydrochar from biomass and also represents the main deficiency of the HTC process. Therefore, it is necessary to additionally treat PW before its release into environments. This obstacle can be overcome by utilizing the obtained chemicals or by recirculating PW, thus reducing water consumption during the HTC process [15,20,21].

This review paper summarizes the impact of HTC parameters on hydrochar structure and characteristics, focusing on lignocellulosic biomass conversion. It discusses challenges

in clean production and potential applications of the produced materials. This paper provides fundamental knowledge and highlights the need for sustainable, environmentally friendly carbonaceous material production.

2. Influence of Process Parameters

The chemical and physical properties of hydrochars produced from the same feedstock can differ considerably if some of the operating parameters are changed. Therefore, it is very important to understand the influence of each parameter to optimize the HTC process and produce the desired product (hydrochar) quality [22,23]. Apart from the set temperature and residence time, which are the most important, the characteristics of the hydrochars are influenced by other factors such as type and amount of feedstock, pressure, and presence of catalysts. Table 1 summarizes the influence of process parameters on the main hydrochar characteristics. A deeper interpretation of the impact is given in the following paragraphs.

Table 1. Influence of process parameters on selected characteristics of hydrochars produced from different precursors.

Biomass	T (°C)	Residence Time (min)	Catalyst	Hydrochar Yield (%)	HHV (MJ/kg)	Fixed Carbon (%)	Reference
Wood chip	240	60	2% Fe(NO ₃) ₃ ·9H ₂ O 4% Fe(NO ₃) ₃ ·9H ₂ O	56.08	26.80	42.95	[24]
				55.32	30.05	44.31	
Sewage sludge	200	120	sulfuric acid	6.20	18.96	10.04	[25]
Municipal solid waste	260	300	acetic acid	45	32.56	38.81	[26]
Sewage sludge/ wheat straw	300	90	Ni@CSB	35.27	36.96	ND	[27]
Spent mushroom substrate	180	60	-	57.2	14.9	11.6	[28]
	200			55.23	15.4	10.42	
	220			43.79	15.82	12.25	
	240			41.98	16.82	13.44	
	260			38.32	17.06	13.5	
Soybean residue	200	120	-	42.9	19.1	42.3	[29]
	250			37.4	20.9	23.7	
	300			32.3	22.0	19.2	
Swine manure	200	0–60	-	58.7	12.4	9.2	[30]
	220			56.3	12.8	11.8	
	240			55.7	13.7	12.6	
	260			51.7	15.9	15.2	
	280			50.2	16.0	15.7	
Banana stalk	160	60	-	75.3	18.1	16.9	[31]
	160	120		73.6	18.4	21.0	
	160	180		72.8	18.4	21.1	
	180	60		68.2	18.5	22.5	
	180	120		65.2	18.6	24.9	
	180	180		61.5	18.7	27.5	
	200	60		61.8	18.8	35.0	
	200	120		60.9	18.8	35.3	
200	180	57.8	18.9	44.3			
<i>Miscanthus</i>	180	60	-	73	19.66	10.83	[19]
	200			54	20.0	16.82	
	220			51	21.18	22.9	
Tobacco stalk	180	120	-	80	18.72	15.6	[32]
	200			67	19.07	18.5	
	220			61	19.65	20.6	
	240			63	21.12	23.02	
	260			59	21.42	26.77	
Grape pomace	180	60	-	86	24.49	25.84	[12]
	200			78	25.71	25.73	
	220			66	26.13	26.64	

2.1. Temperature

Temperature is a crucial parameter that determines the structure and characteristics of the resulting products. It regulates ionic and radical reactions in the supercritical water region as well as the degree of precursor degradation and conversion. Higher temperatures have a significant impact on the degradation process and the number of compounds that can be hydrolyzed [2,33]. When the temperature reaches 180 °C, the degradation process of lignocellulosic biomass becomes more intense. At these operation conditions, hydrolysis of the thermally least stable hemicellulose occurs, while cellulose and lignin degradation require more intense conditions [11,34]. During the hydrolysis stage, biomass materials are degraded into smaller molecules including oligosaccharides and amino acids. These products are further dehydrated and then polymerized and condensed to form hydrochar [33]. Longer reaction times and higher temperatures also increase the intensity of these biomass transformation reactions.

In addition, a higher carbonization temperature affects the production of hydrochar with higher carbon content, but at the same time, it reduces the yield of the solid phase due to increased degradation (Table 1) [2,20,28,32]. In addition, elevated temperature conditions increase the dehydration and decarboxylation reactions, thus reducing oxygen content and causing changes in the O/C and H/C atomic ratios in biomass. The result is the production of hydrochar with improved fuel properties, especially with higher HHV (Table 1) and LHV [11,20,35].

Numerous studies have examined the influence of this process parameter (Table 1). They reveal that each constituent of biomass is individually affected under HTC conditions because their degradation originates at different temperature ranges. Summarizing the literature, temperatures from 180 to 280 °C are most often used to obtain solid hydrochar from biomass precursors. Table 1 shows selected biomasses and their carbonization temperatures. Nakason et al. [36] investigated the effect of temperature (140–200 °C) on fuel characteristics of hydrochars prepared from coconut husk and rice husk. They revealed that an increase in process temperature enhanced the degradation of biomass, leading to a decrease in hydrochar yield, volatile matter, and oxygen content, and this enhanced the carbon content and thermal stability of hydrochar. Moreover, the inorganic element in the raw material could also significantly affect the product characteristics [36]. During thermal treatment of biomass at temperatures above 180 °C, inorganic compounds are leached from biomass constituents, primarily hemicellulose and cellulose, into the process water. This results in lower ash content in hydrochars [12,37]. Nonetheless, higher temperatures can result in the enhanced dissolution of organic compounds into water, leading to an increased inorganic concentration in the hydrochar and greater ash content [38]. Another study monitored the possibility of renewable energy generation from municipal solid food waste by HTC treatment in the temperature regime from 180 to 260 °C [26]. Obtained results indicated that the highest HHV and fixed carbon was acquired at 260 °C but with the lowest mass yield. Further, the highest solid biofuel production rate was attained at 180 °C. Summarizing all the parameters, the authors concluded that the most reliable temperature for obtaining an energy source is 225 °C. Similar results were obtained by other authors who examined the influence of temperature on the characteristics of the obtained hydrocarbons. Petrović et al. [12] and Mihajlović et al. [19] in separate studies revealed that temperature governs energetic potential, increased porosity, and re-adsorption ability while lowering volatiles, ash, and moisture in hydrochars obtained from grape pomace and *Miscanthus × giganteus*, respectively.

Lang et al. [39] studied dissolved organic matter (DOM) from hydrochars made from cow manure, corn stalk, and *Myriophyllum aquaticum* at three temperatures (180, 200, and 220 °C). The study found that the hydrochars' dissolved organic carbon content decreased as HTC temperature increased. On the contrary, increased HTC temperatures increased the relative proportion of aromatic substances and humification degree of cow manure hydrochar DOM, while adversely affecting the DOM from hydrochars made from corn stalk and *Myriophyllum aquaticum* [39].

2.2. Pressure

During the HTC process, pressure is self-generated and primarily influenced by the initial biomass and carbonization temperature. Therefore, this parameter has no considerable impact on the process itself. As the autogenic, pressure increases with a rise in reaction temperature. However, in addition to drawing insight into feedstock–water interactions, more knowledge about obtained pressure is also crucial from the safety and cost aspects for designing effective equipment [23,40]. The amount of pressure that is reached depends on the amount and type of used feedstock, initial feedstock/water ratios, used reaction temperature, and residence time [40]. In pressurized HTC systems, three types of products occur during the chemical destruction of the feedstock: a solid hydrochar, water with dissolved simple organic compounds, and gases [22]. From the gaseous products, CO₂ is the most represented and along with water vapor, its amount affects the pressure increase [40]. Therefore, the pressure at the reaction temperature depends on the saturated water vapor pressure, the amount of partially soluble gases produced by HTC reactions, and some inert, non-soluble gas if it is added to a pre-pressurized system (such as nitrogen). Also, the pressure is higher with a decreased density of biomass and free headspace of the reactor and increased volume of liquid phase [23,40]. HTC systems use reaction temperatures lower than many alternative thermochemical processes, but much higher pressures (10–65 bar) are needed since combustion, pyrolysis, or gasification are performed at atmospheric pressure [40].

Although pressure is a consequent parameter, a few papers describe its influence on the HTC process. Güleç et al. [41] reported that, in addition to higher temperatures, an increase in pressure (temperature is set to 250 °C while pressure is set to 50 or 240 bar) leads to the better transformation of biomass into hydrochars. However, the degree of these structural modifications depends on feedstock composition. The higher hemicellulose–cellulose biomass structures were more affected by the influence of changing temperature and pressure than those with higher cellulose–lignin structures [41]. Also, Minaret and Dutta [42] in their BET analysis evaluated that the surface area of corn husk hydrochar reduced when raising the pressure of the HTC process (from 7.4 to 4.8 m²/g). The HHV of the sewage sludge hydrochar showed a continual decrease (from 8.0 to almost 6.5 MJ/kg) with increasing pressure (from 0.1–0.9 to 3.1–5.4 MPa), while the dewatering performance was improved [43].

2.3. Residence Time

A longer residence time increases the severity of the reaction, affecting solid recovery and forming more stable hydrochars with a polyaromatic structure. For lignocellulosic biomass, secondary hydrochar formation depends on the residence time, while non-dissolved monomers rely more on temperature [44,45]. The process of hydrochar formation is enhanced by the increase in residence time, which leads to the release of more intermediate products. A study conducted by Gao et al. [46] found that the characteristics of hydrochar from water hyacinth were influenced by the residence time, while Zhang et al. revealed that shorter residence times resulted in cracks on the hydrochar surface, while microspheres were formed after 6 h [47]. The residence time controls both polymerization and hydrolysis, and after 24 h, the formed microspheres aggregate, providing different textures of hydrochar. Furthermore, the diameter of the microspheres was also affected by the residence time [44]. However, from the results summarized in Table 1, it can be concluded that residence time shows a smaller influence on the hydrochar characteristics than temperature. Islam et al. [31] found that, during the carbonization of banana stalks, an increase in reaction time from 60 to 180 min (200 °C) decreased hydrochar yield from 61.8 to 57.8%, while HHV and fixed carbon content increased from 18.7 to 18.9 MJ/kg and from 35.0 to 44.3%, respectively. On the other hand, an increase in reaction temperature from 160 to 200 °C (180 min) in the same study significantly affected the mentioned parameters, and yield was reduced from 72.8 to 57.8%, while HHV and fixed carbon were increased from 18.4 to 18.9 MJ/kg and from 22.5 to 44.3%. In conclusion, the residence time

must be considered to polymerize the hydrochar at a specific temperature, based on the obtained hydrochar.

2.4. Catalyst

Catalysts, categorized as organic and inorganic, can speed up a chemical reaction in hydrothermal carbonization and improve hydrochar properties. Their addition promotes a reduction in reaction temperature, enhances hydrolysis, upgrades denitrogenation and deoxygenation, increases hydrochar yield, and functionalizes the hydrochar. An organic catalyst (organic acids, alcohols, etc.) is a type of organic compound that can initiate or accelerate a chemical reaction. Organic acids dissociate in water, creating an acidic solvent that significantly enhances reaction rates [48]. Citric acid is a safe and inexpensive organic acid catalyst that promotes biomass transformation during the HTC process by hydrolysis of biopolymers, dehydration, and carbonization, which enhances hydrochar formation and increases its carbon content [38]. Sarrion et al. reveal that increasing the concentration of citric acid from 0.1 to 0.5 M during HTC of dewatered waste-activated sludge significantly increases the carbon content and mass yield of hydrochar [49]. Furthermore, the inclusion of citric acid during the carbonization of sludge provokes the formation of additional acids, such as formic or acetic acid. These acids interact with mineral compounds, impacting hydrolysis, dehydration, condensation, and polymerization processes, making the process autocatalytic [49]. Further, citric acid may introduce more functional groups into the carbon skeleton and remove some minerals and organic groups in the biomass feedstock, leading to more rough and porous structures [50,51]. Faradilla et al. [52] showed that the addition of citric acid during the HTC treatment of cellulose nanofiber and softwood pulp increased the diameter of formed carbon spheres. The addition of citric acid as a catalyst significantly enhances the hydrolysis of cellulose into soluble oligomers and glucose. These molecules then underwent subsequent dehydration, condensation, and polymerization processes, ultimately resulting in the formation of carbon spheres [52]. Another acid that affects the hydrothermal carbonization process and hydrochar properties is acetic acid. Although this catalyst increased thermal stability and carbon content, it added a lower hydrochar yield than other catalysts. Thus, acetic acid may be better for reducing yield via fragmentation reactions, not promoting polymerization. Citric acid's structure leads to more carbon content during HTC, and its three acid functionalities enhance the dissolution of inorganic materials in the feedstock more than acetic acid's single functionality. In addition to organic acids, a protic solvent (methanol, ethanol, and other lower-molecular-weight alcohols) has hydrogen bound to electronegative atoms like oxygen or nitrogen. It can participate in hydrogen bonding and hydrogen donation, promoting dehydration reactions and improving hydrochar from high-protein and carbohydrate feedstocks [38].

The addition of inorganic acidic reagents improves hydrochar properties by leaching inorganic compounds to process water, provide acidic mineral conditions, remove ash from hydrochar, depolymerize cellulose, and enhance hydrolysis and dehydration. Inorganic catalysts include strong mineral acids and bases, metal chlorides, sulfate and nitrate salts, metal oxides, and hydrogen peroxide. Strong mineral acids improved the fuel properties of hydrochar and enhanced nutrient release and solubilization of nitrogen and phosphorus, enhancing porosity while lowering volatile matter content during HTC, making the hydrochar more stable. Wilk et al. [25] investigated the addition of sulfuric acid as a catalyst during the carbonization of sewage sludge. The authors reveal that specific surface area was significantly increased upon the addition of the catalyst as a result of pronounced degradation and transformation of feedstock. Furthermore, the addition of the catalyst improves the migration of elements, so increases in zinc, copper, and lead oxides and decreases in chromium and nickel compounds in hydrochars were noticed, while an abundance of phosphorous, magnesium, calcium, and zinc were observed in post-processing water. Strong mineral bases, like CaO, raise the hydrochar yield and ash content while reducing the organic matter and polycyclic aromatic hydrochar content,

while NaOH can reduce emission of sulfur dioxide and nitrogen oxide emissions during hydrochar combustion and hydrochar moisture diffusivity [2,53]. Metal chlorides impact hydrochar morphology and surface properties, lower the starting temperature, catalyze dehydration and decarboxylation, and enhance the thermal characteristics and combustion properties by facilitating furfural derivatives formation and further pseudo-lignin structure development [53,54].

In general, studies show that the feedstock type and HTC temperature have the most significant effects on hydrochar properties [1–3,7]. Thus, optimization of the process is crucial in achieving characteristic products for specific applications based on the precursor biomass and the end use of the material.

3. Environmental Applications of Hydrochar

3.1. Solid Fuel

The valorization of waste biomass as a renewable energy source and raw material for biofuel production has become one of the goals of many advanced countries that have adopted the concept of a bio-based economy. HTC is widely recognized as a highly suitable method for the improvement of biomass fuel properties and the preparation of novel biofuels. Hydrochar shows superior fuel performance, increased carbon content and energy density, lower ash and volatiles, better reactivity, dewaterability, and material stability, and overall improved fuel properties in comparison to raw biomass. In addition, produced hydrochars exhibit comparable or better properties than those of commercial coal and lignite. An important feature of the HTC process is the possibility of leaching inorganic elements from the starting biomass [12,39]. This results in a reduction in the ash content in the obtained hydrochars. Petrović et al. [12] reveal that carbonization of grape pomace at 200 °C causes a reduction in ash content in produced hydrochar (from 6.48% in grape pomace to 3.55% in hydrochar) due to partial leaching of inorganics (K, Mg, Ca, Fe, Si, P) into process water. Lower ash content is a highly recommended characteristic for solid fuels since the increased amount of specific inorganic elements (Si, K, Na, S, Cl, P, Ca, Mg, and Fe) in fuels and biomass can cause emission issues or corrosion, clogging, fouling, and/or clinkers formation in combustors during direct combustion [7,17]. The abovementioned problems increase maintenance costs and the combustion efficiency of the fuel. Raw biomass has a highly volatile nature, resulting in inefficient combustion and increased GHG emissions compared to coal. Results from the literature indicate that HTC decreases the volatile content in biomass [12,39,55]. However, Ischia et al. [56] reported that, during HTC of municipal solid waste at 180 °C, volatile matter increases from 80.7% to 82.2%. This result was unexpected since lignocellulose starts to hydrolyze at 180 °C. A possible cause is the accumulation of leached volatile compounds from process water onto the formed hydrochar surface [57]. Wang et al. [58] found that volatile adsorption was most prominent during HTC treatment of sludge at 180 °C, while higher HTC temperatures reduced the peak of hydrochar devolatilization rate. The authors suggest that HTC of biomass above 220 °C leads to the devolatilization of biomass macromolecules and the creation of more stable forms of hydrochars. This could have a positive impact on the environment by improving the production and use of biomass-based products as solid fuel. According to the authors, during HTC, the carbonization of biomass begins with hydrolysis, which leads to the devolatilization of biomass macromolecules into oligomers and monomers. These fragments undergo subsequent degradation mechanisms, including dehydration and decarboxylation, followed by aromatization, which results in the formation of a carbon-rich solid. These degradation reactions occur simultaneously during HTC, leading to the formation of hydrochars with a lower volatile content compared to their corresponding biomasses [2,12,44,45].

Hydrochars as biofuels exploit additional significant advantages over fossil fuels and biomass itself that include higher HHV and LHV. This characteristic makes them eligible to be utilized as a solid fuel. Temperature is again the factor that affects these pa-

rameters the most. Petrović et al. [7] found that an increase in temperature (180–260 °C) provides hydrochars from corn cob, olive pomace, and paulownia with significantly elevated HHV (17.31–27.33 MJ kg⁻¹, 24.35–30.55 MJ kg⁻¹, and 18.99–28.06 MJ kg⁻¹, respectively). A similar trend was also noticed for agricultural, algal, organic municipal solid wastes, plant, and woody biomass (16–29, 30–32, 14–32, 17–32, and 21–30 MJ kg⁻¹, respectively) [43]. Increased HHVs were also noticed during HTC treatment of *Miscanthus × giganteus*, cotton stalk, and paulownia leaves [19,39,55], while Kojic et al. [28] reported increases in both HHV and LHV (58% and 65%) in comparison with raw spent mushroom substrate.

3.2. Adsorbent of Pollutants from Aqueous Solutions

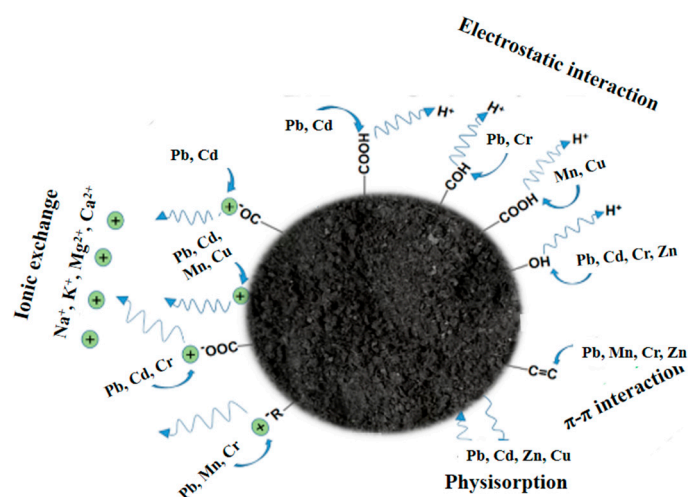
Among other potential applications, hydrochars pose a prospective ability to remove different pollutants from aqueous solutions. Their structure, abundant in different oxygenated functional groups, proved to be very suitable for additional functionalization and surface area modification using various physical and chemical processes. For this purpose, various modification methods, including alkali (KOH, NaOH), acidic (H₃PO₄, HCl), metal salt (ZnCl₂, MgCl, FeCl₃, K₂CO₃), and polymerization treatments, have been adopted so far [45,56–61]. KOH, as a commonly used activator, cleans partly blocked pores and incorporates novel ions onto hydrochar surfaces [58]. In addition, alkali treatment increases surface area due to the removal of organic fragments from prepared hydrochars, while acidic treatment affects the mesoporous structure. Moreover, suggested treatments incorporate new functional groups to hydrochar surfaces and provide more sites for the binding of selected pollutants [1,3,45]. The appropriate modification provides the preparation of novel, effective sorbent materials with tailored structures and advanced performances toward the removal of a wide range of contaminants.

3.2.1. Heavy Metals

Over the years, industrial water contaminated with heavy metals has represented a serious threat to the environment and humans. With the increasing development of industrialization and urbanization, the continuous discharge of pollutants like heavy metals, organic dyes, pesticides, and other organic compounds into river watercourses has become a huge concern. These pollutants come from industrial and mining wastewater, such as that from the textile industry, electroplating, paper production, leather tanning, and food technology [45,59–61]. These toxic and non-biodegradable pollutants tend to accumulate in plant and animal tissues, as well as in the human body, causing significant harm that includes damage to the central nervous system, dermatitis, cancer, kidney dysfunction, and damage to the liver and reproductive organs [61–63]. Therefore, the development of efficient and economical methods for the removal of heavy metals and other contaminants from industrial wastewater before discharge into watercourses becomes essential. In order to overcome the shortcomings of traditional purification methods, the application of new sorbents obtained from renewable sources, such as hydrochars, has recently been extensively investigated [1,3]. Although they exhibit low surface area and porosity, the chemically active functional groups on hydrochars' surfaces (ketones, COOH groups, and hydroxyl) provide satisfying adsorption capability [57]. Numerous studies so far have tested the ability of hydrochars from different precursors to remove heavy metals from aqueous solutions. Moreover, to increase capacity towards selected pollutants, a number of modification methods were applied. Table 2 summarizes the application of hydrochars obtained from different precursors as heavy metals sorbents, while Figure 2 shows potential binding mechanisms.

Table 2. Application of different hydrochars as heavy metal sorbents.

Hydrochar	Pollutant	Capacity (mg/g)	Reference
phosphate-modified poplar sawdust	Pb(II)	119.61	[64]
grape pomace	Pb(II)	27.8	[61]
KOH-modified grape pomace		137	
<i>Sedum alfredii</i> Hance	Cd(II)	1.52	[65]
KOH <i>Sedum alfredii</i> Hance		25.69	
magnetic watermelon seed waste	Cd(II)	347.2	[66]
magnetic pineapple leaves	Mn(II)	2.99	[67]
Paulownia leaves	Pb(II)	82.37	[68]
NaOH paulownia leaves		174.75	
NH ₄ Cl-modified corncob	Cu(II)	77.75	[69]
	Cr(VI)	103.82	
amino-modified bamboo hydrochar	Cr(VI)	523.57	[70]
MgSi sawdust	Cu(II)	214.7	[71]
	Zn(II)	227.3	
Ca-doped spent mushroom substrate	Pb(II)	297	[72]
	Cd(II)	131	

**Figure 2.** Potential interaction between hydrochar surface and heavy metals.

Qin et al. investigated phosphate-modified poplar sawdust hydrochar as a potential adsorbent for Pb(II) ions [64]. FTIR analysis revealed that P-containing groups were involved in Pb(II) removal by surface complexes, while aromatic structures participated in cation- π interaction. Qin et al. [64] also show that the -COOH in the P-hydrochar can more easily adsorb Pb(II) compared to the -OH group. The achieved adsorption capacity for Pb(II) ions was 119.61 mg/g (Table 2), and the main mechanisms include precipitation, π - π interaction, and complexation. Examining the effect of the modification on the hydrochar adsorption capacity, Petrović et al. [61] reveal that KOH-modified grape pomace hydrochar achieves a five times better lead removal capacity (137 mg/g) than unmodified grape pomace hydrochar (27.8 mg/g) (Table 2). Alkali modification caused different structural changes that included the incorporation of oxygenate functional groups to the hydrochar's surface, binding of K⁺ ions that participates in ion exchange reactions with heavy metals, and the cleaning of partially blocked pores. All mentioned structural modifications provided more active sites for the binding of Pb²⁺ ions and, thus, enabled significantly better adsorption. Adsorption of selected ions was achieved through the ion exchange mechanism, chemisorption, and Pb(II)- π interaction, while the Sips isotherm

model gave the best fit with the experimental data [61]. KOH-modified hydrochar from *Sedum alfredii Hance* also showed a higher adsorption performance (17 times) towards Cd(II) ions in comparison to pristine hydrochar [65]. Cd(II) ions were also effectively removed from an aqueous solution by using magnetic watermelon seed hydrochar [66], while Mn(II) ions were treated by a magnetic hydrochar nanocomposite from pineapple leaves (Table 2) [67]. Moreover, alkali modification using NaOH proved to be an effective direction towards the production of highly effective sorbents from a hydrochar derived from paulownia leaves for Pb(II) ion removal. Mechanisms responsible for the binding include complexation and/or Pb- π electron interaction [68].

In order to provide environmental sustainability, Kim et al. simultaneously removed Cu(II) and Cr(VI) ions using a N-doped hydrochar derived from corncob [69]. The hydrochar was modified by NH₄Cl which contributed to a better adsorption ability (1.223 mmol/g for Cu(II) and 1.995 mmol/g for Cr(VI)) than that of the pristine hydrochar. Findings from the infrared spectra suggest that the redox reaction caused an increase in the number of deprotonated imine groups on the surface of the N-doped hydrochar, which could provide additional binding sites for Cu(II), while under pH < pHPzc, the N-doped hydrochar possessed a greater adsorption affinity toward Cr(VI) than Cu(II) due to electrostatic attraction [69]. In addition, a protonated amino-modified bamboo hydrochar was prepared during the interaction of bamboo hydrochar with acryloyl chloride, amine, and hydrochloric acid and employed to adsorb Cr(VI) ions [70]. The authors stated that the incorporation of amine groups onto the hydrochar surface was pivotal for high adsorption capacity (523.57 mg/g) due to the elimination of pollutants by electrostatic interaction.

A novel cost-effective sawdust hydrochar composite (MgSi-HC) was used to remove Cu(II) and Zn(II). The modification provides a large specific surface area and a well-developed pore structure, while adsorption isotherms showed that the maximum adsorption capacity of MgSi-HC for Cu(II) and Zn(II) was 214.7 mg/g and 227.3 mg/g, respectively (Table 2) [71]. The adsorption mechanism suggested that electrostatic interaction, hydrogen bonding, π - π interaction, and pore filling were involved in the adsorption process [71]. Composite hydrochar, a calcium-pyro-hydrochar from spent mushroom substrate, was tested as a functional sorbent of Pb(II) and Cd(II) ions from aqueous solutions. According to the Freundlich isotherm model, the maximum sorption capacities of Ca-modified hydrochar for Pb(II) and Cd(II) were 297 mg/g and 131 mg/g, respectively (Table 2), while the binding was achieved by the ion exchange mechanism, surface complexation, mineral precipitation, and cation- π interaction [72].

3.2.2. Dyes

Among heavy metals, dyes represent an additional frequent group of industrial pollutants. Even at low concentrations, most dyes are serious contaminants and pose a significant threat to all living organisms due to their high toxicity, carcinogenicity, and non-biodegradable effects [1,2]. Textile industries use various synthetic dyes that can degrade water bodies and enter the food chain, posing a threat to aquatic organisms. Therefore, it is essential to remove dyes and purify industrial water before discharging to prevent environmental contamination. Previous studies confirmed that hydrochar can be considered to adsorb these molecules from aqueous systems.

Table 3 summarizes the application of hydrochars obtained from different precursors as dye sorbents, while potential binding mechanisms are shown in Figure 3. A functional hydrochar from olive waste was prepared by HTC at 250 °C and tested for removal of Methylene blue (MB) and Congo red (CR). NMR analysis revealed that hydrochar produced at 250 °C exhibited pronounced functionality, especially in carbonyl and carboxylic functional groups, compared to the raw olive waste. Almost 100% dye removal was achieved within 120 min (MB) and 180 min (CR), due to the presence of carbonyl and carboxylic functional groups on the hydrochar surface [73]. The removal of MB was also investigated using oxone-treated pine wood hydrochar and KHCO₃-modified hydrochar from industrial laundry sludge [74,75]. The highest adsorption capacities for MB sourced from separate

studies were 86.7 mg/g and 808.83 mg/g (Table 3) [74,75]. Pine wood hydrochar showed a substantial increase in carboxylic content upon oxidation. This surface modification provides more sites for pollutant binding and, thus, a higher adsorption capacity [74]. Camilo et al. [75] revealed that increased surface area (3005.57 m²/g) upon activation was the reason for such a high adsorption capacity. In the study of Petrović et al. [60], it was pointed out that Mg-doped pyro-hydrochars prepared from waste grape pomace, corn cobs, and *Miscanthus × giganteus* can be used as efficient MB sorbents with capacities of 289.65 mg/g, 262.30 mg/g, and 232.48 mg/g, respectively (Table 3). It was confirmed that magnesium (Mg) was bound to the surface of the hydrochars, contributing to ion exchange with MB ions. Further analysis referred to the complex mechanism involved in dye removal (hydrogen bonding, the π - π interaction between aromatic groups of Mg-hydrochar surface and MB, electrostatic interaction, and surface complexation) [60]. In addition, Kozhadi et al. [76] investigated the removal of Rhodamin B from an aqueous solution by an Fe-modified wheat straw hydrochar. Furthermore, magnetic watermelon seed hydrochar-grafted chitosan was successfully prepared and applied for the adsorption of malachite green [77]. The optimal parameters for reaching a capacity of 420.02 mg/g were pH 7.5, 420 min, and adsorbent dose of 20 mg at 298 K [77]. Bimetal organic framework (NiFe-MOF) incorporation on sugarcane bagasse hydrochar provides a dual 3-D morphological structure of material with numerous functional groups and high removal ability towards Cristal violet dye (395.9 mg/g) [78]. Modification results in a material with a 2.3 times higher surface area enriched in carboxylic and metal-carboxylate groups, displaying high thermal stability and adsorption through chemisorption [78]. Similarly, Cristal violet was adsorbed using a NaOH-activated sugarcane bagasse hydrochar. Cold alkali modification was chosen to increase oxygenated functional groups and enhance material porosity by removing pore blockages. Authors report that modified hydrochar has a porous structure with microsphere-like particles, functional groups, strong π - π interaction, and high thermal stability [79].

Table 3. Application of different hydrochars as dye sorbents.

Hydrochar	Pollutant	Capacity (mg/g)	Reference
olive waste	Methylene blue (MB) Congo red (CR)	14.26 11.58	[73]
pine wood	Methylene blue (MB)	86.70	[74]
KHCO ₃ -modified hydrochar from industrial laundry sludge	Methylene blue (MB)	808.83	[75]
Mg-doped grape pomace Mg-doped corn cob Mg-doped <i>Miscanthus × giganteus</i>	Methylene blue (MB)	289.65 262.30 232.48	[60]
Fe-modified wheat straw	Rhodamin B	80.00	[76]
magnetic watermelon seed-grafted chitosan	Malachite green (MG)	420.02	[77]
NiFe-MOF incorporation on sugarcane bagasse	Cristal violet (CV)	395.90	[78]
NaOH-activated sugarcane bagasse	Cristal violet (CV)	47.97	[79]

The knowledge of several studies indicates that removal of cationic dye is achieved by a complex mechanism involving the electrostatic attraction between positively charged MB amino groups and negatively charged functional groups onto hydrochar surfaces, hydrogen bonding, π - π dispersion interactions between the aromatic hydrochar structure and MB rings, surface complexation, and the ion exchange mechanism (Figure 3). In general, studies have shown that hydrochar can be an effective material for dye removal, regardless of the mechanism of adsorption. Hydrochars can easily be further tailored and modified to specifically remove a targeted dye. This carbonaceous material exhibits great potential for treating wastewater that contains dyes, particularly from the textile industry.

However, more research is required to determine the remedial effectiveness of hydrochars in wastewater with multiple contaminants as well as their recyclability.

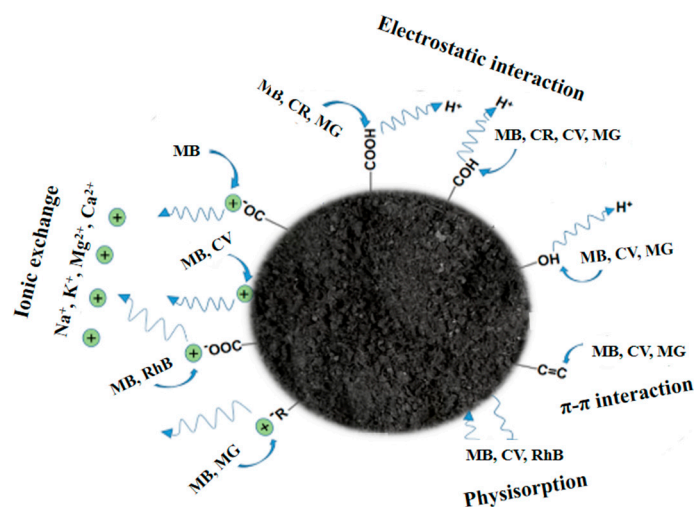


Figure 3. Potential interaction between hydrochar surface and dyes.

3.2.3. Pharmaceuticals

Pharmaceuticals and personal care products, which include antibiotics, analgesics, antidepressants, and more, are a growing concern in many countries due to their classification as emerging organic pollutants [80]. These substances are widely used for the improvement of human and animal health and daily life. In addition, a significant portion (30% to 90%) ends up in domestic sewage through urine, feces, and baths since it cannot be absorbed by humans or animals [80]. For this reason, pharmaceuticals are frequently detected in wastewater. To avoid their adverse impacts, it is necessary to remove them. So far, different methods (precipitation, barrier separation, and adsorption) have been used for this purpose [64,80,81]. Currently, hydrochars obtained by the HTC process are being examined as effective adsorbents for this group of pollutants. The application of different hydrochars and achieved adsorption capacities for pharmaceutical removal are shown in Table 4.

Table 4. Application of different hydrochars as pharmaceutical sorbents.

Hydrochar	Pollutant	Capacity (mg/g)	Reference
unmodified biochar from olive oil waste	Diclofenac	10.00	[81]
	Ibuprofen	2.50	
hydrochar from olive oil waste	Diclofenac	11.00	[82]
	Ibuprofen	10.00	
green tea waste	Ibuprofen	63.69	[77]
phosphate-modified poplar sawdust	Ciprofloxacin	98.38	[64]
NaOH-treated sugarcane bagasse	Tetracycline	22.60	[79]
immobilized bamboo	Paracetamol	48.12	[83]
loquat cores	Diclofenac	8.586	[84]
	Antipyrine	11.369	
	Prednisolone	9.629	

Delgado-Moreno et al. [81] compared the adsorption capability of unmodified biochars and a hydrochar from olive oil waste for diclofenac and ibuprofen removal (Table 4) and revealed that the hydrochar had a higher adsorption capacity despite a lower surface area. Due to the pronounced functionality, the hydrochar removed 68% of diclofenac and 43% of

ibuprofen, while chemisorption mechanisms governed the adsorption capacity. In addition, an unmodified hydrochar from green tea waste produced at 200 °C also demonstrated removal of ibuprofen [82]. Lowering the pH increases ibuprofen adsorption due to electrostatic interactions. Adsorption remains stable after six regeneration cycles [82]. Along with unmodified hydrochars, Qin et al. [64] demonstrated ciprofloxacin adsorption behavior by utilizing a phosphate-modified poplar sawdust hydrochar. According to the Hill model, an achieved adsorption capacity of 98.38 mg/g was influenced by hydrogen bonding, pores filling, and electrostatic attraction between the hydrochar's surface and the selected antibiotic. In addition, NaOH activation was applied on a sugarcane bagasse hydrochar to provide a valuable sorbent for tetracycline removal [79]. Higher NaOH concentrations lower the mass ratio, and longer activation times increase hydroxyl functional groups, pores, and surface area, leading to increased tetracycline removal [79]. A batch adsorption test using an immobilized bamboo hydrochar was performed for the investigation of potential paracetamol removal from water. An adsorption capacity of 48.12 mg/g (Table 4) was estimated during homogenous interaction between the pharmaceutical and the beads' surface [83]. In addition, Hayoun et al. [84] prepared a high-performance hydrochar from loquat cores and examined its potential for the removal of diclofenac, antipyrine, and prednisolone (Table 4). The prepared hydrochar was modified using citric acid, H_3PO_4 , and HCl. The results showed that treatment with 3 M citric acid was significantly better compared to the other two agents, with a removal efficiency of 95.88% for diclofenac, 76.21% for antipyrine, and 80.29% for prednisolone. Treatment with 3 M citric acid increases surface area from 0.0048 to 19.2261 m^2/g and provides a porous and irrigated structure abundant with oxygenated active sites. The structural changes caused by citric acid treatment improved the hydrochar's pollutant removal efficiency [84].

In general, based on the knowledge from numerous previous studies, it can be concluded that the mechanisms responsible for the removal of pollutants from aqueous solutions using hydrochars include the ion exchange mechanism, hydrogen bonding, surface complexation, strong π - π interaction, and electrostatic interaction. Figure 4 shows the aforementioned interactions.

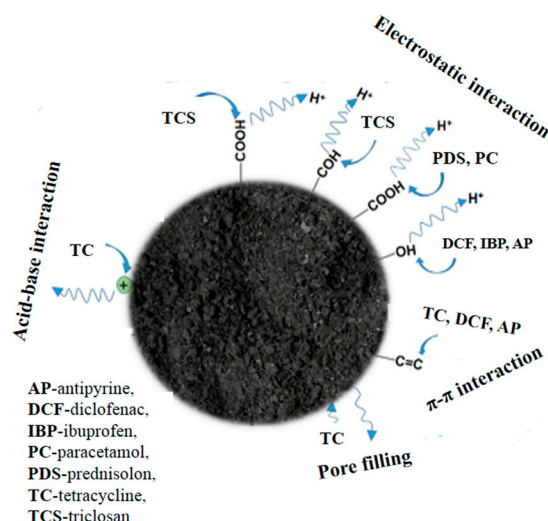


Figure 4. Potential interaction between hydrochar surface and pharmaceuticals.

4. Conclusions

HTC represents an efficient thermochemical transformation of wet biomass into valuable products, hydrochars, suitable for various applications such as solid biofuels, adsorbents, carbon sequestration agents, and soil remediators/conditioners. This article summarizes the knowledge about hydrothermal process variables that influence hydrochar formation (temperature, pressure, residence time, catalyst) and different methods of tailoring hydrochar surfaces for specific environmental applications. Considerable strides

have already been made in comprehending the hydrothermal conversion process, hydrochar formation mechanisms, and its crucial structural characteristics. The performance of hydrochars has been influenced by their specific physical, chemical, and structural characteristics. In addition, hydrochars can be easily adapted to particular applications since their surface is highly susceptible to modification and improvement.

Considering the activation of hydrochars' structure, acquiring additional knowledge of tailoring the surface and its regeneration is crucial in promoting the stability and utilization of hydrochars as sorbents of pollutants from aqueous environments in large-scale applications.

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References

1. Cavali, M.; Libardi Junior, N.; Dutra de Sena, J.; Lorenci Woiciechowski, A.; Soccol, C.R.; Belli Filho, P.; Bayard, R.; Benbelkacem, H.; de Castilhos Junior, A.B. A review on hydrothermal carbonization of potential biomass wastes, characterization and environmental applications of hydrochar, and biorefinery perspectives of the process. *Sci. Total Environ.* **2023**, *857*, 159627. [[CrossRef](#)] [[PubMed](#)]
2. Wang, T.; Zhai, Y.; Zhu, Y.; Li, C.; Zeng, G. A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties. *Renew. Sust. Energ. Rev.* **2018**, *90*, 223–247. [[CrossRef](#)]
3. Masoumi, S.; Borugadda, V.B.; Nanda, S.; Dalai, A.K. Hydrochar: A Review on Its Production Technologies and Applications. *Catalysts* **2021**, *11*, 939. [[CrossRef](#)]
4. Li, Q.; Han, Y.; Liu, X.; Ansari, U.; Cheng, Y.; Yan, C. Hydrate as a by-product in CO₂ leakage during the long-term sub-seabed sequestration and its role in preventing further leakage. *Environ. Sci. Pollut. Res.* **2022**, *29*, 77737–77754. [[CrossRef](#)]
5. Li, Q.; Wang, F.; Wang, Y.; Forson, K.; Cao, L.; Zhang, C.; Zhou, C.; Zhao, B.; Chen, J. Experimental investigation on the high-pressure sand suspension and adsorption capacity of guar gum fracturing fluid in low-permeability shale reservoirs: Factor analysis and mechanism disclosure. *Environ. Sci. Pollut. Res.* **2022**, *29*, 53050–53062. [[CrossRef](#)] [[PubMed](#)]
6. Hillier, J.; Whittaker, C.; Dailey, G.; Aylott, M.; Casella, E.; Richter, G.M.; Riche, A.; Murphy, R.; Taylor, G.; Smith, P. Greenhouse gas emissions from four bioenergy crops in England and Wales: Integrating spatial estimates of yield and soil carbon balance in life cycle analyses. *GCB Bioenergy* **2009**, *1*, 267–281. [[CrossRef](#)]
7. Petrović, J.; Simić, M.; Mihajlović, M.; Koprivica, M.; Kojić, M.; Nuić, I. Upgrading fuel potentials of waste biomass via hydrothermal carbonization. *Hem. Ind.* **2021**, *75*, 297–305. [[CrossRef](#)]
8. Satira, A.; Paone, E.; Bressi, V.; Innazzo, D.; Marra, F.; Calabro, P.S.; Mauriello, F.; Espro, C. Hydrothermal Carbonization as Sustainable Process for the Complete Upgrading of Orange Peel Waste into Value-Added Chemicals and Bio-Carbon Materials. *Appl. Sci.* **2021**, *11*, 10983. [[CrossRef](#)]
9. Yang, J.; Zhang, Z.; Wang, J.; Zhao, X.; Zhao, Y.; Qian, J.; Wang, T. Pyrolysis and hydrothermal carbonization of biowaste: A comparative review on the conversion pathways and potential applications of char product. *Sustain. Chem. Pharm.* **2023**, *33*, 101106. [[CrossRef](#)]
10. Zhai, Y.; Peng, C.; Xu, B.; Wang, T.; Li, C.; Zeng, G.; Zhu, Y. Hydrothermal carbonisation of sewage sludge for char production with different waste biomass: Effects of reaction temperature and energy recycling. *Energy* **2017**, *127*, 167–174. [[CrossRef](#)]
11. Jung, K.W.; Lee, S.Y.; Choi, J.W.; Lee, Y.J. A facile one-pot hydrothermal synthesis of hydroxyapatite/biochar nanocomposites: Adsorption behavior and mechanisms for the removal of copper(II) from aqueous media. *Chem. Eng. J.* **2019**, *369*, 529–541. [[CrossRef](#)]
12. Petrović, J.; Perišić, N.; Dragišić-Maksimović, J.; Maksimović, V.; Kragović, M.; Stojanović, M.; Laušević, M.; Mihajlović, M. Hydrothermal conversion of grape pomace: Detailed characterization of obtained hydrochar and liquid phase. *J. Anal. Appl. Pyrol.* **2016**, *118*, 267–277. [[CrossRef](#)]
13. Xu, Q.; Qian, Q.; Quek, A.; Ai, N.; Zeng, G.; Wang, J. Hydrothermal carbonization of macroalgae and the effects of experimental parameters on the properties of hydrochars. *ACS Sustain. Chem. Eng.* **2013**, *1*, 1092–1101. [[CrossRef](#)]
14. Zhang, Z.; Zhu, Z.; Shen, B.; Liu, L. Insights into biochar and hydrochar production and applications: A review. *Energy* **2019**, *171*, 581–598. [[CrossRef](#)]
15. Antero, R.V.P.; Alves, A.C.F.; de Oliveira, S.B.; Ojala, S.A.; Brum, S.S. Challenges and alternatives for the adequacy of hydrothermal carbonization of lignocellulosic biomass in cleaner production systems: A review. *J. Clean. Prod.* **2020**, *252*, 119899. [[CrossRef](#)]

16. Zhang, S.; Zhu, X.; Zhou, S.; Shang, H.; Luo, J.; Tsang, D.C.W. Hydrothermal carbonization for hydrochar production and its application. In *Biochar from Biomass and Waste: Fundamentals and Applications*; Elsevier Inc.: Amsterdam, The Netherlands, 2018; pp. 275–294. [CrossRef]
17. Jain, A.; Balasubramanian, R.; Srinivasan, M.P. Tuning hydrochar properties for enhanced mesopore development in activated carbon by hydrothermal carbonization. *Microporous Mesoporous Mater.* **2015**, *203*, 178–185. [CrossRef]
18. Knez, Ž.; Markočič, E.; Hrnčič, M.K.; Ravber, M.; Škerget, M. High pressure water reforming of biomass for energy and chemicals: A short review. *J. Supercrit. Fluids* **2015**, *96*, 46–52. [CrossRef]
19. Mihajlović, M.; Petrović, J.; Maletić, S.; Kragulj Isakovski, M.; Stojanović, M.; Lopičić, Z.; Trifunović, S. Hydrothermal carbonization of *Miscanthus × giganteus*: Structural and fuel properties of hydrochars and organic profile with the ecotoxicological assessment of the liquid phase. *Energy Convers. Manag.* **2018**, *159*, 254–263. [CrossRef]
20. Nobre, C.; Alves, O.; Durao, L.; Sen, A.; Vilarinho, C.; Goncalves, M. Characterization of hydrochar and process water from the hydrothermal carbonization of Refuse Derived Fuel. *Waste Manag.* **2021**, *120*, 303–313. [CrossRef] [PubMed]
21. dos Santos, J.V.; Fregolente, L.G.; Laranja, M.J.; Moreira, A.B.; Ferreira, O.P.; Bisinoti, M.C. Hydrothermal carbonization of sugarcane industry by-products and process water reuse: Structural, morphological, and fuel properties of hydrochars. *Biomass Convers. Biorefin.* **2022**, *12*, 153–161. [CrossRef]
22. Wilk, M.; Sliz, M.; Lubieniecki, B. Hydrothermal co-carbonization of sewage sludge and fuel additives: Combustion performance of hydrochar. *Renew. Energy* **2021**, *178*, 1046–1056. [CrossRef]
23. Ro, K.S.; Libra, J.A.; Alvarez-Murillo, A. Comparative Studies on Water- and Vapor-Based Hydrothermal Carbonization: Process Analysis. *Energies* **2020**, *13*, 5733. [CrossRef]
24. Wang, G.; Li, D.; Xiong, L.; Dan, J.; Xu, K.; Yuan, X.; Kan, G.; Ning, X.; Wang, C. Application of catalysts in biomass hydrothermal carbonization for the preparation of high-quality blast furnace injection fuel. *Energy* **2023**, *283*, 129147. [CrossRef]
25. Wilk, M.; Śliz, M.; Czerwińska, K.; Śledź, M. The effect of an acid catalyst on the hydrothermal carbonization of sewage sludge. *J. Environ. Manag.* **2023**, *345*, 118820. [CrossRef]
26. Fallah, S.; Alavi, N.; Tavakoli, O.; Shahsavani, A.; Sadani, M. Optimization of hydrothermal carbonization of food waste as sustainable energy conversion approach: Enhancing the properties of hydrochar by landfill leachate substitution as reaction medium and acetic acid catalyst addition. *Energy Convers. Manag.* **2023**, *297*, 117647. [CrossRef]
27. Zhang, G.; Liu, Q.; Li, X.; Kong, G.; Cao, T.; Cheng, Q.; Zhang, Z.; Zhang, X.; Han, L. Catalytic hydrothermal co-liquefaction of sewage sludge and agricultural biomass for promoting advanced biocrude production. *J. Clean. Prod.* **2023**, *428*, 139470. [CrossRef]
28. Kojić, M.; Petrović, J.; Petrović, M.; Stanković, S.; Porobić, S.; Marinović-Cincović, M.; Mihajlović, M. Hydrothermal carbonization of spent mushroom substrate: Physicochemical characterization, combustion behavior, kinetic and thermodynamic study. *J. Anal. Appl. Pyrol.* **2021**, *155*, 105028. [CrossRef]
29. Ahmad, S.; Zhu, X.; Wei, X.; Zhang, S. Influence of process parameters on hydrothermal modification of soybean residue: Insight into the nutrient, solid biofuel, and thermal properties of hydrochars. *J. Environ. Manag.* **2021**, *283*, 111981. [CrossRef]
30. Xiong, J.B.; Pan, Z.Q.; Xiao, Z.F.; Huang, H.; Lai, F.Y.; Wang, J.X.; Chen, S.W. Study on the hydrothermal carbonization of swine manure: The effect of process parameters on the yield/properties of hydrochar and process water. *J. Anal. Appl. Pyrol.* **2019**, *144*, 104692. [CrossRef]
31. Islam, M.A.; Akber, M.A.; Limon, S.H.; Akbor, A.; Islam, A. Characterization of solid biofuel produced from banana stalk via hydrothermal carbonization. *Biomass Conv. Bioref.* **2019**, *9*, 651–658. [CrossRef]
32. Cai, J.; Li, B.; Chen, C.; Wang, J.; Zhao, M.; Zhang, K. Hydrothermal carbonization of tobacco stalk for fuel application. *Bioresour. Technol.* **2016**, *220*, 305–311. [CrossRef] [PubMed]
33. Funke, A.; Ziegler, F. Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuel. Bioprod. Biorefin.* **2010**, *4*, 160–177. [CrossRef]
34. Kambo, H.S.; Dutta, A. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sust. Energ. Rev.* **2015**, *45*, 359–378. [CrossRef]
35. Parshetti, G.K.; Hoekman, K.S.; Balasubramanian, R. Chemical, structural and combustion characteristics of carbonaceous products obtained by hydrothermal carbonization of palm empty fruit bunches. *Bioresour. Technol.* **2013**, *135*, 683–689. [CrossRef] [PubMed]
36. Nakason, K.; Panyapinyopol, B.; Kanokkantung, V.; Viriya-empikul, N.; Kraithong, W.; Pavasan, P. Hydrothermal carbonization of unwanted biomass materials: Effect of process temperature and retention time on hydrochar and liquid fraction. *J. Energy Inst.* **2018**, *91*, 786–796. [CrossRef]
37. Kambo, H.S.; Dutta, A. Strength, storage, and combustion characteristics of densified lignocellulosic biomass produced via torrefaction and hydrothermal carbonization. *Appl. Energy* **2014**, *135*, 182–191. [CrossRef]
38. Djandja, O.S.; Liew, R.K.; Liu, C.; Liang, J.; Yuan, H.; He, W.; Feng, Y.; Lougou, B.G.; Duan, P.G.; Lu, X.; et al. Catalytic hydrothermal carbonization of wet organic solid waste: A review. *Sci. Total Environ.* **2023**, *873*, 162119. [CrossRef]
39. Lang, Q.; Guo, X.; Wang, C.; Li, L.; Li, Y.; Xu, J.; Zhao, X.; Li, J.; Liu, B.; Sun, Q.; et al. Characteristics and phytotoxicity of hydrochar-derived dissolved organic matter: Effects of feedstock type and hydrothermal temperature. *J. Environ. Sci.* **2023**, *in press*. [CrossRef]

40. Alvarez-Murillo, A.; Libra, J.A.; Ro, K.S. Theoretical framework for estimating design reactor pressure for water-based hydrothermal carbonization (HTC) systems. *Therm. Sci. Eng. Prog.* **2022**, *30*, 101241. [CrossRef]
41. Güleç, F.; Garsia Riesco, L.M.; Williams, O.; Kostas, E.; Samson, A.; Lester, E. Hydrothermal conversion of different lignocellulosic biomass feedstocks—Effect of the process conditions on hydrochar structures. *Fuel* **2021**, *302*, 121166. [CrossRef]
42. Minaret, J.; Dutta, A. Comparison of liquid and vapor hydrothermal carbonization of corn husk for the use as a solid fuel. *Bioresour. Technol.* **2016**, *200*, 804–811. [CrossRef] [PubMed]
43. Yan, M.; He, L.; Prabowo, B.; Fang, Z.; Lin, J.; Xu, Z.; Hu, Y. Effect of pressure and atmosphere during hydrothermal treatment on the properties of sewage sludge-derived solid fuel. *J. Mater. Cycles Waste Manag.* **2018**, *20*, 1594–1604. [CrossRef]
44. Khan, N.; Mohan, S.; Dinesha, P. Regimes of hydrochar yield from hydrothermal degradation of various lignocellulosic biomass: A review. *J. Clean. Prod.* **2021**, *288*, 125629. [CrossRef]
45. Azzaz, A.A.; Khiari, B.; Jellali, S.; Ghimbeu, C.M.; Jeguirim, M. Hydrochars production, characterization and application for wastewater treatment: A review. *Renew. Sust. Energ. Rev.* **2020**, *127*, 109882. [CrossRef]
46. Gao, Y.; Wang, X.; Wang, J.; Li, X.; Cheng, J.; Yang, H. Effect of residence time on chemical and structural properties of hydrochar obtained by hydrothermal carbonization of water hyacinth. *Energy* **2013**, *58*, 376–383. [CrossRef]
47. Zhang, T.; Kumar, R.; Tsai, Y.D.; Elander, R.T.; Wyman, C.E. Xylose yields and relationship to combined severity for dilute acid post-hydrolysis of xylooligomers from hydrothermal pretreatment of corn stover. *Green Chem.* **2015**, *17*, 394–403. [CrossRef]
48. He, M.; Cao, Y.; Xu, Z.; You, S.; Ruan, R.; Gao, B.; Wong, K.H.; Tsang, D.C.W. Process water recirculation for catalytic hydrothermal carbonization of anaerobic digestate: Water-Energy-Nutrient Nexus. *Bioresour. Technol.* **2022**, *361*, 127694. [CrossRef]
49. Sarrion, A.; de la Rubia, A.; Coronella, C.; Mohedano, A.F.; Diaz, E. Acid-mediated hydrothermal treatment of sewage sludge for nutrient recovery. *Sci. Total Environ.* **2022**, *838*, 156494. [CrossRef]
50. Chen, F.; Zhang, Y.; Zheng, M.; Xiao, Y.; Hu, H.; Liang, Y.; Liu, Y.; Dong, L. Preparation of High-Performance Porous Carbon Materials by Citric Acid-Assisted Hydrothermal Carbonization of Bamboo and Their Application in Electrode Materials. *Energ. Fuel.* **2022**, *36*, 9303–9312. Available online: <https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c01828> (accessed on 30 November 2023). [CrossRef]
51. Ma, R.; Fakudz, S.; Shang, Q.; Wei, Y.; Chen, J.; Liu, C.; Han, J.; Chu, Q. Catalytic hydrothermal carbonization of pomelo peel for enhanced combustibility of coal/hydrochar blends and reduced CO₂ emission. *Fuel* **2021**, *304*, 121422. [CrossRef]
52. Faradilla, R.H.F.; Lucia, L.; Hakovirta, M. Remarkable physical and thermal properties of hydrothermal carbonized nanoscale cellulose observed from citric acid catalysis and acetone rinsing. *Nanomaterials* **2020**, *10*, 1049. [CrossRef] [PubMed]
53. Zhang, C.; Ma, X.; Chen, X.; Tian, Y.; Zhou, Y.; Lu, X.; Huang, T. Conversion of water hyacinth to value-added fuel via hydrothermal carbonization. *Energy* **2020**, *197*, 117193. [CrossRef]
54. Qi, R.; Xu, Z.; Zhou, Y.; Zhang, D.; Sun, Z.; Chen, W.; Xiong, M. Clean solid fuel produced from cotton textiles waste through hydrothermal carbonization with FeCl₃: Upgrading the fuel quality and combustion characteristics. *Energy* **2021**, *214*, 118926. [CrossRef]
55. Koprivica, M.; Petrović, J.; Ercegović, M.; Simić, M.; Milojković, J.; Šoštarić, T.; Dimitrijević, J. Improvement of combustible characteristics of Paulownia leaves via hydrothermal carbonization. *Biomass Conv. Bioref.* **2022**. [CrossRef]
56. Ischia, G.; Fiori, L.; Gao, L.; Goldfarb, J.L. Valorizing municipal solid waste via integrating hydrothermal carbonization and downstream extraction for biofuel production. *J. Clean. Prod.* **2021**, *289*, 125781. [CrossRef]
57. Santos Santana, M.; Pereira Alves, R.; da Silva Borges, W.M.; Francisquini, E.; Guerreiro, M.C. Hydrochar production from defective coffee beans by hydrothermal carbonization. *Bioresour. Technol.* **2020**, *300*, 122653. [CrossRef]
58. Wang, L.; Li, A.; Chang, Y. Hydrothermal treatment coupled with mechanical expression at increased temperature for excess sludge dewatering: Heavy metals, volatile organic compounds and combustion characteristics of hydrochar. *Chem. Eng. J.* **2016**, *297*, 1–10. [CrossRef]
59. Chen, Y.; Huang, S.A.; Yu, K.; Guo, J.Z.; Wang, Y.X.; Li, B. Adsorption of lead ions and methylene blue on acrylate-modified hydrochars. *Bioresour. Technol.* **2023**, *379*, 129067. [CrossRef]
60. Petrović, J.; Ercegović, M.; Simić, M.; Kalderis, D.; Koprivica, M.; Milojković, J.; Radulović, D. Novel Mg-doped pyro-hydrochars as methylene blue adsorbents: Adsorption behavior and mechanism. *J. Mol. Liq.* **2023**, *376*, 121424. [CrossRef]
61. Petrović, J.; Stojanović, M.; Milojković, J.; Petrović, M.; Šoštarić, T.; Laušević, M.; Mihajlović, M. Alkali modified hydrochar of grape pomace as a perspective adsorbent of Pb²⁺ from aqueous solution. *J. Environ. Manag.* **2016**, *182*, 292–300. [CrossRef]
62. Ali, H.; Khan, E.; Ilahi, I. Environmental chemistry and ecotoxicology of hazardous heavy metals: Environmental persistence, toxicity, and bioaccumulation. *J. Chem.* **2019**, *2019*, 6730305. [CrossRef]
63. Huang, S.A.; Teng, H.J.; Su, Y.T.; Liu, X.M.; Li, B. Trithiocyanurate-functionalized hydrochar for effectively removing methylene blue and Pb (II) cationic pollutants. *Environ. Pollut.* **2023**, *337*, 122585. [CrossRef] [PubMed]
64. Qin, X.; Meng, W.; Cheng, S.; Xing, B.; Shi, C.; Nie, Y.; Wang, Q.; Xia, H. Efficient removal of heavy metal and antibiotics from wastewater by phosphate-modified hydrochar. *Chemosphere* **2023**, *345*, 140484. [CrossRef]
65. Jiang, L.; Li, K.; Xia, L.; Gao, J.; Tang, L.; Jia, Y. KOH-modified hydrochar produced from Cd/Zn hyperaccumulator *Sedum Alfredii* Hance for aqueous Cd(II) removal: Behavior and mechanism. *J. Environ. Chem. Eng.* **2023**, *11*, 110925. [CrossRef]
66. Algethami, J.S.; Alhamami, M.A.M.; Alqadami, A.A.; Melhi, S.; Seliem, A.F. Adsorptive performance of a new magnetic hydrochar nanocomposite for highly efficient removal of cadmium ions from water: Mechanism, modeling, and reusability studies. *Environ. Technol. Innov.* **2023**, *32*, 103404. [CrossRef]

67. Fouda-Mbanga, B.G.; Velepini, T.; Pillay, K.; Tywabi-Ngeva, Z. Hydrothermal development of magnetic-hydrochar nanocomposite from pineapple leaves and its performance as an adsorbent for the uptake of Mn^{2+} and reuse of the metal loaded adsorbent in latent fingerprint. *J. Saudi Chem. Soc.* **2023**, *27*, 101624. [[CrossRef](#)]
68. Koprivica, M.; Simić, M.; Petrović, J.; Ercegović, M.; Dimitrijević, J. Evaluation of Adsorption Efficiency on Pb(II) Ions Removal Using Alkali-Modified Hydrochar from *Paulownia* Leaves. *Processes* **2023**, *11*, 1327. [[CrossRef](#)]
69. Kim, H.; Lee, S.Y.; Choi, J.W.; Jung, K.W. Synergistic effect in simultaneous removal of cationic and anionic heavy metals by nitrogen heteroatom doped hydrochar from aqueous solutions. *Chemosphere* **2023**, *323*, 138269. [[CrossRef](#)]
70. Chen, Z.L.; Xu, H.; Bai, L.Q.; Feng, Y.L.; Li, B. Protonated-amino-functionalized bamboo hydrochar for efficient removal of hexavalent chromium and methyl orange. *Prog. Nat. Sci. Mater.* **2023**, *33*, 501–507. [[CrossRef](#)]
71. Deng, J.; Li, X.; Wei, X.; Liu, Y.; Liang, J.; Song, B.; Shao, Y.; Huang, W. Hybrid silicate-hydrochar composite for highly efficient removal of heavy metal and antibiotics: Coadsorption and mechanism. *Chem. Eng. J.* **2020**, *387*, 124097. [[CrossRef](#)]
72. Kojić, M.; Mihajlović, M.; Marinović-Cincović, M.; Petrović, J.; Katanić, Đ.; Krstić, A.; Butulija, S.; Onija, A. Calcium-pyrohydrochar derived from the spent mushroom substrate as a functional sorbent of Pb^{2+} and Cd^{2+} from aqueous solutions. *Waste Manag. Res.* **2022**, *40*, 1629–1636. [[CrossRef](#)] [[PubMed](#)]
73. Haris, M.; Khan, M.W.; Paz-Ferreiro, J.; Mahmood, N.; Eshtiaghi, N. Synthesis of functional hydrochar from olive waste for simultaneous removal of azo and non-azo dyes from water. *Chem. Eng. J. Adv.* **2022**, *9*, 100233. [[CrossRef](#)]
74. Madduri, S.; Elsayed, I.; Hassan, E.B. Novel oxone treated hydrochar for the removal of Pb(II) and methylene blue (MB) dye from aqueous solutions. *Chemosphere* **2020**, *260*, 127683. [[CrossRef](#)] [[PubMed](#)]
75. Camilo, F.C.; de Araújo, T.P.; Quesada, H.B.; Moura, A.A.; Murilo Pereira, M.; Bergamasco, R.; Faria, S.H.; Simões Dornellas de Barros, M.A. Synthesis of hydrochars derived from industrial laundry sludge and its application in the removal of cationic dye. *J. Water Process. Eng.* **2021**, *40*, 101999. [[CrossRef](#)]
76. Kohzadi, S.; Marzban, N.; Libra, J.A.; Bundschuh, M.; Maleki, A. Removal of RhB from water by Fe-modified hydrochar and biochar—An experimental evaluation supported by genetic programming. *J. Mol. Liq.* **2023**, *369*, 120971. [[CrossRef](#)]
77. Algethami, J.S.; Alhamami, M.A.M.; Alqadami, A.A.; Melhi, S.; Seliem, A.F. Magnetic hydrochar grafted-chitosan for enhanced efficient adsorption of malachite green dye from aqueous solutions: Modeling, adsorption behavior, and mechanism analysis. *Int. J. Biol. Macromol.* **2024**, *254*, 127767. [[CrossRef](#)]
78. Jais, F.J.; Ibrahim, S.; Chee, C.Y.; Ismail, Z. Solvothermal growth of the bimetal organic framework (NiFe-MOF) on sugarcane bagasse hydrochar for the removal of dye and antibiotic. *J. Environ. Chem. Eng.* **2021**, *9*, 106367. [[CrossRef](#)]
79. Jais, F.M.; Chee, C.Y.; Ismail, Z.; Ibrahim, S. Experimental design via NaOH activation process and statistical analysis for activated sugarcane bagasse hydrochar for removal of dye and antibiotic. *J. Environ. Chem. Eng.* **2021**, *9*, 104829. [[CrossRef](#)]
80. Wang, J.; Wang, S. Removal of pharmaceuticals and personal care products (PPCPs) from wastewater: A review. *J. Environ. Manag.* **2016**, *182*, 620–640.
81. Delgado-Moreno, L.; Bazhari, S.; Gasco, G.; Méndez, A.; Azzouzi, M.E.; Romero, E. New insights into the efficient removal of emerging contaminants by biochars and hydrochars derived from olive oil wastes. *Sci. Total Environ.* **2021**, *752*, 141838. [[CrossRef](#)]
82. Yudha, S.P.; Tekasakul, S.; Phoungthong, K.; Chuenchom, L. Green synthesis of low-cost and eco-friendly adsorbent for dye and pharmaceutical adsorption: Kinetic, isotherm, thermodynamic and regeneration studies. *Mater. Res. Express* **2019**, *6*, 125526. [[CrossRef](#)]
83. Kumar, P.S.; Shanmugapriya, M.; Prasannamedha, G.; Rangasamy, G. Immobilization of hydrochar in cellulose beads for eradicating paracetamol from synthetic and sewage water. *Environ. Pollut.* **2023**, *342*, 123035. [[CrossRef](#)] [[PubMed](#)]
84. Hayoun, B.; Escudero-Curiel, S.; Bourouina, M.; Bourouina-Bacha, S.; Angeles Sanromán, M.; Pazos, M. Preparation and characterization of high performance hydrochar for efficient adsorption of drugs mixture. *J. Mol. Liq.* **2022**, *353*, 118797. [[CrossRef](#)]

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