

# Activated Biochar as an Effective Sorbent for Organic and Inorganic Contaminants in Water

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**Abstract** Adsorption is acknowledged as effective for the removal of pollutants from drinking water and wastewater. Biochar, as a widely available material, holds promises for pollutant adsorption. So far, biochar has been found to be effective for multiple purposes, including carbon sequestration, nutrient storage, and water-holding capacity. However,

its limited porosity restricts its use in water treatment. Activation of biochars, when performed at a high temperature (i.e., 900 °C) and in the presence of certain chemicals (H<sub>3</sub>PO<sub>4</sub>, KOH) and/or gases (CO<sub>2</sub>, steam), improves the development of porosity through the selective gasification of carbon atoms. Physicochemical activation process is appropriate for the production of highly porous materials. As well, the morphological and chemical structure of feedstock together with pyro-gasification operating conditions for the biochar production can greatly impact the porosity of the final materials. The effectiveness of activated biochar as adsorbent depends on porosity and 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 biochars when applied to the treatment of organic and inorganic contaminants in water. Results show that high aromaticity and porosity are essential for the sorption of organic contaminants, while the presence of oxygen-containing functional groups and optimum pH are crucial for the sorption of inorganic contaminants, especially metals. Finally, although activated biochar is a 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.

## Highlights

- Activated biochars are highly efficient for the removal of various contaminants in water
- The variation of feedstock and operating conditions of pyro-gasification can affect the porosity of activated biochars
- Physicochemical and chemical activation are appropriate techniques for production of activated biochars
- High aromaticity and surface area are important characteristics for the removal of organic contaminants
- The presence of surface functionalities in activated biochars is required for interactions between sorbent and inorganic contaminants

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## 1 Introduction

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

Several regulatory bodies (e.g., United States Environmental Protection Agency, Health Canada, World Health Organization, etc.) monitor the levels of contaminants in wastewater treatment plants, drinking water, and effluent industries. Therefore, the discharge criteria should be below a level at which there is no known or expected risk to health. For example, according to Health Canada, metals such as copper and iron can be present in drinking water at maximum concentrations of 1.0 and 0.3 mg/L, respectively (Health Canada 2017). To maintain such low levels of contaminants, several methods are employed, such as chemical precipitation (Li et al. 1999), ion exchange (Chiavola et al. 2012; Li et al. 2015), reverse osmosis (Greenlee et al. 2009; Vaneeckhaute et al. 2012), electrochemical treatment

(Martínez-Huitle and Ferro 2006; Moriwaki et al. 2017), membrane processes (ultra-, micro-, and nanofiltration) (Katsou et al. 2012; Sözen et al. 2016), coagulation-flocculation (Verma et al. 2012), flotation (Rubio et al. 2002), ozonation (Wang et al. 2017), etc. Likewise, the combination of methods such as electro-Fenton process and chemical precipitation (Ghosh et al. 2011), membrane bio-reactor with reverse osmosis (Dialynas and Diamadopoulos 2009), or flotation with membrane filtration showed very high efficiency for metals removal (Sudilovskiy et al. 2008). All these methods have advantages but they also have disadvantages, including the chemicals and energy required, the increase in residual salinity of treated water, the generation of toxic sludge, high cost, and incomplete contaminants removal (Gaspard and Ncibi 2013).

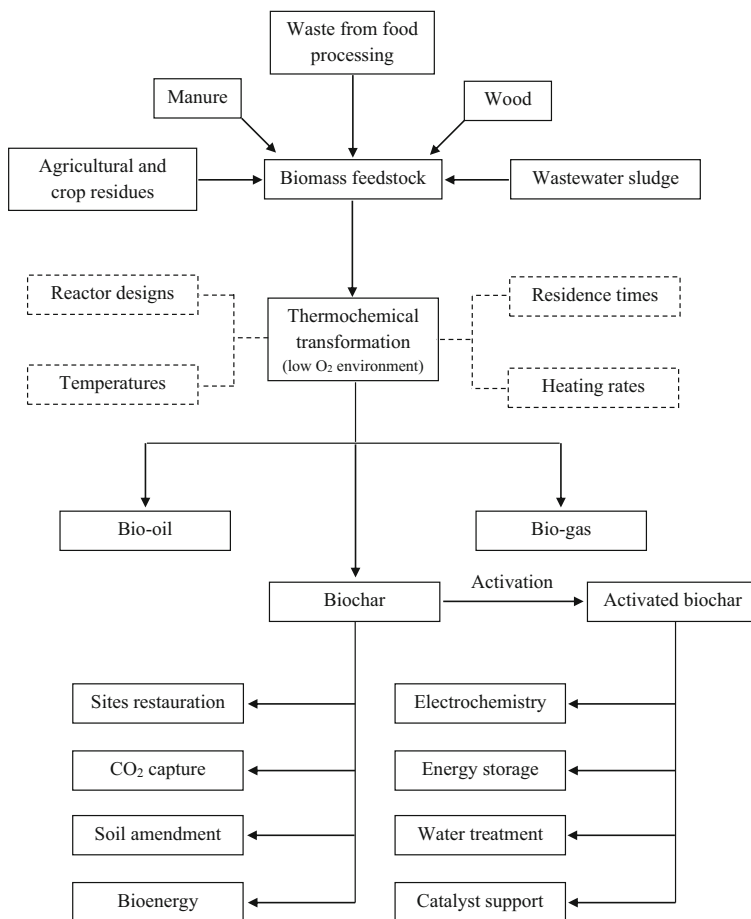
One effective and widely used method for removing toxic contaminants from aqueous solutions is adsorption process. It is the most versatile process to remove contaminants due to its simplicity of design and ease of operation; it also provides high removal capacity (Babel and Kurniawan 2003; Anastopoulos and Kyzas 2015; Hasan and Jung 2015). The growing demand for adsorbent materials for environmentally protective processes (mining and metallurgy) calls for more research on the production of activated carbons from inexpensive materials (González-García 2018). The thermochemical conversion of biomass feedstock (e.g., crop residues, manure, wood, wastewater sludge) offers an efficient means to produce gaseous (biogas), liquid (bio-oil), and solid fuels (Fig. 1) compared to fossil fuel-derived materials. In various places, biomass waste thermochemical conversion is an economically feasible alternative to deal with millions of tons of waste generated by manufacturing activities in different industrial sectors (Dufour 2016; Pandey et al. 2015). The solid fuels produced are also called biochar, defined by the International Biochar Initiative (IBI) as a solid material obtained from the thermochemical conversion of biomass in a zero- or low-oxygen environment (IBI 2012). Indeed, there is growing interest in research communities, biorefineries, and related industries in converting biochar into activated biochar due to (i) its low-cost availability, (ii) potential economic feasibility in large-scale production, (iii) the increased profitability of existing thermochemical conversion processes for the production of diversified products (biochar, bio-oil, or syngas, and activated biochar), and (iv) its effectiveness in several applications such as the treatment (sorption) of

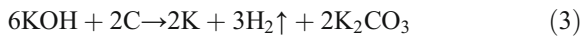
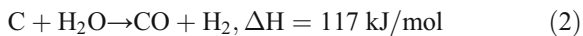
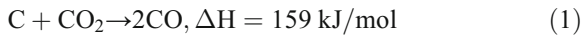
drinking water and wastewater, energy storage, as electrodes in batteries and supercapacitors, and as catalyst support (Fig. 1) (Tan et al. 2017).

Activation is considered the most common method for tailoring the pore structure of biochar. Different pores sizes are created or developed by this approach: ultramicropores (<0.7 nm), micropores (between 0 and 2 nm), and mesopores (between 2 and 50 nm). An appropriate pore size distribution is crucial in order to adsorb molecules of different sizes. There are three types of activation: (1) physical (in the presence of gases: CO<sub>2</sub> or vapor water), (2) chemical (biochars impregnated with solutions of acids, salts, or bases), and (3) physicochemical (biochars impregnated with solutions of acids, salts, or bases in the presence of gases: CO<sub>2</sub> or vapor water) at high temperatures (in an inert atmosphere), for the generation of a selective gasification of carbon atoms and consequently, the development of porosity (Marsh and Rodríguez-Reinoso 2006). In physical activation, the

mechanism involved is as follows: the physical agents, CO<sub>2</sub> or steam, remove the carbon atoms from the structure of the biochar according to Boudouard reaction Eq. 1 and Eq. 2, respectively (Calo and Perkins 1987). On the contrary, in chemical activation, different reactions occur simultaneously, depending on the chemical used. In general, chemicals such as acids (e.g., H<sub>3</sub>PO<sub>4</sub>) can act as a dehydration agent, whereas bases (e.g., KOH) can act as oxidant agents (Ozoemena and Chen 2016). Acids (e.g., H<sub>3</sub>PO<sub>4</sub>) can also act as catalysts, favoring activation, in the thermal treatment of biochar, whereas alkalis (e.g., KOH) can decompose in the form of metallic compounds (i.e., K, boiling-point elevation: 759 °C) (Eqs. 3 6). In addition, the metallic compounds can be intercalated in the carbon lattice by thermal treatment, while gases (CO<sub>2</sub> and CO) could form and act as physical agents to the latter activation (Eqs. 4 6), thus favoring porosity development (Guo et al. 2002; Lozano-Castelló et al. 2007; Armandi et al. 2010).

**Fig. 1** Thermochemical modification of biomass waste feedstock to produce biochar and activated biochar, along with their most relevant applications





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 biochar made from corn straw yielded a maximum sorption capacity 47 times higher compared to biochar due to its higher surface area and higher aromaticity (Tan et al. 2016). Broiler litter biochar and activated broiler litter biochar were applied by Lima et al. (2010) as adsorbents for the removal of metals ( $\text{Cu}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ) separately dispersed in water. In all cases, activated biochar performed better in the removal of metals, compared to biochars: 80% against 75% ( $\text{Cu}^{2+}$ ), 85% against 22% ( $\text{Cd}^{2+}$ ), and 96% against 10% ( $\text{Ni}^{2+}$ ). Thus, porosity plays a major role in the performance of carbonaceous adsorbents. Indeed, activated biochars have higher surface area and porosity compared to biochars as well as fewer functional groups connected to their carbonaceous structure. Thus, the main mechanism involved in contaminant removal is related to physical sorption (pores diffusion). However, depending on the chemical structures, characteristics of activated biochar, and the type of contaminants, additional mechanisms for adsorbent-contaminant interactions may also be involved during contaminant removal. In the case of inorganic contaminants, several interactions (physical sorption, ion exchange, metals electrostatic attraction, and metal precipitation) may be involved. Oppositely, in the case of organic pollutants, the main mechanisms involved are partitioning or adsorption and electrostatic interactions (Ahmad et al. 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.

## 2 Activated Biochar for Water Treatment

### 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  $\text{pK}_a$ , polarity, functional groups, and molecular size), and finally (iii) the solution conditions (e.g., pH, concentration, ion strength) (Haghseresht et al. 2002).

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

Furthermore, additional studies are needed for the treatment of real effluents that usually contain several classes of contaminants. The majority of scientific

**Table 1** Activated biochars applied to organic and inorganic (metals) contaminants removal from water

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ capacity ( $m^2/g$ )	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, $T = 20\text{ }^\circ\text{C}$	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 $^\circ\text{C}$ ), higher activation temperature (e.g., 900 $^\circ\text{C}$ ), 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) $Pb^{2+}$	Comcobs	Steam (607)	MB:- I: 325 Ph: 164 $Pb^{2+}$ : 155	Synthetic effluent, $pH \leq 5.5$ ( $Pb^{2+}$ )	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 $Pb^{2+}$ ions was highly dependent on pH solution. At $pH \geq 6.5$ , surface precipitation occurred. Higher adsorption of $Pb^{2+}$ ions occurred at solution $pH \leq 5.5$	(El-Hendawy et al. 2001)
MB Iodine	Rice straw	KOH (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 $^\circ\text{C}$ due to the development of micropores (< 1 nm), whereas MB adsorption increased between 800 and 900 $^\circ\text{C}$ 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	$CO_2$ (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, $pH = 6.2$ , $T = 27\text{ }^\circ\text{C}$	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	(Rengaraj et al. 2002)

Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ ( $m^2/g$ )	Adsorption capacity activated biochar ( $mg/g$ )	Experimental conditions	Relevant results	Reference
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 3 h (RH), pH = 3, $T = 30\text{ }^\circ\text{C}$	wastewater that may have interfered in the phenol adsorption process 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 adsorbate and the adsorbent	(Malik 2003)
Acid blue 74 Basic brown 1 MB p-nitrophenol 4-chlorophenol p-cresol phenol	Fir wood	KOH/ $CO_2$ (2821)	359 1476 653 543 417 333 275	Synthetic effluent, $T = 30\text{ }^\circ\text{C}$	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 $CO_2$ 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 $CO_2$ gasification	(Wu and Tseng 2006)
Phenol	Rattan sawdust	KOH/ $CO_2$ (-)	149	Synthetic effluent 25–200 mg/L, equilibrium time 4 h, pH < 8, $T = 30\text{ }^\circ\text{C}$	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 ( $pK_a \approx 9.89$ ), 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	$K_2CO_3$ (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	(Li et al. 2008)

Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ ( $m^2/g$ )	Adsorption capacity activated biochar ( $mg/g$ )	Experimental conditions	Relevant results	Reference
Herbicide atrazine; deisopropylatrazine $Cu^{2+}$	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	macropores. The iodine number and MB adsorption increased to 1834 and 517 mg/g, respectively, with an increase of the $K_2CO_3$ /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 $K_2CO_3$ to $K_2O$ and $CO_2$ molecules, which are then reduced by carbons to K and $CO_2$ , causes the development of pores but only until a certain point; after that point, they widened and burned off 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 sorption of deisopropylatrazine, even though its sorption capacity was greater in single contaminant experiments	(Uchimiya et al. 2010)
MB	Oil seed hulls: soybean, cottonseed, sunflower, peanut; bean coats of lupine and broad beans	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 the presence of	(Angun et al. 2013)

Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ ( $m^2/g$ )	Adsorption capacity activated biochar ( $mg/g$ )	Experimental conditions	Relevant results	Reference
Bisphenol A (BPA) Atrazine (ATR) 17 $\alpha$ -ethynylestradiol (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, $pH < pK_a$ , $T = 20$ °C	adsorbent amount from 0.05 to 0.6 g in 50 mL of dye solution. The adsorption 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 $pK_a$ , the adsorption of contaminants significantly increased; whereas at pH above $pK_a$ 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 was suitable for the sorption of larger contaminants. The activated biochar exhibited a good initial sorption (156 mg/g) after 30 min compared to 130 mg/g for the commercially available activated carbon ( $S_{BET}$ not shown)	(Park et al. 2013)
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; $S_{BET}$ : 1021 $m^2/g$ )	(Jung and Kim 2014)
Diclofenac (DCF) Naproxen (NPX)	Loblolly pine chips containing bark	NaOH (1360)	372 290	Synthetic effluent, single and multiple contaminants, $pH = 7$	The interaction energy between the surface of the activated biochar and the adsorbate was	(Jung et al. 2015a)



Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ ( $m^2/g$ )	Adsorption capacity activated biochar ( $mg/g$ )	Experimental conditions	Relevant results	Reference
Ibuprofen (IBP)			311		measured by $^{13}C$ 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. 2015b)
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	
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 (38 mg/g) at pH 3. Chemisorption 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 °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> ,	(Iriarte-Velasco et al. 2016)

Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ (m <sup>2</sup> /g)	Adsorption capacity activated biochar (mg/g)	Experimental conditions	Relevant results	Reference
Ranitidine hydrochloride (RH)	Mung bean husk	Steam (405)	12	Column testing, synthetic effluent 100–200 mg/L, pH = 2, $T = 28\text{ }^{\circ}\text{C}$	<p>respectively, which could be related to surface area in the 1.7–5.0 nm pore range (large micropores and small mesopores)</p> <p>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</p> <p>The optimized conditions for ~99% IBP removal were as follows: adsorbent dose 0.1 g/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</p>	(Mondal et al. 2016a)
Ibuprofen (IBP)	Mung bean husk	Steam (405)	60	Synthetic effluent 1–100 mg/L, equilibrium time 2 h, pH = 2, $T = 20\text{ }^{\circ}\text{C}$	<p><math>\text{Na}_2\text{S}</math>-modified biochar showed the highest <math>\text{Hg}^{2+}</math> removal compared to KOH-activated biochar due to the formation of <math>\text{HgS}</math> 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</p>	(Mondal et al. 2016b)
Atrazine $\text{Hg}^{2+}$	Com straw ( <i>Zea mays L.</i> )	KOH (466)	92 5	Synthetic effluent 0.5–30 mg/L (atrazine) and 0–500 $\mu\text{g/L}$ ( $\text{Hg}^{2+}$ ), single and multiple contaminants, pH = 3 (atrazine) and pH = 4–6 ( $\text{Hg}^{2+}$ ), $T = 25\text{ }^{\circ}\text{C}$	<p><math>\text{Na}_2\text{S}</math>-modified biochar showed the highest <math>\text{Hg}^{2+}</math> removal compared to KOH-activated biochar due to the formation of <math>\text{HgS}</math> 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</p>	(Tan et al. 2016)

**Table 1** (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ ( $m^2/g$ )	Adsorption capacity activated biochar ( $mg/g$ )	Experimental conditions	Relevant results	Reference
Herbicide: 2,4-Dichlorophenoxy acetic acid (2,4-D)	Tea waste, burcucumber, oak wood, and bamboo	Steam (576)	59	Synthetic effluent 10–500 mg/L, pH = 7, $T = 23\text{ }^\circ\text{C}$	(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 $Hg^{2+}$ removal were electrostatic interactions, cation ion exchange, and $Hg^{2+}$ precipitation. The polyaromatic surfaces of the sorbents influenced the $\pi$ - $\pi$ electron donor-receptor force, occurring mostly for materials that have more aromatic structures and higher surface areas The highest pyrolysis temperature (700 vs. 400 $^\circ\text{C}$ ) 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, $T = 20\text{ }^\circ\text{C}$	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 $cm^3/g$ ). 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 limiting 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), $T = 30\text{ }^\circ\text{C}$	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 chemisorption, whereas APAP adsorption was simultaneously controlled by physical (i.e., electrostatic interactions) and chemical	(Sumalinog et al. 2018)

Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	Adsorption capacity activated biochar ( $\text{mg}/\text{g}$ )	Experimental conditions	Relevant results	Reference
Inorganic/metal contaminants					interactions [i.e., chemical surface reactions with the oxygen-containing functional groups ( $-\text{OH}$ and $-\text{COOH}$ )]	
$\text{Cu}^{2+}$ $\text{Cd}^{2+}$ $\text{Ni}^{2+}$ $\text{Zn}^{2+}$	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. $\text{Cu}^{2+}$ 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)
$\text{Cu}^{2+}$ $\text{Fe}^{3+}$	Date pits	Steam (1467)	203 307	Synthetic effluent, equilibrium time 10 min, $T = 18^\circ\text{C}$	Pyrolysis temperature ( $700^\circ\text{C}$ ) and activation hold time (4 h) were optimal parameter conditions applied for the production of activated biochars reaching $S_{\text{BET}}$ of $1467\text{ m}^2/\text{g}$ . 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	(Bouchelta et al. 2012)
$\text{Cu}^{2+}$	Waste peels of mangosteen fruits	$\text{CO}_2/\text{KOH}$ (367)	19	Synthetic effluent 50–100 mg/L, pH = 5.5, $T = 30^\circ\text{C}$	$\text{Cu}^{2+}$ 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 $\text{Cu}^{2+}$ 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 $70^\circ\text{C}$ ) increased the velocity of adsorbate species toward the internal structure of the adsorbent	(Hamid et al. 2014)
$\text{Cu}^{2+}$			104	Synthetic effluent 0.02 M,		

Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ (m <sup>2</sup> /g)	Adsorption capacity activated biochar (mg/g)	Experimental conditions	Relevant results	Reference
NH <sup>4+</sup>	Broiler litter and broiler cake	Steam (up to 425)	49	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)
		Steam (320)	55	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 <sub>3</sub> > steam > CO <sub>2</sub> . 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)
		CO <sub>2</sub> (403) KOH (1230) NH <sub>3</sub> (19)	18 149 57		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)
Na <sup>+</sup>	Rice husk	KOH (K) (2201)	134	Synthetic effluent 0.2 M		
		Steam (S) (317) K/S (1169)	74 102			
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 m <sup>2</sup> /g, respectively). However, Cu <sup>2+</sup> 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 Cu <sup>2+</sup> 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> Cu <sup>2+</sup> As(V)	<i>Cobocasia esculenta</i> roots	Steam (102)	6.2	Synthetic effluent, Fe <sup>2+</sup> : 50 mg/L, equilibrium time 30 min, pH 3, Cu <sup>2+</sup> : 30 mg/L, equilibrium time 180 min, pH 5,	Activated biochar was capable of removing 97% of Fe <sup>2+</sup> , 95% of Cu <sup>2+</sup> , and 84% of As(V) from aqueous solutions. The mechanism involved followed monolayer adsorption with maximum uptake of 6.2, 2.3, and 2.2 mg/g at initial	(Banerjee et al. 2016)
			2.3			
			2.2			

Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ (m <sup>2</sup> /g)	Adsorption capacity activated biochar (mg/g)	Experimental conditions	Relevant results	Reference
Pb <sup>2+</sup> Cd <sup>2+</sup> Cu <sup>2+</sup> Zn <sup>2+</sup> Ni <sup>2+</sup>	Hickory chips	NaOH (873)	Batch: Multiple: 19 1.0 18 1.8 0.9 Single: Cu <sup>2+</sup> : 54	As(V): 50 mg/L, equilibrium time 1440 min, pH 6 T = 25 °C  Batch (2–250 mg/L) and column (100 mg/L) testing, single and multiple contaminants, equilibrium time 140 min, pH = 5, T = 20 °C	concentrations of 50, 30, and 50 mg/L for Fe <sup>2+</sup> , Cu <sup>2+</sup> , and As(V), respectively. At pH 5 and 6, maximum removal of Cu <sup>2+</sup> and As(V) was observed, whereas a decrease in Fe <sup>2+</sup> adsorption was seen with an increase of pH from 3 to 7. Thus, activated biochar was capable of adsorbing various metals at different pHs NaOH-activated biochar had increased surface area, high oxygen-containing surface functional groups, and high cation-exchange capacity. Activated biochar also presented 2.6–5.8 times greater adsorption capacity for all heavy metal ions compared to biochar in single or multiple solutions. Pb <sup>2+</sup> and Cu <sup>2+</sup> were preferable metals from the competitive batch adsorption of mixed metal ions	(Ding et al. 2016)
PO <sub>4</sub> <sup>3-</sup>	Holm oak and greenhouse paprika waste	KOH (67.8) FeCl <sub>3</sub> .6H <sub>2</sub> O (-) O (-) MgCl <sub>2</sub> .6H <sub>2</sub> O (-)	26 102 25	Synthetic effluent 21–400 mg/L, pH = 7	The surface adsorption of biochars with or without pretreatment was sufficient for improving PO <sub>4</sub> <sup>3-</sup> removal. An additional thermal treatment on Fe-impregnated biochars was not necessary, but low pH seems to influence Fe-loaded adsorbent for PO <sub>4</sub> <sup>3-</sup> 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 influences PO <sub>4</sub> <sup>3-</sup> uptake much more than does porosity	(Takaya et al. 2016)
As(III)	Biogas residue from pig manure	ZnCl <sub>2</sub> (163)	28	Synthetic effluent 40 mg/L, equilibrium time 1.5 h, pH = 7, T = 25 °C	ZnCl <sub>2</sub> -activated biochar presented excellent adsorption efficiency for the removal of As(III) from solution. Adsorption was found to occur through ligand exchange (Zn <sup>2+</sup> ) which was loaded on hydroxyl groups present on the surface of the adsorbent (Zn-OH) as well as through porous adsorption. Based on FTIR 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 significantly	(Xia et al. 2016)
Cd <sup>2+</sup>	Debarked loblolly pine chips	NaOH (1151)	167	Synthetic effluent 2 mg/L, equilibrium time 6 h, pH = 7.5, T = 25 °C	The maximum Cd <sup>2+</sup> adsorption capacity was obtained at pH 7.5. The main mechanisms involved during Cd <sup>2+</sup> adsorption were	(Park et al. 2017)

Table 1 (continued)

Contaminant	Biochar feedstock	Activated biochar/ $S_{BET}$ ( $m^2/g$ )	Adsorption capacity activated biochar ( $mg/g$ )	Experimental conditions	Relevant results	Reference
$Cd^{2+}$ $Cu^{2+}$	Pine sawdust	$H_3PO_4$ (900)	5 2	Synthetic effluent 1–10 mg/L, equilibrium time 6 h, pH = 4.5	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 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 $H_3PO_4$ -activated biochar was controlled by the mechanism of surface complexation	(Peng et al. 2017)
As(V) F <sup>-</sup>	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 chemisorption process	(Saikia et al. 2017)

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

In addition, the type of activation (physical, chemical, or physicochemical), diversity of feedstock, and pyro-gasification operating conditions applied for the preparation of biochars have great effect on the porosity of activated biochars (Table 1). Steam-activated broiler litter biochar synthesized after pyrolysis at 350 and 700 °C showed that for both materials, the same surface area of 335 m<sup>2</sup>/g was attained. The chemical composition of broiler litter (high ash content) is completely different from lignocellulosic precursors (low ash content). However, higher adsorption capacity of deisopropylatrazine (a herbicide) was reached by applying high pyrolysis temperature and subsequent activation (Uchimiya et al. 2010). Activated biochar has higher aromaticity, which is an important parameter related to enhanced removal of organic

pollutants due to its higher hydrophobicity and  $\pi$ - $\pi$  interactions (Boving and Zhang 2004; Moreno-Castilla 2004; Park et al. 2013). The same findings were observed for phenanthrene removal: faster initial sorption rate and higher equilibrium concentration for phenanthrene adsorption were reported when using activated biochar prepared at low pyrolysis temperature (300 °C;  $S_{\text{BET}} = 1250 \text{ m}^2/\text{g}$ ), whereas stronger binding with the sorbate was noted with the material pyrolyzed at 700 °C ( $S_{\text{BET}} = 57 \text{ m}^2/\text{g}$ ). The considerable decrease in surface area of the activated biochar pyrolyzed at 700 °C was due to the presence of condensed aromatic structures, which were more stable and had fewer oxygen-containing groups at the surface. Consequently, its carbon framework was resistant to thermal degradation (even when impregnated with harsh chemicals, e.g., NaOH) inhibiting the development of a porous structure. Although the activated biochar pyrolyzed at 700 °C presented higher aromaticity, the material having the highest surface area (pyrolyzed at 300 °C) exhibited higher initial sorption efficiency (156 mg/g) compared to a commercial activated carbon NORIT (130 mg/g) (Park et al. 2013).

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

## 2.2 Inorganic Contaminants

Most of the compounds included in the inorganic contaminant group are present in mining effluents; they include both cations and anions  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , As(III), and  $\text{NH}_4^+$ , as well as  $\text{Na}^+$  and  $\text{PO}_4^{3-}$ . 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 ( $-\text{COOH}$ ), phenol ( $-\text{OH}$ ), and amino groups ( $-\text{NH}_2$ ) 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  $\text{Cu}^{2+}$  was reported through the use of biochar and steam-activated biochar from 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  $\text{Cu}(\text{OH})_2$  formation takes place at higher pH levels. The surface area of the activated biochar doubled compared to biochar (322 vs. 181  $\text{m}^2/\text{g}$ ), while its polarity index  $[(\text{O} + \text{N})/\text{C}]$  decreased.  $\text{Cu}^{2+}$  adsorption was better fitted to the Freundlich and Langmuir models by using biochar and activated biochar, respectively, but they presented almost the same adsorption capacity for  $\text{Cu}^{2+}$  in water (14 vs. 15  $\text{mg}/\text{g}$ ). The greater efficiency of biochar for  $\text{Cu}^{2+}$  could be because of the formation of metal complexes or chelates due to the presence of more oxygenated functional groups connected to it compared to activated biochar.  $\text{Cu}^{2+}$  may have been adsorbed through different mechanisms in both materials: intraparticle diffusion and  $\pi$ -cation interactions in activated biochar, and surface complexation 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.,  $\text{Fe}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{As}(\text{V})$  within the pH range of 2–7, was reported by Banerjee et al. (2016). At lower pH (equal to 3),  $\text{Fe}^{2+}$  was highly adsorbed by the activated biochar, whereas at higher pH, its adsorption decreased due to the formation of ferrous species such as  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^+$ , as well as the precipitation of  $\text{Fe}(\text{OH})_3$ , resulting in less adsorption of  $\text{Fe}^{2+}$  (Panday et al. 1985; Mohan and Pittman Jr. 2006; Hove et al. 2007; Banerjee et al. 2016). In relation to the contaminants  $\text{As}(\text{V})$  and  $\text{Cu}^{2+}$ ,

the maximum removals of 80 and 75%, respectively, were reached at pH 5 and 6, whereas low contaminants removal was found at low pH. In other cases, it was reported that  $\text{Cu}^{2+}$  was the most adsorbed metal ion in single solutions but the adsorption capacity of the activated biochar was reduced when other metals ( $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ) were found in the same environment (Lima et al. 2010). A probable metals competition may have lowered the sorption of  $\text{Cu}^{2+}$ .

The type of pyro-gasification process and operating conditions were also found to have an influence on the porosity of activated biochars and, consequently, on the removal of inorganic contaminants. The proper choice of pyrolysis temperature (500 vs. 700  $^\circ\text{C}$ ) may influence the porosity of biochars (50 vs. 300  $\text{m}^2/\text{g}$ ), and may have been responsible for the presence of carboxylic and phenolic groups at the surface of the material, improving the cation-exchange and complexation properties of the adsorbents for the removal of  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$ , in addition to physical sorption (Bouchelta et al. 2012). These findings were also confirmed by  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ -activated biochars prepared after first-step pyrolysis at 600  $^\circ\text{C}$ , producing higher  $\text{PO}_4^{3-}$  (102  $\text{mg}/\text{g}$ ) removal compared to a material made at 400  $^\circ\text{C}$  (17  $\text{mg}/\text{g}$ ) (Takaya et al. 2016). Different biochars made from slow and fast pyrolysis of the same feedstock also presented great differences in relation to 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  $\text{NH}_4^+$  from water through activated biochar prepared at different types of activation using steam,  $\text{CO}_2$ ,  $\text{KOH}$ , and  $\text{NH}_3$  was reported by Rambabu et al. (2015). By using  $\text{NH}_4^+$  solution at 260 ppm, the sorption capacity was found to be 55, 18, 149, and 57  $\text{mg}/\text{g}$ , respectively. Chemical activation was shown to be an effective approach for the development of porosity for the sorption of  $\text{NH}_4^+$ . However, the presence of minerals (high ash content), the presence of oxygenated and nitrogenated functional groups connected to the surface of activated biochar, and the chemical surface of modified materials [e.g.,  $\text{Na}_2\text{S}$ -modified biochar (Tan et al. 2016),  $\text{ZnCl}_2$ -activated biochar (Xia et al. 2016)] were also found to be determinant for better heavy metals adsorption. In activated biochars, the overall metal interaction mechanisms with these surface functionalities are electrostatic interactions, ion exchange, surface

complexation, and metal precipitation in addition to physical sorption.

### 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.
- ii. The pH of the solution may also affect the sorption of organics and inorganics onto activated biochar. Specifically, metals at precisely pH range can lead to precipitation mostly in a form of hydroxides, which may solubilize afterwards depending on the pH conditions. Therefore, an optimization study on the effect of the pH on the adsorption process is recommended.
- iii. The pyro-gasification conditions, reactor design, as well as the quality of feedstock used for the preparation of biochars have considerable influence on the textural properties (porosity) of activated biochars as well on the environmental remediation applications. Optimization of operating conditions and physicochemical characterization of biochars are recommended 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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