2	Activated biochar as an effective sorbent for
3	organic and inorganic contaminants in water
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#### 22 Abstract

23 Adsorption is acknowledged as effective for the removal of pollutants from drinking water 24 and wastewater. Biochar, as a widely available material, holds promises for pollutant 25 adsorption. So far, biochar has been found to be effective for multiple purposes, including 26 carbon sequestration, nutrient storage, and water-holding capacity. However, its limited 27 porosity restricts its use in water treatment. Activation of biochars, when performed at a high 28 temperature (i.e., 900°C) and in presence of certain chemicals (H<sub>3</sub>PO<sub>4</sub>, KOH) and/or gases 29 (CO<sub>2</sub>, steam), improves the development of porosity through the selective gasification of carbon 30 atoms. Physicochemical activation process is appropriate for the production of highly porous 31 materials. As well, the morphological and chemical structure of feedstock together with pyro-32 gasification operating conditions for the biochar production can greatly impact the porosity of 33 the final materials. The effectiveness of activated biochar as adsorbent depends on porosity and 34 on some functional groups connected to its structure, both of these are developed during activation. This study provides a comprehensive synthesis of the effect of several activated 35 36 biochars when applied to the treatment of organic and inorganic contaminants in water. Results 37 show that high aromaticity and porosity are essential for the sorption of organic contaminants, 38 while the presence of oxygen-containing functional groups and optimum pH are crucial for the 39 sorption of inorganic contaminants, especially metals. Finally, although activated biochar is a 40 promising option for the treatment of contaminants in water, further research is required to evaluate its performance with real effluents containing contaminants of emerging concern. 41

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Keywords: Biomass waste, biochar, activation, adsorption, water treatment, organic and
 inorganic contaminants

#### 1. Introduction

48 Due to extensive anthropogenic activities, including industrial operations (such as mining), 49 agricultural processes, and disposal of industrial wastewater materials, the concentration of 50 contaminants in water is progressively increasing. A large number of anthropogenic and natural 51 substances are present in water, including pharmaceuticals (prescriptions, over-the-counter drugs, 52 and veterinary drugs), personal care products (fragrances, cosmetics, and sunscreens), steroid 53 hormones, radioactive elements, metals (e.g., Pb, Hg, As), industrial chemicals (hydrocarbons and 54 solvents), and pesticides. Most of these compounds have been recently defined as contaminants of 55 emerging concern (CEC) because they are subject to critical action by regulatory agencies. CEC 56 refer to naturally occurring, manufactured or manmade chemicals or materials that have been 57 recently discovered, or persist in the environment for some time, posing toxicity concerns for living 58 organisms (Sauvé and Desrosiers 2014). Potential leaching of organic and inorganic CEC from 59 poorly managed residual waste sites (e.g., landfills, septic tanks) is also a concern. The main 60 challenge is that, due to their very low concentrations, most wastewater treatment plants are not 61 specifically designed to eliminate such contaminants, although they can have a chronic or long-62 term harmful impact on the environment. Given their persistence and continuous input, the CEC 63 pass through treatment processes without being affected. Consequently, they end up in the aquatic 64 environment and become dangerous to wildlife and probably are of concern with regard to drinking 65 water (Sauvé and Desrosiers 2014; Petrie et al. 2015; Fairbairn et al. 2016).

66 Several regulatory bodies (e.g., United States Environmental Protection Agency, Health 67 Canada, World Health Organization, etc.) monitor the levels of contaminants in wastewater 68 treatment plants, drinking water, and effluent industries. Therefore, the discharge criteria should be 69 below a level at which there is no known or expected risk to health. For example, according to

70	Health Canada, metals such as copper and iron can be present in drinking water at maximum
71	concentrations of 1.0 mg/L and 0.3 mg/L, respectively (Health Canada 2017). To maintain such low
72	levels of contaminants, several methods are employed, such as chemical precipitation (Li et al.
73	1999), ion exchange (Chiavola et al. 2012; Li et al. 2015), reverse osmosis (Greenlee et al. 2009;
74	Vaneeckhaute et al. 2012), electrochemical treatment (Martínez-Huitle and Ferro 2006; Moriwaki
75	et al. 2017), membrane processes (ultra-, micro- and nano-filtration) (Katsou et al. 2012; Sözen et
76	al. 2016), coagulation-floculation (Verma et al. 2012), flottation (Rubio et al. 2002), ozonation
77	(Wang et al. 2017), etc. Likewise, the combination of methods such as electro-Fenton process and
78	chemical precipitation (Ghosh et al. 2011), membrane bio-reactor with reverse osmosis (Dialynas
79	and Diamadopoulos 2009) or flotation with membrane filtration showed very high efficiency for
80	metals removal (Sudilovskiy et al. 2008). All these methods have advantages but they also have
81	disadvantages, including the chemicals and energy required, the increase in residual salinity of
82	treated water, the generation of toxic sludge, high cost, and incomplete contaminants removal
83	(Gaspard and Ncibi 2013).

84 One effective and widely used method for removing toxic contaminants from aqueous solutions 85 is adsorption process. It is the most versatile process to remove contaminants due to its simplicity 86 of design and ease of operation; it also provides high removal capacity (Babel and Kurniawan 2003; 87 Anastopoulos and Kyzas 2015; Hasan and Jhung 2015). The growing demand for adsorbent 88 materials for environmentally protective processes (mining and metallurgy) calls for more research 89 on the production of activated carbons from inexpensive materials (González-García 2018). The 90 thermochemical conversion of biomass feedstock (e.g., crop residues, manure, wood, wastewater 91 sludge) offers an efficient means to produce gaseous (biogas), liquid (bio-oil) and solid fuels (Fig. 92 1) compared to fossil-fuel-derived-materials. In various places, biomass waste thermochemical

93 conversion is an economically feasible alternative to deal with millions of tons of waste generated 94 by manufacturing activities in different industrial sectors (Dufour 2016; Pandey et al. 2015). The 95 solid fuels produced are also called biochar, defined by the International Biochar Initiative (IBI) as 96 a solid material obtained from the thermochemical conversion of biomass in a zero- or low-oxygen 97 environment (IBI 2012). Indeed, there is growing interest in research communities, biorefineries 98 and related industries in converting biochar into activated biochar due to: i) its low-cost availability; 99 ii) potential economic feasibility in large-scale production; iii) the increased profitability of existing 100 thermochemical conversion processes for the production of diversified products (biochar, bio-oil, 101 or syngas, and activated biochar); and iv) its effectiveness in several applications such as the 102 treatment (sorption) of drinking water and wastewater, energy storage, as electrodes in batteries 103 and supercapacitors, and as catalyst support (Fig. 1) (Tan et al. 2017).

104 Activation is considered the most common method for tailoring the pore structure of biochar. 105 Different pores sizes are created or developed by this approach: ultramicropores (< 0.7 nm), 106 micropores (between 0 and 2 nm), and mesopores (between 2 and 50 nm). An appropriate pore size 107 distribution is crucial in order to adsorb molecules of different sizes. There are three types of 108 activation: 1) physical (in presence of gases: CO<sub>2</sub> or vapor water), 2) chemical (biochars 109 impregnated with solutions of acids, salts, or bases) and 3) physicochemical (biochars impregnated 110 with solutions of acids, salts, or bases in presence of gases: CO<sub>2</sub> or vapor water) at high 111 temperatures (in an inert atmosphere), for the generation of a selective gasification of carbon atoms 112 and consequently, the development of porosity (Marsh and Rodríguez-Reinoso 2006). In physical 113 activation, the mechanism involved is as follows: the physical agents, CO<sub>2</sub> or steam, remove the 114 carbon atoms from the structure of the biochar according to Boudouard reaction Eq. 1 and Eq. 2, 115 respectively (Calo and Perkins 1987). On the contrary, in chemical activation, different reactions

116	occur simultaneously, depending on the chemical used. In general,	chemicals such as acids (e.g.,
117	H <sub>3</sub> PO <sub>4</sub> ) can act as a dehydration agent, whereas bases (e.g., KO	H) can act as oxidant agents
118	(Ozoemena and Chen 2016). Acids (e.g., H <sub>3</sub> PO <sub>4</sub> ) can also act as ca	talysts, favoring activation, in
119	the thermal treatment of biochar, whereas alkalis (e.g., KOH) can dec	compose in the form of metallic
120	compounds (i.e., K, boiling-point elevation: 759°C) (Eqs. 3-6). In ad	dition, the metallic compounds
121	can be intercalated in the carbon lattice by thermal treatment, while g	ases ( $CO_2$ and $CO$ ) could form
122	and act as physical agents to the latter activation (Eqs. 4-6), thus f	avoring porosity development
123	(Guo et al. 2002; Lozano-Castelló et al. 2007; Armandi et al. 2010).	
124	$C + CO_2 \rightarrow 2CO, \Delta H = 159 \text{ kJ/mol}$	(1)
125	$C + H_2O \rightarrow CO + H_2, \Delta H = 117 \text{ kJ/mol}$	(2)
126	$6\text{KOH} + 2\text{C} \rightarrow 2\text{K} + 3\text{H}_2 \uparrow + 2\text{K}_2\text{CO}_3$	(3)
127	$K_2CO_3 \rightarrow K_2O + CO_2 \uparrow$	(4)
128	$K_2CO_3 + 2C \rightarrow 2K \uparrow + 3CO \uparrow$	(5)
129	$K_2O + C \rightarrow 2K \uparrow + CO \uparrow$	(6)

130 The limited surface area and porosity of biochars restrain their potential to be applied in adsorptive processes. Removal of atrazine (the active substance in a pesticide) by KOH-activated 131 biochar made from corn straw yielded a maximum sorption capacity 47 times higher compared to 132 biochar due to its the higher surface area and higher aromaticity (Tan et al. 2016). Broiler litter 133 biochar and activated broiler litter biochar were applied by Lima et al. (2010) as adsorbents for the 134 removal of metals (Cu<sup>2+</sup>, Cd<sup>2+</sup>, Ni<sup>2+</sup>) separately dispersed in water. In all cases, activated biochar 135 performed better in the removal of metals, compared to biochars: 80% against 75% (Cu<sup>2+</sup>), 85% 136 against 22% (Cd<sup>2+</sup>), and 96% against 10% (Ni<sup>2+</sup>). Thus, porosity plays a major role in the 137 138 performance of carbonaceous adsorbents. Indeed, activated biochars have higher surface area and 139 porosity compared to biochars as well as fewer functional groups connected to their carbonaceous 140 structure. Thus, the main mechanism involved in contaminant removal is related to physical 141 sorption (pores diffusion). However, depending on the chemical structures, characteristics of 142 activated biochar, and the type of contaminants, additional mechanisms for adsorbent-contaminant 143 interactions may also be involved during contaminant removal. In the case of inorganic 144 contaminants, several interactions (physical sorption, ion exchange, metals electrostatic attraction, 145 and metal precipitation) may be involved. Oppositely, in the case of organic pollutants, the main 146 mechanisms involved are partitioning or adsorption and electrostatic interactions (Ahmad et al. 147 2014; Liu et al. 2015; Tan et al. 2017).

In the following sections, the contaminants removed by activated biochars are discussed separately (inorganics versus organics). A comprehensive list of such contaminants, together with the type of wastewater used (e.g., synthetic vs. real effluent), the biochar feedstock, the activation method used, as well as the corresponding surface area of the activated biochar, is compiled in Table 1. This table also includes the adsorption capacity for contaminants by activated biochar (mg/g), their experimental conditions, and a summary of the relevant results for each study.

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## 2. Activated biochar for water treatment

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### 2.1. Organic contaminants

Among the organic contaminants listed in Table 1 are methylene blue, phenol, and dyestuff, which have been extensively studied as contaminants removed through adsorption by the use of activated carbons (Dąbrowski et al. 2005; Demirbas 2009; Rafatullah et al. 2010). Other organic contaminants compiled in Table 1 are relatively new structures that have been recently studied, since they are part of the emerging contaminants concern such as herbicides (Uchimiya et al. 2010) and pharmaceutical compounds (Jung et al. 2013; Mondal et al. 2016b). In liquid-phase systems, the adsorption capacity of activated carbons for aromatic compounds depends on a number of
factors: i) the nature of the adsorbent (e.g., its porous structure, ash content, and functional groups);
ii) the nature of adsorbate (e.g., its pK<sub>a</sub>, polarity, functional groups, and molecular size); and finally,
iii) the solution conditions (e.g., pH, concentration, ion strength) (Haghseresht et al. 2002).

166 The greatest concern in water treatment is mixes of contaminants. Probable competition can 167 drastically reduce the adsorption capacity of adsorbents, even though contaminants are easily 168 removed from uni-component solutions. Jung et al. (2015a) studied the removal of single and 169 multiple contaminants present in solution such as diclofenac (DCF), naproxen (NPX), and 170 ibuprofen (IBP) through NaOH-activated biochar made from loblolly pine chips. The presence of 171 several contaminants in the same environment caused lower contaminant adsorption due to a 172 combination of a series of mechanisms: lower binding energy, polarity, and  $\pi$ -energy (i.e., energy 173 of molecular orbital of  $\pi$  electrons present in conjugated hydrocarbon systems), and electrostatic 174 repulsion from the contaminants occupying adsorption sites.

175 Furthermore, additional studies are needed for the treatment of real effluents that usually 176 contain several classes of contaminants. The majority of scientific works cited in Table 1 examined 177 single solutions prepared in the laboratory and studied mostly in batch sorption experiments. 178 Ranitidine hydrochloride (RH), however, was adsorbed from fixed-bed columns (Mondal et al. 179 2016a). In this testing, the adsorbate is in continuous contact with the adsorbent, a method that has 180 been widely used in industry for the removal of organic compounds by carbon adsorption 181 (Unuabonah et al. 2010; Karunarathne and Amarasinghe 2013). This contaminant is a medicine 182 normally used for gastric and intestinal problems, which is excreted through urine and feces and 183 therefore reaches a sewage system and ends up in rivers because wastewater plants cannot 184 completely remove it. Researchers also evaluated the influence of parameters such as bed depths, 185 initial concentration of contaminant, and volumetric flow rates on the performance of the adsorbent. 186 The main findings of sorption experiments with flow (column reactor type) were as follows: i) At 187 the highest bed-adsorbent height (3 cm), adsorption capacity was increased. A high amount of 188 adsorbent offered more binding sites, thus increasing the adsorption and other interactions with RH 189 molecules (Gupta et al. 1998; Al-Degs et al. 2009); ii) At the highest flow rate (6 mL/min), 190 adsorption capacity decreased due to adsorbate residence time insufficient to diffuse into the pores 191 or interact with the functional groups present in the adsorbent (Charumathi and Das 2012; Sadaf 192 and Bhatti 2014); iii) At the highest initial concentration, the sorption of the column was enhanced 193 due to the increased driving force for the mass transfer and RH loading rate (Han et al. 2007; Sancho 194 et al. 2012).

195 In addition, the type of activation (physical, chemical or physicochemical), diversity of 196 feedstock and pyro-gasification operating conditions applied for the preparation of biochars have 197 great effect on the porosity of activated biochars (Table 1). Steam-activated broiler litter biochar 198 synthesized after pyrolysis at 350°C and 700°C showed that for both materials the same surface 199 area of 335  $m^2/g$  was attained. The chemical composition of broiler litter (high ash content) is 200 completely different from lignocellulosic precursors (low ash content). However, higher adsorption 201 capacity of deisopropylatrazine (a herbicide) was reached by applying high pyrolysis temperature 202 and subsequent activation (Uchimiya et al. 2010). Activated biochar has higher aromaticity, which 203 is an important parameter related to enhanced removal of organic pollutants due to its higher 204 hydrophobicity and  $\pi$ - $\pi$  interactions (Boving and Zhang 2004; Moreno-Castilla 2004; Park et al. 205 2013). The same findings were observed for phenanthrene removal: faster initial sorption rate and 206 higher equilibrium concentration for phenanthrene adsorption were reported when using activated biochar prepared at low pyrolysis temperature (300°C;  $S_{BET} = 1250 \text{ m}^2/\text{g}$ ), whereas stronger binding 207

208 with the sorbate was noted with the material pyrolyzed at 700°C ( $S_{BET} = 57 \text{ m}^2/\text{g}$ ). The considerable 209 decrease in surface area of the activated biochar pyrolyzed at 700°C was due to the presence of 210 condensed aromatic structures, which were more stable and had fewer oxygen-containing groups 211 at the surface. Consequently, its carbon framework was resistant to thermal degradation (even when 212 impregnated with harsh chemicals, e.g., NaOH) inhibiting the development of a porous structure. 213 Although the activated biochar pyrolyzed at 700°C presented higher aromaticity, the material 214 having the highest surface area (pyrolyzed at 300°C) exhibited higher initial sorption efficiency 215 (156 mg/g) compared to a commercial activated carbon NORIT (130 mg/g) (Park et al. 2013).

216 In summary, surface area and aromaticity of activated biochars are the most important factors 217 for enhancing the sorption capacity of organic pollutants in water. Physicochemical and chemical 218 activation were found to be highly effective in producing these properties in activated biochars and, 219 consequently, increased their efficiency in the removal of organic compounds. Materials pore size distribution [e.g., highly microporous ( $\emptyset < 2.0 \text{ nm}$ ) or even ultramicroporous ( $\emptyset < 0.7 \text{ nm}$ )] play an 220 221 important role on the sorption of differently sized organic molecules. For example, iodine was 222 successfully adsorbed by activated biochars having smaller pores, compared to methylene blue, 223 which due to its high-size molecule, was found by most studies to need to be adsorbed by materials 224 with larger micropores and mesopores (Oh and Park 2002).

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#### 2.1. Inorganic contaminants

Most of the compounds included in the inorganic contaminant group are present in mining effluents; they include both cations and anions  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cu^{2+}$ ,  $Ni^{2+}$ ,  $Cd^{2+}$ ,  $Zn^{2+}$ , As(III), and  $NH_4^+$ , as well as Na<sup>+</sup> and PO<sub>4</sub><sup>3-</sup>. In fact, globally, the mining industry is responsible for the generation of the largest amount of waste material. The main problem is the exposure of chemically reactive minerals to air and water, leading to contaminated mine drainage, either acid (AMD) or neutral (CND) which generates pollution in surface water and groundwater (Westholm et al. 2014; Rakotonimaro et al. 2017; Calugaru et al. 2018). In inorganic contaminants removal, in addition to the porosity of the adsorbent materials, the presence of functional groups, such as carboxyl (– COOH), phenol (–OH), and amino groups (–NH<sub>2</sub>) on the surface of the adsorbents may help in the removal of metals. In addition, the majority of studies listed in Table 1 reported that there is an optimal pH at which activated biochars most effectively adsorbed inorganic contaminants in water media.

The removal of  $Cu^{2+}$  was reported through the use of biochar and steam-activated biochar from 238 239 the Miscanthus plant (Shim et al. 2015). Surface sorption occurs beginning at pH 5, but the pH level must be maintained below 7.5, since surface precipitation through Cu(OH)<sub>2</sub> formation takes 240 241 place at higher pH levels. The surface area of the activated biochar doubled compared to biochar  $(322 \text{ m}^2/\text{g vs } 181 \text{ m}^2/\text{g})$ , while its polarity index [(O+N)/C] decreased. Cu<sup>2+</sup> adsorption was better 242 fitted to the Freundlich and Langmuir models by using biochar and activated biochar, respectively, 243 but they presented almost the same adsorption capacity for  $Cu^{2+}$  in water (14 vs 15 mg/g). The 244 greater efficiency of biochar for  $Cu^{2+}$  could be because of the formation of metal complexes or 245 chelates due to the presence of more oxygenated functional groups connected to it compared to 246 activated biochar. Cu<sup>2+</sup> may have been adsorbed through different mechanisms in both materials: 247 intra-particle diffusion and  $\pi$ -cation interactions in activated biochar, and surface complexation 248 249 with the metal in biochar.

The presence of several metals in the same environment may make the sorption of metal contaminants quite complex once each metal is removed at different pH ranges. The adsorption of three pollutants normally found in mining water, i.e.,  $Fe^{2+}$ ,  $Cu^{2+}$ , and As(V) within the pH range of 2–7, was reported by Banerjee et al. (2016). At lower pH (equal to 3),  $Fe^{2+}$  was highly adsorbed by 254 the activated biochar, whereas at higher pH, its adsorption decreased due to the formation of ferrous species such as  $[Fe(H_2O)_6]^{2+}$  and  $[Fe(OH)(H_2O)_5]^+$ , as well as the precipitation of  $Fe(OH)_3$ , 255 resulting in less adsorption of Fe<sup>2+</sup> (Panday et al. 1985; Mohan and Pittman Jr. 2006; Hove et al. 256 2007: Banerjee et al. 2016). In relation to the contaminants As(V) and Cu<sup>2+</sup>, the maximum removals 257 of 80% and 75%, respectively, were reached at pH 5 and 6, whereas low contaminants removal was 258 found at low pH. In other cases, it was reported that Cu<sup>2+</sup> was the most adsorbed metal ion in single 259 solutions but the adsorption capacity of the activated biochar was reduced when other metals ( $Cd^{2+}$ , 260  $Ni^{2+}$ ,  $Zn^{2+}$ ) were found in the same environment (Lima et al. 2010). A probable metals competition 261 may have lowered the sorption of  $Cu^{2+}$ . 262

263 The type of pyro-gasification process and operating conditions were also found to have an 264 influence on the porosity of activated biochars and, consequently, on the removal of inorganic contaminants. The proper choice of pyrolysis temperature (500 vs. 700°C) may influence the 265 porosity of biochars (50 vs.  $300 \text{ m}^2/\text{g}$ ), and may have been responsible for the presence of 266 carboxylic and phenolic groups at the surface of the material, improving the cation-exchange and 267 complexation properties of the adsorbents for the removal of Fe<sup>3+</sup> and Cu<sup>2+</sup>, in addition to physical 268 sorption (Bouchelta et al. 2012). These findings were also confirmed by MgCl<sub>2</sub>.6H<sub>2</sub>O-activated 269 biochars prepared after first-step pyrolysis at 600°C, producing higher  $PO_4^{3-}$  (102 mg/g) removal 270 271 compared to a material made at 400°C (17 mg/g) (Takaya et al. 2016). Different biochars made from slow and fast pyrolysis of the same feedstock also presented great differences in relation to 272 273 physicochemical properties and consequently, in metal ion uptake (Lima et al. 2010).

The type of activation was also found to play a role in the development of porosity of activated biochars for the sorption of inorganic contaminants. For example, the removal of  $NH_4^+$  from water through activated biochar prepared at different types of activation using steam, CO<sub>2</sub>, KOH, and 277 NH<sub>3</sub> was reported by Rambabu et al. (2015). By using NH<sub>4</sub><sup>+</sup> solution at 260 ppm, the sorption 278 capacity was found to be 55, 18, 149, and 57 mg/g, respectively. Chemical activation was shown 279 to be an effective approach for the development of porosity for the sorption of NH<sub>4</sub><sup>+</sup>. However, the 280 presence of minerals (high ash content), the presence of oxygenated and nitrogenated functional 281 groups connected to the surface of activated biochar, and the chemical surface of modified materials 282 [e.g., Na<sub>2</sub>S-modified biochar (Tan et al. 2016), ZnCl<sub>2</sub>-activated biochar (Xia et al. 2016)] were also 283 found to be determinant for better heavy metals adsorption. In activated biochars, the overall metal 284 interaction mechanisms with these surface functionalities are electrostatic interactions, ion 285 exchange, surface complexation, and metal precipitation in addition to physical sorption.

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#### 3. Conclusions and future research needs

The present study reviewed the pertinent literature dedicated to the application of activated biochars prepared from various feedstock and different pyro-gasification and activation operating conditions, for the sorption of organic and inorganic contaminants in water media. The main findings are outlined below:

i. The developed porosity (surface area and pore volume) and higher aromaticity were important properties of activated biochars for the enhanced sorption of organic contaminants in water due to higher hydrophobicity and  $\pi$ - $\pi$  interactions. For inorganic contaminants, activated biochar surface chemistry (e.g., the presence of oxygenated functional groups, minerals) is an important property for enhancement of the interactions with inorganics in water by various mechanisms: electrostatic interactions, ion exchange, and surface complexation.

298 ii. The pH of the solution may also affect the sorption of organics and inorganics onto activated
 299 biochar. Specifically, metals at precisely pH range can lead to precipitation mostly in a form

300 of hydroxides, which may solubilize afterwards depending on the pH conditions. Therefore,
301 an optimization study on the effect of the pH on the adsorption process is recommended.

- 302 iii. The pyro-gasification conditions, reactor design, as well as the quality of feedstock used for
   303 the preparation of biochars have considerable influence on the textural properties (porosity)
   304 of activated biochars as well on the environmental remediation applications. Optimization
   305 of operating conditions and physicochemical characterization of biochars are recommended
   306 for designing biochars for specific applications.
- iv. The majority of studies on the application of activated biochars for the removal of organic
  or inorganic contaminants in water were based on synthetic solutions in batch tests.
  Therefore further studies should investigate column tests with real effluents characterized
  by a mixture of contaminants of emerging concern (CEC), and various heavy metals from
  mining industries, pharmaceuticals and pesticides, since they pose an increasing concern to
  the environment, wildlife and drinking water systems.
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623	Captions of the tables:
624	Table 1 Activated biochars applied to organic and inorganic (metals) contaminants removal from
625	water
626	Captions of the figures:
627	Fig. 1 Thermochemical modification of biomass waste feedstock to produce biochar and activated
628	biochar, along with their most relevant applications
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# Table 1 Activated biochars applied to organic and inorganic (metals) contaminants removal from water

Contaminant	Biochar feedstock	Activated biochar / S <sub>BET</sub> (m <sup>2</sup> /g)	Adsorption capacity activated biochar (mg/g)	Experimental conditions	Relevant results	Reference
Organic contaminants						
Methylene blue (MB) Iodine	Olive waste	Steam (-)	MB: 403 I: 1131	Synthetic effluent, T= 20°C	Adsorption of iodine and MB was enhanced by the use of highly porous activated biochars. Several parameters were involved in the development of porosity of activated olive waste biochar: lower pyrolysis temperature (e.g., 400°C), higher activation temperature (e.g., 900°C), and longer activation residence time (e.g., 2 h). The increase in activation temperature causes an opening and enlargement of the pores. However, iodine molecules were better adsorbed compared to MB due to its smaller size (well fitted in micropores)	(Baçaoui et al. 1998)
MB Phenol (Ph) Iodine (I) Pb <sup>2+</sup>	Corncobs	Steam (607)	MB:- I: 325 Ph: 164 Pb <sup>2+</sup> : 155	Synthetic effluent, pH $\leq$ 5.5 (Pb <sup>2+</sup> )	Steam-activated biochar developed microporosity when temperature is increased. Consequently, it exhibited good adsorption affinities in solutions having iodine, phenol, and MB. The removal of Pb <sup>2+</sup> ions was highly dependent on pH solution. At pH $\geq$ 6.5, surface precipitation occurred. Higher adsorption of Pb <sup>2+</sup> ions occurred at solution pH $\leq$ 5.5	(El-Hendawy et al. 2001)
MB Iodine	Rice straw	КОН (2410)	I: 1720 MB: 820	Synthetic effluent 0.02 N (I) and 1.2 g/L (MB)	Iodine adsorption increased with activation temperature between 600 and 800°C due to the development of micropores (< 1 nm), whereas MB adsorption increased between 800 and 900°C due to the development of larger micropores (up to 2 nm). These porous materials made at different conditions were favorable to the sorption of both contaminants: MB (molecule diameter of 1.5 nm) and iodine (molecule diameter of 0.5 nm, three times smaller than MB)	(Oh and Park 2002)
Phenol	Palm seed coat	CO <sub>2</sub> (577)	Batch: 18 Column: Synthetic effluent: 72; real effluent: 55	Batch and column testing, synthetic (10–60 mg/L) and real effluent (122 mg/L), equilibrium time 3 h, pH = 6.2, $T = 27^{\circ}C$	The removal of phenol was greater at pH range 4–9. The adsorption of phenol on activated palm-seed-coat-biochar follows the Freundlich model based on the formation of a monolayer or film diffusion process. Adsorption of phenol in synthetic solution (72 mg/L) was higher in column tests compared to real phenol wastewater (55 mg/L). This may be due to the presence of other impurities or contaminants in wastewater that may have interfered in the phenol adsorption process	(Rengaraj et al. 2002)

Acid yellow 36	Sawdust (SD) and rice rusk (RH)	Steam SD: 516 RH: 272	SD: 184 RH: 87	Synthetic effluent 1000 mg/L, equilibrium time 1 h (SD) and 3h (RH), pH = 3, T = 30°C	Adsorption was highly dependent on contact time, adsorbent dose, and pH. The optimal pH for favorable adsorption of acid yellow 36 was 3 or below when high electrostatic attraction exists between the positively charged of the adsorbent and anionic dye. Two possible mechanisms for adsorption of dye into activated biochar are: 1) electrostatic interaction between the protonated group of carbon and acidic dye; and 2) chemical interaction between the adsorbert	(Malik 2003)
Acid blue 74 Basic brown 1 MB p-nitrophenol 4-chlorophenol p-cresol phenol	Fir wood	KOH/CO <sub>2</sub> (2821)	359 1476 653 543 417 333 275	Synthetic effluent, T = 30°C	Physicochemical activation was a suitable technique for the production of highly porous materials. The presence of functional groups on the carbon surface (e.g., carbonyl, carboxylic, hydroxyl) indicates that there are many types of adsorbate– adsorbent interactions. Increasing CO <sub>2</sub> gasification time decreased micropore volume, but did not increase the adsorption capacity for phenol, for example. Contrary to other studies, these authors reported that the presence of higher amount of mesopores did not result in the material adsorbing a greater quantity of larger organic molecules. The low phenol adsorption might be due to the alteration of functional groups on the surface of the carbon through CO <sub>2</sub> gasification	(Wu and Tseng 2006)
Phenol	Rattan sawdust	KOH/CO <sub>2</sub> (-)	149	Synthetic effluent 25–200 mg/L, equilibrium time 4 h, pH < 8, T = 30°C	The maximum adsorption capacity of activated biochar was 149 mg/g. An important role on the sorption of phenol from aqueous solution was played by pH. Adsorption decreased at high pH values due to ionization of phenol molecules (pKa $\approx$ 9.89), whereas at acidic pH, the percentage of phenol removal was higher since its molecule did not dissociate and the dispersion interaction dominated	(Hameed and Rahman 2008)
MB Iodine (I)	Tobacco stems	K <sub>2</sub> CO <sub>3</sub> (2557)	I: 1834 MB: 518	Synthetic effluent	Chemical activation was suitable for the production of activated biochar having a porous structure of 60% micropores and 40% meso- and macropores. The iodine number and MB adsorption increased to 1834 and 517 mg/g, respectively, with an increase of the K <sub>2</sub> CO <sub>3</sub> /biochar ratio from 0.5 to 1.5, and then the adsorption decreased to 1350 and 290 mg/g, respectively, at a ratio of 3. The decomposition of K <sub>2</sub> CO <sub>3</sub> to K <sub>2</sub> O and CO <sub>2</sub> molecules, which are then reduced by carbons to K and CO <sub>2</sub> , causes the development of pores but only until a certain point; after that point, they widened and burned off	(Li et al. 2008)
Herbicide atrazine: deisopropylatrazine Cu <sup>2+</sup>	Broiler litter	Steam (335)	-	Synthetic effluent 0–200 mg/L (atrazine) and 0–800 mg/L ( $Cu^{2+}$ ), single and multiple contaminants, equilibrium time after 72 h, pH = 5.5	The pyrolysis temperature (700°C) and steam activation were responsible for increasing the aromaticity and surface area of activated broiler litter biochars. Deisopropylatrazine sorption was positively correlated with these parameters. In binary experiments, the presence of $Cu^{2+}$ significantly diminished the	(Uchimiya et al. 2010)

					sorption of deisopropylatrazine, even though its sorption capacity was greater in single contaminant experiments	
MB	Oil seed hulls: soybean, cottonseed, sunflower, peanut; bean coats of lupine	Steam (600)	18	Synthetic effluent 50–400 mg/L	The removal of MB was influenced by the acidic surface of activated biochar as well as its proportion of mesoporosity. Steam-activated biochar had high surface area with a high percentage of micropores that inhibited dye diffusion. In addition, its surface basicity (above $pH_{PZC} = 4$ ) resulted in low MB uptake (18 mg/g)	(Girgis et al. 2011)
Dyestuff	Safflower seed press cake	KOH (1277)	18	Synthetic effluent 20–100 mg/L, pH = 2, T = 25°C	Highly porous materials having surface area of $1277m^2/g$ consisting of 75% of micropores had a strong effect on dyestuff removal. Maximum dyestuff removal was obtained at pH 2. At low pH, the negative charge on the surface of activated biochar was reduced due to the excess of protons in solution. Therefore, a positive charge surface of activated biochar favored the adsorption of dyestuff due to electrostatic attraction. The dyestuff removal efficiency was varied from 46 to 96% in presence of adsorbent amount from 0.05 to 0.6 g in 50 mL of dye solution.	(Angin et al. 2013)
Bisphenol A (BPA) Atrazine (ATR) $17 \alpha$ -ethinylestradiol (EE2) Pharmaceutical active compounds (PhACs) Sulfamethoxazole (SMX) Carbamazepine (CBM) Diclofenac (DCF) Ibuprofen (IBP)	Loblolly pine chips containing bark	NaOH (1360)	-	Synthetic effluent 10 $\mu$ M, single and multiple contaminants, pH < pK <sub>a</sub> , T = 20°C	The adsorbeint another from 0.05 to 0.05 g m 50 million dye solution The adsorbeint kinetics of these pharmaceutical compounds was very complex, especially when all species were found in the same environment and due to the desorption of some compounds having weak adsorption bonding energy. At pH values below their pKa, the adsorption of contaminants significantly increased; whereas at pH above pKa values, the adsorption was reduced significantly. The pseudo-second-order model implied that the mechanism involved in their removal was due to the chemical adsorption involving electronic forces through sharing or exchanging of electrons between the adsorbent and ionized species. The aromatic rings in all contaminants and adsorbents formed a $\pi$ -system and enabled $\pi$ - $\pi$ interactions, which were positively correlated to the adsorption capacity for hydrophobic compounds	(Jung et al. 2013)
Phenanthrene (PAH)	Debarked loblolly pine chips	NaOH (1250)	156	Synthetic effluent 0.05–6.5 mg/L, equilibrium time 30 min, T = 25°C	Activated biochar prepared at low-temperature pyrolysis (300°C) presented a faster initial sorption rate and higher equilibrium concentration for phenanthrene removal. The sorption kinetics of the activated biochar seemed to be correlated with high surface area and pore volume. The presence of mesopores or larger pores were suitable for the sorption of larger contaminants. The activated biochar exhibited a good initial sorption (156 mg/g)	(Park et al. 2013)

					after 30 min compared to 130 mg/g for the commercially available activated carbon (S <sub>BET</sub> not shown)	
Iodine	Oak	CO <sub>2</sub> (1126)	830	Synthetic effluent 0.1 N	Iodine adsorption indicated that the highest activation temperature had a great effect on the development of microporosity in activated biochars. The material synthesized at 900°C for 1 h had very high iodine number (830 mg/g) compared to commercial coal-based activated carbon (724 mg/g; $S_{BET}$ : $1021m^2/g$ )	(Jung and Kim 2014)
Diclofenac (DCF) Naproxen (NPX) Ibuprofen (IBP)	Loblolly pine chips containing bark	NaOH (1360)	372 290 311	Synthetic effluent, single and multiple contaminants, pH = 7	The interaction energy between the surface of the activated biochar and the adsorbate was measured by <sup>13</sup> C nuclear magnetic resonance (NMR) analysis. DCF showed the highest adsorption capacity, interacting much better with the activated biochar compared to NPX and IBP. This strong interaction resulted in the occupation of effective adsorption sites as compared to the small-sized solutes (NPX and IBP) that blocked the pores. The coexistent tri-solute had a complex configuration. The presence of adsorption competitors lowered the adsorption capacity of the solutes due to low binding energy, low polarity, low $\pi$ -energy, and electrostatic repulsion from cosolutes that occupied sites (in the case of deprotonated IBP that had very low adsorption capacity and negatively charged adsorbent surfaces)	(Jung et al. 2015a)
Humic acid (HA) Tannic acid (TA)	Loblolly pine chips containing bark	NaOH (1360)	9 19	Synthetic effluent 10 mg/L, single and multiple contaminants, pH = 7	Higher TA adsorption capacity onto activated biochar was observed due to its superior chemisorption tendencies and size- exclusion effects (its smaller molecular size provided access to inner pores present in the adsorbent). On the other hand, HA adsorption had much lower capacity due to hydrophobic interactions between the adsorbent and adsorbate	(Jung et al. 2015b)
Sulfamethazine (SMT)	Burcucumber plants	Steam (7)	38	Synthetic effluent 2.5–50 mg/L, pH = 3, T = 25°C	Steam-activated burcucumber biochar produced at 700°C showed the highest adsorption capacity (38mg/g) at pH 3. Chemiosorption was the major mechanism involved in SMT removal by activated biochar due to its very high ash content and very low surface area (7 m <sup>2</sup> /g). The mechanisms involved were electrostatic interactions, but various other mechanisms may also have participated, including hydrophobicity, hydrogen bonding, and $\pi$ - $\pi$ interactions simultaneously	(Rajapaksha et al. 2015)

Methylene blue (MB)	Pork chop bones	H <sub>3</sub> PO <sub>4</sub> (136) H <sub>2</sub> SO <sub>4</sub> (140)	61 54	Synthetic effluent 50 mg/L, equilibrium time 1 h, pH = 5.8, $T = 20^{\circ}C$	Higher impregnation rates enhanced microporosity when using H <sub>2</sub> SO <sub>4</sub> , whereas a dramatic reduction of porosity was reported when using H <sub>3</sub> PO <sub>4</sub> . The maximum uptake of MB was achieved at impregnation ratios of 0.2 mmol/g and 1 mmol/g using H <sub>3</sub> PO <sub>4</sub> and H <sub>2</sub> SO <sub>4</sub> , respectively, which could be related to surface area in the 1.7-5.0nm pore range (large micropores and small mesonores)	(Iriarte-Velasco et al. 2016)
Ranitidine hydrochloride (RH)	Mung bean husk	Steam (405)	12	Column testing, synthetic effluent 100–200 mg/L, pH = 2, T = 28°C	The shape of the breakthrough curves on the adsorption of RH in column is strongly dependent on operation parameters. The highest adsorptive capacity of the sorbent was around 12 mg/g using bed height of 3 cm, flow rate of 2 mL/min, and RH concentration of 200 mg/L. It was reported that a variation in the initial concentration or flow rate changed the slope of the breakthrough curve of RH uptake	(Mondal et al. 2016a)
Ibuprofen (IBP)	Mung bean husk	Steam (405)	60	Synthetic effluent 1–100 mg/L, equilibrium time 2 h, pH = 2, $T = 20^{\circ}C$	The optimized conditions for ~ 99% IBP removal were as follows: adsorbent dose $0.1g/L$ , agitation speed 200 rpm, pH 2, initial IBP concentration 20 mg/L, equilibrium time 2 h, and temperature 20°C. Studies on thermodynamic parameters show that the removal of IBP was exothermic, spontaneous, and feasible. At lower temperature, adsorption was more likely to occur. The growth of <i>Scenedesmus abundans</i> was observed to be affected by IBP solution, whereas the activated biochar treated with IBP solution did not significantly affect its growth	(Mondal et al. 2016b)
Atrazine Hg <sup>2+</sup>	Corn straw (Zea mays L.)	KOH (466)	92 5	Synthetic effluent 0.5–30 mg/L (atrazine) and 0–500 $\mu$ g/L (Hg <sup>2+</sup> ), single and multiple contaminants, pH = 3 (atrazine) and pH = 4–6 (Hg <sup>2+</sup> ), T = 25°C	Na <sub>2</sub> S-modified biochar showed the highest $Hg^{2+}$ removal compared to KOH-activated biochar due to the formation of HgS precipitate. The presence of oxygen-containing functional groups on the char surface also had a positive effect on contaminant removal. For the atrazine removal, the KOH-activated biochar yield the maximum sorption capacity, 47 times higher than that of biochar. The main reasons could be the higher surface area, higher aromaticity, and porous structure with the presence of mesopores that favor the hydrophobicity effect and specific interactions. When both contaminants coexisted, the uptake removal for both materials was reduced, indicating the competition sorption between organic and inorganic adsorbates (probably both negatively charged). The surface functional groups (phenolic hydroxyl and carboxylic groups) played an important role in metals removal, with the formation of surface complexes between them. The main mechanisms involved in Hg <sup>2+</sup> removal were electrostatic interactions, cation ion exchange, and Hg <sup>2+</sup> precipitation. The polyaromatic surfaces of the sorbents influenced the $\pi$ - $\pi$ electron donor-receptor force,	(Tan et al. 2016)

					occurring mostly for materials that have more aromatic structures and higher surface areas	
Herbicide: 2,4- Dichlorophynoxy acetic acid (2,4-D)	Tea waste, burcucumber, oak wood, and bamboo	Steam (576)	59	Synthetic effluent 10-500  mg/L, pH = 7, T = 23 °C	The highest pyrolysis temperature (700 vs. 400°C) seems to have an effect on increasing surface area of activated biochar, probably due to the opening of pore spaces with the removal of organic matter. The reason that steam-activated tea waste biochar adsorbed 2,4-D more efficiently compared to the biochar is the increased pore volume and pore diameter (micropores), higher surface area and aromatic carbon structure	(Mandal et al. 2017)
Tetracycline (TC)	Debarked loblolly pine	NaOH (960)	275	Synthetic effluent 10-100  mg/L, pH = 6, $\text{T} = 20^{\circ}\text{C}$	NaOH-activated pine biochar showed higher TC adsorption capacity compared to biochar and various other activated biochars due to its developed porous structure having high surface area and mesopore volume (0.13 cm <sup>3</sup> /g). Elovich kinetics and Freundlich isotherm models well fitted the data, indicating that hydrogen bonding and $\pi$ - $\pi$ interaction on the heterogeneous surface might be the possible mechanisms while intra-particle diffusion would be the major limitating factor for TC adsorption on the activated biochar	(Jang et al. 2018)
Acetyl-para- aminophenol (acetaminophen or APAP) MB	Municipal solid waste	KOH (662)	APAP: 31 MB: 33	Synthetic effluent 50 mg/L, pH = 4 (APAP) and pH = 6.5 (MB), T = 30°C	The adsorption capacity of APAP highly decreased (about 89%) when pH increased from 2 to 12, whereas the variation of pH had little effect on MB adsorption. MB uptake was controlled by chemiosorption, whereas APAP adsorption was simultaneously controlled by physical (i.e., electrostatic interactions) and chemical interactions [i.e., chemical surface reactions with the oxygen-containing functional groups (-OH and -COOH)]	(Sumalinog et al. 2018)
Inorganic/Metal contan	ninants					
$\begin{array}{c} Cu^{2+} \\ Cd^{2+} \\ Ni^{2+} \\ Zn^{2+} \end{array}$	Broiler litter, alfalfa stems, switchgrass, corn cob, corn stover, guayule bagasse, guayule shrub, soybean straw	Steam (up to 793)	Removal of up to: 96% 85% 96% 40%	Synthetic effluent 1 mmol/L, single and multiple contaminants	Activated biochars showed improved uptake of metal ions compared to biochars. The improvement was associated with increased surface area (highly porous materials) and improved access of functional groups connected to the surface of activated biochars. Adsorption capacities were reduced once metal ions were in competition, compared to single metal solutions. Cu <sup>2+</sup> was found to be the preferable metal ion to be adsorbed in single or multiple solutions. The pH was also found to play an important role in metals adsorption; precipitation of metals occurred at pH values higher than 6, in addition to adsorption	(Lima et al. 2010)
$Cu^{2+}$ Fe <sup>3+</sup>	Date pits	Steam (1467)	203 307	Synthetic effluent, equilibrium time 10 min, $T = 18^{\circ}C$	Pyrolysis temperature (700°C) and activation hold time (4 h) were optimal parameter conditions applied for the production of	(Bouchelta et al. 2012)

<b>a</b> 24	W. c. l. C	CO ///OU//2/7)	10		activated biochars reaching S <sub>BET</sub> of 1467 m <sup>2</sup> /g. High adsorption capacity of both metals was attributed to the presence of both carboxylic and phenolic groups on activated biochars, improving cation-exchange and complexation properties of such materials as well as greater surface area	
Cu	waste peels of mangosteen fruits	CO <sub>2</sub> /KOH (367)	19	Synthetic effluent 50-100  mg/L,  pH = 5.5, $T = 30^{\circ}\text{C}$	Cu <sup>2+</sup> cations in synthetic solution were adsorbed mainly by chemical interactions with the surface active sites of activated biochar. The adsorption uptake at equilibrium was found to increase with increasing initial $Cu^{2+}$ concentration solutions. The higher the initial concentration, the larger was the driving force for mass transfer. The agitation time influenced the formation of an external film, which created a boundary layer over the surface of the adsorbent. Finally, the increase of the temperature (from 30 to 70°C) increased the velocity of adsorbate species toward the internal structure of the adsorbent	(Hamid et al. 2014)
Cu <sup>2+</sup>	Broiler litter and broiler cake	Steam (up to 425)	104 49	Synthetic effluent 0.02 M, equilibrium time 24 h, pH = 4.8	Manure precursor presents high ash content which plays a role in the development of specific surface functionalities and consequently in the adsorption of Cu <sup>2+</sup> ions. Adsorption is enhanced with the increase of the steam flow rate injected during activation (3 mL/min). Cu <sup>2+</sup> uptake also increased with the presence of certain elements connected to the activated biochar: phosphorus, sulfur, calcium, and sodium	(Lima et al. 2014)
NH <sup>4+</sup>	Canola meal	Steam (320) CO <sub>2</sub> (403) KOH (1230) NH <sub>3</sub> (19)	55 18 149 57	Synthetic effluent 260 mg/L, equilibrium time 30–240 min, pH = 9, T = 20°C	In terms of ammonium ion adsorption in relation to the type of activation at optimum $pH = 9$ , $KOH > NH_3 > steam > CO_2$ . Ammonium adsorption depended not only on pH and initial concentration but also on surface area and surface functional groups due to surface-related reactions such as adsorption, absorption, complexation, precipitation, and ion exchange	(Rambabu et al. 2015)
Na <sup>+</sup>	Rice husk	KOH (K) (2201) Steam (S) (317) K/S (1169)	134 74 102	Synthetic effluent 0.2 M	Na <sup>+</sup> sorption increased with increasing surface area and pore volume. The K/S material was the most effective adsorbent for Na <sup>+</sup> sorption, having the highest percentage of micropores (effective pores to adsorb this cation). Researchers also reported intra-particle diffusion involved in the sorption process	(Rostamian et al. 2015)
Cu <sup>2+</sup>	<i>Miscanthus</i> plant	Steam (322)	14	Synthetic effluent 0.2–150 mg/L, equilibrium time 120 h, pH = 6	Biochar made via slow pyrolysis presented a lower surface area compared to the activated biochar (181 vs. $322 \text{ m}^2/\text{g}$ , respectively). However, $\text{Cu}^{2+}$ sorption capacities were not significantly different. Fast sorption due to surface complexation dominated for biochar, whereas slow sorption due to intra- particle diffusion dominated for activated biochar. Both of them decreased the toxicity of $\text{Cu}^{2+}$ but the activated material showed clear toxicity to <i>Daphnia magna</i> , possibly due to increased aromaticity upon steam activation	(Shim et al. 2015)

Fe <sup>2+</sup>	Colocasia	Steam (102)	6.2	Synthetic effluent,	Activated biochar was capable of removing 97% of Fe <sup>2+</sup> , 95% of	(Banerjee et al.
Cu <sup>2+</sup>	esculenta roots		2.3	$Fe^{2+}$ : 50 mg/L, equilibrium time	$Cu^{2+}$ , and 84% of As(V) from aqueous solutions. The mechanism	2016)
As(V)			2.2	30  mm, pH  3, $Cu^{2+}: 30 \text{ mg/L}$ equilibrium	involved followed monolayer adsorption with maximum uptake of 6.2, 2.3, and 2.2 mg/g at initial concentrations of 50, 30, and	
				time 180 min, pH 5.	50  mg/L for Fe <sup>2+</sup> , Cu <sup>2+</sup> , and As(V), respectively. At pH 5 and 6.	
				As(V): 50 mg/L, equilibrium	maximum removal of Cu <sup>2+</sup> and As(V) was observed, whereas a	
				time 1440 min, pH 6	decrease in $Fe^{2+}$ adsorption was seen with an increase of pH from	
				$\Gamma = 25^{\circ}C$	3 to 7. Thus, activated biochar was capable of adsorbing various metals at different pHs	
Pb <sup>2+</sup>	Hickory chips	NaOH (873)	Batch:	Batch $(2-250 \text{ mg/L})$	NaOH-activated biochar had increased surface area, high	(Ding et al.
$Cd^{2+}$	2 1		Multiple:	and column (100 mg/L) testing,	oxygen-containing surface functional groups, and high cation-	2016)
$Cu^{2+}$			19	single and multiple	exchange capacity. Activated biochar also presented 2.6–5.8	
Zn <sup>2+</sup> Ni <sup>2+</sup>			1.0	contaminants, equilibrium time	times greater adsorption capacity for all neavy metal ions compared to biochar in single or multiple solutions. $Pb^{2+}$ and	
111			1.8	140 min, pH = 5, $I = 20^{\circ}C$	$Cu^{2+}$ were preferable metals from the competitive batch	
			0.9		adsorption of mixed metal ions	
			Single: $Cu^{2+}$ 54			
PO4 <sup>3-</sup>	Holm oak and	KOH (67.8)	26	Synthetic effluent	The surface adsorption of biochars with or without pretreatment	(Takaya et al.
	greenhouse	FeCl <sub>3</sub> .6H <sub>2</sub> O (-)	102	21-400  mg/L, pH = 7	was sufficient for improving PO43- removal. An additional	2016)
	paprika waste	$MgCl_2.6H_2O(-)$	25		thermal treatment on Fe-impregnated biochars was not necessary, but low pH seems to influence Fe-loaded adsorbent for $POv^{-3}$	
					removal. Phosphate uptake capacities were enhanced from 2.1–	
					3.6% to 66.4–70.3% by impregnation with magnesium. These	
					findings show that the presence of minerals on activated biochar	
As(III)	Biogas residue	$ZnCl_{2}(163)$	28	Synthetic effluent 40 mg/L.	ZnCl2-activated biochar presented excellent adsorption efficiency	(Xia et al. 2016)
	from pig	211012 (100)	-0	equilibrium time 1.5 h, $pH = 7$ ,	for the removal of As(III) from solution. Adsorption was found to	(110 00 00 2010)
	manure			$T = 25^{\circ}C$	occur through ligand exchange $(Zn^{2+})$ which was loaded on	
					hydroxyl groups present on the surface of the adsorbent (Zn- OH)) as well as through porous adsorption. Based on ETIR and	
					XPS results, once in contact with As(III), the surface of the	
					adsorbent becomes Zn-O-As(III). In this way, equilibrium was	
					reached much faster and adsorption capacity increased	
$Cd^{2+}$	Debarked	NaOH (1151)	167	Synthetic effluent 2 mg/L.	The maximum $Cd^{2+}$ adsorption capacity was obtained at pH 7.5.	(Park et al.
	loblolly pine	()		equilibrium time 6 h, $pH = 7.5$ ,	The main mechanisms involved during Cd <sup>2+</sup> adsorption were	2017)
	chips			$T = 25^{\circ}C$	inner-sphere surface complexation and cation exchange. The ion	
					strength was associated with particle aggregation and the affinity of the surface complexes with $Cd^{2+}$ The pseudo-second-order	
					kinetic model fits the data well, whereas the sorption was	
					controlled by a diffusion-limited mechanism	

Cd <sup>2+</sup> Cu <sup>2+</sup>	Pine sawdust	H3PO4 (900)	5 2	Synthetic effluent 1–10 mg/L, equilibrium time 6 h, pH = 4.5	The surface area of activated biochars increased with the increasing of pyrolysis temperature (from 200 to 650°C) during biochar production. Activated biochar had higher affinity for the sorption of heavy metals due to the increased surface area and oxygen-containing functional groups compared to biochars. Carboxyl and hydroxyl functional groups, and phosphorus-containing groups (P=O and P=OOH) formed complexes with metal ions, enhancing metals adsorption. Thus, sorption of metals by H <sub>3</sub> PO <sub>4</sub> -activated biochar was controlled by the mechanism of surface complexation	(Peng et al. 2017)
As(V) F	Perennial grass	KOH (1248)	Removal (%): 72 25	Synthetic effluent 100 mg/L (As(V)) and 25 mg/L (F <sup>-</sup> ), equilibrium time 60 min, pH = 7, T = 26°C	The optimal conditions for the maximum As(V) removal was: initial concentration, 100 mg/L; adsorbent dosage, 0.2 g/50 mL; and contact time of 60 min. In contrast, for F <sup>-</sup> removal, the conditions were 25 mg/L, 0.2 g/50 mL and 60 min, respectively. Among these variables, adsorbent dosage was found to be the most influential parameter for the removal of both contaminants. Pseudo-first-order best fitted the data, indicating that adsorption was probably a chemiosorption process	(Saikia et al. 2017)