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Hydrochars production, characterization and application for wastewater treatment: A review

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ABSTRACT

Hydrothermal carbonization (HTC) of wet solid wastes has been pointed out as an eco-friendly, flexible and highly efficient technology for the sustainable valorization of multiple sourced wastes. In this review paper, most recent studies on hydrochars (solid residue of the HTC process) production, characterization and application for wastewaters treatment was summarized and deeply discussed. The role of initial feedstock source nature and characteristics as well as the HTC experimental conditions including the temperature, the residence time and the pH media was assessed. Physical and chemical activation methods including the use of oxygen, steam, microwave, acids, alkaline, organics and salty solutions for the improvement of the physicochemical properties of the produced hydrochars are compared. The efficiency of these raw/modified hydrochars along with the involved mechanisms during organic (dyes) and mineral pollutants (heavy metals and nutrients) removal from aqueous solutions is also reviewed. Finally, this paper addresses the main challenges and also demonstrates insights on new directions for hydrochars research and development in the future.

1. Introduction

The energy production from fossil fuels has raised several environmental and health problems. Therefore, numerous studies have explored the potential of various sustainable energy sources such as wind, sun and biomass [1]. The latter includes the exploitation of abundant and low-cost by-products issued from vegetal, animal and industrial processing sources. These different feedstocks present very interesting physico-chemical properties that can be employed in both energetic and environmental applications [2]. Despite their relative potential when used in their raw state, it has been found that the thermal/chemical/biological conversion of these resources could significantly alter their properties towards an efficient energy production and environmental applications [3].

The selection of the appropriate conversion method depends on the biomass properties, on pretreatments techniques (drying, densification, ...) and logistics (transport, storage) [4]. For instance, the biological techniques are sensitive to the input feedstock because, the role of microorganisms could be easily inhibited by toxic substances in the biomass [5]. In addition, these methods require long residence times resulting in higher volumes and manufacturing costs [6]. On the contrary, thermochemical methods require from a few minutes to a few hours for the process and does not rely on microorganisms [7]. This property encourages the treatment of heterogeneous materials or substrates of low purity (e.g. organic wastes, sewage sludge, etc ...). Among the thermochemical processes, the slow pyrolysis has the advantage of producing both liquid and gaseous fractions (bio-oil and syngas) that can be upgraded as biofuels as well as a solid fraction (biochar). The later

Abbreviations: HHV, High Heating Values (kJ/kg); LHV, Low Heating Values (kJ/kg); HTC, Hydrothermal Carbonization; TG, Thermogravimetry; DTG, Derivative Thermogravimetry; AC, Activated Carbon; BET, Brunauer-Emmett-Teller; SSA, Specific Surface Area (m²/g); VM, Volatile Matter; FC, Fixed Carbon; T, Temperature (K); HIU, High-Intensity Ultrasound; pH_{ZPC}, pH of Zero Point Charge; CEC, Cation Exchange Capacity; MWe, Megawatt electrical.

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ones can be used in many applications such as soils amendment, water and gas treatment, energy storage, etc. [8]. However, the slow pyrolysis could be economically limited when the raw biomass has high moisture contents (greater than 60%) since a controlled drying step is necessary and larger volumes for storage are needed. Such constraint could be faced for industrial organic wastes such as agri-food residues, paper, woodcrafts, etc. [9,10].

The hydrothermal carbonization (HTC) technology could be a promising alternative for converting wet biomasses. This process taking place in water, under thermal and self-pressure generated conditions, allows the generation of relatively high fraction of carbon residue named hydrochar (>60%) exhibiting a high carbon sequestration potential [11].

Owing to their interesting physico-chemical properties, the application of hydrochars in multiple fields was assessed [12] and a growing number of publications dealt with this topic (Fig. 1). Their applications could be found in energy storage, supercapacitors and batteries (Li/Naion batteries) [13], CO₂ and H₂ gas storage [14], soil amendments [15] and pollutants removal [16]. The latter investigation increase is

explained by the physico-chemical characteristics of hydrochars favoring the effective adsorption of various ions/molecules.

This review paper aims: i) to provide an introduction on the hydrothermal carbonization and the main parameters governing this process, ii) to give an overview of the hydrochar modification methods and their effect on the physico-chemical properties, and finally iii) to provide the main hydrochars application for the removal of pollutants from aqueous effluents.

2. Hydrothermal carbonization

The hydrothermal carbonization represents an innovative pathway to the thermal conversion -at moderate temperature and autogenous pressure-of wet biomasses [17]. It consists in converting organic feedstock, in presence of water, into bio-oil, gas and a rich carbon solid product (called hydrochar). Their yields and physico-chemical characteristics are related to the feedstock nature and the operating conditions [18]. For example, at temperature range varying between 140 and 350 °C, the moisture trapped in a sealed reactor (Fig. 2) undergoes

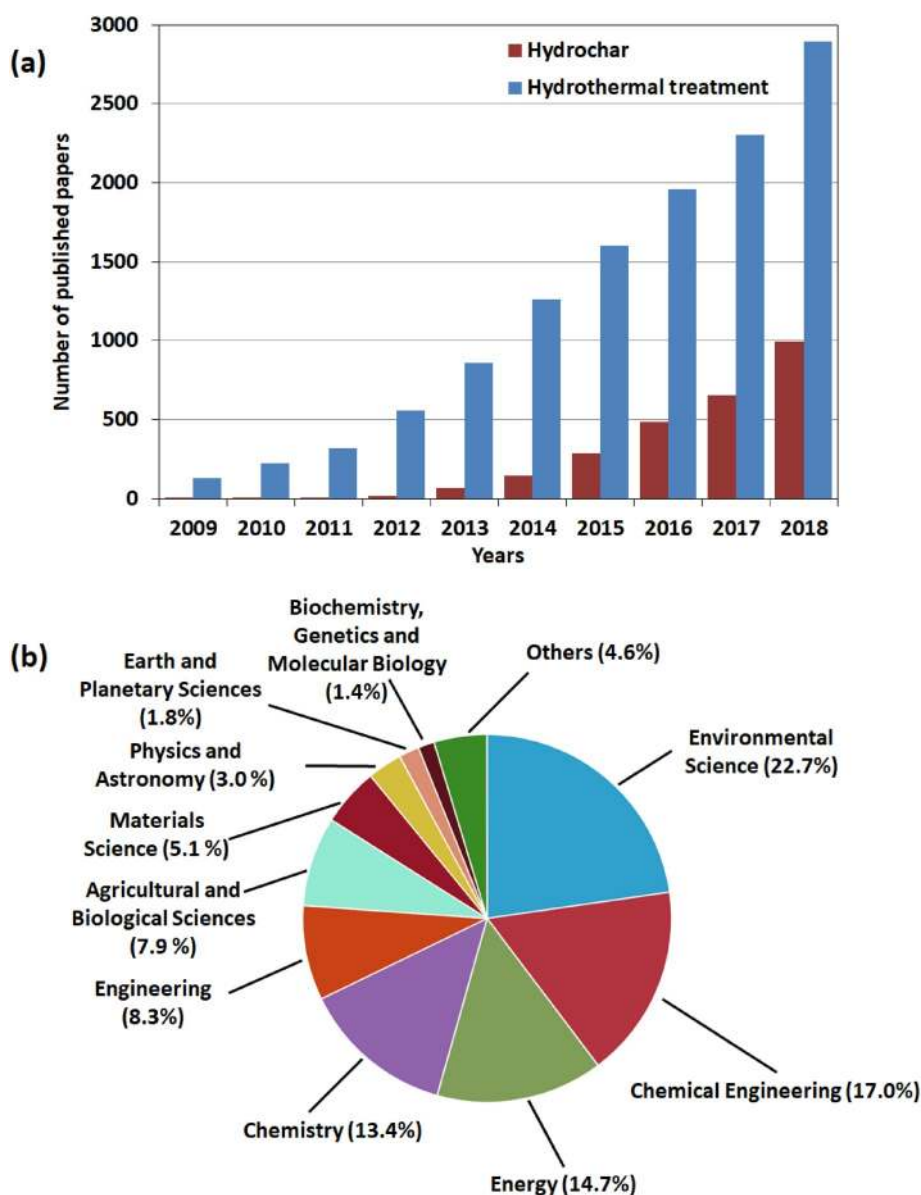


Fig. 1. (a) Evolution of the number of papers dealing with the hydrothermal carbonization and hydrochars production topics from 2009 to 2018 and (b) papers partition about hydrochar topic by respective research field (Source: Scopus 2018).

significant thermodynamic changes within the subcritical phase region [19]. An anoxic reaction is thereby triggered as, in absence of atmospheric air feed, the added water and the initial biomass moisture are considered as the reaction media. The exothermic reaction causes the intrinsic moisture transformation present in the feedstock into water vapor which further enhances the feedstock carbonization [20]. The quick change in the water phase generally causes a dramatic increase in the reactor's inner pressure varying between 2 and 10 MPa [21]. These critical phase modifications could engender the instability of the liquid fraction. It has been highlighted that under high pressure and temperature, water molecules undergo a deionization process leading to the

generation of more stable entities, i.e. H_3O^+ and OH^- [22].

The final hydrochar yield thorough HTC depends mainly on the initial feedstock properties. In fact, the carbon and minerals contents, as well as the polymeric structure of the feedstock will guide the degradation pathway of the solid matrix.

2.1. Feedstock nature

In the current emerging context of clean energy, a special attention is paid to the HTC applied to large varieties of feedstock such as lignocellulosic residues [21], agricultural residues [24], animal wastes [25],

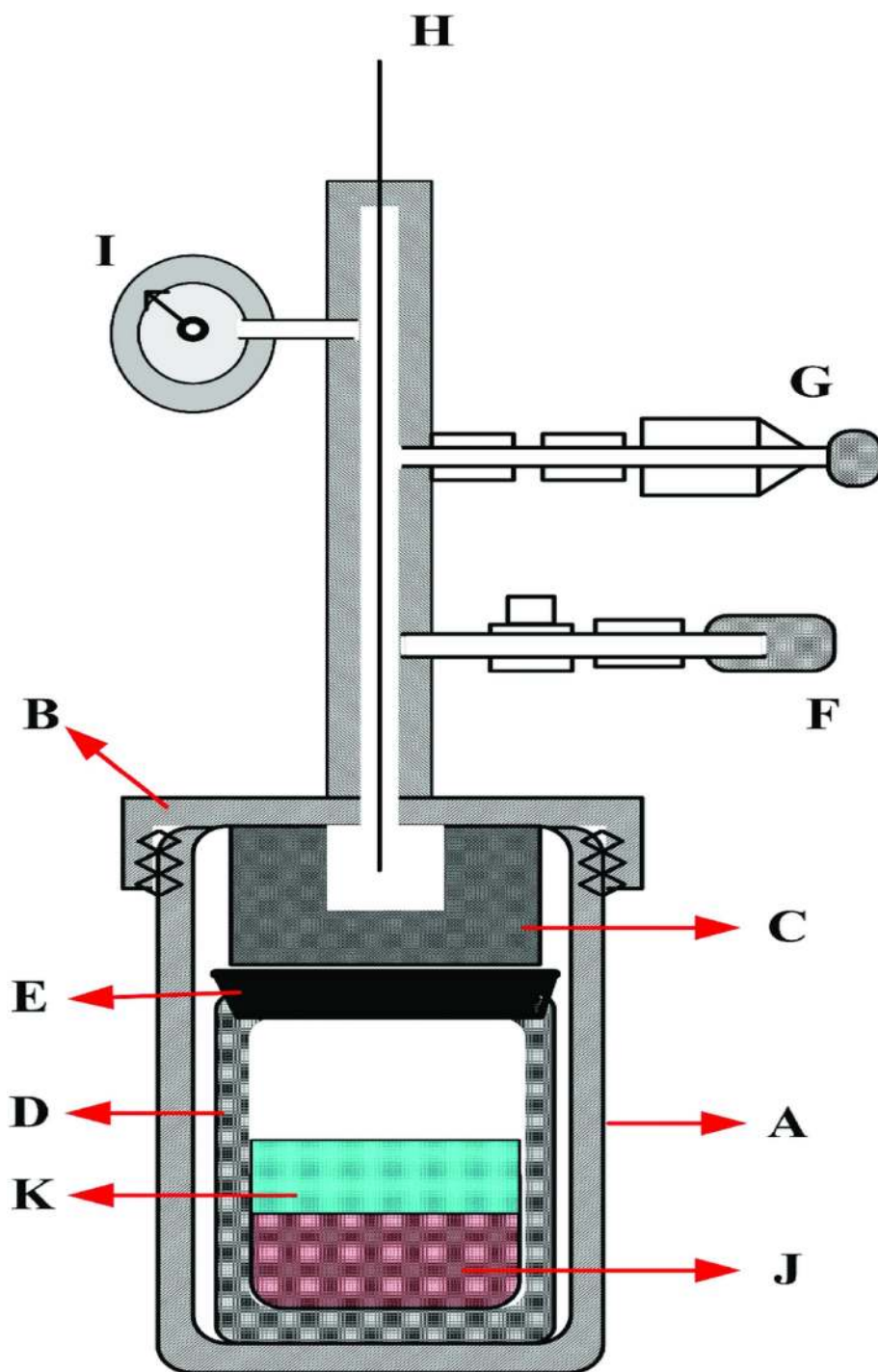


Fig. 2. The structure of hydrothermal carbonization (HTC) reactor. A: Stainless steel vessel, B: pressure vessel closure, C: Fixing iron, D: Teflon cylinder, E: Teflon seal cover, F: Pressure valve, G: Relieve valve, H: Thermocouple, I: Pressure gauge, J: Biomass material, K: Water (Reproduced with permission from Ref. [23]).

food wastes [26], food processing by-products [27], municipal wastes [28], and wastewater treatment plants' (WWTPs) activated sludge [29]. In the next part, the main feedstock along with their hydrochar derived properties will be described in details.

2.1.1. Livestock wastes

That initial feedstock is generally characterized by low amounts in fixed carbon and an important content in volatile matter (Table 1) [30]. After HTC, specific changes in the morphological and chemical properties could be noticed (Fig. 3). Manure based hydrochars present low porosities with heterogeneous chemical similar to natural charcoal. This finding could be attributed to the applied low carbonization temperatures that generally do not exceed 350 °C. Such heat uptake is not sufficient enough for significant porosity development in the feedstock's aromatic structure [31]. Furthermore, the high content in volatile matter initially present in the feedstock could negatively affect the development of micro and meso-porosity due to their possible recombination with the aromatic structure. However, differently composed animal sourced hydrochars could present among them some differences due to their content in outsourced compounds. This could be remarked for example when examining dairy manure (Fig. 3a and b,c.) and poultry litter (Fig. 3d and e,f,g). As the latter one usually contains higher lignocellulosic compounds, the corresponding hydrochar shows the development of micro carbonaceous spheres on the surface, related to the dehydration of polymers (mainly, cellulose and polysaccharides) [32]. In the dairy manure, however, the morphology is significantly changing with the temperature: from macroporous, to spheres then to tube-like structure. The SEM pictures lead to the conclusion that these different aspects seem to be related more to the feedstock nature than to the temperature.

The carbonization mechanism of animal wastes could be explained by following their combustion kinetics. Zhou et al. [34] investigated the effect of HTC temperature (180–240 °C) on the combustion characteristics of five animal sourced hydrochars using thermogravimetric analyses. Results showed that swine (SM), dairy (DM) and cattle beef (BM) manure presented similar combustion peaks at 1st to 2nd stages that gradually decrease with increasing the HTC temperature (Fig. 4). This is mainly attributed to the reduction of volatile matter content and the increase in fixed carbon percentage [35]. However, when using broiler (BL) feedstock, these peaks became tighter compared to manure based hydrochars. This could be explained by the presence of lignocellulosic materials that increased the fixed carbon content, the degree of carbonization and thus decreasing the O/C and H/C ratios. In fact, the carbon yield depends on the feedstock type but also on the temperature. Nevertheless, the highest temperature does not always give the highest yield. This may suggest that some inorganics are not kept in the material.

2.1.2. Agricultural feedstock

Agricultural biomasses are composed of cellulose (40–60%, wt.%), hemicellulose (20–40%, wt.%) and lignin (10–25%, wt.%) along with other lipid extracts [36]. They present heterogeneous surfaces with low specific surface areas and non-developed porous structures. The high concentration of hydroxyl, carboxylic and phenolic functional groups [37] together with the initial low content in C explain the high content of volatile matter and low percentage of fixed carbon in the agricultural biomass-hydrochar (Table 1).

During hydrothermal carbonization of agricultural feedstocks, hemicellulose undergoes a series of dehydration and decarboxylation reactions characterized by the liberation of H₂O molecules then followed by the decomposition of long chained polymers into a large spectrum of organic compounds such as organic acids (acetic, lactic, phenolic, oleic ...), alcohols (phenols, methanol ...) and saturated hydrocarbons and aromatic compounds (decane, methyltetrahydrofuran ...). For cellulose, hydrolysis by-products undergo isomerization, dehydration, and fragmentation followed by further polymerization and condensation reactions. The lignin degradation may be also simplified as

being the succession of a fast degradation into soluble fragments and a slow repolymerization (Fig. 5).

The produced hydrochars generally present *hydrophobic* aromatic inner structures and *hydrophilic* heterogeneous surfaces [32]. This succession of reactions leads to a significant mass loss translated in an increase of the volatile matter emissions, composed generally of CO, CO₂, H₂, CH₄, NO_x and NH₃ [39], which explains the decrease in the H/C and O/C ratios during the carbonization reactions.

In Fig. 6, the van Krevelen diagram for the hydrochar (data in Table 1) shows that these hydrochars have the ratios within the limit of 0.6, recommended by the European Biochar Certificate (EBC) except for the sewage sludge. As a comparison between two feedstock types, the hydrothermal carbonization of two wastes at 200 and 250 °C for 1h conducted by Han et al. [40] (Sawdust) and Li et al. [41] (Swine manure) showed a significant difference in terms of H/C and O/C ratio (H/C: 1.26 vs. 0.12; O/C: 0.22 vs. 0.98, for sawdust and swine manure, respectively). The cellulose and lignin fractions present in the sawdust undergoes a depolymerization accompanied with the outer carbohydrate separation. The corresponding step is quickly followed by a re-condensation of the re-polymerized lignin compounds with an acidification of the hydrochar surface. On the other side, the high content in minerals and amine groups engendered the loss reduction in volatile matter and therefore the increase in fixed carbon contents [42].

2.1.3. Municipal solid wastes

Municipal solid wastes (MSW) is usually referred to wastes collected from urban and suburban commercial places, localities and households. It is a mixture of feedstocks, making the prediction of their degradation pattern fairly difficult. In fact, MSW could contain recyclable materials (organics: paper, clothes; minerals: glass, metallic wastes: batteries, cans ...), petrochemical materials (plastic, rubber, ...), biodegradable wastes (animal and vegetal leftovers), electronic wastes, biomedical and personal care wastes, toxic wastes (pesticides, herbicides ...), chemical hazardous wastes (paints, organic solvents ...) as well some inert compounds such as soil and rocks. The co-existence of organic and mineral elements at different concentrations impacts the mechanisms involved in the degradation of organic compounds [54]. The complexity of this feedstock relies on the diverse MSW composition and their physical properties. In fact, the collected wastes generally present very broad particle size distributions ranged between 0.02 and 60 cm [31]. Therefore, a supplementary processing step is required during investigation. It consists in sorting, shredding then sieving the MSW to obtain uniform final carbonaceous materials [31].

The MSW composition depends generally on its collection source, the consumption habits and socio-economical level of the agglomerations, regions and countries [55]. It is generally composed of a high percentage of volatile matter and medium to low content in fixed carbon. Ash content, on the other hand, could present very low (0.28%, Lin et al. [56]) to high (43.11%, Gai et al. [57]) percentages depending on the mineral content of the feedstock (Table 2). The MSW management was carried out using different methods. They include physical [58], chemical [59], biological [60] and thermal conversion methods (pyrolysis and HTC [56,61]). The HTC application allows the MSW conversion and ensures its carbonization at low temperatures. Therefore, it affects the final gaseous composition of the by-product (less emissions of CO₂ was reported) as well as the carbonization yield and the final physico-chemical properties [62].

In this context, Kim et al. [63] performed the HTC of digested sludge at different temperatures. The corresponding results showed that the energetic capacity of the produced hydrochar was densified by about 22% when increasing carbonization temperature from 180 to 280 °C. This finding was correlated by an increase in fixed carbon (+34.1%) contents. However, the increase in ashes (+26.6%) had probably mitigated the calorific value (15–20 kJ/kg).

Similarly, Lokahita et al. [64] investigated the degradation of wastes issued from food packaging industry. The results showed that fixed

Table 1

Chemical properties of some raw feedstock and their derived hydrochars (db, %: dry basis percentage; VM: Volatile Matter; FC: Fixed Carbon; –: not determined).

	Feedstock	Temperature (°C)	Residence time (h)	Hydrochar yield (db, %)	Proximate analysis (%)			Ultimate analysis (%)					Atomic ratio			Reference
					VM	Ash	FC	C	H	O	N	S	H/C	O/C	C/N	
Animal waste	Swine manure	Uncarbonized	10	55.54	81.41	17.16	1.43	39.57	5.78	33.65	3.37	0.48	1.75	0.64	13.70	[43]
		220			68.67	23.27	8.06	50.64	5.44	17.05	3.16	0.44	1.29	0.25	18.70	
	Poultry litter	Uncarbonized	4	33.34	72.95	16.37	10.67	42.22	5.59	30.96	4.19	0.65	1.59	0.55	11.76	[33]
		225			47.31	26.73	25.96	52.66	5.23	11.05	4.57	0.39	1.18	0.16	13.44	
Agricultural waste	Dairy manure	Uncarbonized	4	51.55	70.72	5.10	24.18	36.21	5.14	30.76	2.39	1.32	1.70	0.64	17.68	[30]
		220			50.95	35.14	13.91	41.60	4.15	17.00	1.75	0.37	1.20	0.31	27.73	
	Watermelon peel	Uncarbonized	6	90.32	–	9.17	–	41.18	6.56	41.45	1.63	–	1.91	0.75	29.47	[37]
		190			–	6.24	–	58.80	5.95	26.79	2.22	–	1.21	0.34	30.90	
		225			47.31	26.73	25.96	52.66	5.23	11.05	4.57	0.39	1.18	0.16	13.44	
	Algae	Uncarbonized	0.5	72.56	87.65	2.66	9.69	50.63	6.66	31.99	9.02	0.47	1.58	0.47	6.55	[44]
		200			79.65	4.10	16.25	59.66	8.04	21.08	8.10	0.36	1.62	0.27	8.59	
	Corn stover	Uncarbonized	12	49.78	79.34	3.51	17.15	45.12	5.77	45.19	0.41	–	1.54	0.74	128.39	[16]
		220			50.95	2.97	46.08	67.36	5.01	24.26	0.40	–	0.91	0.25	196.47	
	Coconut husk	Uncarbonized	4	67.50	61.80	3.40	34.80	48.30	5.60	42.10	0.40	0.10	1.42	0.67	140.88	[45]
		200			54.00	39.57	5.78	33.65	3.37	0.48	0.50	0.10	1.16	0.43	138.60	
	Waste rubber	Uncarbonized	1	97.67	63.26	4.90	31.84	50.64	5.44	17.05	3.16	0.44	1.20	0.04	196.24	[46]
		280			61.93	41.18	6.56	41.45	1.63	–	0.20	1.15	1.18	0.02	481.31	
Urban waste	Sugarcane industry residues	Uncarbonized	13	17.60	–	6.50	93.50	58.80	5.95	26.79	2.22	–	1.63	1.01	–	[47]
		190			–	42.22	5.59	30.96	4.19	0.65	3.80	1.50	1.31	0.10	20.42	
	Grape pomace	Uncarbonized	1	78.00	75.49	6.48	17.29	52.66	5.23	11.05	4.57	0.39	1.71	0.51	20.33	[48]
		200			66.60	50.63	6.66	31.99	9.02	0.47	1.97	0.16	1.46	0.36	34.72	
	Organic fraction of municipal solid waste	Uncarbonized	6	55.70	80.70	5.40	13.90	59.66	8.04	21.08	8.10	0.36	1.86	0.46	16.85	[49]
		220			66.90	45.12	5.77	45.19	0.41	–	3.90	–	1.20	0.15	20.82	
	Waste textile	Uncarbonized	1.5	67.00	81.13	0.28	18.59	67.36	5.01	24.26	0.40	–	1.23	0.62	29.63	[50]
		280			74.35	36.21	5.14	30.76	2.39	1.32	0.69	0.00	0.81	0.43	101.70	
	Municipal solid waste pulp	Uncarbonized	2	48.10	65.70	24.30	10.00	41.60	4.15	17.00	1.75	0.37	1.71	1.20	23.88	[51]
		300			40.20	39.50	20.30	43.90	4.00	15.70	2.30	<0.1	0.87	0.28	22.27	
	Sewage sludge	Uncarbonized	12	53.80	69.98	28.60	1.42	39.57	5.78	33.65	3.37	0.48	0.75	0.47	7.78	[52]
		200			45.00	50.64	5.44	17.05	3.16	0.44	2.20	3.90	2.12	1.60	17.23	

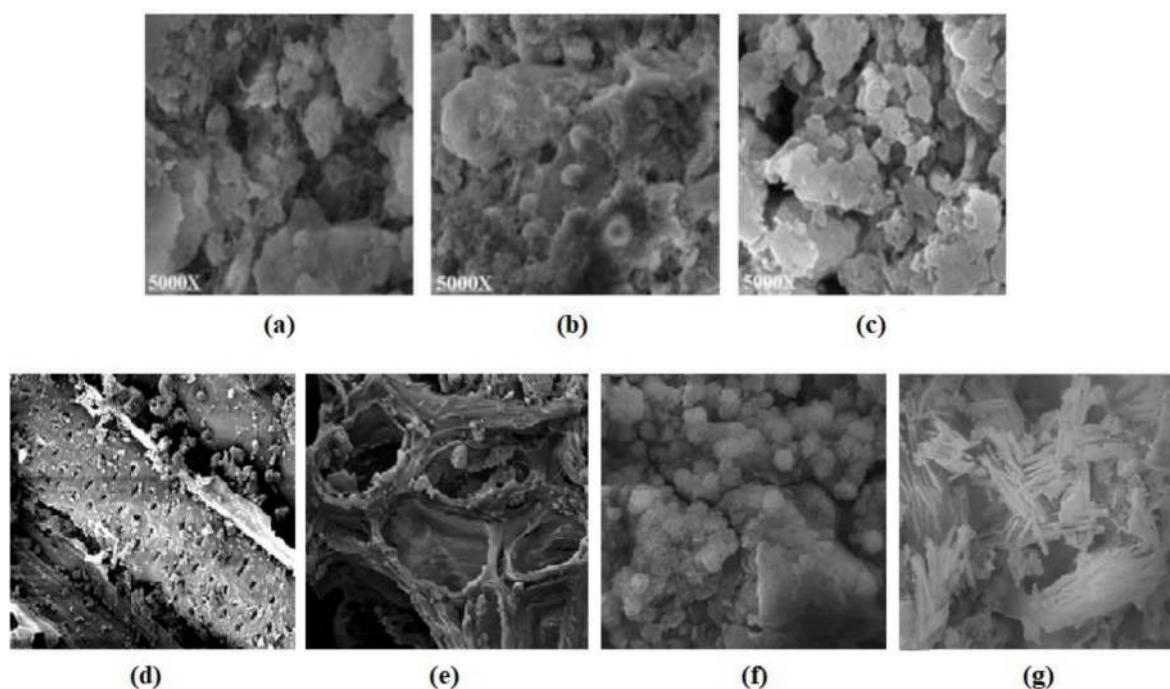


Fig. 3. SEM images of hydrochars obtained from dairy manure (a,b,c) and poultry litter (d,e,f,g) at different temperatures (a. 180 °C, b. 200 °C, c. 240 °C, d. 150 °C, e. 175 °C, f. 200 °C and g. 300 °C) (Reprinted from Ref. [30,33], Copyright (2017, 2016), with permission from Elsevier).

carbon content varying from 1.0% to 35.4% when increasing carbonization temperature and residence time. Furthermore, the hydrochar produced at 260 °C during 60 min, presented a very important HHV of 25.2 kJ/kg, which is similar to bituminous coal..

2.2. HTC experimental conditions

2.2.1. Carbonization temperature

The carbonization temperature is the main parameter governing the water phase status in the reactor. In particular, it affects the level of the inner pressure and the thermodynamic equilibrium between the solid, liquid and gaseous phases [28]. The subsequent products production depends mainly on the isotherm temperature. Indeed, higher heating rates at ion-dominated HTC reactions induce the disintegration of the solid matrix by the action of low water viscosity, which significantly enhances mass-transfer driven reactions [65]. This might result in a change in the final by-products percentage, and therefore, a constant decrease in the char yield (Table 3). In fact, such conditions promote the production of either bio-oil, the reaction is thereby called liquefaction, or gas with a gasification reaction controlling the carbonization tendency [66]. For instance, the food wastes HTC at temperatures varying between 150 and 350 °C showed a significant decrease in the hydrochar yield by about 49%, while the bio-oil final fraction increased by 10% [67]. For temperatures higher than 350 °C, both the hydrochar (29%) and bio-oil (31%) fractions decrease in the favor of non condensable gases fractions which significantly increases up to 67%. This behavior is related to the thermal decomposition of hydrochar with the formation of CO_x, H₂, H₂O ... gaseous species.

Furthermore, recurrent studies investigating the HTC of biomasses reported that the increase in operating temperatures causes a constant decrease in the O/C and H/C ratio (Fig. 7). For instance, Yao and Ma [70] reported that carbon content in fan palm hydrochars increased from 48.99% to 66.52% when increasing the temperature from 180 to 240 °C for 100 min, respectively. This is due to the synchronized reactions of dehydration and decarboxylation occurring at higher temperatures accompanied with the migration of minerals to the liquid and gaseous phases. Other studies suggested also that the selected

temperature determines the affected matrix by the heating gradient. In fact, this finding is not seen for animal wastes due to their heterogeneity. However, the effect of temperature on the feedstock issued from lignocellulosic materials could drive the carbonization reaction pathway, thus the final by-products [71]. Indeed, in the case of carbonization of lignocellulosic materials at low temperatures (<220 °C), the firstly affected components are the cellulose and the hemicellulose, which are transformed into simple acidic compounds [71]. Once the temperature increases (>220 °C), the ligninic structure is then affected under the presence of highly acidic molecules and undergoes a depolymerization and dehydration reaction. This operation is characterized by an increase in the amount of the released volatile matter, a formation of acid molecules (i.e., phenolic and lactonic free molecules, usually present in the bio-oil) and a significant rise in the fixed carbon content [72].

On the other hand, these chemical changes affect the hydrochars energy contents .. The raise in HTC temperature led to the increase of the carbon content and the decrease of the percentage of O and H contents. Yang et al. [73] showed that the reduction in oxygen content by 16% and hydrogen by 7% enhanced the high heating value from 17.1 to 20.3 MJ/kg during bamboo fibers HTC.

2.2.2. Residence time

The residence time is a determinant factor in the HTC process since exposure to longer heat periods contributes in higher conversion rates [16,42]. It has been reported that hydrochars production yields decrease when increasing heating time while fixed carbon fractions becomes more significant leading to the formation of a more stable hydrochars (Fig. 7).

In this context, Gao et al. [83] demonstrated that the structure of cellulose, xylan and rice straw during HTC have undergone an important modification as they presented altered surfaces with kinky morphologies and the apparition of micro-sphere particles. A significant decrease in the percentage of volatile matter and an increase in fixed carbon content were noted, which was mainly attributed to the decarboxylation and the polymerization of the constituent polymers (cellulose and hemicellulose) occurring at longer hydrolysis times. Similar trend was reported by Volpe et al. [84] during the HTC of the *Opuntia ficus-indica* at various

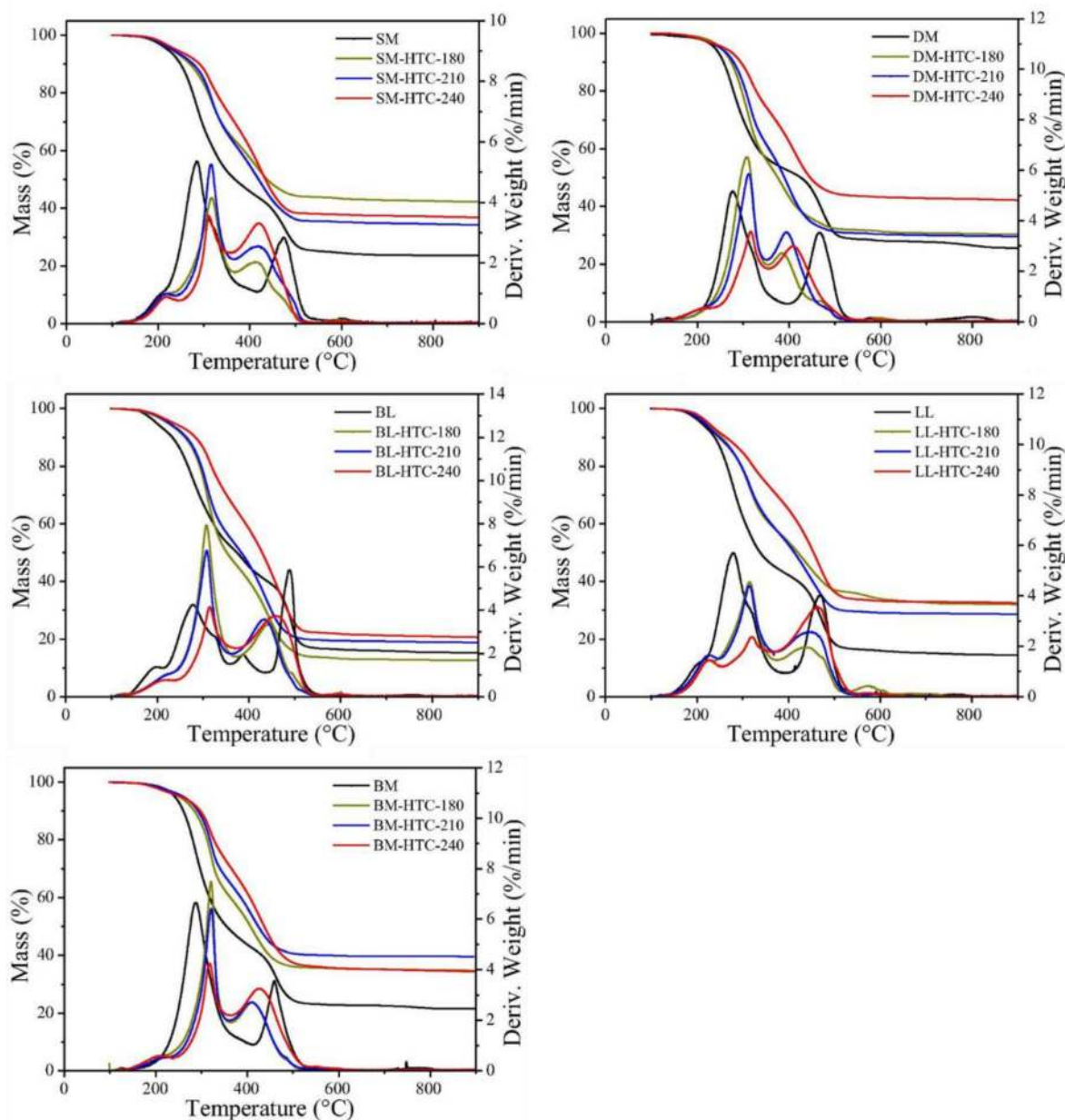


Fig. 4. TG-DTG curves of raw manures (swine manure (SM), dairy cattle manure (DM), broiler litter (BL), layer chicken litter (LL) and beef cattle manure (BM)) and their derived hydrochars at different carbonization temperatures (Reprinted from Ref. [34], Copyright (2019), with permission from Elsevier).

residence times between 30 and 180 min. FTIR analyses performed on the hydrochars showed a decrease in the esters and hydroxyl groups, related to the degradation of cellulose and hemicellulose and an increase in the lignin percentage, characterized with the important concentration of spherical structures.

Gao et al. [76] studied the HTC of water hyacinth at residence times varying between 30 min and 24 h. The results showed a reduction in O and H contents with a significant fluctuation in nitrogen percentages. The detected decrease in H/C and O/C ratios was mainly attributed to a dehydration mechanism and the involvement of H and O atoms in the formation of water molecules in subcritical phase. This could be further explained by the involvement of nitrogen atoms, as gases such as NO_x and NH_3 [85].

2.2.3. Medium pH

Other influencing parameters governing biomasses HTC is the initial acidity of the feed water. As presented earlier, the successive

degradation of the organic compounds generally leads to the formation of organic acids causing a decrease in the bio-oil and hydrochar pHs. Several studies showed that the released organic acids such as oleic, palmitic, benzoic, stearic, etc. [86], play a crucial role. Reza et al. [72] investigated the wheat straw HTC at different feed water pHs and reported an increase in feed water acidity which enhanced the degradation of polysaccharides and notably the xylose ($\text{C}_5\text{H}_{10}\text{O}_5$). This degradation contributes to the formation of furfural molecules ($\text{C}_5\text{H}_4\text{O}_2$), among other volatile compounds, through the following dehydration reaction:



This reaction affected the elemental composition of the produced hydrochars by a significant increase of the elemental carbon content and a decrease of the oxygen and hydrogen concentrations [87] (Fig. 8).

Zhai et al. [93] studied the effect of feedwater pH on the behavior of heavy metals present in a sewage sludge and their recombination patterns during the HTC process. It has been observed that pH variation

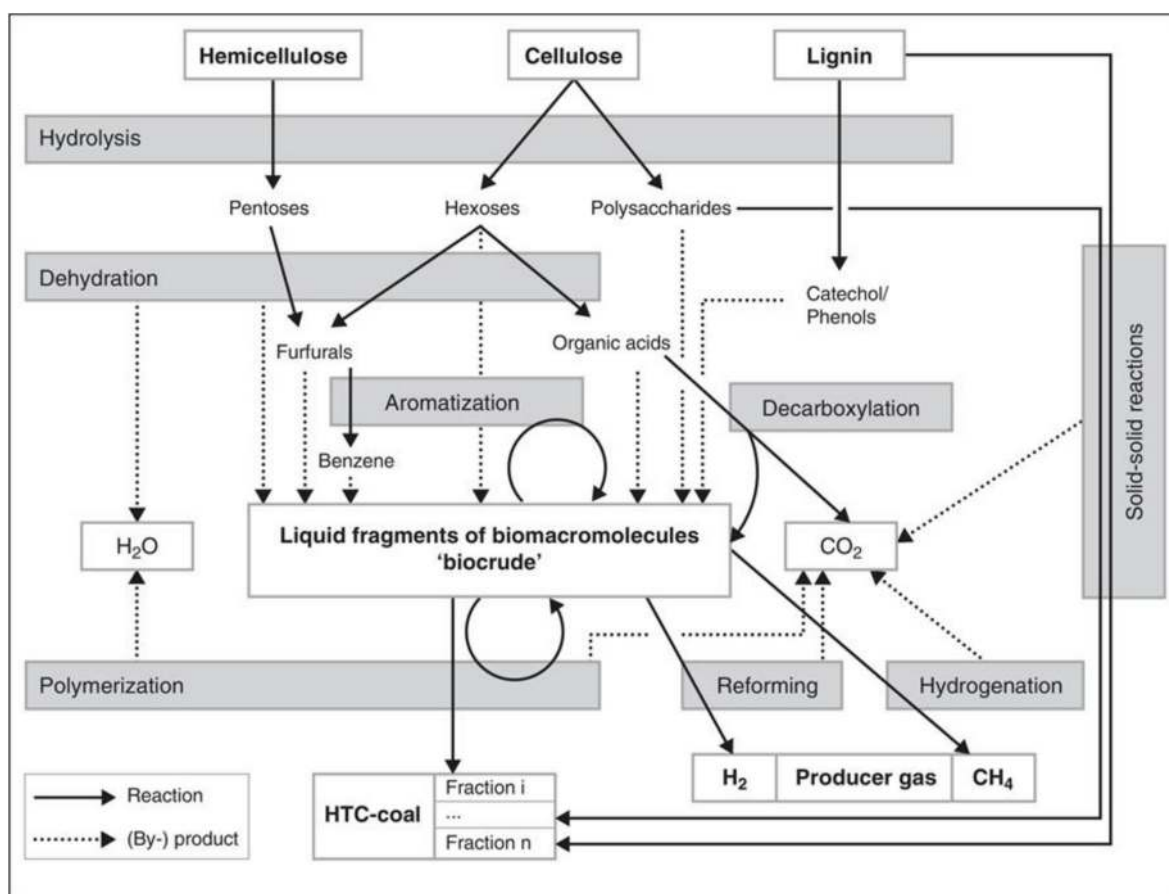


Fig. 5. Example of hydrochar formation mechanism from lignocellulosic biomass (Reprinted from Ref. [38], Copyright (2013), with permission from Elsevier).

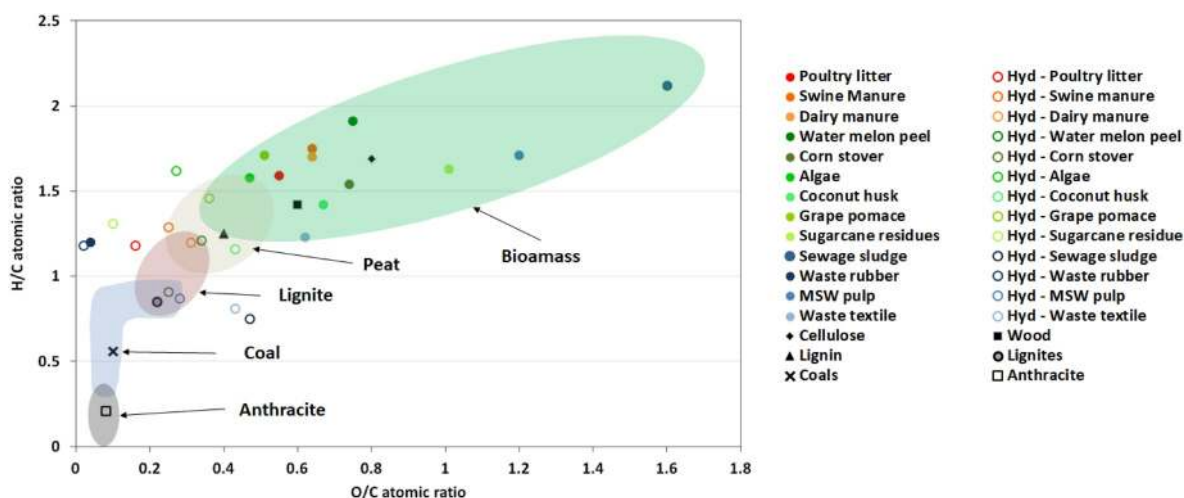


Fig. 6. Van Krevelen diagram for different hydrochars (based on reference data shown in Table 1) in comparison with model precursors (Reproduced with permission from Refs. [53]).

during HTC did not significantly affect the final hydrochar pH (close to neutral) (Fig. 9). In fact, hydrochars reactivity with the feed water depends on the hydrophobicity of their surface as well as the availability of the oxygen functional groups, as they could be either repulsive or attractive towards the produced organic elements [80]. The authors indicated that a decrease in the feed water pH could have negative effects on the stability of the retained heavy metals on the hydrochar surface (Fig. 9). An acidic environment could enhance the reducible and oxidizable heavy metals fractions which could alter the quality of water

and soils during their agricultural or environmental applications.

3. Hydrochar modification

3.1. Physical activation

Physical activation is usually performed to enhance the hydrochars porous properties and to reduce their surface heterogeneity. The main methods applied for hydrochars physical modification are based on

Table 2

Main properties of the raw MSW in literature [49–51,57].

	Composition	Value
Elemental analysis (% dry ash free)	C	27.69–52.00
	H	4.55–6.93
	O	12.81–61.69
	N	1.59–4.36
	S	0.32–1.46
Proximate analysis (db, %)	Fixed Carbon	8.38–13.90
	Volatile matter	48.51–86.94
	Ash	0.28–43.11
	HHV (kJ/kg, dry weight)	8.27–22.00

Table 3

Effect of hydrothermal carbonization temperature of food waste on the percentage of by-products distribution [67–69].

Temperature (°C)	HTC by-products		
	Hydrochar (%)	Bio-oil (%)	Non condensable gas (%)
150–250	35–60	25–38	15–20
250–350	25–43	35–50	25–38
>350 °C	10–29	23–31	44–67

three pathways, namely CO₂, O₂, steam-flow and wave-based treatments.

3.1.1. Oxygen based activation

Modification by oxygen-based molecules (O₂ and CO₂,) is widely used in the literature. The activation gas is selected according to the desired physico-chemical properties of the activated hydrochar and its subsequent use. For instance, CO₂-based activation is applied to ensure an increase of SSA, pore volume and pore size modulation (tuning) while the use of water steam as an activation gas is able to widen the pores diameters even at early activation stages. Román et al. [94] assessed the effect of two oxidizing gases, namely CO₂ and O₂ (substituted by air) on the structural characteristics of three feedstocks. They found that CO₂ enhanced the specific surface area for all hydrochars (e.g. from 204 to 438 m²/g for olive stones) with a significant increase in the micropores volume (e.g. from 0.115 to 0.231 cm³/g for olive stones). However, a significant decrease in the meso and macropores volume was detected after activation by a factor up to 4 (mesopore volume reduced from 0.061 to 0.017 cm³/g for sunflower stems). Ledesma et al. [95] reported a significant increase (about 75 times) in the specific surface of almond shell derived hydrochar treated with O₂ compared to non treated hydrochar. Authors suggested that meso and micropores present on the hydrochar surface were initially filled with volatile matter which blocked the char reactivity with O₂.

3.1.2. Steam activation

Steam is used as an endothermic modification method for impurities removal after HTC such as free radicals and deposited volatile matters. It generally proceeds by applying a constant flow rate of gas on the hydrochar surface at medium to high temperature (from 700 to 950 °C) [96]. This operation generally allows a better surface exposure and increases the hydrochars porosities and specific surface areas [97]. Saetea and Tippayawong showed that [98] that the steam activation of hydrothermally treated sewage sludge generated a hydrochar with a developed specific surface area of 600 m²/g against less than 10 m²/g for the starting raw. However, the intense decarboxylation and dehydration undergone by the hydrochar caused an important stripping of the surface functional groups and an increase in aromaticity [99].

3.1.3. Microwave and ultrasound treatment

Microwave treatment is usually used as a complementary method for the physiochemical properties modification of the hydrochar [100]. It consists in applying an electromagnetic radiation field with frequencies

varying between 300 MHz and 300 GHz coupled with heat temperature variation [101]. The heating mechanism of the materials through microwave radiation is fundamentally different from the conventional hydrothermal treatment. In fact, electromagnetic radiation is able to heat the entire mass simultaneously from surface to core in opposition to the conventional heating method that raises locally the temperature of the material surface until reaching gradually its inner zone [102]. Furthermore, the selective heating possibility through this technique is allowed by the absence of direct interference with the heating source. Such feature is important when carbonization is desired at high temperatures. Dai et al. [103] studied the HTC of bamboo sawdust conventionally and in presence of microwave irradiation. The reported results showed that microwave treatment at a power of 800W led to an increase in carbon (2%) contents of the biomass for the same used heating temperature (230 °C) when compared to conventional HTC. This direct heating gradient is nonetheless characterized with a non-uniform heating distribution due to the screening effect of the usual heterogeneous structure and content of the treated material. Figs. 10 and 11 show the physico-chemical properties (morphology, texture, structure and surface chemistry) of polypropylene hydrochar (from plastic waste) before and after microwave modification. One can see that the modification gave rise to changes in the material, where additional small fragments were formed and covered the matrix in the modified sample. The solid-state heating resulted in an increase in mass yield from 43.7 to 86.2% and, images of the powder implied that the microwave modified product was more homogenous in size as compared to the unmodified product.

Another wave-based technique consists of modifying the physico-chemical characteristics of the feed water using ultrasound activation. It has been suggested by Cravotto et al. [105] that high-intensity ultrasound (HIU) (Frequencies above 20 KHz) could enhance the feedstock swelling and favors their dissolution in water through a depolymerization sonochemical mechanism. The involved reactions did not affect the matter integrity, i.e. the covalent bonds forming the feedstock polymeric matrix since the acoustic beaming energy presents low energy levels of about 10⁻¹⁰ eV [106].

Alternatively, the sonic field triggers a cavitation phenomenon in the feedwater, thus generating homogeneous micro and macro bubbling [106]. At this point, two reactions are simultaneously evolved: (i) The rapid increase in the Reynolds number at high temperatures and pressure leading to the generation of active radicals formed in the water gaseous phase, similarly to a plasma driven reaction (OH•, HO_x, H•, O₂•, ...) [107], and (ii) the kinetic effect of the produced bubbles induces an eroding action during their impact on the feedstock's surface [108].

3.2. Chemical activation

3.2.1. Acidic modification

Hydrochars issued from vegetal or animal sources present very heterogeneous surface chemistry, with a concentrated presence of both basic (mainly hydroxyl) and acidic (carboxyl, phenolic and lactonic) groups. The application of acid activation agents to activate carbonaceous materials are usually performed to enhance the surface concentration in these oxygenated functional groups and to decrease their pH_{ZPC} values. This features could be important in case of a desired reaction with a negatively charged target pollutants [109]. Some studies suggested that the acidic treatment of hydrothermally carbonized feedstock enhanced their textural properties by proliferating their micro-porous structure, and therefore their specific surface area [110].

The hydrogen peroxyde is commonly used to enhance the concentration of oxygen functional groups. This finding was confirmed by Xue et al. [111] when studying the modification of peanut hull based hydrochar using H₂O₂ solutions. The acidic treatment enhanced the specific surface (an increase by 15.3%) and the oxygen content (16.4%–22.3%). This is attributed to the ability of H₂O₂ to oxidize the carboxylic

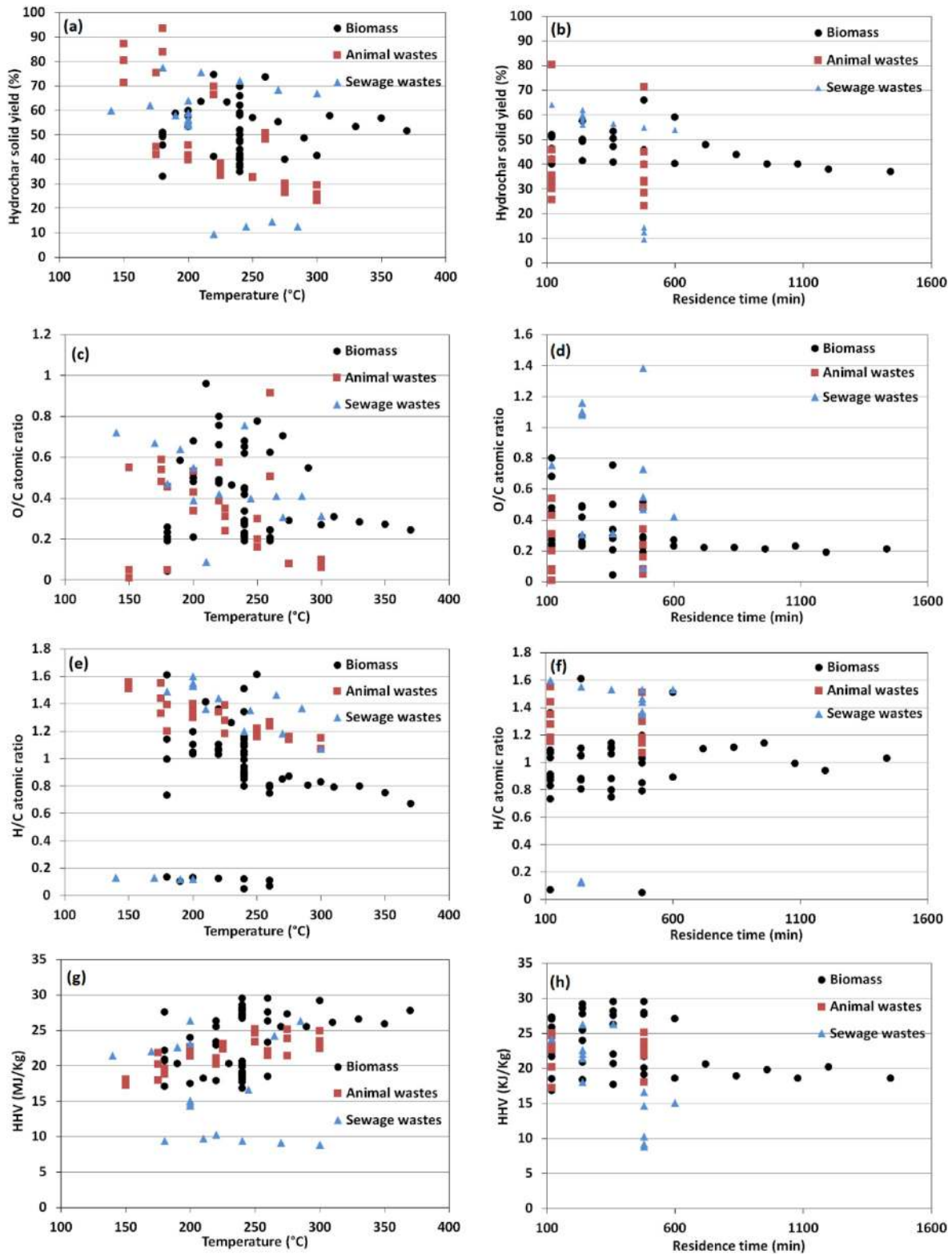


Fig. 7. Effect of carbonization temperature and residence time on the (a–b) final solid yield, (c–d) O/C and (e–f) H/C atomic ratios and (g–h) the high heating value of the produced hydrochars derived from different sourced precursors (adapted from Refs. [33,73–82]).

and phenolic groups.

Dai et al. [112] activated a hydrochar derived from cattle manure with HCl solution at different solid to liquid ratios in order to enhance hydrochar capacities in recovering nutrients from aqueous solutions. Results showed that increasing acid concentrations from 0 to 2%, increases the specific surface area and the pore volume by about 75% and

72%, respectively. Wang et al. [113] suggested performing a pre-treatment and a post-treatment procedure using two different mineral acids for the enhancement of the hydrothermally treated rice husk. Although the surface area of the produced hydrochar increased remarkably, reaching $2610 \text{ m}^2/\text{g}$ (treatment solid to acid ratio 1:2), its mineral concentrations decreased dramatically. This finding was

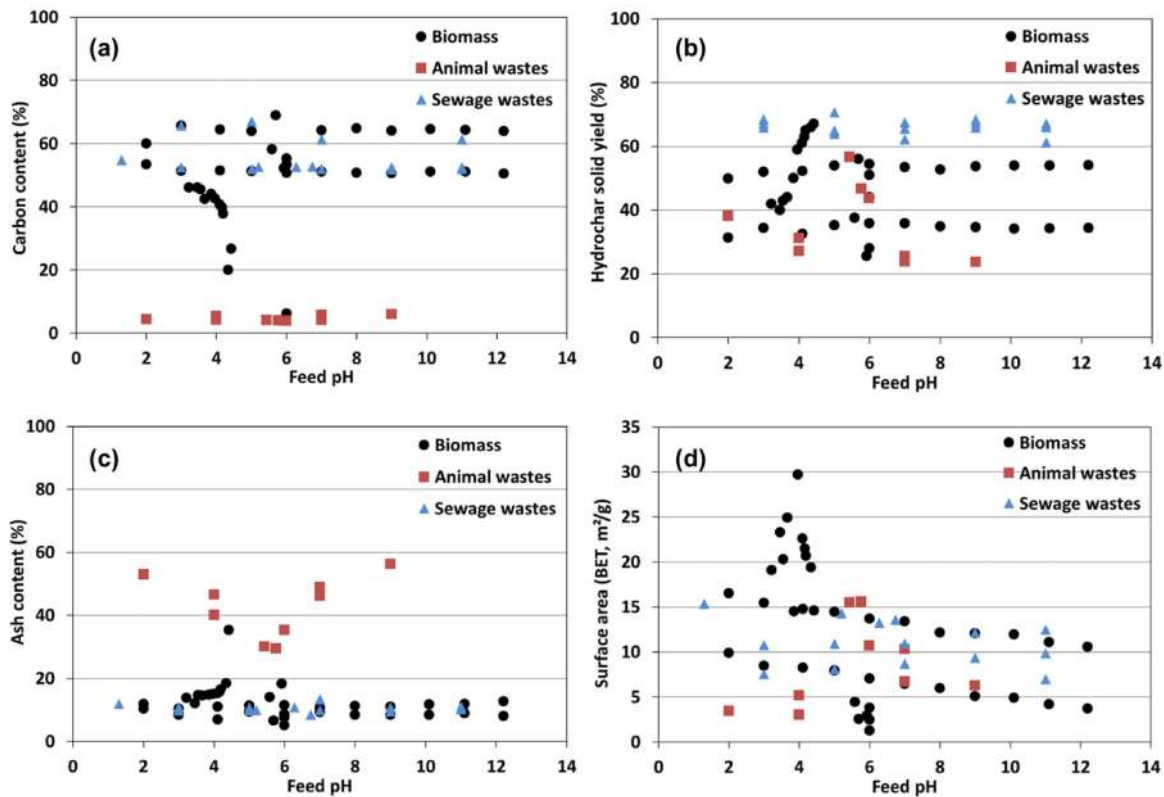


Fig. 8. Effect of feed pH on the (a) Carbon content, (b) final solid yield, (c) ash content and (d) BET surface area of the produced hydrochars derived from differently sourced precursors (adapted from Refs. [72,88–92]).

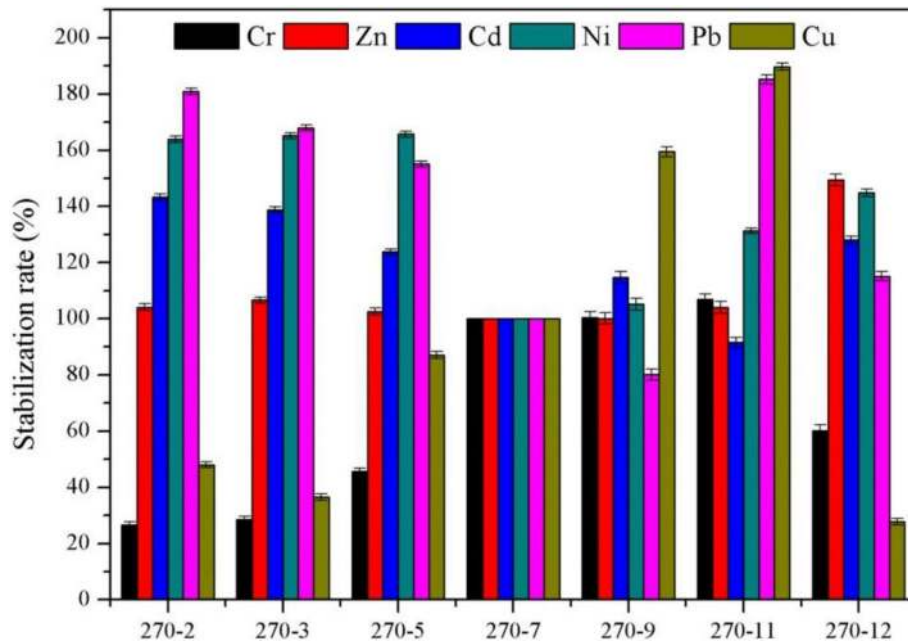


Fig. 9. The stability absorbed Cr, Zn, Cd, Ni, Pb and Cu ions in hydrochars issued from sewage sludge carbonization at T = 270 °C and for different pH values (x) varying between 2 and 12 (samples are denoted as 270-x) (Reprinted from Ref. [93], Copyright (2016), with permission from Elsevier).

confirmed by the drop in its cation exchange capacity (CEC) of 42% compared to the hydrochar produced at a treatment solid to acid ratio of 1:6. It is important to underline that hydrochars treatment by using acid solutions, does not affect the integrity of the feedstock structure but rather react with exposed functional structures through a quick rate mineral leaching Fig. 12.

3.2.2. Alkaline modification

Chemical activation of hydrochars using alkaline solutions is widely applied due to the important modifications that could engender on the feedstock' surface and inner structures (Fig. 13). The majority of research works performed the alkaline modification after hydrothermal carbonization followed by a high temperature treatment (e.g. slow

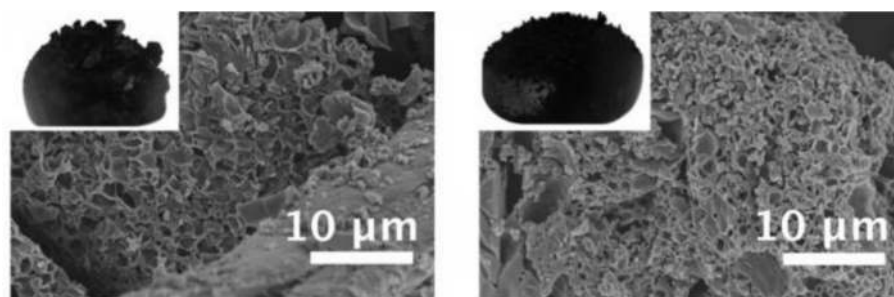


Fig. 10. SEM images and pictures of polypropylene hydrochar before (right) and after (left) microwave modification (Reprinted with permission from Ref. [104]. Copyright 2018 American Chemical Society).

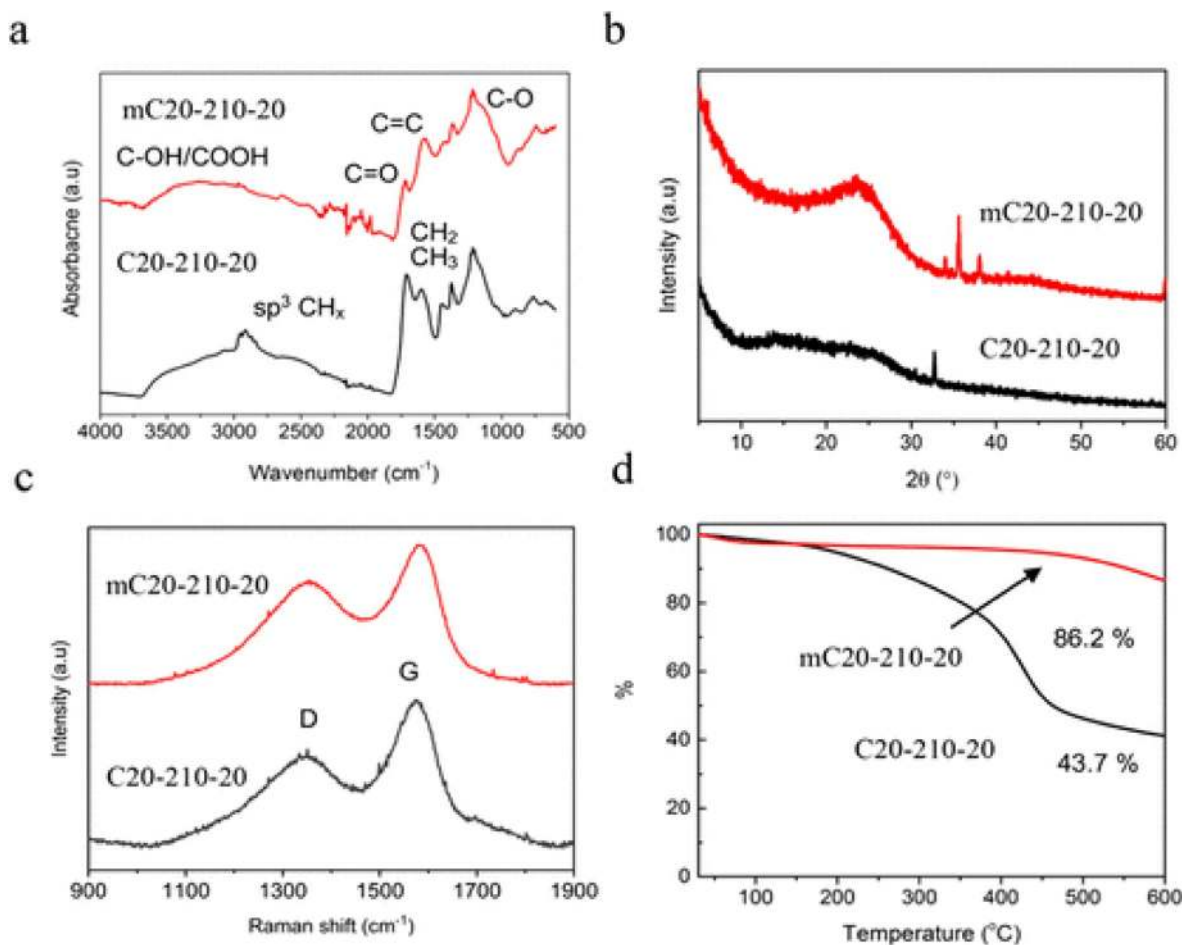


Fig. 11. FTIR (a), WAXS (b), Raman (c) and TGA results (d) of polypropylene hydrochar before (C20- 210–20) and after microwave modification (mC20-210-20) (Reprinted with permission from Ref. [104]. Copyright 2018 American Chemical Society).

pyrolysis between 400 and 900 °C), in order to avoid minerals leaching and thereby reduce the percentage of volatile matter losses [115]. It has been reported that the effect of alkaline treatment on the hydrochars consists of: (i) The increase in pH of zero charge and the presence of hydrophilic functional groups on the surface of the feedstock (i.e., hydroxyl, carboxylic and amine groups) causing a swelling in the solid matrix and therefore enhances the incorporation of metal elements in the solid structure (K, Na, Li, Ca ...) [97]. This treatment induces an increase in the ash content in the final hydrochar and reduces the volatile matter losses. (ii) The increase in the solution pH induces a certain severity on the surface of the hydrochar especially when using strong bases such as KOH, NaOH and LiOH. Ding et al. [116], studied the treatment of rice husk with H₃PO₄, KOH and NaOH and they observed

significant increase of its porosity. This finding was attributed to a redox reaction between metallic ions and the carbonaceous material. However, Fornes and Belda [117] showed that the alkaline aspect of a hydrochar generated from the HTC of olive mill waste and forest waste could be toxic in case of an application in agricultural field due to their capacity of inhibiting the solubilization of certain nutrients. Therefore, a complimentary acidification treatment could be applied in order to neutralize the hydrochar surface.

3.2.3. Metal and salt modification

A novel method could be applied to change the surface electrical properties of hydrochars through the deposition of metal oxides and metal salts. This modification is followed by a pyrolysis step to ensure

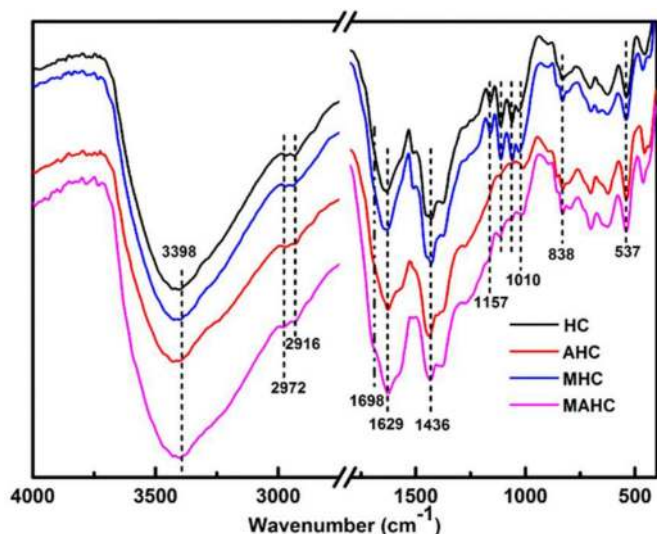


Fig. 12. FT-IR spectra of hydrochar samples issued from bamboo HTC (HC: Untreated hydrochar, AHC: Hydrochloric acid treated hydrochar, MHC: Sodium Chloride treated hydrochar, MAHC: NaOH/HCl treated hydrochar) (Reprinted from Ref. [114], Copyright (2018), with permission from Elsevier).

the homogeneous deposition of the metal ions on the hydrochars surface.. Chen et al. [119] found that the impregnation of sawdust hydrochar with FeCl_3 , increased their specific surface areas from 1.7 to 1710.3 m^2/g . Zhu et al. [120] showed that the hydrochar specific surface area increased from 7.16 to 349 m^2/g with a decrease in the pores volume of about 91% when investigating the application of FeCl_3 on hydrochars issued from *salix psammophila* carbonization. This finding suggests that metallic elements caused the swelling of the solid matrix, then were incorporated in the surface functional groups.

3.2.4. Organic modification

Organic molecules are able to interact with both solid and liquid media by establishing strong covalent bonds through different functional groups. Among these molecules, amino organic molecules are widely used to improve the chemical stability of the hydrochar surface as well as to increase the hydrochar reactivity towards targeted ions/molecules [121]. The linkage between the amino molecules and the carbonaceous support is generally insured by an electrophilic substitution reaction (Fig. 14). Although this treatment decreases the hydrochar specific surface due to the treatment abundance in N and other joint minerals [122], this modification noticeably increases the hydrochar's surface electronegativity and allows a more stable values of pH_{zpc} . Lu et al. [123] investigated the chemical enhancement of taro stalks hydrochar by using diethylenetriamine molecule as a grafting agent. Results showed an important decrease in the zeta potential (≈ 20 mV). Similar results were recorded by Li et al. [121] during the modification of bamboo hydrochar using diethylenetriamine. Authors observed that the zeta potential decreased by about -40 mV. This could be explained by the incorporation of the amine compounds in the inner carbonaceous structure. Vieillard et al. [122] suggested that a partial deprotonation of the hydrochar was followed by the grafting of $-\text{NH}_2$ group by the establishment of a chained covalent bond with silicon atoms that possess a high affinity to oxygen surface functional groups. A similar pathway was proposed by Shi et al. [124] modifying an acid-pretreated-corn-cobs-hydrochar by using polyethylene imine (PEI) solution. The PEI's azote atoms established cross-linking electrophilic bonds with the oxygenic functional groups (mainly hydroxyl, carboxylic and phenolic) through the surface deprotonation, which explains the reported decrease in surface's zeta potential.

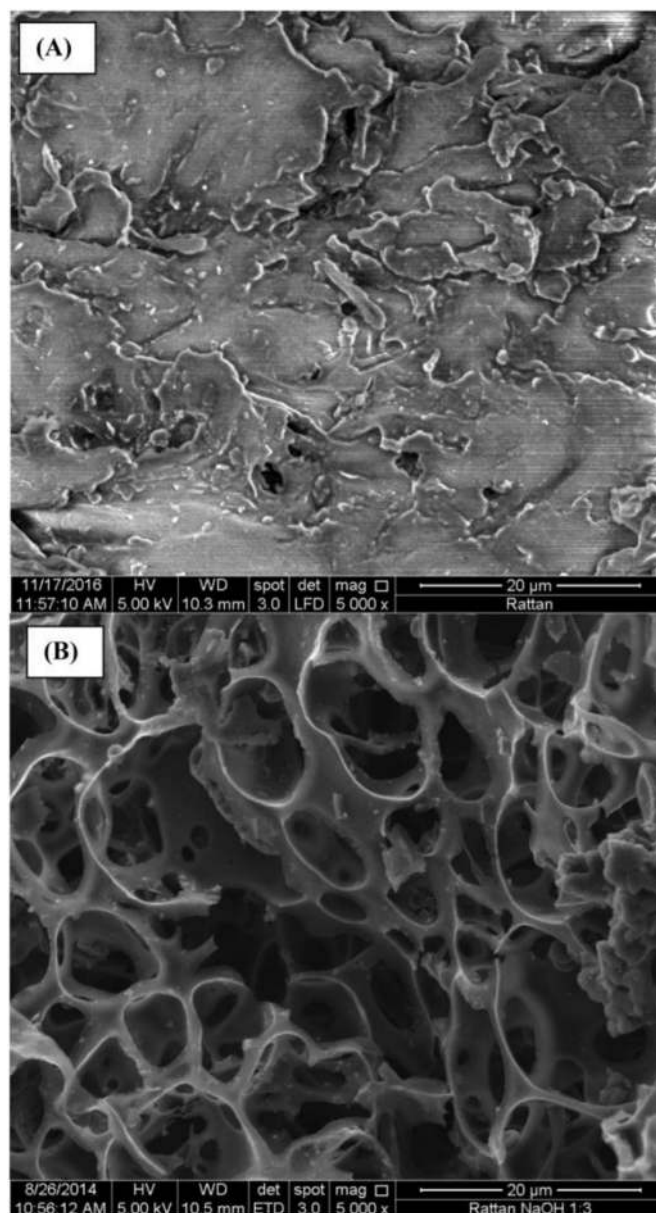


Fig. 13. SEM images of (A) raw rattan and (B) rattan-based activated hydrochar HAC at 5000 \times magnification (Reprinted from Ref. [118], Copyright (2017), with permission from Elsevier).

3.2.5. Carbonaceous materials coating

Recently, two methods are applied for the fabrication of highly dense graphene content through hydrothermal carbonization joined with the valorization of carbon content solids. The first one consists in carbonizing molecules (Sucrose, cellulose, lignin ...), polymers or solids (biomass or animal waste) under specific experimental conditions in order to obtain a hydrochar. Afterwards, the graphene layers are embedded on the hydrochar's surface to enhance its physico-chemical properties for a specific application. The impregnation of the graphene oxides (GO) usually depends on the concentration of oxygen groups on the surface of the used hydrochar [125]. Such coating-like process ensures an equal partition of the graphene layers without affecting the hydrochar's morphological aspect. However, the deposition of long chained carbon matrixes reduces slightly the specific surface (from 479.15 to 432.49 m^2/g) and the micro/meso-porosity of the supporting material [125]. The second one concerns the HTC of the impregnated graphene/graphene content feedstock in order to ensure a total

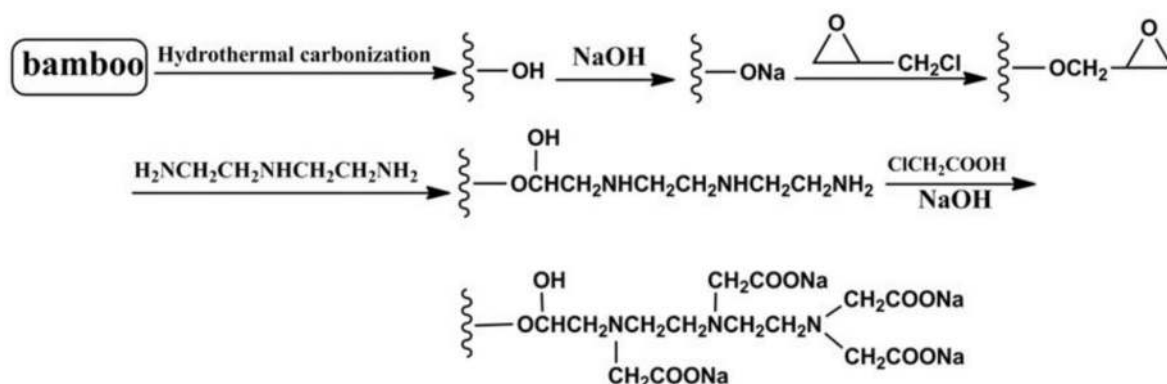


Fig. 14. Reaction pathway for the successive chemical modification of bamboo hydrochar using sodium chloride, epichlorohydrin, diethylenetriamine and monochloroacetic acid (Reprinted from Ref. [121], Copyright (2019), with permission from Elsevier).

embedding of the graphene layer on the supporting solid [126,127]. To ensure the total incorporation of the graphene oxide composites, the HTC of graphene supported feedstock are usually followed by a thermal/chemical activation through pyrolysis carbonization (Fig. 15) at temperatures varying between 400 and 600 °C [125]. This method is usually performed not only to enhance considerably the chemical composition of the hydrochar, but also to increase its specific surface and porosity.

4. Hydrochars valorization for pollutants removal

Hydrochars produced from different wastes were exploited for the removal of organic and mineral pollutants from aqueous solutions [152–154]. The removal efficiency is intimately related to the hydrochars physico-chemical characteristics, the pollutant properties and the experimental conditions [155]. In particular, the increase of hydrochars' dosages leads to an increase in the available functional sites susceptible of reacting with the targeted pollutants, and therefore an enhancement in the removal efficiency [156,157]. In addition, pH solution and the hydrochar surface (pH_{zpc}) control also the removal efficiency of charged pollutants [84,105]. Furthermore, usually, the adsorption

efficiency of hydrochars generally increases with the solution temperature [158,159]. Since the application of the adsorptive capacity of hydrochars is recently exploited, the following section will target the adsorption of dyes as an example of organic molecules and, heavy metals and nutrients as examples of mineral matters (Table 4).

4.1. Dyes and other organic molecules

Several investigations have examined the removal of dyes from aqueous solutions through adsorption onto raw and modified hydrochars (Table 4).

Table 4 shows that the efficiencies of dye adsorption onto hydrochars are medium to low, compared to other materials such as activated carbons [26,128,129]. The use of a raw feedstock and a neutral feeding solution (i.e. distilled water) does not contribute significantly to the development of enhanced physico-chemical properties of the produced hydrochars. For instance, Ronix et al. [130] reported that the removal of methylene blue from aqueous solution using a coffee husk derived hydrochar was 34.85 mg/g. The use of distilled water during HTC did not enhance neither the adsorptive capacity, nor the specific surface area of the produced hydrochar (31.3 m²/g). Similar outcome was

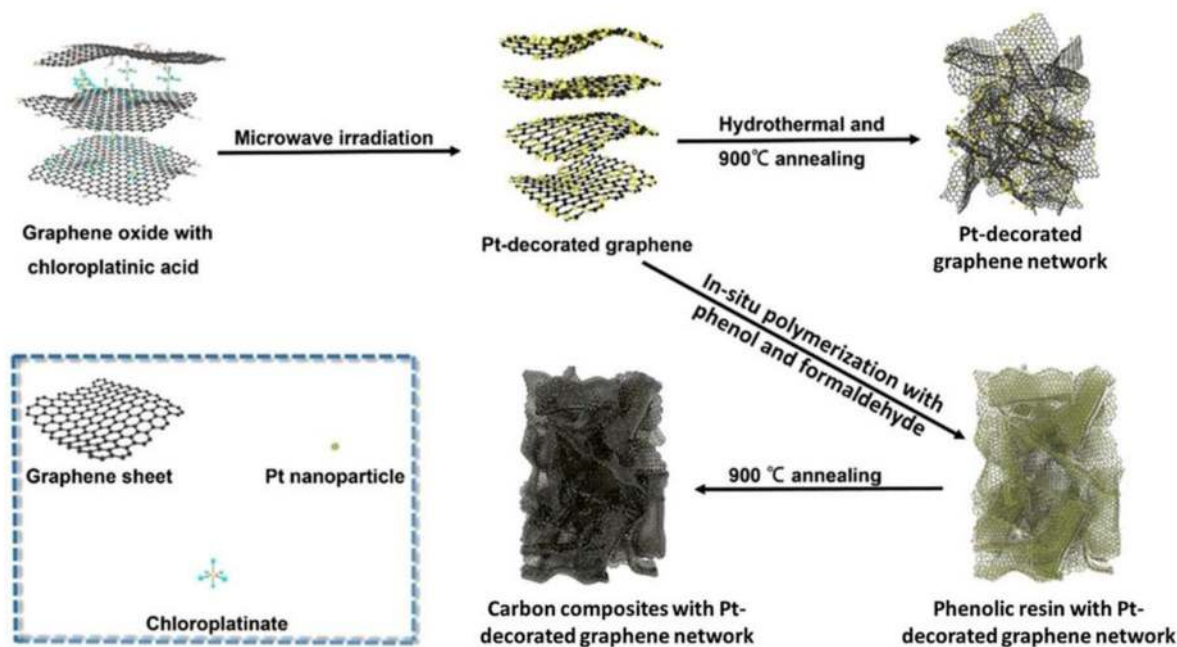


Fig. 15. Preparation set-up for platinum and carbon composites platinum graphene deposited network through thermal treatment (Reprinted from Ref. [127], Copyright (2019), with permission from Elsevier).

Table 4
Summary of studies regarding dyes and other organics removal from aqueous solutions by various hydrochars (where Chem. mod. stands for: Chemical modification; Phys. mod. for: Physical modification; DW: distilled water, Q_{\max} : maximum adsorption capacity, PFO: Pseudo-First Order kinetic model; PSO: Pseudo-Second Order kinetic model).

Feedstock (FS)	Pre-treatment	Hydrothermal treatment conditions	Post-Treatment	BET surface area (m ² /g)	Pollutant	Adsorption conditions	Equilibrium time (min)	Kinetic model	Isotherm	Q_{\max} (mg/g)	Reference
Dyes											
Camellia oleifera seed shells	–	1 g + 30 mL DW 230 °C/12 h	Chem. mod. 1/3 (w/w) KOH over night + activation at 650 °C for 2 h	1882	Methylene blue	0.02 g/40 mL at 100–200 mg/L for 6 h	175	PSO	Langmuir	493	[139]
Factory-rejected tea	–	5 g + 100 mL DW 200 °C/5 h	Chem. mod. 1/3 (w/w) NaOH over night + Activation at 800 °C for 1 h.	369	Methylene blue	0.2 g/200 mL at 25–500 mg/L for 480 min	240	PSO	Langmuir	487	[140]
Coconut shell	–	5 g + 100 mL DW 200 °C/2 h	Chem. mod. 1/3 (w/w) NaOH for 4 h + Activation at 600 °C for 1 h.	876	Methylene blue	0.2 g/200 mL at 25–250 mg/L for 1500 min	1140	PSO	Langmuir	200	[118]
Bamboo	–	1 g + 6 mL DW 240 °C/0.5 h	–	20	Congo red	0.1 g/50 mL for 720 min	–	–	Langmuir and Freundlich	97	[131]
Food waste	–	25% solid waste in 500 mL reactor/250 °C for 20 min	–	6	Acridine orange Rodamine 6G	0.05 g/100 mL at 10–100 mg/L for 120 min	30	PSO	Langmuir	79	[128]
Coffee husk	–	Water precursor ratio of 3.2/1 210 °C for 243 min	–	31	Methylene blue	0.125 g/25 mL at 25–500 mg/L for 240 min	125	Elovich	Langmuir	35	[130]
Bamboo	–	40 g + 160 mL 1 M HCl solution 200 °C for 24 h	Chem. mod. Rinsing with 0.25 M NaOH solution + Etherification + Amination processes	12	Methyl orange	0.04 g/50 mL for 300 min	175	PSO	Langmuir	909	[141]
salix psammophila	–	3.5 Kg + 44 L of DW at 300 °C	Chem. mod. Pyrolyse of hydrochar adding solution K ₂ CO ₃ solution + Rinsing with 0.1 M HCl solution for 720 min + Ferric composites	84	Malachite green	0.04 g/80 mL at 150–250 mg/L for 1500 min	1350	PSO	Langmuir	486	[133]
Algal bloom residues	Phycocyanin-extracted	30 g + 15 mL DW 200 °C for 10 h	–	–	Malachite Green	Dosage 4 g/L at 50–100 mg/L for 1600 min	1440	PSO	Langmuir/Freundlich	89	[142]
Sewage sludge	–	Water to precursor ratio of 1/9 180 °C for 3 h	–	45	Crystal violet	Dosage 6 g/L at 50–350 mg/L for 1440 min	1140	PSO	–	41	[143]
Other organic molecules											
Salix psammophila	–	80 g/L S/L dispersion at 300 °C.	Chem. mod. 20 g of hydrochar +120 mL of FeCl ₃ + pyrolysis at 700 °C at inert atmosphere (N ₂) for 1 h	349	Tetracycline	0.05 g of hydrochar + 50 mL at 5–80 mg/L for 120 h.	70 h	PFO/PSO	Freundlich	25	[120]
Bamboo	–	6 g + 36 mL of 5 wt% of NaOH 200 °C for 3 h.	Chem. mod. 5 wt% HNO ₃	58	2-naphthol	0.01 g of hydrochar +30 mL for 5 h.	3 h	–	Langmuir	93	[144]
Sawdust	–	–	Chem. mod. 10 g of hydrochar +10 g of ZnCl ₂ + 0.02 M FeCl ₃ + 50 mL DW + Pyrolysis at 600 °C at inert atmosphere (N ₂) for 4 h	923	Roxarsone	0.02 g of hydrochar + 50 mL at 50–500 mg/L for 24 h	–	–	Langmuir	417	[145]
Sugarcane bagasse	Chem. mod. 0.1 M NaOH for 3 h Then 15 g + 1/10 wt % of 1/2 M ratio of Fe ₂ +/Fe ₃ + for 2 h.	Mixture heated at 230 °C for 24 h.	Chem. mod. Acetone rinsing	43.29	Tetracycline	0.05 g of hydrochar +25 mL of 0–200 mg/L for 24 h.	12	Intra-particle diffusion	Freundlich	48	[146]
Salix psammophila	–	80 g/L S/L dispersion at 300 °C.	Thermal modification. 5 g of hydrochar pyrolyzed at 700 °C for 4 h.	316	Tetracycline	0.04 g of hydrochar +50 mL at 5–80 mg/L for 120 h.	–	–	Freundlich	29	[138]
Bamboo	–	15 g + 90 mL distilled water. 240 °C for 2 h	–	40.50	2-naphthol	0.1 g of char +50 mL for 12 h	–	–	Freundlich	83	[131]

pointed out by Li et al. [131], as the adsorption capacity of Congo red dye by bamboo derived hydrochar did not exceed 97 mg/g. Besides, the adsorption efficiency of dyes by hydrochars is usually mainly related to the availability of various surface functional groups containing oxygen [121]. The HTC process tends to reduce the concentration of these groups on the surface of the produced hydrochars compared to the raw biomasses [132]. This is due to the possible decarboxylation mechanism occurring at extended carbonization times or relatively high temperatures. Therefore, pre/post treatment steps were implemented to enhance their physicochemical properties and thereby, their dye retention capacities [118]. It has been pointed out, that hydrothermal carbonization at higher temperature increases the fixed carbon content and consequently decreases the content in oxygen and hydrogen by a dehydration mechanism [82]. Therefore, chemical post-treatment was exhaustively applied to restore the oxygen functional groups concentration and to enhance the adsorptive capacity of the hydrochar, using various chemical activators. For instance, Li et al. [121] suggested that the retention of both methylene blue and copper ions involved various mechanisms, where covalent bonding is the most significant one. Although hydrogen bonds were susceptible of contributing in the retention of these pollutants, FTIR spectra suggests the establishment of strong linkage between the dye and hydroxyl ($3600\text{--}3200\text{ cm}^{-1}$) and carboxylic groups ($1600\text{--}1400\text{ cm}^{-1}$) (Fig. 16).

On the other hand, this adsorption mechanism is intimately linked to the hydrochar physical properties and to the development degree of its porous structure. Hydrochars do not usually present significant surface areas since the carbonization in humidified media as well as the conversion process at low to moderate temperatures (compared to pyrolysis) lowers the possibility to develop an important porosity. Therefore, modified hydrochars with important specific surface could present significant adsorption capacity. According to Zhu et al. [133], magnetic prepared hydrochar presenting important specific surface (up to $1541\text{ m}^2/\text{g}$) allowed the removal of malachite green dye at rates reaching 417 mg/g (Fig. 17). Such high capacity was confronted to an enthalpy value of 19.8 kJ/mol which confirms that adsorption is mainly driven by a physical interaction [134]. The smallest porosities ($<2\text{ nm}$) present the highest majority of the surface area of hydrochars. Thereby, the considerable presence of these pores will enhance the adsorption of especially the organic molecules that could be driven by a combination of hydrogen bonding and pore-filling mechanisms. In fact, the

abundance in oxygen containing surface functional groups (e.g., carboxylic, phenolic and lactonic) enhance the surface acidity. Therefore, an abundance in the polar groups on the surface of hydrochar is generally detected which contributes in the sorption of water and mainly electro-negatively charged molecules. This finding was emphasized by Eibisch et al. [135] during the adsorption of Isoproturon pesticide in a soil amended with hydrochars issued from lignocellulosic materials. The retention mechanism was attributed to the electronegativity difference between the hydrochar's H-bond acceptors (ester and azotic groups, δ^+) and the partial electronegativity generated by the hydrogen atom at the Isoproturon molecules (δ^-) [136]. According to Li et al. [146], this mechanism was behind the adsorption of Congo red and 2-naphthol onto bamboo hydrochars. When increasing solution temperature, uptake capacity towards these two molecules decreased suggesting that a possible decrease in adsorption enthalpy could alter the integrity of these weak bonds. Furthermore, pollutants with certain molecular structure could be attracted into the pores due by pressure difference between the inner-pore space and the liquid phase as well as by certain size-exclusion effect especially for bulky molecules [137]. The molecules adsorption in this case is generally described by the multi-layered Freundlich isotherm equilibrium, since the uptake mechanism occurs physically following an accumulative adsorption tendency until the saturation of micropores along with the considerable decrease in the specific surface area.

The hydrothermal carbonization of feedstock and its impact on the elemental composition of the hydrochars could significantly affect their adsorption capacities. Zhu et al. [138] reported that an increase in the carbon content of the *Salix psammophila* hydrochar, was followed up by an increase in the Freundlich parameter related to the adsorption of tetracycline molecules. Moreover, the decrease in the (O + N)/C atomic ratio is attributed to the volatile matter elimination, which enhances the presence of microporosity. The adsorption of tetracycline was found to be mainly driven by a pore-filling mechanism with an adsorption capacity of 28.77 mg/g .

4.2. Heavy metals and nutrients

The removal of heavy metals from aqueous solutions using hydrochars was successfully reached (Table 5). A recent study performed by Li et al. [41] indicated that the removal of zinc and copper ions by rice straw hydrochar reached 216.9 and 226.8 mg/g , respectively. These considerable removal efficiencies were recorded despite the low specific surface area of the carbonized material ($25.5\text{ m}^2/\text{g}$), which suggests that adsorption of heavy metals was not physically driven. In fact, it has been reported that heavy metals uptake from aqueous solutions is attributed to the establishment of covalent bonds with oxygenic and nitric surface functional groups [111]. The effect of heavy metals co-presence was assessed by Sun et al. [147], which investigated the adsorptive capacity of three different activated hydrochars for the removal of four heavy metals ions. Results showed that the adsorption trend of heavy metals was $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$. This tendency was explained by the fact that heavy metals removal is governed by a combination of two adsorption pathways namely cation exchange and intra-particle diffusion (Fig. 18). These two mechanisms, yet different, are more likely privileged for ions presenting low atomic radius. In this context, it has been reported that at multi-heavy metals system, Pb^{2+} adsorption onto carbonaceous matrix could lead to the formation of PbCO_3 that reduces the available functional groups for other ions, even for those presenting lower atomic radius such as cadmium [148].

In order to increase the adsorption capacity of heavy metals, researchers enhanced the physico-chemical properties of the produced hydrochars (Table 5). Petrović et al. [48] found out that lead adsorption onto hydrothermally treated grape pomace has increased by about 392% after chemical activation via 2 M KOH alkaline solution. The chemical modification of hydrochars using bases are susceptible of causing a swelling in the carbonaceous matrix, with an alteration of its

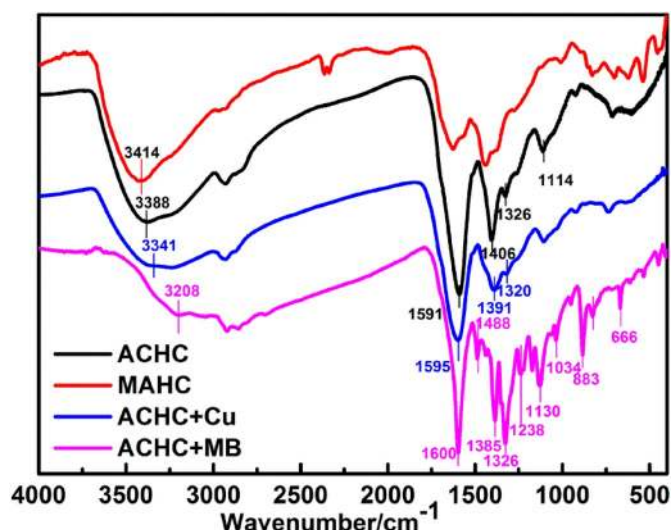


Fig. 16. FT-IR spectra of bamboo modified hydrochar (MHAC), amino-activated hydrochar (ACHC) and Cu(II) and Methylene Blue (MB) loaded ACHC (Reprinted from Ref. [121], Copyright (2019), with permission from Elsevier). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

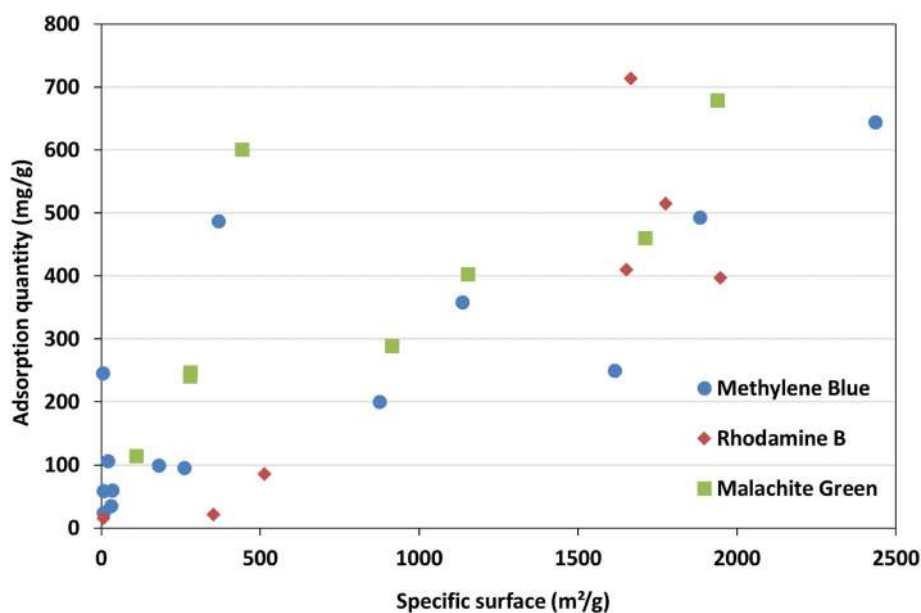


Fig. 17. Correlation between specific surface area of modified and unmodified hydrochars on their adsorptive capacity of three different dyes.

upper surface. This step accompanied by the increase in oxygen functional groups namely phenolic, carboxylic and aromatic. Fang et al. [149] showed that physical activation of hydrochars enhances their capacities for heavy metals removal. In fact, the activation of hickory wood hydrochar at 900 °C under CO₂ increased its uptake of Cu²⁺ from 17.4 to 72.3 mmol/Kg.

Hydrochars could behave at certain thermodynamic conditions as ion-exchange resin, especially when the liquid solution presents high pollutants concentrations [150]. The mechanism depends mainly on the chemical characteristics of the hydrochar's surface, where ions retained to the matrix *via* functional groups could react with entities present in the aqueous solution. The possibility of ion exchange increases in case of similar valence, charge and/or atomic radius for the adsorbed and the released ion/molecule (Fig. 18). Therefore, the ion exchange mechanism is reported as an early stage adsorption process, which includes the breaking and the establishment of strong covalent bonds (>45 KJ/mol). Xue et al. [151] suggested that the saturation of H₂O₂-modified hydrochar with Na⁺ was responsible for about 70% of lead ions removal from aqueous solution. Authors reported that the phenomenon occurred at the oxygen-containing functional groups where sodium ions were initially retained.

On another level, the application of hydrochars for the removal of nutrients was not yet sufficiently exploited. Among the few studies, phosphorus and ammonium are the most followed nutrients. For example, Takaya et al. [153] investigated the adsorption of both ammonium and phosphorus onto hydrochars issued from different feedstock carbonized at 250 °C. Results showed a considerable affinity between the solid fractions and the studied ions as adsorption reached 37.0 mg/g and 146.4 mg/g for PO₄³⁻ and NH₄-N, respectively (Table 5). The authors compared the adsorption capacity of hydrochar with biochars issued from the pyrolysis of the same feedstock at temperatures varying between 450 and 650 °C. A progressive decrease in the removal yield of both nutrients even with a significant increase in the surface area was observed, which confirms the involvement of a chemical driven reaction in the retention of phosphorus and ammonium onto hydrochars (Fig. 19).

4.3. Economical aspect of hydrochars production

The production of hydrochars in order to obtain a carbon support with interesting physico-chemical characteristics is well confirmed by

the multiple methods of synthesis and modifications. The application of these supports is nevertheless decided by the production costs and thus by their economic feasibility. Although no numerical model was set yet for the estimation of the hydrochar production costs, a fair analogy could be derived from the different assessments performed for biochars production [157]. In fact, a multitude of expenses determining the final cost of hydrochars must be taken into account namely the feedstocks acquirement, machinery maintenance and operating costs along with miscellaneous expenses. However, the costs related to transport, distribution and production process present the majority of the reported expenses. To ensure an economic profitability, the thermal transformation industries generally exploit low-cost feedstocks as they come from inexpensive wastes. As an application of the formula reported by Dickinson et al. [158], the price of one ton of hydrochar produced from raw olive pomace, an abundant agricultural by-product, on an average dry basis solid yield of 50% is estimated by about US\$450. While the price of the raw olive pomace does not exceed US\$60/ton, the fees related to the production process and the transport could represent 40% of the final costs [158]. To reach a maximum breakeven cost, industries aim to reduce these costs by two decreasing the costs related to electricity consumption by using the renewable energy sources including solar and wind energy as well as the exploitation of the gaseous fraction released after hydrothermal carbonization. It has been reported that an increase in the process plants capacity from 55 MWe to 550 MWe could decrease the breakeven cost by 20% [159]. In addition, the suitable choice of the HTC reactors as well as the process methodology could be of a strategic importance to reduce the final costs. In general, the choice is based on the initial feedstock properties and the adaptability of the technical features of the reactors [159]. Therefore, an in-depth assessment for the optimization of hydrochar production and transport is highly recommended to reach an economical feasibility of this process.

5. Conclusions, challenges and perspectives

Hydrothermal carbonization is an eco-friendly process of decomposition, at relatively low temperatures and high pressures, of vegetal, animal and waste sourced feedstock in the presence of water. The later one provides a medium for complex series of reactions which generally lead to oxygen and hydrogen reduction contents, colloidal structure modification and, remove of hydroxyl groups through dehydration, elimination of carboxyl and carbonyl groups through decarboxylation,

Table 5
Summary of heavy metals and nutrients removal efficiencies from aqueous solutions by various hydrochars (Chem. mod.: Chemical modification; Phys. mod.: Physical modification; DW: distilled water, Q_{\max} : adsorption capacity).

Feedstock (FS)	Pre-treatment	Hydrothermal treatment conditions	Post-Treatment	BET surface area (m^2/g)	Pollutant	Adsorption Batch conditions	Equilibrium time (min)	Kinetic model	Isotherm	Q_{\max} (mg/g) *, mol/g	Reference
Heavy metals											
Peanut hull	–	60 g + 400 mL DW 300 °C for 5 h	Chem. mod. 3 g of hydrochar + 20 mL H_2O_2 (10%) 2 h	1	Pb^{2+}	0.1 g + 50 mL 1.5/200 ppm	12 h	Elovic	Langmuir	23	[111]
Hickory wood	–	50 g + 290 mL DW 200 °C for 6 h	Phys. mod. 5 g For 1–2 h at 600–900 °C under CO_2 flow of 150 mL/min	445–928	Pb^{2+}	0.1 g/30 mL solution Lead: 500 ppm	24 h	–	–	36–225*	[149]
					Cu^{2+}	0.1 g/30 mL solution Copper: 20 ppm	24 h	–	–	17–72*	
					Cd^{2+}	0.1 g/30 mL solution Cadmium: 20 ppm	24 h	–	–	1–18*	
Sawdust	–	5 g + 60 mL DW 200 °C/20 h	–	4	Cd^{2+}	0.06 g + 30 mL at 2 h 5–300 mg/L for 6 h	2 h	PSO	Langmuir	40	[147]
Wheat Straw	–	–	–	9	–	–	2 h	PSO	Langmuir	38	
Corn Stalk	–	–	–	9	–	–	2 h	PSO	Langmuir	30	
Grape pomace	–	250 g + 1:5 DW ratio 220 °C for 60 min	–	–	Pb^{2+}	0.5 g/L of biomass at 40–180 mg/L for 40–180 min	90 min	Weber-Morris diffusion model	Sips	28	[48]
			Chem. mod. Activation with 2 M KOH solution	–	–	–	60 min	Weber-Morris diffusion model	Sips	137	
Corn cobs	–	40 g + 240 mL of DW 300 °C for 30 min	Chem. mod. 1 M HCl or 3 M KOH + 10% Polyethyleneimine + 1% glutaraldehyde 3 M KOH + 10% Polyethyleneimine + 1% glutaraldehyde	–	Cr^{6+} Ni^{2+}	0.05 g + 20 mL at 10–1000 mg/L for 24 h	450 min	PSO	Langmuir	24	[124]
				–	Cr^{4+} Ni^{2+}	–	200 min	PSO	Langmuir	29	
Anaerobically digested sludge	–	105 g of feedstock + 45 mL of DW 200 °C for 24 h	–	18	Pb^{2+}	50 mg of hydrochar in 25 mL at 4–800 mg/L for 24 h	50 min	Intra-particle diffusion	Sips	11	[154]
Paper Industry sludge	–	–	–	9	–	–	50 min	Intra-particle diffusion	Sips	12	
Nutrients											
Commercial oak	–	10 wt% solid/water	–	<6	PO_4^{3-} NH_4^+	0.1 g of hydrochar in 100 mL at 125 mg/L	7 h	PSO	Langmuir/Freunlich poorly fitted the experimental data at the exception of oak hydrochar (Langmuir & Freundlich; $R^2 = 0.999$) for NH_4^+	27	[153]
Greenhouse waste	–	250 °C for 1 h at 4 MPa	–	–	PO_4^{3-} NH_4^+	P L and 1000 mg/L NH_4^+ for 24 h	10 h	PSO	–	110	
Municipal waste	–	–	–	–	PO_4^{3-} NH_4^+	–	–	PSO	–	10	
Presscake from AD	–	–	–	–	PO_4^{3-} NH_4^+	–	–	PSO	–	122	
Rice straw	Chem. mod. 3 g + 27 mL of 0.2 M of $LaCl_3$ + 6 mL of 6 M KOH	Prepared mixture was heated at 200 °C for 10 h	–	–	PO_4^{3-} NH_4^+	0.03 g of hydrochar in 50 mL of 0–250 mg/L of PO_4^{3-} FOR 48h. pH = 4.5	12 h	PSO	Langmuir	5	[155]
				–	PO_4^{3-}	0.03 g of hydrochar in 50 mL of 0–250 mg/L of PO_4^{3-} FOR 48h. pH = 10.5	36 h	PFO	Langmuir	146	
				–	PO_4^{3-}	–	–	PSO	–	37	
				–	PO_4^{3-}	–	–	PSO	–	129	
				–	PO_4^{3-}	–	–	PSO	–	62	

(continued on next page)

Table 5 (continued)

Feedstock (FS)	Pre-treatment	Hydrothermal treatment conditions	Post-treatment	BET surface area (m ² /g)	Pollutant	Adsorption Batch conditions	Equilibrium time (min)	Kinetic model	Isotherm	Q _{max} (mg/g) ± mol/g	Reference
Sugarcane bagasse	-	40 g + 310 mL of DW. 250 °C for 6 h	-	4	PO ₄ ³⁻	0.1 g of hydrochar in 30 mL of 50 ppm of PO ₄ ³⁻ for 24 h.	-	-	-	3	[156]

and cleavage some ester and ether bonds through facilitated hydrolysis.

The main resulting solid by-product is a dense, friable and hydrophobic carbonaceous material. The yield (determined at wet basis), the quality and the final usage depending on the experimental conditions (feedstock nature, medium pH, carbonization temperature, residence time, etc.). Nevertheless, as long as hydrochar application in wastewaters treatment is concerned, the adsorptive capacity can be enhanced by several modification operations, before, during and/or after the wet torrefaction process. Indeed, the physical/chemical activation process for example could significantly widen the pores, increase the specific surface area, reduce the surface heterogeneity, increase the concentration of oxygenated functional groups and change the surface electrical properties.

Different modifications undergone by produced hydrochars engendered specific physico-chemical peroperties judged interesting for application in field of wastewater treatment. Raw and modified hydrochars exhibited good performance for the removal of organic (dyes, pharmaceuticals, solvents ...) and mineral (heavy metals, nutrients ...) pollution from aqueous solutions.

To sum up and based on the bibliography presented in this review, hydrothermal carbonization presented a very interesting and viable method for different low-cost and sustainable solids conversion. Nevertheless, multiple scientific goals should be further exploited such as:

- Further research and development work is needed in order to optimise the choice of the feedstock, the HTC experimental parameters, and the conditions of the produced hydrochars modification (e.g. the choice of the physical/chemical compound, the experimental settings: concentration of the chemical agent, the solid:solution ratio, the mixing intensity, the temperature) in order to get hydrochars with improved properties that can be applied to efficiently remove various organic/inorganic pollutants. Efforts should be undertaken to more in-depth characterization of hydrochars properties by complementary analyses techniques.
- The new research/development investigations regrading hydrochars use for wastewaters treatment should include also the socio-economic aspect in order to: i) minimise the related costs, including the availability of the feedstock near the industrial site, the preparation of the raw material (cleaning, drying), the used HTC conditions (mainly temperature and residence time) and the modification step (primarily the used chemical/physical agents, energy consumption), ii) make simpler and easier its technical applicability in real sites, and iii) guarantee its social acceptance.
- A particular attention should be paid to the fate of the pollutant-loaded-hydrochars through the test and optimization of efficient desorption methods that could, in some cases, allow the reuse of these recovered pollutants inside the industrial process and therefore promote sustainability and circular economy concepts [160].
- The ecotoxicology of the modified hydrochars should be accurately asseesed in order to prevent the possible adverse effets onto the environment. In fact, the acidic aspect of the majority of the hydrochars and the generation of long-chained organic compounds could present a drawback for their application in agromonic fields. An interesting research axis could include the adaptability of certain agricultures and soils to the amendment of hydrochars and their impact on the plants growth and soil microorganisms behavior.
- Finally, limited interest was shown to the exploitation of bio-oil issued from the HTC of different feedstocks. In fact, the liquid fraction presents important concentrations in fatty acids and minerals issued from the degradation of the feedstocks aromatic structure. The recovery of these components for agricultural and industrial usage could be highly beneficial.

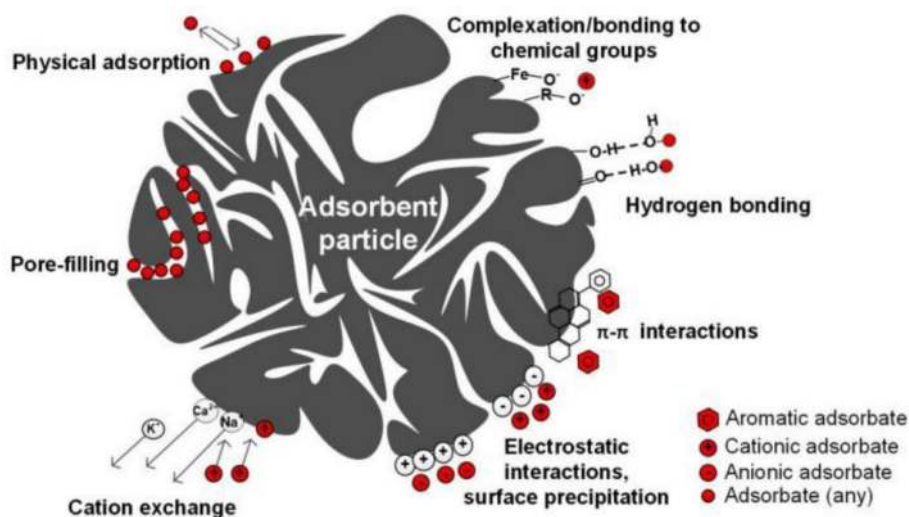


Fig. 18. Possible adsorption mechanisms on a hydrochar adsorbent particle (Reproduced with permission from Ref. [152]).

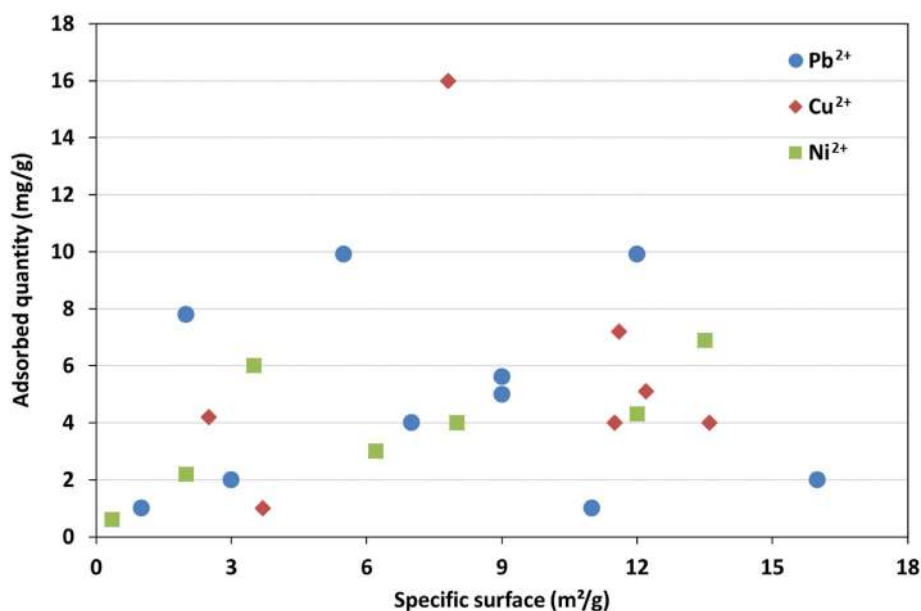


Fig. 19. Correlation between BET specific surface area of modified and unmodified hydrochars on their adsorptive capacity of three different heavy metals.

Declaration of competing interest

None.

CRediT authorship contribution statement

Ahmed Amine Azzaz: Investigation, Writing - original draft. **Besma Khiari:** Formal analysis, Writing - review & editing. **Salah Jellali:** Conceptualization, Methodology, Writing - review & editing, Supervision. **Camélia Matei Ghimbeu:** Writing - review & editing, Supervision, Project administration. **Mejdi Jeguirim:** Conceptualization, Methodology, Funding acquisition, Writing - review & editing, Supervision.

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