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A comprehensive review of biochar in removal of organic pollutants from wastewater: characterization, toxicity, activation/functionalization and influencing treatment factors

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ABSTRACT

The current climate and environmental challenges demand novel and cost-effective sustainable materials with a high efficacy and eco-friendly properties. Biochar (BC) has gathered a great interest in the last years across different research fields, thanks to its special physicochemical characteristics such as high specific surface area, high porosity, ion exchange capacity and because of scientific evidence in removing various contaminants from soil, water, and air. This review aims to give the state of the art on the removal of toxic organic pollutants from wastewater using biochar, activated biochar, functionalized biochar and metal oxide or clay base biochar composites, commenting on

the substrates' physiochemical properties, the role of the most used characterization techniques toxicity, activation/functionalization and influencing treatment factors in organic pollutant removal from wastewater.

The effect of different operating parameters of the water treatment process is summarized and thoroughly discussed. The toxicity of biochar components such as heavy metals, dioxins and polycyclic aromatic hydrocarbons (PAHs) is addressed. The various application processes of biochar in water treatment at both laboratory and pilot scale is also reviewed. The activation techniques, functionalization pathways and biochar based-nanocomposite synthesis methods for enhancing the pollutant elimination efficiency are also extensively discussed. Finally, the paper suggests research directions in the field of biochar application in wastewater treatment.

Keywords: Biochar; Characterization; Toxicity; Contaminant removal; Functionalization; Magnetization.

1. Introduction

The world population increase over the past two decades led to an increasing demand in water volume, both for human consumption and for the industry sector, which results to increased wastewater volumes released in the aquatic environment. A variety of pollutants are detected in wastewater streams and have been reported in literature, such as; carcinogenic heavy metals [1], petroleum hydrocarbons [2], polycyclic aromatic hydrocarbons (PAHs) [3], organic dyes [4], phenols, pesticides, pharmaceuticals and veterinary antibiotics [5]. A diversity of pollutant treatment techniques has been

extensively discussed in literature [6][7][8]. However, the design of optimal, efficient, and operational treatment methods is still considered a challenge. Among different techniques which have been the subject of research, we identified the most promising: chemical oxidation, electrocoagulation, membrane separation, reverse osmosis, filtration, adsorption and biological treatment [9][10][11].

Adsorption is one of the most efficient methods for the removal of a wide variety of pollutants from gaseous and wastewater streams [12][7]. During the adsorption process the pollutants are removed from the effluent by being adsorbed on the active sites on the surface of a solid substrate (adsorbent). Certain parameters such as temperature, pH or the concentration of adsorbate of the liquid phase influence the adsorption capacity and their fluctuations can result to the desorption of the adsorbed species from the surface back into the liquid phase [13].

Common adsorbents include clays, zeolites and active carbon, the latter being widely used for efficient micropollutant removal especially in the potabilization of water.

Active carbon used in Europe is usually produced from biomass transported over long distances, such as coco coir or coco shells, as well as coal. Local residual biomass and well controlled pyrolysis conditions offer the advantage of sustainably produced substrates, biochars, as an alternative to currently used active carbon [14].

The initial interest in biochar focused on the improvement of agricultural productivity via enhancement of soil fertility, increasing soil nutrient levels and water retaining capacity, while decreasing greenhouse gas emissions and carbon sequestration are drivers that gain a lot of attention currently [15][16][17]. Biochar is considered a cost-effective and

environmentally friendly material [9][10], with large surface area, high porosity, functional groups, high cation exchange capacity, stability, reusability [17][18]. These characteristics make it a suitable substrate in environmental applications which have also gained a lot of attention the last years. Some very recently published reviews demonstrate the effective application of biochar for both heavy metals and organic pollutants (pesticides, phenols) removal from contaminated soil [19][20][21]. Regarding the produced biochar properties, these are related to the nature of the feedstock (lignocellulosic biomass: green waste, organic residues, energy crops) and the preparation conditions.

Biochar is a high carbon containing material with high specific surface area and a large porosity which is produced via the carbonization of biomass under a limited oxygen environment [15]. The carbonization process allows the valorization of diverse biomass sources like lignocellulosic residues from agro-industrial and forestry activities, animal manure, dewatered sludges, even micro algae, marine and aquatic species [22][16]. Lignocellulosic biomass pyrolyzed at high temperature ($>600^{\circ}\text{C}$) produces biochars with high aromatic carbon content, high stability and therefore resistance to microbial decomposition. Animal manure conversion produces biochar with high ash content and therefore a very high pH value, due to the nutrients present in the feedstock. As a consequence, biochar may act as a slow-release fertilizer and alkalinity regulator for acidic soils. The high nutrients content of biochar is linked to its potential for soil cation exchange capacity (CEC), water holding capacity and plays a role in the nitrogen cycle in soil.

The term carbonization includes the technologies of pyrolysis, hydrothermal carbonization, flash carbonization, gasification and torrefaction [23][17][24]. These technologies vary with respect to their relative co-products and their maximum yields

which are linked to the operating conditions such as pressure and temperature, its heating rate and its residence time in the reactors [20][25]. Low carbonization temperatures (<300–400 °C) result in low porosity biochars. Medium carbonization temperatures (400–700 °C) yield biochars with the highest porous development and a higher aromaticity, the latter promoting electron donor interaction [12]. At moderate pyrolysis temperature, the biochar surface may contain oxygen and nitrogen surface groups, which add functionalities and could act as electron acceptors. Biochar prepared at temperatures above 700 °C are hydrophobic and recalcitrant, and have no apparent functionality anymore due to the loss of almost all O and H in their structure [25].

The term functional biochar refers to biochars (a) either produced at low temperature and thus still containing some O and H which allow the formation of surface functional groups, but with the drawback of low porosity and surface area, or (b) produced at usual pyrolysis conditions as presented earlier, and further treated either chemically or physically in order to enhance its functional groups while keeping its high surface area porosity and recalcitrance.

By further post treating biochars it is possible to obtain functional materials for environmental applications, in water and air treatment of industrial effluents and off gases. In specific, the application of biochar in wastewater treatment is believed to overcome the problem of cytotoxic, genotoxic and mutagenic activities in living organisms resulting from the application of ozonation, hydrogen peroxide, chlorine dioxide for organics pollutants removal [26].

The adsorption efficiency of organic compounds on biochar is based mainly on electrostatic interaction, partitioning, hydrophobic interaction, pore-filling, hydrogen

113 bonding formation, π - π interaction between biochar and organic pollutants [27].

114 The wide range of biomass feedstock used in the production of biochar in combination
115 with the production conditions applied, lead to a range of products with variable physico-
116 chemical composition and properties. There is a strong interest in linking biochar
117 physicochemical characteristics and their potential application.

118 Concerted efforts are being done to regulate and define quality requirements related to
119 biochar, develop guidelines for biochar and substrates used for its production. At this
120 moment, certain organizations are developing quality standards, namely the European
121 biochar certificates (EBC) in Europe, and the International Biochar Initiative (IBI) at
122 international level. The EBC indeed provides good suggestions to produce biochar that
123 can potentially be used in various applications but it is not their objective to make an
124 elaborate correlation between physicochemical characteristics and potential application.
125 This further elaboration of quality standards is the objective of ongoing research and
126 demonstration projects at EU level (ThreeC, HortiBlueC), to name a few.

127 Recent reviews aim to categorize the large amount of information of biochar
128 physicochemical properties and their effect on removal mechanisms by attributing
129 preparation technologies, functionalization techniques, to certain biochar characteristics
130 and propose specific applications, as for example in Wang et al and Patel et al.[28][29].

131 The knowledge of biochar characteristics and their possible effect on adsorption
132 mechanisms towards various types of pollutants in aqueous media is necessary to clarify
133 what steps to take towards improving biochar characteristics by means of various
134 treatments like activation and functionalization.

Table 1 gives a global overview of biochar properties, their function, their role in pollutant adsorption and relevant production parameter of biochar

Table 1: Global overview of biochar properties, their function, their role in pollutant adsorption and relevant production parameter of biochar

Biochar Property	Function	Application/ mechanism involved	Biochar production parameter
SSA, porosity	sorption capacity	Immobilization of contamination from solid, liquid and gaseous media	Residence time, high temperatures
Ion-exchange properties on surface	electrostatic interactions with polar or non-polar groups	adsorption of organic contaminants	post functionalization (acidic or base treatment)
high mechanical and chemical stability			high temperatures
Surface functional groups	Chemical bonding with certain molecules	Absorption and immobilization of certain toxins and drugs	Low temperature production, post treatment (functionalization)
pH and pH_{pzc}	Negatively or positively charged surface	Attraction/repulsion of ionically charged molecules	Feedstock (high ash content biomass leads to high pH biochars), post functionalization (acidic or base treatment)

This review aims to give the state of the art on the removal of toxic organic pollutants from wastewater using biochar, activated biochar, functionalized biochar and metal oxide or clay base biochar composites, commenting on the substrates' physicochemical characteristics, toxicity, activation/functionalization techniques and the link with the adsorption process parameters.

The impact of adsorption process parameters such as temperature, biochar loading, pollutants initial concentration, initial pH, presence of ions and contact time is discussed, to evaluate the activation/modification of biochars and their effect on the treatment

149 efficiency. This review paper also addresses recent biochar characterization techniques
150 giving information on the interpretation of analysis results mainly for FTIR, XPS, XRD,
151 TGA and Raman. The role of each technique on evaluating biochar properties is
152 underlined. Furthermore, the modification of certain biochar characteristics via activation,
153 functionalization and nanocomposite incorporation is discussed. The link between biochar
154 treatment/post-modification process and biochar proprieties is highlighted. This review
155 aims to contribute to the ongoing discussion and research efforts in EU and globally on
156 biochar quality standards, that may complement and elaborate the existing EBC and IBI
157 standards (European Biochar Certificate and International Biochar Initiative). This review
158 focuses on the applications of biochar in physicochemical treatments and does not
159 address biological processes that may include biochar at some stage.

161 **2. Biochar characterization techniques**

162
163 Recent studies prove the importance of thorough biochar characterizations to help identify
164 agronomic and environmental applications and to distinguish biochar from other organic
165 matter that provide comparable functions, either as soil improver or environmental
166 applications [30][31]. The application area of biochar is large, depending on its
167 characteristics such as specific surface area, surface functional groups, stability and
168 structure and, to a lesser degree, elemental composition [32]. These characteristics make
169 the choice of appropriate characterization techniques for biochar of a great interest and a
170 difficult task at the same time. A judicious and complete characterization of biochar
171 preceding to any target applications requires a high level of understanding the correlations

between biochar production conditions and the physiochemical properties of the biochar [33][34]. The properties of biochar can be classified in four main categories: i) chemical properties (chemical composition, functional groups, pH, ion exchange capacity; ii) physical properties (porosity, pore size distribution, specific surface area); iii) structure and surface and morphology); iv) and thermal stability properties; each category requires specific characterization techniques as shown in figure 1.

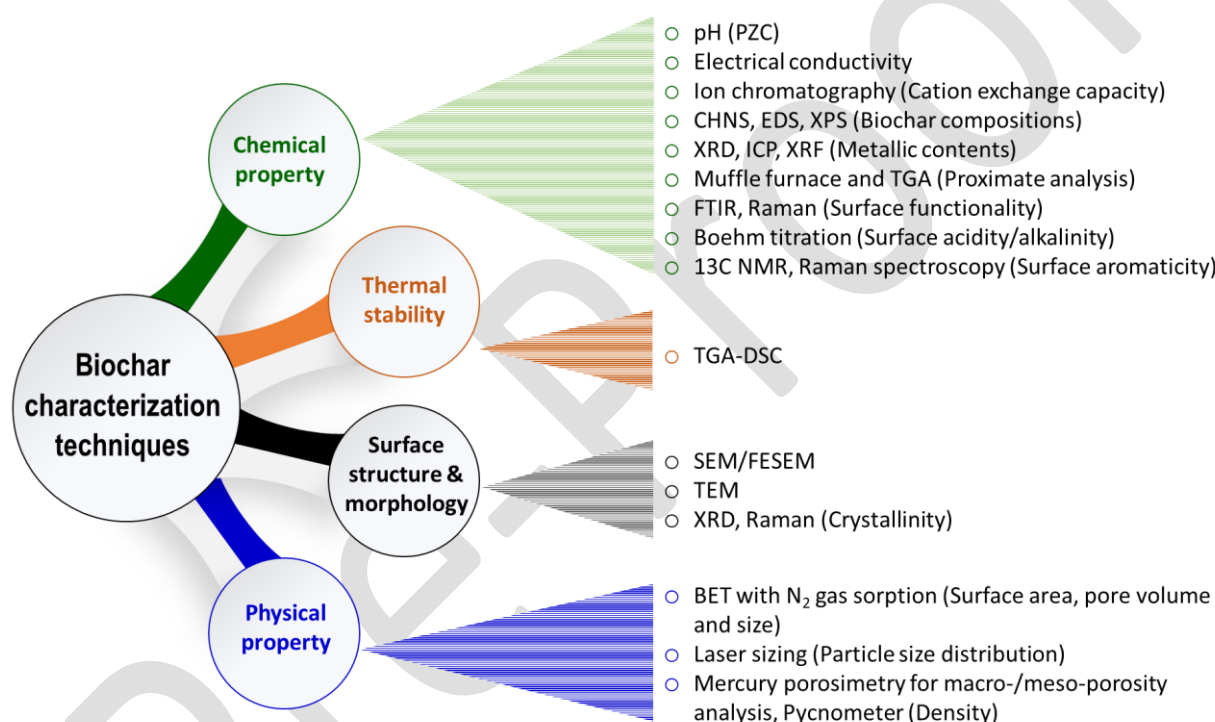


Figure 1: Classification of characterization techniques versus biochar properties reported in biochar literature.

We would like to comment that the stability of biochar may be defined differently if one considers focusing on the evolution of physicochemical properties during applications as

a stability indicator. Stability of biochar in the soil for example, is evaluated in several ways that include protocols of accelerated aging using chemical reagents, the objective of which tests is to estimate the long-term carbon storage capacity of biochars in the carbon credit context, or in GHG emission tests during incubation experiments to estimate the effect of biochar/hydro char in compost. These applications deviate from the objective of this review and will therefore not be further analyzed.

The characterization techniques reported in literature include Fourier Transform Infrared Spectrometer (FTIR), Cation Exchange Capacity (CEC) [35], Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), X-Ray photoelectron spectrometry (XPS) [36], Thermo Gravimetric Analysis (TGA), Differential scanning calorimetry (DSC), Nuclear Magnetic Resonance (NMR), Raman spectroscopy, Brunauer Emmett Teller (BET) [37].

Emerging pollutants appear in very low concentrations, in the range from $\text{ng}\cdot\text{L}^{-1}$ to $\mu\text{g}\cdot\text{L}^{-1}$, so their elimination using conventional water treatment technologies is difficult. Only with the development of novel analytical techniques or the further development of existing ones, such as liquid chromatography coupled with mass spectrometry (LC-MS), can we safeguard detection of micro pollutants. On the other side of the pollutant removal challenge is the necessity for advanced solid materials characterization techniques, to evaluate the effect of various production parameters and treatment techniques on biochar and achieve therefore the necessary links among properties and applications, which is much needed in standardization efforts of biochar quality. Research is advancing in the development of both, accurate analytical techniques to quantify pollutants in very low concentrations and in the development and characterization technologies for novel

functional biochar-based materials. These challenges go hand in hand and the effort to categorize and standardize is a long and tedious task.

Biochar characterization techniques are crucial to evaluate the performance of novel materials and to optimize the treatment process. Advances in characterization technologies help in the direction of novel composites, however a review and deeper analysis of characterization technologies is not in the scope of this article, beside recommendations on the characterization technique chosen that will be commented upon.

Figure 2 shows the reporting frequency (%) of each characterization technique used in biochar literature based on 100 scientific research articles (articles dated from 2018 to 2021). It seems that the surface imaging characterization techniques such as SEM and TEM are the most applied with a frequency of 92/100, followed by specific surface area quantification (BET) with 83/100, FTIR with 81/100 and then XRD, XPS and porosity with 63%, 55% and 47%, respectively. Nevertheless, the CEC, XRF and Boehm titration remain the less used techniques applied to evaluate the physicochemical properties of biochar. It can be concluded that surface morphology, crystallinity, the specific surface area and surface functional groups are the most demanded properties and determining factors in biochar engineering for organic pollutants removal. Concerning heavy metals content quantification, Inductively Coupled Plasma (ICP) is much more broadly applied than XRF.

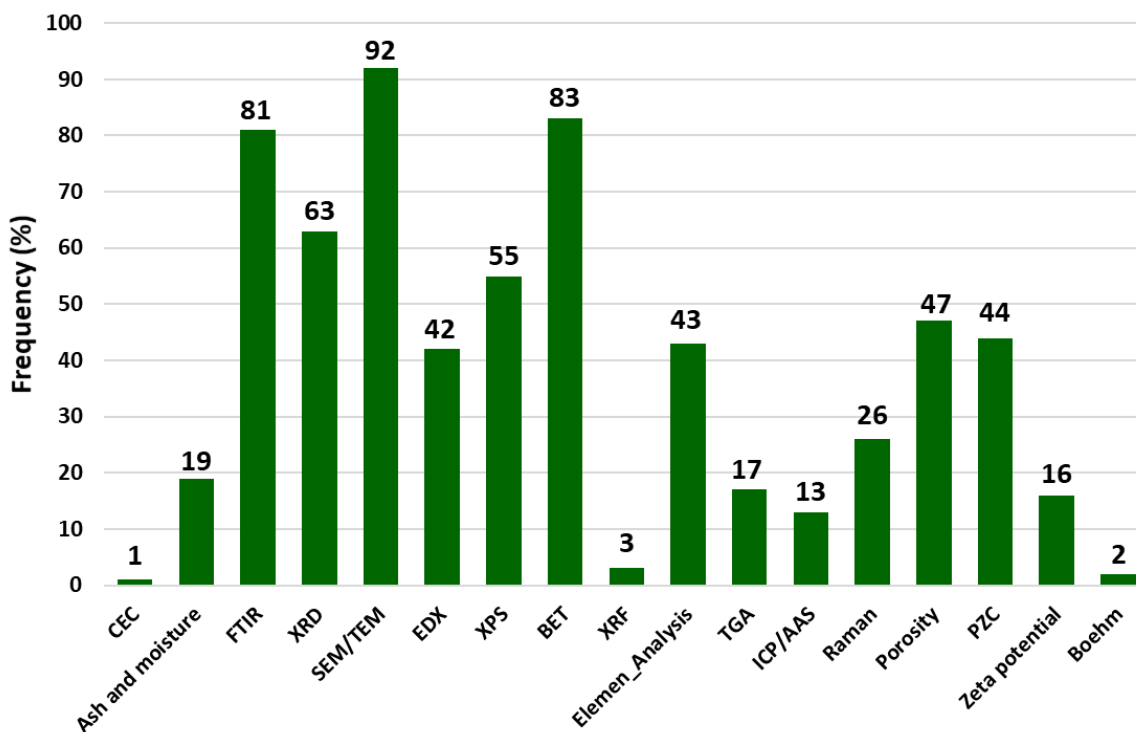


Figure 2: Frequency of applying certain techniques for biochar characterization (data recorded from 100 studies).

Table 2 shows a variety of functionalized novel biochar -based materials, with the potential to eliminate a variety of pollutants (antibiotics, dye, pesticides and steroids) at different treatment conditions. The categorization of table 2 is based on pollutant rather than biochar materials because at this stage of research it is not yet possible to discuss categories of novel functional materials and link “products” to pollutants to be removed. In the reported literature the efficiency of biochar in eliminating a pollutant is expressed both, as a removal efficiency (%) or as an adsorption capacity (mg/g). We observed that the acidic treatment is the most applied one for biochar modification/activation.

244 **Table 2:** Biochars applied in the treatment of organic pollutants.

Biochar material	Treatment of biochar	Pollutant (initial Concentration)	Removal yield or adsorption capacity (q _{max})	References
Medicine (antibiotics)				
Cobalt-gadolinium modified biochar		Ciprofloxacin (20 mg/L) Tetracycline (20 mg/L)	99.55% (6 h) 99.23% (6 h)	[38]
Sulfamic acid modified biochar		Tetracycline (100 mg/L)	412.95 mg/g biochar	[39]
Activated biochar derived from cotton shell		Sulfadiazine (10 mg/L)	≈95% (1400 min)	[36]
Rice husk Carbonization at 500 °C	H ₂ SO ₄ or KOH treatments activation biochar	Tetracycline (20 mg/L)	93.1% (180 min)	[40]
Rice straw and swine manure Carbonization at 700 °C	H ₃ PO ₄ modified biochar	Tetracycline (C ₀ = 30–200 mg·L ⁻¹)	T = 25 °C pH = 5.0–9.0 q _{max} = 167.5 mg·g ⁻¹	[41]
Iron oxide nanoparticle loaded biochar		Ofloxacin (30 mg/L)	96% (5 h)	[42]
Bamboo Carbonization at 380 °C	H ₃ PO ₄ treatment	Sulfamethoxazole, sulfathiazole and sulfamethazine	T = 21–30 °C pH = 1.0–10.0 q _{max} SMX = 88.1 mg·g ⁻¹ q _{max} STZ = 237 mg·g ⁻¹ q _{max} SMZ = 65.7 mg·g ⁻¹	[43]
Anthriscus sylvestris-derived activated biochar	NaOH treatment	Diclofenac (DF) Cephalexin (CPX)	q _{max} = 392.94 mg g ⁻¹ for DF q _{max} = 724.54 mg g ⁻¹ for CPX	[44]
Dyes				
CaWO ₄ -biochar nanocomposites		Rhodamine (0.01 mM) Methyl orange (0.05 mM)	71% (30 min) 73% (30 min)	[45]
ZnO/biochar nanocomposites		Methylene blue (160 mg/L)	95.19% (225 min)	[46]
Fe, N codoped biochar		Acid orange (20 mg/L)	93.4% (20 min)	[47]
Pinecone biochar		Black-3	346.856 mg g ⁻¹	[48]
Pesticides				
P doped biochar		Triazine (2 mg/L)	>96% (20 min)	[49]

Sawdust-coal biochar		Epoxiconazole (10 mg/L)	97 % (400 min)	[50]
Grape pomace-derived biochar		Cymoxanil pesticide (100 mg/L)	q _{max} =161 mg /g biochar	[51]
CO ₂ activated biochar		Phenol (0.5 mM) Chlorophenol (0.5 mM)	50 – 60% (60 min)	[52]
Activated magnetic loofah sponge biochar	KOH treatment	Imidacloprid	q _{max} =738 mg.g ⁻¹	[53]
Steroides				
Graphene oxide supported on activated magnetic biochar		17 β -estradiol (6 mg/L)	q _{max} =46.22 mg/g biochar	[54]
Iron loaded porous graphitized biochar		17b-estradiol (3 mg/L)	100 % (45 min)	[55]

2.1. Physical proprieties.

Physical properties include the specific surface area (SSA), particle size distribution, the bulk density, pore size and pore volume distribution [55]. These parameters are directly linked to the biochar production conditions such as reactor temperature and residence time, addition of oxygen containing media in the process (air, pure oxygen, CO₂ and steam) and/or post production processing to modify the product [38]. In the work of Xiong et al., five different biochars from various feedstocks were applied on the adsorption of epoxiconazole (EPC) fungicide. The results showed that the adsorption capacity of these five biochars towards EPC is closely related to the total pore volume and specific surface area [50]. Patel et al. also reported a positive correlation between the biochar sorptive potential toward ciprofloxacin/acetaminophen, the biochar surface area, and the total pore volume [33].

Beside total surface area also biochar surface heterogeneity plays an important role in the sorption behavior. The BET analysis is applied to study the effect of biochar modification on SSA as discussed in Figure 5 or to evaluate the effect of pyrolysis temperature on SSA of produced biochar. In their work Liu et al. reported the increase of SSA and total pore volume with increasing pyrolysis temperature. In the presence of acid the accumulation of inorganic content and the formation of new minerals at the biochar surface further increased the SSA [39]. In addition to an increase in total pore volume, Cai et al. reported a reduction in pore size [56].

2.2. Chemical properties.

Chemical properties of biochar include the point of zero charge (PZC), Cation Exchange Capacity (CEC), surface functional groups and electrical conductivity. The structural and elemental analysis are important to predict the impact of biochar on the environment [57].

The SEM technique is coupled with energy-dispersive X-ray spectroscopy (EDX or EDS) to obtain insight to the O/C atomic ratio, elemental components composition and distribution at the surface, and further on to explain the relationship between biochar preparation parameters and its resulting properties. For example, the O/C atomic ratio reflects the carbonization degree of the biochar, and indicates the degree of aromaticity of biochars, which is linked to their stability and therefore to its carbon sequestration potential [58].

On the other hand, EDX is reported as a potential tool for the direct O/C atomic ratio measurement rather than applying the CHNS elemental measurement [58][59]. Some

works reported that the H/C and O/C atomic ratios in biochar have a positive correlation with the concentration of hydroxyl, carboxyl, and carbonyl groups and thereby to CEC [60][61]. The elemental ratios of H/C refer to the aromatization degree of carbonization [62]. However, the value of O/C also represents the hydrophilicity of biochar [63].

XPS analysis is a very valuable characterization technique to identify the components functional groups on the biochar surface and their metallic state of compounds, before and after biochar composite synthesis [64]. XPS spectral lines (C 1s, O 1s and N 1s photoelectron lines) are rich in chemical information (Table 3). Their precise positions on the energy axis reflect the local electronic environment of the photoemitting atom, a clear shift for C-O, C = O, COO⁻ and CO₃²⁻ carbons can be seen [65]. Zhang et al confirmed the presence of Fe-O in biochar/Fe_xO_y composite by XPS at binding energies of 711.3 and 725.0 eV for the Fe 2p_{3/2} and Fe 2p_{1/2} core levels, respectively. Moreover, the adsorption of methylene blue leads to a decrease in peaks intensities for the majority of C 1s and O 1s spectrum [66]. On the other hand, the appearance of N 1s in the XPS spectrum of biochar/Fe_xO_y-MB suggested that the adsorption involves N electrostatic attraction [66][67]. The incorporation of Mn on Nano-zerovalent manganese/biochar composite resulted to the detection of Mn²⁺ and Mn³⁺ present at binding energy values of 642.5 eV (Mn 2p_{3/2}), 653.5 eV (Mn 2p_{1/2}) for Mn²⁺ and 645.3 eV that corresponds to Mn³⁺ [68]. Other works reported the presence of; i) O-Fe (530.12–530.26 eV) in O 1s XPS spectra of biochar/Fe composites [69]; ii) Fe2p and Co2p at 711.3 eV and 779.8 eV, respectively [70]; iii) Cr³⁺ at 584.20 and 575.04 eV [71].

Table 3: Binding energy in XPS spectra for the main surface functional groups on biochars reported in literature.

Biochar	C 1s Line					O 1s Line		N 1s Line	Reference
	C–C	C = C	C–O	O–C–O	C=O	Organic C=O	Organic C–O	C–N	
Biochar/Fe _x O _y composite	284.8	284.8	286.1	288.3		533.3	531.62	399.6 and 402.0	[66]
Biochar	284.4–284.7 285.0–285.2		286.3 – 286.6	289.1–289.3	287.8–288.0	531.3–532.3	533.3–533.9	399–401	[65]
Biochar/Fe composites						531.44–531.57	532.23–533.08		[69]
Graphene oxide /CoFe ₂ O ₄ sludge biochar composite	284.8	284.8	286.5						[70]
Iron-loaded biochar	284.8	284.8						400.2	[71]
Biochar-based iron oxide	284.4		285.6		288.5				[72]

Sludge-derived biochar			285.9 – 286.4	288.7– 289.0	287.1– 287.2				[73]
N-doped graphite-like mesoporous structure biochar			285.0 286.4		288.8			398.4, 400.0, 400.9	[74]
Magnetic sludge biochar	284.8	284.8	286.5		288.7				[75]
Ga ₂ S ₃ /S-modified biochar	285.62 283.77	285.6 2 283.7 7	284.0 3 285.3 4			532.27, 531.71, and 530.32			[76]
Hickory chip biochars	284.8	284.8	286		288.5	531.5	533.0		[77]

XPS can also be used to evaluate the elemental O/C molar ratio that may be considered as an indication for biochar stability [78].

The use of Fourier Transform Infrared spectroscopy (FTIR) in biochar surface characterization is also very common. This technique gives detailed information on the oxygen-containing functional groups present on the surface of biochar (Table 4), evaluates the success of metal binding during surface treatment and/or the surface functional groups transformation after pollutants adsorption [54]. Al-Wabel et al reported the increase of the broad absorption band attributed to O–H stretching vibrations (at

around 3320 cm⁻¹) in biochar with the moisture increase, however the presence of C–O–C stretching vibrations band indicated the occurrence of non-decomposed oxygenated groups [79]. FTIR can analyze organic functional groups commonly observed in biochars, as carbon-hydrogen (C-H), C = C, C=O, C-O, and silicon-oxygen (Si-O)[80][81]. Table 4 shows the functional groups and their wavenumber in published literature on biochar and biochar composites.

Table 4: Peak positions of the main surface functions in FTIR spectra of biochar and biochar-based composites reported in literature.

Biochar	O–H	C–O–C	C = C	Carboxyl C=O	C–O	C–H aromatic	C–N	Reference
Biochar/Fe _x O _y composite	3368-3429		1620	1386	1049	826		[66]
Alkali-modified SCG biochars	3160-3430	1150-1050		1600 – 1450				[82]
Nano-zerovalent manganese/biochar	3320		1580					[68]
Graphene oxide /CoFe ₂ O ₄ sludge biochar composite	3423–3444		1562– 1628		1035– 1081			[70]
Biochar derived from sugarcane bagasse	3430		1625	1710	1030	865– 750		[83]

Biochar-supported MnFe_2O_4	3361		1495 and 1283			875		[84]
Bidirectional activated biochar from sugarcane	3744		1615, 1580, 1582, 1497		1415 and 1381		1384, 1379	[85]
Biochar-based iron oxide	3400–3500		1500	1600	1040			[72]
Sludge-derived biochar	3420	1035		1590	1035	700–900		[73]
Natural iron ore – biochar	3426		1588		1099	807		[86]
Pyrrolic N-rich biochar	3428		1592	1714	1064		1236	[56]
N-doped graphite-like mesoporous structure biochar	3160			1683–1590			1344	[74]
Magnetic Pristine biochar	3451		1584		1118			[87]
Biochar from oil palm frond	3460		1615	1736		878, 809 and 764		[88]
Biochars produced from rice straw, bagasse, and eucalyptus wood	3400		1620	1730	1100			[89]

Cornstalk, orange peel, and peanut hull derived biochar	3430		1620	1580	1080			[90]
Biochars from forest and agri-food wastes	3440		1633			877		[91]
Modified magnetic biochar from pine nut shells	3360	1030	1640				1050	[92]
Magnetic sludge biochar	3429– 3432	1031– 1090	1618– 1649					[75]
Cassava ethanol sludge derived biochar	3425– 3433	1066– 1087		1633– 1635				[93]

2.3. Surface structure and morphology

The surface morphology and chemical composition are important attributes of biochar. Scanning electron microscope (SEM) and transmission electron microscope (TEM) are valuable tools to evaluate the development of surface structure, porosity and pores distribution of biochar before and after modification [38].

Raman spectroscopy is considered a powerful technique for exploring the graphitization or defects on carbonaceous materials. In biochar engineering and development, the interest focuses on two bands; i) the D band which represents the disorder and defect degree caused by vacancies, edges and functional groups, ii) the G band which is related

to the crystalline and graphitic structures [94]. Meanwhile, the estimated intensity ratio of the D band relative to the G band (ID/IG) reflects the disorder and level of defect of the analyzed biochar (Table 5). It is suggested that an increase in ID/IG ratio due to the addition of iron suggests an increase of defective sites [95]. It is also reported that the increase in pyrolysis temperature until a certain value increases the defected sites formed on biochar [73]. Also a low ID/IG ratio meant a relatively high degree of graphitization [93]. Generally, the ID/IG value increases with increasing pyrolysis temperatures, indicating that high pyrolysis temperatures are beneficial for the growth of defect structures in produced biochar [96][97].

Table 5: The position of D band and G band in Raman spectra of biochar reported in literature.

Biochar	D band position (cm ⁻¹)	G band position (cm ⁻¹)	ID/IG	Reference
Sludge-derived biochar	1350	1580	0.84 and 1.06	[73]
Magnetic biochar derived from banana peels	1338	1589	0.94 and 0.99	[95]
Pyrrolic N-rich biochar	1343	1588	0.79 and 1.07	[56]

Multi-porous biochar from lotus biomass	1340	1585	1.67, 1.48, 1.30, and 1.56	[98]
Cassava ethanol sludge derived biochar	1368	1594	0.389 and 0.407	[93]
Graphitic biochar	1310	1590	1.94–2.56	[99]
Nanoscale zero- valent iron (nZVI) supported on rice stalk (RS) derived biochar composite	1309.1 1349.6	1561.7 1590.6	0.99, 1.04, 1.08, 1.05 and 1.10	[97]

348

349 The X-Ray Diffraction (XRD) technique is applied to determine the crystal structures and
350 phase composition in a solid material. It can also evaluate the ratio of crystalline and
351 amorphous phase and define the material modification such as metal oxide loading [64],
352 magnetic biochar composite synthesis [70]. The technique can evaluate the stability of
353 biochar components after modifications, for example SiO₂ modification [66]. The use of
354 XRD spectra is reported to evaluate the interlayer spacing of the activated biochar
355 according to Bragg's formula and/or the average crystalline size with the help of the
356 Scherrer equation [83].

357 **Bragg's equation:**

$$d = \frac{\lambda}{2\sin\theta}$$

In which λ is the X-ray wavelength whose value is 0.154 nm generally, and θ is the angle of the peak position.

Scherrer equation

This equation is used to evaluate the average crystalline size along c-axis (L_c) and the size of the layer planes (L_a).

$$L = \frac{k\lambda}{B\cos\theta}$$

In which k is the value of the shape factor ($k = 0.9$ and 1.84) which are used frequently for the purpose of calculation of L_c and L_a respectively. B is the value of line broadening at half width of the peak known as FWHM (Full width half maximum) in radians.

2.4. Biochar stability

Thermogravimetry analysis (TGA) is applied to evaluate the thermal stability of biochar [74] and characterize its structure, as it gives information about the pyrolysis yield, the content of moisture and the different structural components such as hemicellulose, cellulose, and lignin [100]. Generally, the weight loss in TG analysis can be divided into three stages shown in Table 6 below; the first stage represents the loss due the water evaporation, and decomposition of bonded hydrated compounds, during the second stage the major loss observed is explained by the thermal decomposition of polar organic compounds derived from most cellulose, hemicellulose and holocellulosic precursors

[101]. Finally the last weight loss stage was attributed to the slow and gradual thermal decomposition of high molecular weight components present in the biomass [89].

Table 6: The main weight loss stages of biochars in thermogravimetry analysis reported in literature.

Biochar	1st weight loss	2nd weight loss	3rd weight loss	Reference
Biochars produced from rice straw, bagasse, and eucalyptus wood	7 to 9 % (0-150 °C)	60 to 81 % (200-450 °C)	(450-900 °C)	[89]
Maple leaf-derived biochars	10 % (40-300 °C)	45 % (300-400 °C)	5 % (400-1000 °C)	[101]
Multi-porous biochar from lotus biomass	10 % (0-160 °C)	58 % (160-365 °C) dehydration and condensation of cellulose and hemicelluloses	20 % (350-900 °C)	[98]
Functionalized magnetic biochar from waste poplar sawdust (CoFe ₂ O ₄ @PBC-LDH)	11 % (20-200 °C) loss of hygroscopic water and light components	12-14 % (200-415 °C) dehydroxylation of LDHs and the release of volatile substances by the	17 % (415-980 °C) decomposition of biochar	[102]

		interlayer CO_3^{2-} anions		
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3. Toxicity of biochar

Biochar has an active role in environmental remediation as an adsorbent, filter medium or active catalytic composite [103], nonetheless it is imperative to systematically discuss its potentially negative environmental effects and prevent risks during application. Some studies focus on the evaluation of harmful components of biochar such as dioxins [104], heavy metals [105], polycyclic aromatic hydrocarbons (PAHs) [106][107], environmentally persistent free radicals (EPFRs) [108], volatile organic compounds (VOCs) and perfluorochemicals (PFCs) [109].

The content of heavy metals in biochar differs with biomass type and source [105][110], for example sludge biochar, which has a high heavy metal content [111]. The concentration of heavy metals in biochar is therefore linked to the origin biomass and is retained during pyrolysis [112]. In addition, PAHs in biochar are reported to have high biotoxicity effect on plants and microorganisms in different environmental media. The content of PAHs in biochar depends on the process itself, namely residence time, temperature and special attention should be given to avoiding the condensation of tar loaded gases on the biochar. In specific, PAH formation i) varies with the feedstock type or nature [57], ii) is reduced at sufficient heating rate during pyrolysis [107], iii) decreases while pyrolysis temperature and/or residence time in reactor increase [113].

Dioxins also form during the biochar production process, the factors that influence are; i) Chloride (Cl) content in feedstock, as reported by Wiedner et al. [114], ii) reactor

temperature, with dioxins forming as temperature reduces, usually when the flue gas cools down [107]. EPFRs can be produced during pyrolysis process with lignin, cellulose and hemicellulose in biomass fibers acting as a precursor [115], [116]. In addition, the content of these free radicals increases with the pyrolysis temperature [117]. It may pose a potential environmental risk since they can induce the formation of reactive oxygen species with high cytotoxicity and phytotoxicity within environmental media [118].

Other potential risks of biochar are due to adsorbed pollutants on the biochar surface, the presence of residual chemicals in biochar originating from the plant residues persisting the pyrolysis process, and finally the leaching out of various components from the biodegradation under natural conditions of aged biochar [119].

The voluntary biochar quality standards that apply in Europe with the European Biochar Certificate (EBC) [120], in the UK with the biochar quality mandate (BQM) and in the USA with the International Biochar Initiative-Biochar Standard (IBI-BS) propose limits for certain harmful components in biochar such as; PAH, benzo (a) pyrene, polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans and heavy metals [120][121]. However, these standards are safeguarding biochar production rather than final applications, therefore prior to applying novel adsorbents with potential ecotoxic effects the national safety regulations for air, soil and water need to be secured at all times.

4. Factors influencing pollutants removal

The elimination of pollutants and the adsorption capacity of biochar are greatly affected by its physicochemical properties as well as of the target pollutants nature, and the operating conditions of the treatment, as reported in Tables 1 and 2 [122]. Several works report the effect of different parameters and their interaction on the removal efficiency of pollutants with the help of multivariate optimization approach [123][124]. Figure 3 shows the factors influencing the removal of organic pollutants by biochar. In general, biochar concentration and initial pH of the solution are the most discussed.

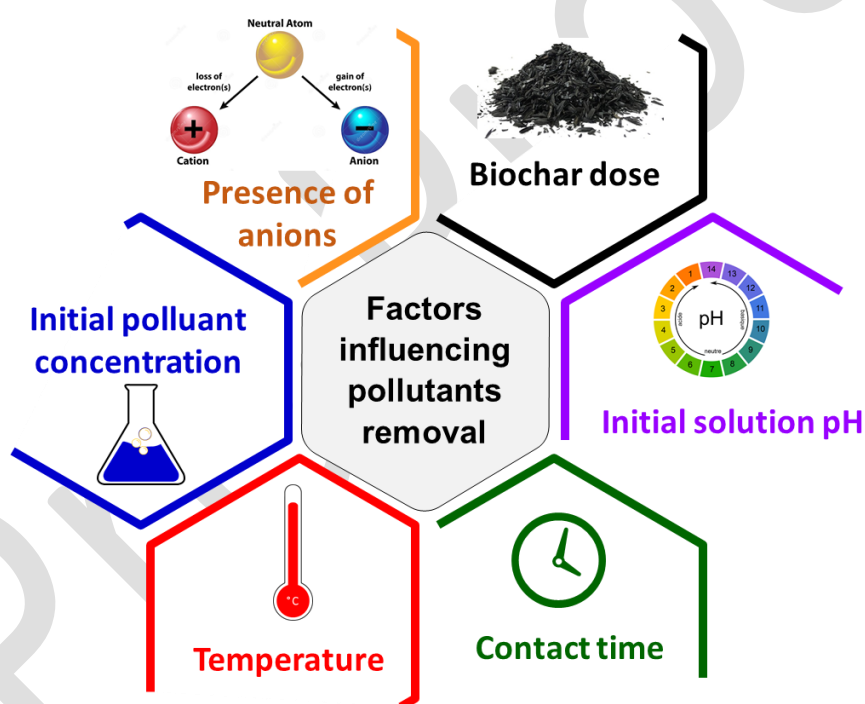


Figure 3: The main influencing parameters in organic pollutants removal by biochar.

4.1. Effect of biochar dose

The impact of biochar dose on pollutant removal efficiency is reported in detail in most of the adsorption studies, because of the high correlation observed between adsorbent dosage and adsorption capacity. However there is an optimum value of biochar dose, beyond this threshold there is no enhancement in the pollutant elimination anymore [42]. This tendency is explained by the optimum use of the active adsorption sites for pollutant adsorption [125]. Beyond the optimum point, the decrease in the adsorption capacity may be due to the inadequate availability of pollutant molecules for spare active sites [126]. In another study the increased biochar quantity results to a faster achievement of the reaction equilibrium, indicating the increased availability of vacant reactive sites on the adsorbent surface, which leads to a high adsorption rate at the beginning of the process [127]. However the increase in biochar dosage decreases the adsorption capacity exponentially but moderately at lower dosages and slightly at higher dosages [128].

4.2. Effect of initial solution pH

The pH of pollutant solution is a factor which influences the removal efficiency because of the predominant role on the charge characteristics through the protonation and deprotonation of oxygen-containing groups on the biochar or biochar composite surface [129]. The pH value also influences the degree of ionization of the adsorbate [130]. Wang et al reported that anion adsorption is favored at pH less than the point of zero charge (PZC) because the adsorbent surface is positively charged. However, when the surface is negatively charged at pH values above the PZC the cation adsorption is favored [131].

In the work of Chaukura et al, a maximum adsorption of methyl orange was recorded at pH value lower than the PZC of biochar, this was explained by possible electrostatic attraction of the dye molecules to biochar surface since the dye molecules existed as anions at the reported conditions [132]. Generally, the organic dyes adsorption capacity by biochar or nano-metal biochar composites decrease with increasing solution pH values [133].

4.3. Effect of pollutant concentration

The initial concentration of the adsorbate plays a crucial role in the efficiency of the adsorption process. It is reported that the adsorption capacity decreases with the increase in the initial concentration of pollutants [134]. This is attributed to the occupation of active sites on the adsorbent material surface by the targeted pollutants [127]. Some works reported a proportional relationship between pollutant initial concentration and adsorption capacity of biochar; however, the removal yield of pollutant decreases [135][136]. An explanation of this can be that at higher concentration, the mass transfer driving force increased [85], which enhanced the diffusion rate and the probability that molecules reached the material surface increases [137]. We would like to comment that if the diffusion rate is enhanced, one may observe positive correlation between concentration and rate of adsorption, instead of adsorption capacity [135][136], as the latter should be dependent of the total available sorption site amount on biochar.

Sayin et al. reported a decrease of adsorption efficiency with increasing the ciprofloxacin initial concentration from 50 to 150 mg/L, and this was explained by the gradual saturation of specific active site for antibiotic molecules adsorption [138]. Nnadozie and P.A. Ajibade

studied the adsorption of Indigo Carmine (IC) dye using *C. odorata* biochar, the result showed a decrease in the removal efficiency with increasing dye concentration from 10 to 100 mg/L with the same biochar dose [139].

4.4. Effect of anions presence

The pollutant molecules may compete with various coexisting anions such as NO_3^- , Cl^- , SO_4^{2-} and PO_4^{3-} during adsorption in aqueous environment. Wang et al reported a decrease in the removal efficiency of p-arsanilic acid in the presence of PO_4^{3-} because of the stronger competitiveness for the adsorptive sites on the surface of biochar [140]. The increase in NaCl content decrease the adsorption capacity of biochar [54], which was explained by the reduction of repulsion force between adsorbent particles and hence the increase of aggregation of nanomaterials [141]. However, beyond a certain dose of NaCl increase, the adsorption capacity increases, which was attributed to the increase of ionic strength which improved the activity coefficient of hydrophobic organic compounds, resulting in a decrease in solubility (i.e. salting-out effect), thus was conducive to pollutant adsorption [142]. It can also be explained by surface charge neutralization of the carbonaceous adsorbents by the double layer compression and the reduced solubility of the micropollutants in the presence of high Na^+ concentration [82].

4.5. Effect of contact time

The effect of contact time needs to be considered in the evaluation of the biochar adsorption system. Published research reports a fast increase in the adsorption capacity at the beginning of the treatment and a gradual slow-down of the adsorption capacity until

adsorption equilibrium is reached, when the sorption sites were fully occupied [135][143]. This can be explained by the gradual adsorption saturation of active sites on biochar and the gradual decrease in the differential concentration between solution bulk phase and the surface of the adsorbent [144]. Similar results were observed by Velusamy et al. [145] and Li et al., in the removal of ciprofloxacin [146]. Sayin et al., in their work on the removal of ciprofloxacin by H₃PO₄ modified biochar, reported the decrease of the adsorption rate of antibiotic molecules with increasing time of treatment and that until the equilibrium point of time [138]. Nguyen et al. in their study tested diverse Metal salt-modified biochars derived from different agro-waste for the removal of Congo red dye. The results revealed the different equilibrium times needed for the different biochars applied at the same initial concentration of the dye [13].

4.6. Effect of temperature

The adsorption temperature can also affect the pollutants removal capacity by biochar and its composites. However, the majority of water treatment experiments are conducted at ambient temperature (25 °C) to simulate the temperature predominant in the environments [147]. It is reported that the adsorption increases with increasing temperature in the range of 15-35°C [71], which reflects an endothermic process [148]. Similar results on the endothermicity of : i) p-nitrophenol adsorption by pine sawdust biochar was reported in the work of Liu et al [149] and ii) diclofenac adsorption by pine wood biochar [150]. The increase in temperature increased the probability of pollutant molecules contacting the active sites [148]. However, the increase of temperature in the same range can reduce the adsorption capacity in an exothermic process [136][145]. On

the other hand there is a proportional relationship between temperature and the molecular movement acceleration, which promotes adsorbent-ion interaction and reduction of the Gibbs free energy [151][152]. The increase of temperature can enhance the formation of aromatic carbon present on the surface of biochar resulting to improved surface characteristics for adsorbing an extensive range of pollutants [153].

4.7. Effect of chemical impregnation ratio on the removal of pollutants

The ratio of the non-processed to magnetic material was studied in several works to evaluate its effect on pollutant removal efficiency. It is found that the increase of this ratio increases the adsorption capacity of magnetic biochar until an optimum value but further increase leads to a decrease of the adsorption capacity [154]. However, Son et al report that copper removal capacities decrease with decreasing biochar/Iron ratio and Fe recovery efficiency, explained by the plugging of biochar's surface pores with iron oxide particles [155]. In addition, Yang et al. found that the increase in FeCl_3 /sawdust impregnation mass ratio increases the removal efficiency of mercury which was attributed to oxygen-rich functional groups formation at biochar surface and especially C=O group. However, an excess of FeCl_3 can lead to; i) the aggregation of Fe_3O_4 particles on the magnetic biochar surface, and/or ii) the variation of textural properties and therefore a decrease in mercury removal yield [156].

5. Post-processing modification of biochar: Activation and functionalization

The thermal decomposition of biomass in the absence of oxygen, or at very limited oxygen environment, produces biochars that still contain various refractory oxides, depending on

the biomass feedstock, such as Fe_2O_3 , SiO_2 , KCl , Al_2O_3 , CaSO_4 , CaCO_3 [157]. Furthermore, the surface of most pristine biochars are often negatively charged in association with its abundant oxygen-containing function groups, thus exhibiting specific sorption to cations (e.g., heavy metals ions) [158]. However, sorption toward anionic species (i.e., oxyanion, anionic dyes and organics) is limited [159]. This limits the applications of biochar which drives researchers to introduce new and additional metal oxides with different methods to modify biochar for targeted applications [160].

In addition, biochar prepared by conventional pyrolysis of biomass may have poor physicochemical properties such as surface oxygenated groups, surface area, pore volume, and pore width. These properties fluctuate considerably and depend on feedstock types and production conditions [161]. Nevertheless, the available functional groups (carboxyl ($-\text{COOH}$), hydroxyl ($-\text{OH}$), and carbonyl ($\text{C}=\text{O}$)), are quite important in water treatment [162]. The hydrophilic (polarity index) or hydrophobic property (aromaticity) of biochar highly depends upon the type and nature of existing functional groups on the surface. Different techniques available have been reported to boost the abundance of this last, such as steam activation, impregnation method, chemical and heat treatments [163].

Biochar can also act as an excellent photocatalyst when combined with other catalysts, because of the resulting favorable physicochemical properties such as; high surface area with high active site, enhanced charge separation, higher availability of functional groups, high porous volume, better catalyzing ability, stability and recoverability [164]. However, the synthesis of photocatalyst-based biochar must be optimized [165]. As reported by Yu et al., the addition of an appropriate amount of ZnO into biochar enhanced both the adsorption capacity and the photocatalytic ability of the nanocomposites [46]. Similar

569 results were reported in the application of Mn-loaded and Fe-loaded biochar for the
570 atrazine elimination in aqueous solution with heterogeneous catalytic ozonation [166].
571 Ahmaruzzaman reported a different synthesis technique of biochar supported
572 photocatalyst like Sol-gel method, Ultrasound assisted synthesis, Thermal
573 polycondensation technique, Solvothermal process, Hydrothermal process [164].

574 As seen in the Figure 4, the different post-modification methods of biochar are classified
575 into four main categories; 1) modifications to increase the surface area and porosity; 2)
576 modifications to render the biochar surface positively charged; 3) Increasing surface
577 oxygen-containing functional groups and 4) magnetization of biochar in order to
578 facilitate/enhance the biochar particles recovery. It may be that one treatment can
579 enhance two or more proprieties at the same time, for example the case of H_2SO_4
580 treatment which enhances the specific surface area and increases the oxygen-containing
581 functional groups. There are different classifications for these modifications reported in
582 literature [167][18] such as the classification according to physicochemical characteristics
583 of biochar targeted by the modification [161], or according to the nature of process
584 (chemical, physical or composite) [168].

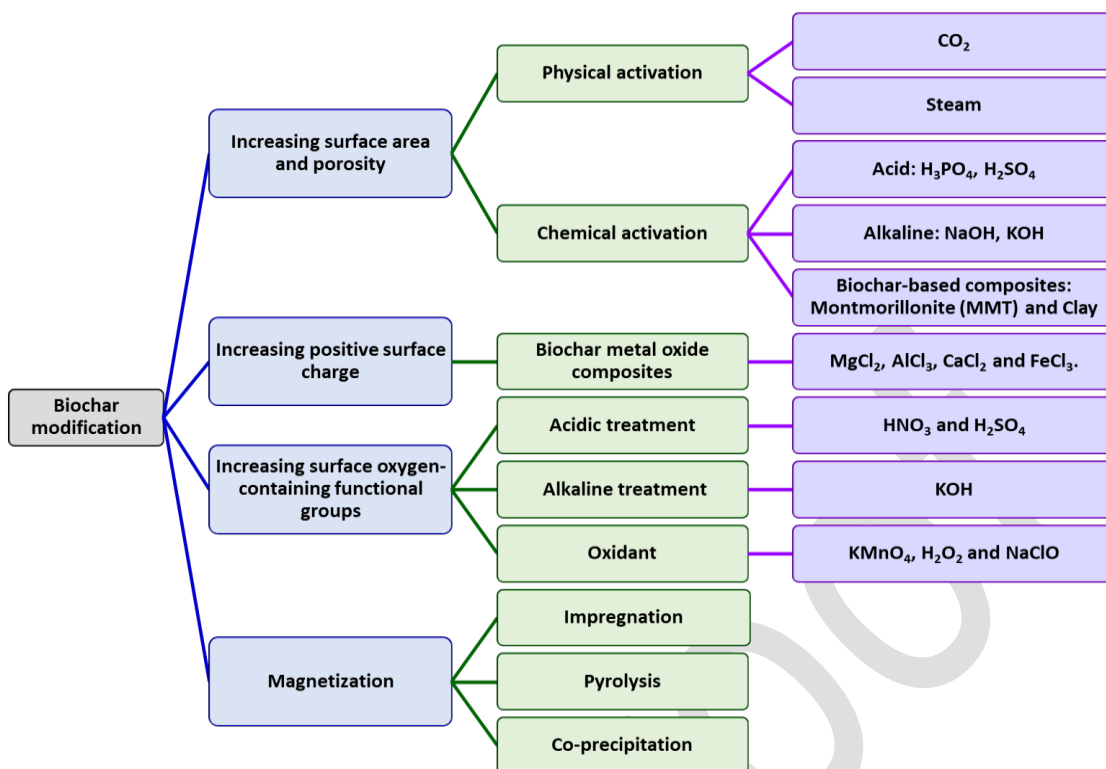


Figure 4: Typical engineered biochar modifications and its classification.

Figure 5 shows the effect of different modification treatments on the biochars' specific surface area (SSA) as reported in literature. We observe that: i) the result for a treatment technique varies from one biochar to another (case of Mn-BC modification and H_3PO_4 treatment for example); ii) some treatments lead to a decrease in SSA (case of FeCl_3 -BC and AlCl_3 -BC); iii) some techniques presented a considerable increase in the SSA such as CO_2 activation and K_2CO_3 treatment. The Increase of biochar SSA resulting from different posttreatment techniques does not always mean the improvement of its performance towards the removal of organic pollutants.

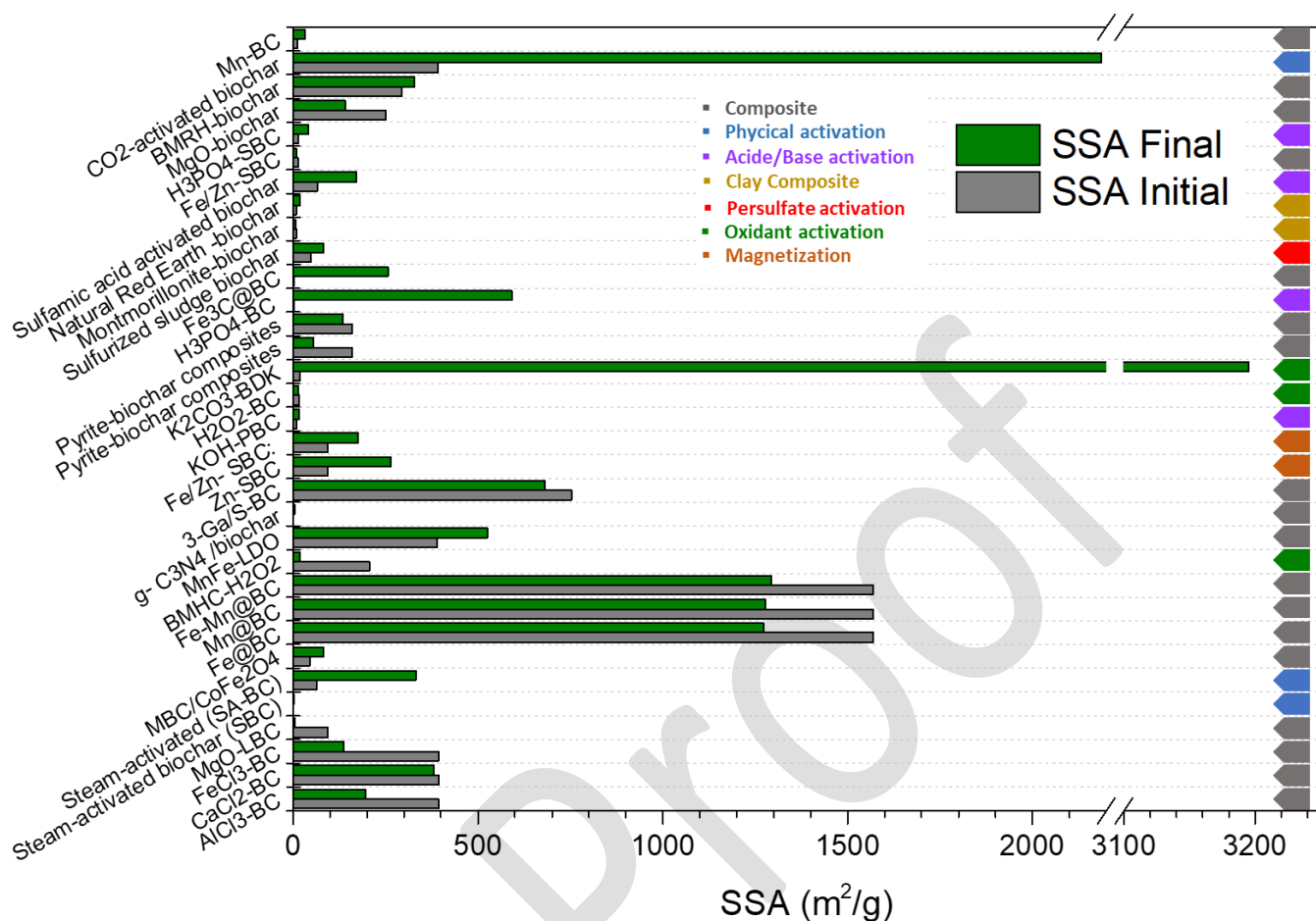


Figure 5: The evolution of specific surface area (SSA) of biochar according to different modification techniques in some reported works ([13], [169], [170], [171], [172], [173], [77], [174], [175], [76], [75], [90], [90], [56], [86], [69], [176], [177], [39], [178], [179], [180], [52], [64]).

Moreover, as reported in detail by Barquilha and Braga, organic and inorganic pollutants adsorption on biochars can involve different mechanisms, including physical and chemical interactions. The interaction between biochars and adsorbate species is not simple and may involve different adsorption mechanisms, such as van der Waals forces, electrostatic interactions, surface complexation, ion-exchange, hydrophobic interactions, π -interactions, co-precipitation, partition, and pore-filling [181]. Other studies report on the

mechanisms of dye adsorption by sewage sludge-biochar [182] and adsorption mechanisms of modified biochar on typical emerging contaminants [167].

5.1. Acid-base activation/decoration

Generally, biochar modification by acidic treatment occurs in two main ways: activation and decoration. Activation is to develop porous structure and increase specific surface area by using chemical activating agents with highly etching ability. Whereas, decoration emphasizes on enhancing surface activity, by using zero-valent iron nanoparticles [183], Fe_3O_4 and FeOOH as additives [184]. Another work reported the enhancement of sorbent hydrophobicity by decoration with different acid and fatty acids such as; pure lauric acid, acetic anhydride, phosphoric acid and citric acid [185][186][187].

Gurav et al., reported the application of pinewood biochar decorated with coconut oil-derived fatty acids for adsorptive removal of crude petroleum oil from water. Fatty acids composition attached to the resulted biochar (mg/g of biochar) was reported as: lauric acid (9.024), myristic acid (5.065), palmitic acid (2.769), capric acid (1.639), oleic acid (1.362), stearic acid (1.114), and linoleic acid (0.130). Decorated biochar presented a higher hydrophobicity and a good reusability with stable adsorption efficiency at 51.40% after fifth adsorption-desorption cycles [188]. The sulfamic acid modified biochar reported in the work of Liu et al., presented a specific surface area with 2.6 times larger than that of the original biochar introducing more functional groups on the biochar. Furthermore, the resulted biochar shows an improved performance for tetracycline adsorption [39].

Many studies have proved that biochar treated with a strong oxidizing agent (e.g., $\text{HNO}_3/\text{H}_2\text{SO}_4$, HNO_3 , HF/HNO_3 , KMnO_4 , H_2O_2 and NaClO) enhance its sorption capacity,

creates charged and hydrophilic surface functional groups, and increases their colloidal stability and mobility [189]. The activation of biochar in one step and two steps by KOH and KMnO_4 as a green activator was found to give a large pore volume, pore channel and proportion of aromatized structure, it revealed to have a high adsorption capacity for methylene blue removal [190]. The oxidation of corncob biochar by of $\text{HNO}_3\text{-H}_2\text{SO}_4$ mixture was found to boost the adsorption capacity of biochar, decrease hydrophobicity and increase the amounts of oxygen-containing groups [191]. The treatment of sludge biochar modified by $\text{Fe/Zn} + \text{H}_3\text{PO}_4$ presented an adsorption capacity for ciprofloxacin (CIP), norfloxacin (NOR) and ofloxacin (OFL) from water up to 20 times of those of sludge biochar only or H_3PO_4 modified biochar [178].

Some works reported the NaOH activation of biochar or biomass before pyrolysis in order to well-developed mesoporous structure [192], enhance the higher specific surface area, total pore volume, aromaticity [193], and graphitized orderly carbon layer in biochar [135]. The KOH treatment was also reported to increase the surface area and pore volume [194]. Apparently, biochar modification with a strong inorganic acid is one of a simple and effective processes for biochar activation. However, the scaling-up into an industrial scale will produce a large amount of acidic or basic wastewater, with negative impact to the aquatic environment.

5.2. Persulfate activation

Persulfate (PS) activated biochar was reported in many studies in the last years [173][195], due to the increased pollutant removal efficiency from water by combining the advantage of PS radicals effect and the high specific surface area of biochar [196][197].

It is noticed that, compared with the traditional hydroxyl radical-based AOP, Sulfate radicals-AOP has a higher redox potential (2.5–3.1 V ($\text{SO}_4^{\cdot-}$) vs. 2.7 V ($\cdot\text{OH}$)), but longer half-life time (30–40 μs ($\text{SO}_4^{\cdot-}$) vs. <1 μs ($\cdot\text{OH}$)) and wide pH adaptability [198]. Fan et al. reported the slight adsorption of bisphenol A (8.1%) by sludge-derived biochar (SBC) alone and limited direct oxidation (2.4%) by sole peroxymonosulfate (PMS), nevertheless, the removal efficiency of bisphenol A was boosted to 94.5% within 60 min in the presence of both SBC and PMS. that the explanation is that PMS is bound to SBC and forming a surface reactive complex (SBC-PMS*), which would abstract the electrons from the adsorbed pollutant through the conductive carbon tunnel [199].

Furthermore, different biochar modification options can be combined to promote the elimination of aqueous pollutants, such as magnetization and peroxymonosulfate (PMS) activation, reported by You et al. [172].

5.3. Physical activation

Physical activation of biochar is the partial oxidation of the material to increase its porosity, under low to medium heat treatment ($<250^\circ\text{C}$) under air conditions or high temperature ($>750^\circ\text{C}$) treatment with CO_2 , steam, blends thereof. At high temperatures H_2O and CO_2 become reactive and therefore allow for chemical reactions with the biochar matrix [200]. Jellali et al. reported the increase of the surface area and total pore volume after CO_2 activation by about 5.9 and 1.5 times, respectively [122]. Meanwhile the activation process with air at a low temperature ($\approx 275^\circ\text{C}$) for 4 h significantly enhanced the structure and texture of the biochar generated from different sewage sludge types [201]. Sewu et al. reported that the steam activation of biochar enhances the porosity and increases the

specific surface area by 5 times and the adsorption capacity of crystal violet by 4.1 time [171]. Similar results were reported by Wang et al. for the synergistic removal of Cu^{2+} and tetracycline (TC) with steam-activated bamboo-derived biochar [170]. Ibrahim et al reported that steam activation of carbonized Oil Palm Mesocarp Fiber presents a high removal of the chemical oxygen demand and suspended solids from 395 mg/L and 117 mg/L to 122 mg/L and 7 mg/L, respectively in a treated wastewater after 6 consecutive treatment cycles [202]. Some works reported that alkali and steam treatments can be used to increase porosity and clean blocked pores [203][204].

5.4. Biochar-based composites

It is reported that producing biochar-based composites allows to combine the advantages of biochar with nano-materials, where the resulting composites usually exhibit great improvement in functional groups, pore properties, surface active sites, adjusted net surface charges, catalytic degradation ability and easy for recovery [204][180]. These composites can be classified into three categories based on their synthesis process towards biochar-based nano-materials; i) nano-metal oxide/hydroxide-biochar composites, ii) magnetic biochar composites [159], and iii) clay mineral based-biochar [205].

5.4.1. Nano-metal oxide/hydroxide-biochar composites

Several chemical additives have been used in the synthesis of these composites, like H_3PO_4 , NaCl, K_2CO_3 , MgCl_2 , ZnCl_2 , KOH, CaCl_2 and FeCl_3 , which may be added before

or after biomass carbonization [161], in powder forms or dissolved, as shown in figure 5. Table 6 summarizes some works reported on nano-metal oxide- biochar composite synthesized to treat organic pollutants, where it can be seen that there are different preparation methods for these composites under diverse operating conditions. So, for example we find co-precipitation, pyrolysis, impregnation, sol-gel method and chemical reduction. Using a different classification method, in their review Zhao et al classified the nano-metal oxide-biochar composites preparation into four methods as presented in the figure 6; i) Impregnation which is characterized by its simplicity and a large capacity of obtained composites, ii) Chemical coprecipitation characterized by low cost, high purity, homogeneous nanoparticles, both these methods have the disadvantage of causing chemical pollution, iii) direct pyrolysis characterized by the easy preparation and the prior biomass enriched with target heavy metals but it is difficult to control the nano-metal oxides/biochar ratio in the composites, iv) Ball milling with various advantages like Low cost, easy to operate, no chemical pollution, effective reduction of particle size of metal oxides. In the downside, during the ball milling preparation particles are easily dispersed in water and move to surface runoff, pollutants can migrate out of the contaminated site, posing potential risks to groundwater [133].



Figure 6: Different pathways for Nano-metal oxide/hydroxide-biochar composites synthesis.

Special attention is given to the ball milling technique, during which samples including biochars are crushed to nanometer size in the presence of metal oxide particles [206]. Ball milling has the capacity to increase the SSA, probably by revealing pores [207], and to increase the oxygen-containing functional groups (e.g., carboxyl, lactone, and hydroxyl) [208]. Zheng et al. developed a new ball-milling process to synthesize MgO/biochar nanocomposites with a dual- functional adsorbent to remove both cationic and anionic pollutants. The developed materials enhanced the adsorption of methylene blue (MB) for about 8.4 times, likely due to increased surface area and pore volume [179].

Table 6: Reported work on Nano-metal oxide-biochar composites synthesis for organic pollutants removal.

Biochar	Synthesis method	Reagent	Operating Conditions	Reference
MnOx-coated rice straw biochar	Co-precipitation	KMnO ₄	The mixed solution was vibrating continuously at 30 °C for 8 h and then oven-dried at 80 °C for 24 h after washing.	[129]
Fe ₂ O ₃ – Paper and pulp sludge biochar	One-step pyrolysis	FeCl ₃	Pyrolysis of FeCl ₃ -impregnated Paper and pulp sludge (1:3, m/v) at 750 C for 2 h in a one-step pyrolysis method.	[132]
Mg-biochar, Al-biochar, Fe-biochar and Ca-biochar	Pyrolysis (impregnation)	MgCl ₂ .6H ₂ O, AlCl ₃ .6H ₂ O, CaCl ₂ .2H ₂ O and FeCl ₃ .6H ₂ O	A dry mixture of biomass and MgCl ₂ (or AlCl ₃ , CaCl ₂ , FeCl ₃) was heated at 10 C/min up to 600 C under N ₂ flow for 1 h.	[147]
Nano-MgO modified fallen leaf biochar	Sol-gel method	MgCl ₂ .6H ₂ O	MgCl ₂ .6H ₂ O mixed with biochar suspension, stirred at 25 °C for 6 h and then centrifuged and dried at 80°C	[169]
AlCl ₃ - agro-waste biochar, FeCl ₃ -agro-waste biochar,	Pre-pyrolysis treatment	AlCl ₃ .6H ₂ O, FeCl ₃ .6H ₂ O, and CaCl ₂	Biochar added to salt solution, stirred (ambient Temperature for 24h),	[13]

CaCl ₂ - agro-waste biochar	followed by pyrolysis		filtered, dried at 80°C and the pyrolyzed at 500 °C.	
Nano-zerovalent manganese/biochar composite (nZVMn/PBC)	Chemical reduction method	MnCl ₂ , NaBH ₄	MnCl ₂ was dissolved in water and ethanol mixture, biochar was added simultaneously, NaBH ₄ was added drip by drop to the mixture, and then sonicated, followed by water remove and drying.	[68]

Finally Sewu and his co-workers reported that using non-magnetic goethite mineral (α -FeOOH) in co-pyrolysis with firwood biomass to produce biochar proved as a green process when compared to the ubiquitous and conventionally used FeCl₃, which has a negative impact due to toxicity [209].

5.4.2. Magnetic biochar composites

Significant research efforts have been carried out to improve the adsorption capacity of biochar. However, due to the small particle sizes and lower density, the separation and reuse of biochar after water pollutants elimination remain one of the main problems to be resolved [210]. Magnetic biochar has been successfully produced by various methods as reported in literature [211], presented in figure 7, showing the impregnation-pyrolysis, chemical co-precipitation, solvothermal and reductive co-precipitation methods. It is shown that these biochar composites provide effective absorptivity, ready separation by

using external magnets and easy recycling [212]. Nevertheless, the traditional loading-
 process of magnetic medium increases the cost of the sorbent [213]. Thines et al reported
 three main common techniques employed to produce magnetic material such as pyrolysis,
 co-precipitation and calcination method [214]. An additional common production method
 was reported in literature such as, conventional heating in an electrical furnace [215],
 microwave heating in a modified furnace [216][154].

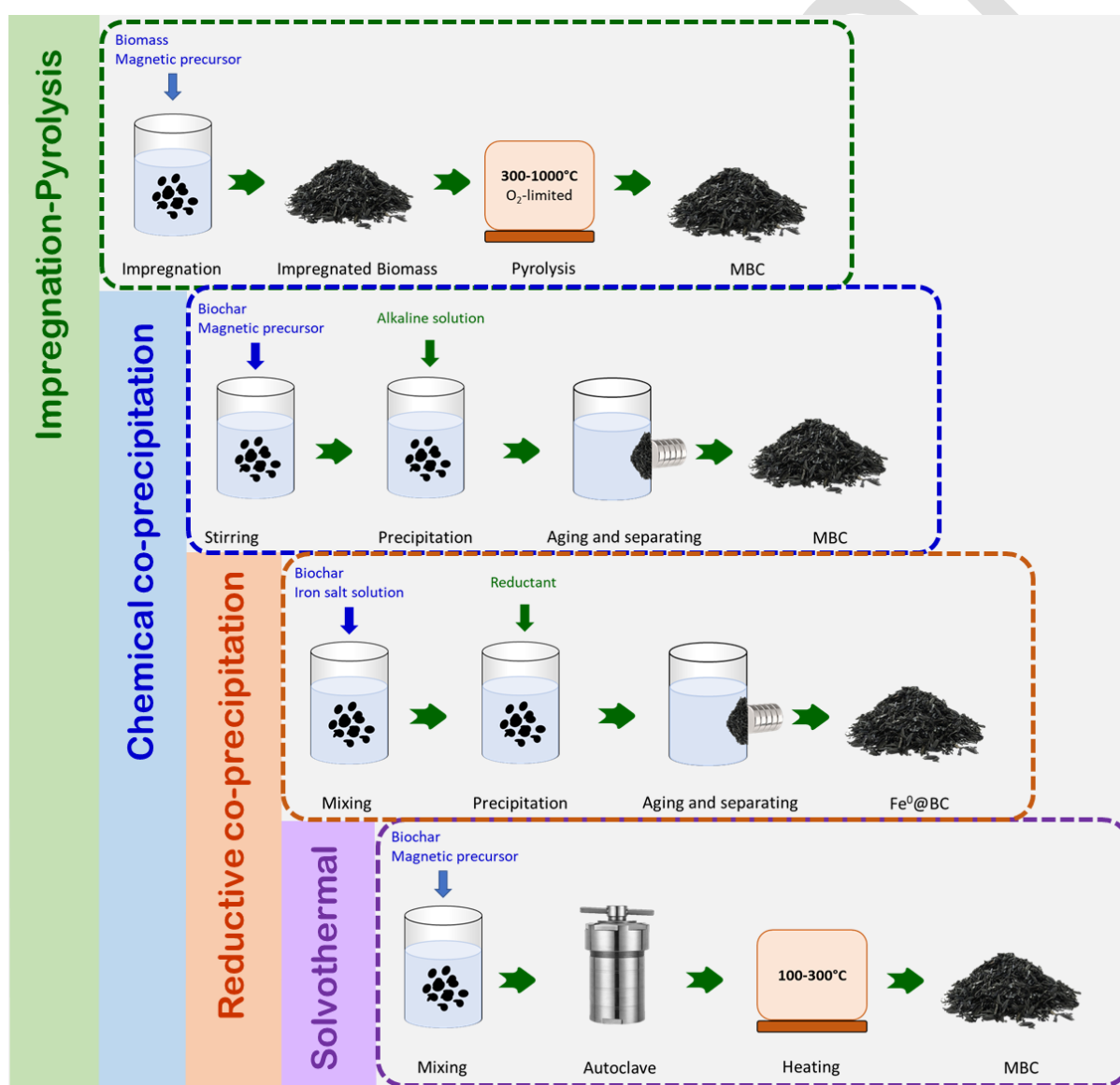


Figure 7: Schematic diagram of common Magnetic biochar preparation methods.

The co-precipitation method was found to be the simplest due to its easy step of mixing and heating. This process focuses on the molar ratio of transition metal's ion being used during the mixing for improving the characteristics of the magnetic biochar produced, in terms of magnetism and porosity [214]. Co-precipitation methods result to coating the surface of biochar with different iron oxides such as, Fe_3O_4 , $\alpha\text{-Fe}_2\text{O}_3$, and CoFe_2O_4 particles, which give magnetic properties for active sites of iron oxide for pollutant elimination [212][217][218].

It has been reported that additives with a high decomposition capacity (e.g., AlCl_3 , FeCl_2 and MgCl_2) exhibits catalytic activity, higher sorption capability, increasing porosity and creating positively charged adsorption sites [161][219][220]. Table 7 summarizes some results on the preparation of magnetic biochars following different synthesis pathways, different metal reagents and different operating conditions.

Table 7: Literature on magnetic biochar composites synthesis for organic pollutants removal.

Magnetic biochar	Synthesis method	Reagent	Operating Condition	reference
Magnetic activated sawdust hydrochar	Slow thermal pyrolysis	$\text{Fe}(\text{NO}_3)_3$	Pyrolysis under N_2 flow for 1h at 700°C with a heating rate 3 K min^{-1} .	[221]

Cottonwood biochar/ γ - Fe_2O_3	Thermal pyrolysis	Ferric chloride hexahydrate, $\text{FeCl}_3, 6\text{H}_2\text{O}$	Biomass were immersed into FeCl_3 solution for 2 h and dried at 80 °C for 2 h followed by pyrolyzing the biomass mixture in a furnace at 600 °C with the flow of N_2 for 1 h.	[222]
Fe_3O_4 -loaded hydrochar magnetic biochar	Thermal pyrolysis	$\text{FeCl}_3, 6\text{H}_2\text{O}$ and ZnCl_2	Pyrolysed under N_2 flow of 1 L/min for 30 min at a temperature range of 500°C to 800°C	[223]
Humic acid coated magnetic biochar	Thermal pyrolysis	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and humic acid	Pyrolysis with a heating rate of 20 °C min^{-1} at 500 °C for 6 h. humic acid and magnetic biochar obtained was stirred at 25 °C with 170 r min^{-1} for 24 h and kept quiescent for 48 h.	[224]
Magnetic greigite/biochar composites	Co- precipitation /solvothermal method	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	Suspension was heated at 180 C for 12 h.	[225]

CuFe ₂ O ₄ -loaded magnetic biochar	Co-precipitation process	CuCl ₂ and FeCl ₃	Process were carried out at pH10 and the suspension were heated to 98–100 °C for 2 h. Molar ratio of 1:2 of Cu ²⁺ : Fe ³⁺ .	[226]
Fe and Mn ions onto pinewood biochar	Co-precipitation process	MnCl ₂ ·4H ₂ O and FeCl ₃ ·6H ₂ O	Under N ₂ flow, reaction of suspension for 4 h at 80 °C. Then resulting biochar dried at 80 °C for 12 hours.	[227]
Ca-Mg/biochar	Co-precipitation process	MgCl ₂ and CaCl ₂	Corn cob was suspended in MgCl ₂ (ratio of 1:3) and CaCl ₂ (ratio of 1:3) and were further heated under N ₂ flow.	[228]
Magnetic modified sugarcane bagasse (MSCB)	Co-precipitation process	FeCl ₃ and FeSO ₄	Mixture dissolved in an ammonia solution and proceed with ultrasound irradiation at 60°C. Molar ratio of Fe ³⁺ : Fe ²⁺ is 1:2	[229]
Fe ₃ O ₄ -loaded bentonite magnetic biochar	Calcination process	FeCl ₃ ·6H ₂ O	Calcined at 190°C for 8 h.	[230]
Fe ₃ O ₄ -loaded microalgae magnetic biochar	Calcination process	FeSO ₄ ·6H ₂ O	Calcined at different temperatures for 6 h.	[231]

5.4.3. Clay mineral modification

Clay-biochar composite is the result of pre-mixing the raw biomass before pyrolysis or the post mixing of produced biochar with clay minerals [232]. The synthesis methods, characteristics of clay minerals-biochar and the surface interactions with contaminants during treatment has been reviewed by Arif et al [205]. This composite is characterized by high porosity and a great compatibility with water pollutants [233]. Premarathna, et al. reported the synthesis of a novel clay-biochar composite from montmorillonite (MMT) and red earth (RE) clay materials with municipal solid waste (MSW) biochar in pyrolysis. The obtained composites exhibit a high adsorption capacity towards removing tetracycline antibiotic in aqueous media [234]. Similar results were reported by Borthakur et al. for tetracycline removal from wastewater [177]. It is noticed that the surface properties of the biochar samples are considerably affected by the incorporation of different clay material. Zhao and Zhou revealed that clay-mineral modification enhanced the micro-pore area of biochar by more than 200% while only a slight growth in the mesopore area was observed [235]. It is also reported that organo-mineral layer of clay increases the biochar stability and its ability to resist the process of decomposition when biochar is applied to soil [236].

From a mechanistic point of view, interactions of BC-clay/mineral composites with inorganic and organic contaminants can be established according to different mechanisms including ion exchange, physical adsorption, precipitation, complexation, electrostatic interaction, H-bonding, partitioning, electron-donor-acceptor (EDA) interaction, hydrophobic interaction and pore-filling [237].

6. Biochar applications for organic pollutants removal from water

6.1. Adsorption

There is a high research interest in the adsorption as a technique for mineral and/or organic contaminated water treatment, reflected by the high number of publications in the area [238][239][240]. Lu et al. reported the simultaneous elimination of metal ions and organic compounds from aqueous solutions by rice bran, bamboo and their derived biochars. These biochars presented a high sorption capacity for acenaphthene removal compared to the original biomass whereas the coexisting Cu^{2+} and Cr^{6+} both inhibited the sorption of acenaphthene by the biochar [136]. Similar results were reported by Cheng et al. for the adsorption of methyl orange in the presence of Cr^{6+} from dye wastewater [71]. The simultaneous removal of toxic $\text{Pb}(\text{II})$ ions, poly(acrylic acid) and Triton X-100 from their mixed solution was achieved by using engineered acid activated biochars obtained from horsetail herb precursor [241]. Shin et al. investigated the competitive adsorption of three pharmaceuticals; naproxen (NPX), diclofenac (DCF), and ibuprofen (IBU) from lake water and wastewater effluent. The results revealed that the competitive adsorption of NPX, DCF, and IBU for the NaOH-activated SCW biochar was more spontaneously endothermic than that for the pristine SCW biochar [193].

6.2. Filtration

The filtration technique was also studied and tested for the removal of different pollutants from wastewater. Wang et al., reported the removal of microplastic spheres by different biochar filters in a column system. In their study, biochar was packed in a 7 cm height bed

between two sand layers of 3 cm height each. The results show that the biochar filters provide significant capacity for the removal and immobilization of 10 μm diameter microplastic spheres (more than 95% removal efficiency) which is much higher than that of similar grain-sized sand filter studied [242]. Biochar can also be used for the pathogens removal (such as *Escherichia coli* and *Enterococci*) of as a common sand filter [243]. Kaetzi et al., studied the elimination of organic pollutant from raw sewage by using Miscanthus-biochar based filter media. Some works reported that the filtration removal is more dominant than adsorption where the result showed $74 \pm 18\%$ of chemical oxygen demand (COD) removal by biochar filters when only $61 \pm 12\%$ of COD reduction was recorded for sand filters [244]. Reddy et al., have used a filtration column with an inner diameter of 7 cm and a length of 61 cm for the elimination of different contaminants from urban storm water runoff. The results proved that biochar-filter reduced the total suspended solids (TSS), nitrate, phosphate and polycyclic aromatic hydrocarbons (PAHs) by an average of 86%, 86%, 47% and 68%, respectively [245].

6.3. Coupled Adsorption and advanced oxidation processes (AOPs)

Recently, the application of biochar (BC)-based composite materials in catalytic oxidation treatment has been proposed for organic contaminants elimination and degradation [245][246]. The introduction of these composites in the AOPs is due to the dual benefits of adsorption and catalytic degradation [247]. Huang et al. revealed that morphological and chemical features of biochar played an important role in hydroxyl radical ($^{\circ}\text{OH}$) generation [248]. Various methods have been tested and validated by researchers to develop biochar supported catalyst for the activation of hydrogen peroxide and persulfate

such as; co-precipitation, impregnation, liquid phase reduction, hydrothermal and pyrolysis [249][250]. Meanwhile, the role of biochar in hydroxyl radical based AOPs can be classified in three categories; biochar as a catalyst, biochar as supporting material and biochar as cathode in electro-Fenton process [251].

Some works reported the synthesis of biochar composite with a double function of adsorption and photocatalytic degradation. Leichtweis et al., reported the preparation of biochar derived from pecan nutshell with ZnO (biochar-ZnO) for the treatment of acid red 97 in aqueous solution. The obtained material degraded 100% of acid red 97 in only 67 min of treatment (30 min with biosorption + 37 min with photocatalysis) [252]. Similar results reported by Xiao et al., on the treatment of enrofloxacin with 50% g-C₃N₄/biochar, report a removal of 45.2% and 81.1% of enrofloxacin (C₀=10 mg/L) under darkness and light with a material dosage of 1 mg/mL, respectively [175]. It is worth mentioning that about 98 % of tetracycline removal was achieved by MnFe-LDO–biochar catalyst within 240 min upon exposure to a UV light [174]. On the other hand, Luo et al., reviewed the formation mechanisms of persistent free radicals in biochar and their interactions with organic and inorganic contaminants. They reported the combination of biochar with different oxidation processes such as; H₂O₂, photocatalysis, peroxydisulfate, persulfates, peroxymonosulfate [9]. It is also reported that the effect of some typical anions such as; SO₄²⁻, H₂PO₄⁻, HCO₃⁻ and Cl⁻ can act as inhibitors by trapping the radicals and therefore compete with the adsorption [253].

The electrical discharge plasma was also coupled with biochar as reported by Lou et al., for the degradation of tetracycline hydrochloride in aqueous medium [254]. The result showed that during discharge plasma process, the specific surface area and the amount

of oxygen-containing functional groups of biochar increased due to the interaction of biochar and reactive species generated by the plasma. The amount of generated $\cdot\text{OH}$ radicals was higher in the combined system due to the decomposition of O_3 and H_2O_2 . Furthermore, this process leads to the elimination of tetracycline hydrochloride ($\text{C}_0=50$ mg/L) at 89.36% in only 5 min [254].

7. Water treatment by biochar at pilot scale

Nowadays, the development of biochar based pilot or industrial plant reactors for contaminated water treatment is of great importance, because of the large amount of wastewater daily generated in the world [255]. There are only very few works reported on the organic/inorganic pollutants removal at pilot scale biochar reactors. Ashoori et al. reported the removal of nitrate, metals, and trace organic contaminants from urban stormwater runoff by pilot-scale biochar-amended woodchip bioreactor, composed of 9 parallel columns of 10 cm in diameter and 50 cm length, where every three columns are filled with the same adsorbent (Woodchips, Woodchips + biochar and Woodchips + straw). The results showed a high capacity of removing nitrate and four of the five metals tested (i.e., Cd, Cu, Ni and Pb but not Zn), however a weak adsorption capacity for organic pollutant was recorded [256]. Finally, scientific advances on the extrapolation of results present a significant challenge requiring more investigations to be conducted within the framework of a reusability over several cycles.

8. Conclusion and future research directions

Biochar has been recommended as a promising adsorbent material for organic contaminants removal from wastewater. Some works estimated the costs incurred in the production of biochar based adsorbents; a cheaper process and a reusability ability with multiple cycles of biochar is possible [85]. Nevertheless, supplementary research in several perspectives is necessary to ensure the efficacy and cost-effectiveness of biochar to scale-up it into a large-scale application, mostly in the following areas:

- 1) Some of the reported biochar sorbents (such as Coir pith, Coconut coir dust, Pandanus leaves and paper waste) showed low efficiency and elimination capacity to organic pollutants. It is expected that surface modifications will help increase their capacity.
- 2) To achieve optimal environmental remediation activity for biochars it is essential to further explore the relationships between certain factors; production process, activation, functionalization, and treatment all in an environmental ecofriendly manner.
- 3) It is important to keep in mind that a promising bio based sorbent successfully applicable at industrial scale should be economically attractive and raw materials should be extensively available in large quantities in nature or as a by-product (bio-residues) [257]. Regenerating and reusing using these sorbents for several cycles at an industrial scale can reduce the cost and energy consumption for production and offer a sustainable product.

915 Combined modified-clay/biochar composites revealed noteworthy advantages over
916 single-modified-clays, due to their high adsorption capacity, low cost and more suitable
917 for removing anionic dyes and phenolic compounds.

918 There are a very few studies on pilot/large-scale application of biochar for organic
919 pollutants removal in literature.

920 The progress of research on magnetic biochar with catalytic degradation activity for
921 organic contaminants elimination from aqueous medium is an important and a new
922 research direction and will become a research focus soon. Studies on the toxic
923 components produced during magnetic biochar synthesis should be carefully considered.

924 The implementation of a sustainable management plan for pollutant-loaded Sewage
925 derived biochars (SDBs) is critical. This strategy should follow the circular economy
926 concept and would permit: i) an eco-friendly and low-cost regeneration and reuse of these
927 SDBs in upcoming adsorption cycles, ii) the recovery of the adsorbed chemicals and it
928 reprocess in an industry as resources, and iii) the preservation of the environment counter
929 to further pollution.

930 Two strategies concepts should be explored to achieve functional and cost-effective
931 modified biochars for the efficient elimination of organic compounds from wastewater: i)
932 The first one is optimizing the biochar physicochemical activation process using a variety
933 of eco-friendly reagents, ii) The second option concerns the exploitation of the high
934 specific surface areas of prepared biochar to impregnate nano-composites. The
935 application of an experience plan software to optimize the influencing parameter is a
936 powerful and innovative tool in the experiment design and analysis phase. Machine

learning (ML) is a subdivision of artificial intelligence (AI) that aims to reduce explicit computers programming by learning from experience and prediction [258]. Predictive models that use machine learning can reduce the workload, cost, space requirement and time consumption for remediation of effluents [259]. For example ML can be applied to develop prediction models for optimizing the pyrolysis process and predict biochar yield and C-char according to biomass characteristics and pyrolysis conditions [260]. As stated in [261], science-informed design of biochar substrates with high removal capacity for organic contaminants can prove a valuable tool for designing sustainable wastewater treatment systems. The developed models based on data from advanced microscopic and spectroscopic techniques (biochar surface functionality and porous structure) gave accurate predictions on the adsorption capacity of the considered materials.

The conception of more compact reactors that can accommodate biochar supported catalysts are necessary for real scale applications. Future research must be devoted to implement biochar-based catalysts in pilot scale reactors that can be used also at industrial level.

Optimizing biochar properties and activation techniques and parameters is important for obtaining maximum efficiency for organic pollutant elimination, less post-treatment by-products and less energy consumption.

Well-coordinated actions currently going on, guided by the European biochar certificate (EBC) in Europe, and the IBI at international level, to regulate and standardize quality requirements and develop guidelines or good practices concerning the biomass supply, biochar production and biochar applications which mainly are limited to agriculture and organic farming. One needs to keep in mind that the first concern of the EBC has been to

safeguard health and safety while producing and using biochar in a sustainable way. Biochar based substrates for environmental applications are a promising alternative to currently applied substrates for wastewater treatment and organic pollutant elimination, but there is yet no set of criteria on the physicochemical properties of the substrates that guarantee satisfactory adsorption efficiencies. Such well-coordinated actions are currently still in the form of literature reviews that try to draw conclusions and offer a suggestions and guidelines for researchers that need to build upon the existing but very dispersed knowledge on the potential applications of biochar and biochar composites in environmental applications.

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