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Biochar modification to enhance sorption of inorganics from water

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Abstract

Biochar can be used as a sorbent to remove inorganic pollutants from water but the efficiency of sorption can be improved by activation or modification. This review evaluates various methods to increase the sorption efficiency of biochar including activation with steam, acids and bases and the production of biochar-based composites with metal oxides, carbonaceous materials, clays, organic compounds, and biofilms. We describe the approaches, and explain how each modification alters the sorption capacity. Physical and chemical activation enhances the surface area or functionality of biochar, whereas modification to produce biochar-based composites uses the biochar as a scaffold to embed new materials to create surfaces with novel surface properties upon which inorganic pollutants can sorb. Many of these approaches enhanced the retention of a wide range of inorganic pollutants in waters, but here we provide a comparative assessment for Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, NH_4^+, NO_3^-, PO_4^{3-}, CrO_4^{2-} and AsO_4^{3-}.

Keywords: Modification, sorption, inorganic, pollution, activation

1. Introduction

Biochar is produced by heating organic materials in the partial or total absence of oxygen (pyrolysis). The objective of biochar production is usually to generate energy or to reduce the mass or volume of waste materials. However, considerable interest has been paid to optimising the pyrolysis conditions to improve the yield (Tripathi et al., 2016) and properties (Mukherjee et al., 2011) of the resulting biochar. Biochar is resistant to degradation, has a high surface area and a considerable negative charge (Sizmur et al., 2016). It has therefore been proposed as a sustainable means to remove positively charged ions (e.g. Cd^{2+}, Cu^{2+}, Pb^{2+}, Zn^{2+}) and polar organic molecules (e.g. phenolics, halogenated compounds, solvents) from water by ion exchange, electrostatic attraction, physical sorption and precipitation (Tan et al., 2015).

There are several methodologies by which the properties of biochar can be chemically, physically or biologically modified by treating the feedstock or, more commonly, the resulting biochar (Rajapaksha et al., 2016). These methodologies include treatments with steam, acids, bases, metal oxides, carbonaceous materials, clay minerals, organic compounds, and biofilms. The objectives of these treatments are broadly to either, (i) increase the surface area of the biochar, (ii) modify or enhance the surface properties of the biochar, or (iii) use the surface as a platform to embed another material (or organism) with beneficial surface properties. The tools available to modify biochars increase the breadth of chemical pollutants which can be removed from water using biochar.

This review will provide an introduction to common inorganic pollutants, describe the surface properties of unmodified biochar, introduce the various modification approaches, explain how the pyrolysis process and the modifications alter the surface properties of biochar, and demonstrate how these modifications enhance the removal of inorganic contaminants from aqueous solutions.

2. Common inorganic pollutants in water

The prevention and remediation of freshwater pollution is one of the greatest global challenges facing humanity in the 21st century (Dudgeon et al., 2006). Anthropogenic disruption of biogeochemical cycling of elements has increased the concentrations, or changed the chemical form, of several elements in terrestrial ground and surface waters. The inorganic contaminants of primary concern are classified by their chemical behavior and discussed below. Efficient, sustainable, and cost-effective remediation strategies for these elements are urgently required.

Potentially toxic elements, such as As, Cd, Cr, Cu, Hg, Pb and Zn are often present discharges from mining and smelting, sewage treatment, road runoff and the manufacture of batteries, pigments and dyes, electronics and alloys (Moore & Ramamoorthy, 2012). In sufficient concentrations, these elements can cause ecotoxicological effects to freshwater ecology and can bioaccumulate through food webs resulting in chronic toxicity to higher tropic levels, including humans. Most of these elements (Cd, Cu, Hg, Pb, and Zn) occur primarily in the environment as divalent cations. Cd and Zn have a larger radius and thus a lower charge-to-radius ratio and lower ionic potential than Cu, Hg and Pb. For this reason, Cu, Hg and Pb more readily form bonds with functional groups on surfaces and are thus less mobile than Cd and Zn.

Concentrations of nutrients (NH_4^+, NO_3^- and PO_4^{3-}) are elevated in surface and ground waters globally, largely due to sewage effluent and inefficient application of agricultural fertilizers, (Mueller & Helsel, 1996). The elevated nutrient status of freshwater discharges to oceans causes ecological damage in estuaries and coastal zones by promoting harmful algal blooms, and reducing dissolved oxygen concentrations, resulting hypoxic ‘dead zones’ (Conley et al., 2009).

While NH_4^+ is positively charged and is attracted to the negatively charged surfaces, it has a much lower charge-to-radius ratio than the metal cations discussed above. NH_4^+ thus behaves similarly to alkali metal cations (e.g. Na^+, K^+) and so does not form as stable bonds with surfaces as the divalent metal cations. Unlike NH_4^+, NO_3^- and PO_4^{3-} are oxyanions with contrasting behavior to each other. Both are negatively charged and therefore attracted to positively charged surfaces but NO_3^- is much more mobile than PO_4^{3-}, which readily binds to colloids in water.

As and Cr are redox sensitive elements that exhibit contrasting changes to mobility and toxicity in response to changes in redox conditions. Inorganic As can be found in the environment as pentavalent arsenate, As(V), or as trivalent arsenite, As(III). Arsenate (AsO_4^{3-}) is found in aerobic environments, and arsenite (AsO_3^{3-}), which is more toxic to humans, is more mobile, and occurs in anaerobic conditions, including groundwater (Moore & Ramamoorthy, 2012). The use of naturally occurring As contaminated groundwater as drinking water and to irrigate rice paddies has resulted in widespread poisoning of human populations, especially in Bangladesh. Cr can be found as trivalent Cr(III) and hexavalent Cr(VI). In contrast to As, the reduced species, Cr(III) is considered a beneficial element in humans as it enhances insulin production, whereas Cr(VI), usually present as chromate (CrO_4^{2-}) or dichromate ($Cr_2O_7^{2-}$) is a strong oxidising agent, is carcinogenic, and is more mobile and much more toxic than Cr(III) (Kotaś & Stasicka, 2000). Chromium most notoriously contaminates surface waters due to discharge of tannery effluent .

To reduce the concentrations of these inorganic contaminants of concern in aquatic ecosystems it is essential to treat point source discharges of agricultural, domestic and industrial wastewater before disposal into the freshwater environment. Current wastewater treatment technologies to remove inorganic contaminants are costly, energy intensive, and require disposal of resulting toxic waste (Shannon et al., 2008). These limitations of the

currently available technologies provide a demand for an efficient, selective, cost-effective adsorbent material. The modification of biochar could provide the versatile, low cost and sustainable solution to point source pollution of freshwater with inorganic pollutants.

3. How biochar properties influence the sorption of inorganic pollutants from aqueous solutions

Biochar can be used as a sorbent to remove pollutants from water and may be removed from solution when saturated, treated appropriately and replaced with new or recycled biochar. There are several mechanisms responsible for the high sorption capacity of biochar for specific pollutants.

Biochars have a high surface area due to a large distribution of micro or mesopores. The greater the number of micropores, the greater the surface area of the biochar and the more surface sites upon which pollutants can adsorb. Several authors have observed a relationship between pollutant adsorption capacities and biochar surface area (Kim et al., 2013; Tan et al., 2015).

Surface functionality also affects biochar sorption capacity (Fletcher et al., 2014; Niu et al., 2017). Sorption of inorganic pollutants by biochar is a result of (i) stoichiometric ionic exchange, (ii) electrostatic attraction, or (iii) surface precipitation (Beesley et al., 2015; Gomez-Eyles et al., 2013; Sizmur et al., 2016).

(i) Chemical sorption occurs due to ion exchange with the abundant functional groups on the carbonaceous surface of biochar, such as carboxylic, hydroxylic or phenolic groups (Lee et al., 2010; Liang et al., 2006). These groups confer cation exchange capacity (CEC) to biochar depending on feedstock and pyrolysis temperature, with a peak of CEC at around 350-400 ºC (Gomez-Eyles et al., 2013), probably due to the loss of oxygenated functional groups above this temperature (Lee et al., 2010). Chemical sorption of cations relies on releases of protons and base cations (Na, K, Ca or Mg) from the biochar (Uchimiya et al., 2010). Since chemical

sorption is stoichiometric, sorption efficiency is pH dependent and thus dictated by the pH of the medium.

(ii) Physical (electrostatic) sorption occurs between positively charged ions in water and the delocalised cloud of electrons associated with aromatic groups on the surface of carbonaceous biochars, creating cation-π interactions with the C=C aromatic bonds (Harvey et al., 2011). Unlike chemical sorption, physical adsorption does not require stoichiometric release of cations or protons from the biochar.

(iii) Precipitation (or co-precipitation) of inorganic pollutants (particularly metal cations) with insoluble salts occurs on the surface of biochars with a high mineral ash content. For example, precipitation of Pb has been demonstrated on the surface of phosphate rich biochars derived from manures (Cao et al., 2009). Biochar may also raise the pH of the solution (depending on its starting pH), leading to the precipitation of metal (hydr)oxides, which are generally sparingly soluble.

Surface area and functionality can be manipulated by the modification of biochar to enhance sorption capacities for specific pollutants. Modifications often have the objective of increasing the anion sorption capacity while activation usually increases the metal cation sorption capacity of biochars. However, considerable differences in the surface area and functionality of biochars can result from altering the pyrolysis temperature.

4. Effect of pyrolysis temperature on biochar properties and sorption capacity

Although modifications of biochars (post-pyrolysis) or their feedstocks (pre-pyrolysis) can alter their physico-chemical properties, pyrolysis conditions can also affect the biochar structure and composition and thus its metal sorption capacity (Figure 1). Pyrolysis temperature influences the adsorption characteristics of biochar by changing the surface area, surface functionality, pore distribution and mineral concentration of biochar (Ahmad et al.,

2012; Chen et al., 2014; Jung et al., 2016b; Kim et al., 2012). It is important to produce biochar at optimum pyrolysis temperatures to maximise inorganic contaminant adsorption.

The development of microstructure and an increase in the surface area of biochar upon increasing pyrolysis temperature has been widely observed, regardless of the feedstock used (Cantrell et al., 2012; Fletcher et al., 2014; Uchimiya et al., 2010). Fletcher et al. (2014) observed an opening of the internal structure when the pyrolysis temperature of willow biochar was ≥450 ºC. At higher temperature (≥550 ºC), the width of mesopores increased and new micropores were created. However, Jung et al. (2016b) found a decrease in total pore volume, surface area and phosphate sorption capacity of a biochar produced from a marine macroalgae when pyrolysis temperature increased to 600 and 800 ºC, likely due to blockage and collapse of the pore structures (Paethanom & Yoshikawa, 2012) by melting of the material during pyrolysis.

Biochars produced at higher temperatures often contain greater amounts of C fixed in the biochar structure (i.e. higher C content) as a result of greater loss of volatile matter at high pyrolysis temperatures (Cantrell et al., 2012; Kim et al., 2012). Increasing pyrolysis temperatures also increases the aromaticity and decreases the polarity of the biochar, so the biochar surface becomes less hydrophilic. Lower O and H contents have been reported when increasing pyrolysis temperature due to loss of surface functional groups. The decrease in oxygen-containing functional groups can affect the metals sorption capacity of biochars, as observed by Ding et al. (2014), who found higher Pb adsorption capacity of biochar when produced at lower temperature. The authors suggest that for lower temperature biochars, oxygen-containing functional groups were responsible for Pb sorption, whereas for high temperature biochars, Pb sorption was dominated by intraparticle diffusion and was thus affected by the abundant pores.

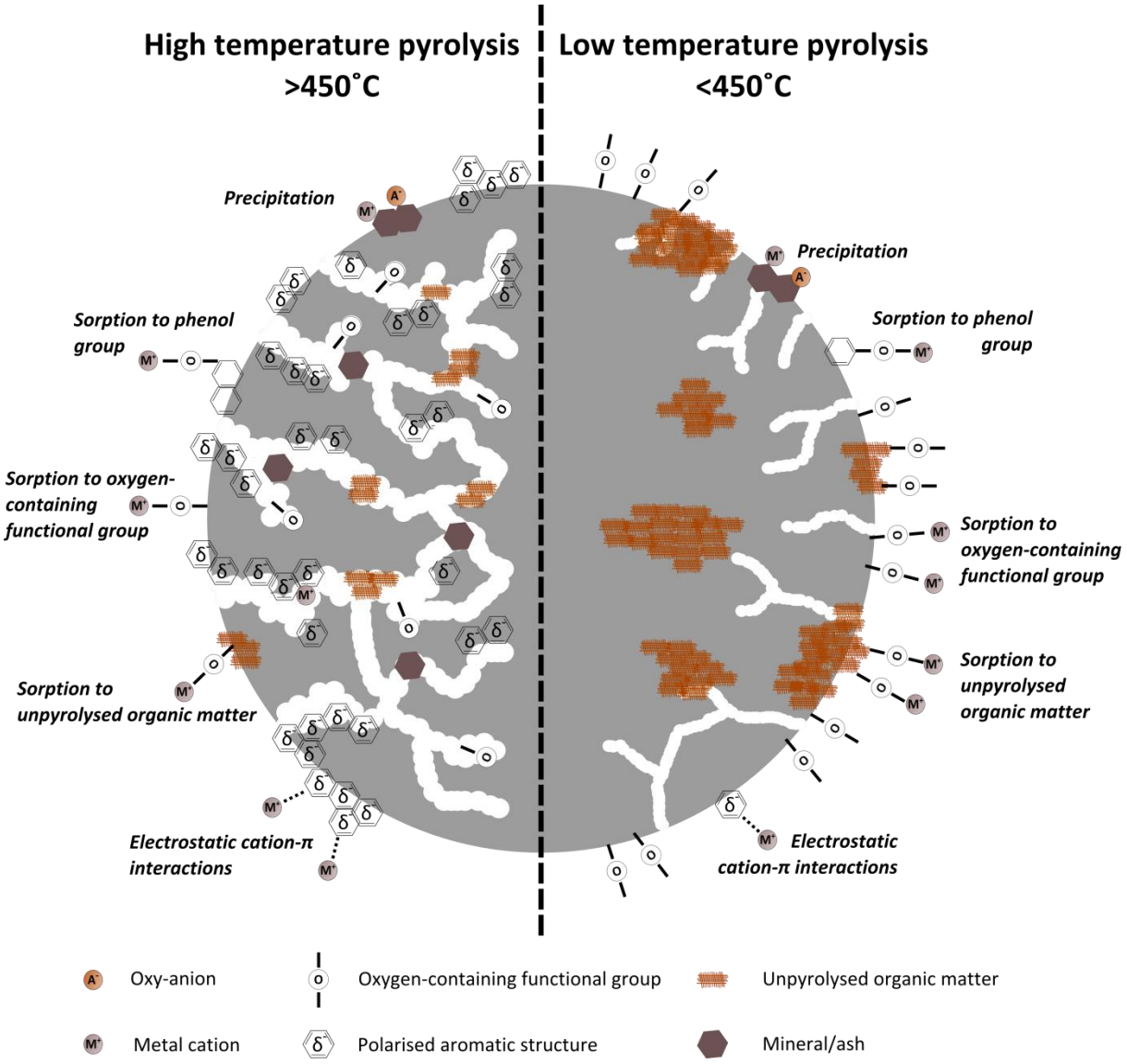

Figure 1. Conceptual model identifying the mechanisms of metal cation (e.g. Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}) and oxyanion (e.g. PO_4^{3-}, AsO_4^{3-}) sorption to biochar pyrolysed at high temperature (>450˚C) and low temperature (<450˚C). High temperature biochar has a higher surface area, pores previously blocked by unpyrolysed organic matter are unblocked, and there are more aromatic groups and less oxygen containing functional groups on the biochar surface.

The yield of biochar production decreases as pyrolysis temperature increases, generally by about 10% for every temperature increase of 100 ºC (Chen et al., 2014; Fletcher et al., 2014). As the pyrolysis temperature increases and the biochar yield decreases, the mineral ash content becomes more concentrated. Consequently, biochars produced at higher pyrolysis temperatures have more total, soluble and exchangeable base cations and carbonates, less

oxygenated functional groups and greater pH (Fletcher et al., 2014; Qian et al., 2013; Yuan et al., 2011). Thus, more alkaline biochar can be produced by increasing the pyrolysis temperature, which can lead to greater precipitation of metal cations (Kim et al., 2013). Chen et al. (2014) reported higher Cd removal from an aqueous solution by biochar produced with a mixture of sewage sludge and pine bark when biochar was produced at higher pyrolysis temperature. The authors suggested that Cd^{2+} sorption onto biochar was likely due to surface precipitation with $Ca^{2+}$and thus attributed the higher Cd removal to the enhanced cation exchange capacity in higher temperature-biochar due to concentrated alkaline-earth metals, such as Ca^{2+}, in the ash during pyrolysis.

5. Methods of modifying Biochar

Innovative methodologies for modifying biochar have been developed to enhance the adsorption of inorganic pollutants from water. Modifications are performed either pre-or post-pyrolysis of the biochar (or both). Whilst pre-pyrolysis modifications involve the treatment of the biochar feedstock, post-pyrolysis modifications are more common and involve the treatment of biochar after it has already been produced. Figure 2 provides a classification system of the most common modification methods reported in the literature. The physical activation of biochar using steam and chemical activation using acidic and alkaline solutions is usually undertaken post-pyrolysis, although promising results have been reported also when chemical activation is conducted pre-pyrolysis. The production of biochar-based composites, the modification method that has received the most research attention for creating sorbents for remediation of polluted waters, is performed by embedding different materials into the biochar structure pre- or post-pyrolysis. The primary aim of all these modification methods is to enhance the efficacy by which the biochar removes pollutants from water, generally by changing its physical or chemical properties, such as surface area, or surface functionality.

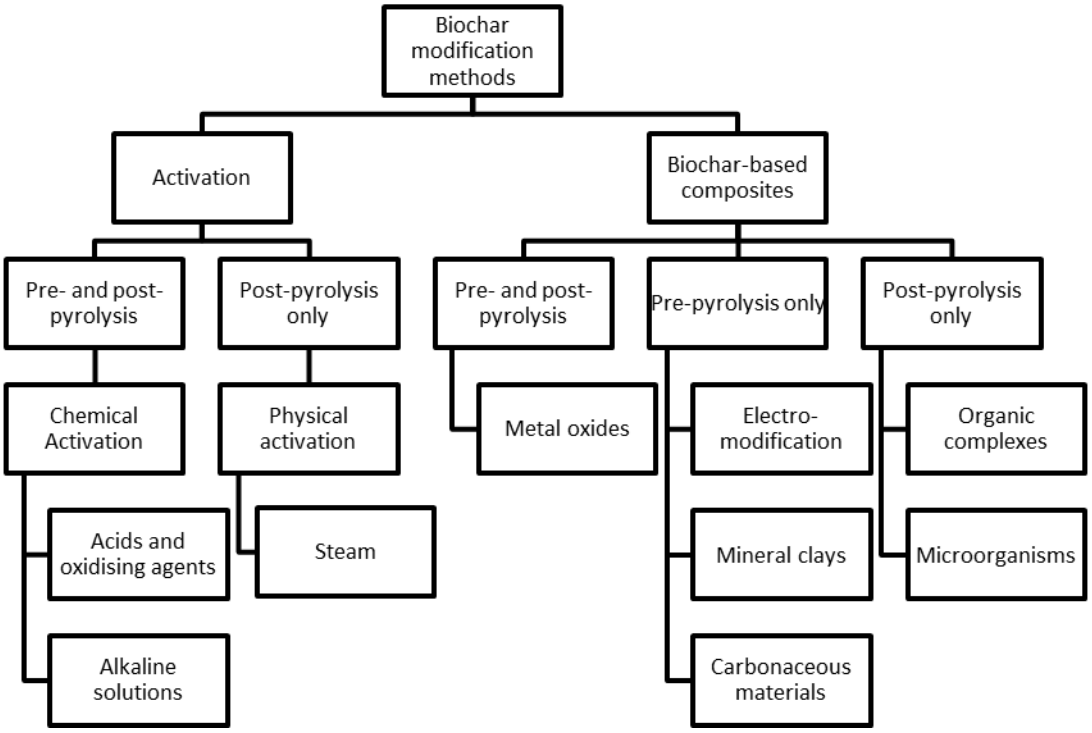

Figure 2. Chart defining a classification system of biochar modification methods to physically and chemically activate biochars and produce biochar based composites

The properties of biochar can be altered by physical and chemical activation. While the acid and alkali treatments are the most common chemical activation methods, steam is the primary physical activation method. Biochar-based composites are prepared by impregnation or coating the surface of the biochar with metal oxides (Micháleková-Richveisová et al., 2017), clay minerals (Chen et al., 2017), carbonaceous structures such as graphene oxide (Shang et al., 2016) or carbon nanotubes (Inyang et al., 2015), complex organic compounds, such as chitosan (Zhou et al., 2013) or amino acids (Yang & Jiang, 2014), or inoculation with microorganisms (Frankel et al., 2016). These modification methods are explained in detail in the following sections and their impact on the sorption of selected inorganic pollutants in water are summarised in Table 1.

253 **Table 1. Effect of biochar modifications on common inorganic pollutants in water. The modifications were sorted as Physical**
254 **activation with steam (Phy. A. – Steam); Chemical activation with acids or oxidants (Ch. A. - Acids/oxidants) or with bases (Ch. A. -**
255 **Acids/oxidants); Biochar-based composites (Comp.) modified with metals (Metals), carbonaceous materials (C materials), electrical**
256 **field (Electromodified), organic molecules (Organics) and Biofilms (microorganisms).**

Target pollutant	Type of biochar modification	Treatment / Feedstock	Treatment stage	Effect on metal sorption capacity	References
Cd^{2+}	Phy. A. - Steam	Steam / Poultry manure)	Post-pyrolysis	+	Lima and Marshall (2005)
	Ch. A. - Bases	KOH / Ipomoea biomass	Post-pyrolysis	+	Goswami et al., (2016)
	Comp. - Metals	Fe / Several feedstocks	Post-pyrolysis	+	Mohan et al., (2014); Trakal et al., (2016)
	Comp. - Organics	Chitosan / Bamboo, hickory wood, sugarcane bagasse	Post-pyrolysis	+	Zhou et al., (2013)
	Comp. - Organics	Chitosan / Peanut hull	Post-pyrolysis	-	Zhou et al., (2013)
Zn^{2+}	Phy. A. - Steam	Steam / poultry manure	Post-pyrolysis	+	Lima and Marshall (2005)
Cu^{2+}	Phy. A. - Steam	Steam / Pine sawdust	Post-pyrolysis	=	Lou et al., (2016)
	Phy. A. - Steam	Steam / poultry manure	Post-pyrolysis	+	Lima and Marshall (2005)
	Ch. A. - Acids/oxidants	HNO_3 / Cactus cladodes	Post-pyrolysis	+	Hadjitoffi et al., (2014)
	Ch. A. - Bases	KOH / Fruit peel	Post-pyrolysis	+	Hamid et al., (2014)
	Comp. - Metals	Mn / Corn straw	Post-pyrolysis	+	Song et al., (2014)
	Comp. - Organics	Amino-modification by nitrification and reduction / Commercial sawdust	Post-pyrolysis	+	Yang and Jiang, (2014)
	Comp. - Organics	Chitosan / Bamboo, hickory wood, sugarcane bagasse, peanut hull	Post-pyrolysis	-	Zhou et al., (2013)
Hg^{2+}	Comp. - C materials	Graphene oxide / Wheat straw	Pre-pyrolysis	+	Tang et al., (2015)
Pb^{2+}	Ch. A. - Acids/oxidants	H_3PO_4 / Pine sawdust	Pre-pyrolysis	+	Zhao et al., (2017)
	Ch. A. - Acids/oxidants	H_2O_2 / Peanut hull hydrochar	Post-hydrothermal treatment	+	Xue et al., (2012)
	Comp. - Metals	Mn / Pine wood	Pre-pyrolysis	+	Wang et al., (2015a)
	Comp. - Metals	Mn / Pine wood	Post-pyrolysis	+	Wang et al., (2015a)
	Comp. - Metals	Fe / Several feedstocks	Post-pyrolysis	+	Mohan et al.,(2014); Trakal et al., (2016)

	Comp. - Metals	Mg / Cypress sawdust	Pre-pyrolysis	+	Jellali et al., (2016)
	Comp. - C materials	Carbon nanotubes / Sugarcane bagasse	Pre-pyrolysis	=	Inyang et al., (2015)
	Comp. - C materials	Carbon nanotubes / Hickory chips	Pre-pyrolysis	+	Inayng et al., (2015)
	Comp. - Organics	Chitosan / Bamboo, hickory wood	Post-pyrolysis	+	Zhou et al., (2013)
	Comp. - Organics	Chitosan / Sugarcane bagasse, peanut hull	Post-pyrolysis	-	Zhou et al., (2013)
	Comp. - Organics	Chitosan + ZVI particles / Bamboo	Post-pyrolysis	+	Zhou et al., (2014)
NH_4^+	Ch. A. - Acids/oxidants	HNO_3 + NaOH / Corncob waste	Post-pyrolysis	+	Vu et al., (2017)
	Comp. - Clays	Montmorillonite / Bamboo	Pre-pyrolysis	+	Chen et al., (2017)
	Comp. - Clays	Bentonite / Cassava peel	Pre-pyrolysis	+	Ismadji et al., (2016)
NO_3^-	Comp. - Metals	Mg / Several feedstocks	Pre-pyrolysis	+	Zhang et al., (2012)
PO_4^{3-}	Comp. - Metals	Fe / Several feedstocks	Post-pyrolysis	+	Ren et al., (2015); Micháleková-Richveisová et. al (2017)
	Comp. - Metals	Fe / Several feedstocks	Pre-pyrolysis	+	Cai et al.,(2017); Chen et al., (2011)
	Comp. - Metals	Mg / Several feedstocks	Pre-pyrolysis	+	Yu et al.,(2016); Zhang et al., (2012)
	Comp. - Metals	Mg-enriched tomato	Pre-pyrolysis	+	Yao et al., (2013)
	Comp. - Metals	Ca / Ramie biomass	Pre-pyrolysis	+	Liu et al., (2016)
	Comp. - Electromodified	Al electrode / *Laminaria japonica*	Pre-pyrolysis	+	Jung et al.,(2015a; 2015b; 2016a)
	Comp. - Clays	Montmorillonite / Bamboo	Pre-pyrolysis	+	Chen et al., (2017)
	Comp. - Clays	Layered double hydroxides / Cotton wood	Post-pyrolysis	+	Zhang et al., (2013b)
	Comp. - Organics	Chitosan + ZVI particles / Bamboo	Post-pyrolysis	+	Zhou et al., (2014)
	Comp. - Microorganisms	Indigenous microbial community / Several feedstocks	Post-pyrolysis	+	Frankel et al., (2016)
As (V)	Ch. A. - Bases	KOH / Municipal solid wastes	Post-pyrolysis	+	Jin et al., (2014)
	Comp. - Metals	Fe / Several feedstocks	Pre-pyrolysis	+	Hu et al,(2015); Zhang et

	Comp. - Metals	Fe / Several feedstocks	Post-pyrolysis	+	al.,(2016); Zhang et al., (2013a)
	Comp. - Metals	Magnetic gelatin / Chestnut shell	Post-pyrolysis	+	Agrafioti et al.,(2014); Fristak et al.,(2017); Wang et al.,(2015b); Wang et al., (2017b)
	Comp. - Metals	Al / Several feedstocks	Pre-pyrolysis	+	Zhou et al., (2017b)
	Comp. - Metals	Mn / Pine wood	Pre-pyrolysis	+	Zhang and Gao, (2013)
	Comp. - Metals	Mn / Pine wood	Post-pyrolysis	+	Wang et al.,(2015a);
	Comp. - Metals	Mn + Ni / Pine wood	Pre- and post-pyrolysis	+	Wang et al.,(2015a);
	Comp. - Organics	Chitosan + ZVI particles / Bamboo	Post-pyrolysis	+	Wang et al., (2016)
	Comp. - Microorganisms	Indigenous microbial community / Several feedstocks	Post-pyrolysis	+	Zhou et al., (2014)
	Comp. - Metals	Fe / Rice straw	Post-pyrolysis	+	Frankel et al., (2016)
	Comp. - Metals	Fe / Eucalyptus	Post-pyrolysis	-	Quian et al.,(2017); Wang et al., (2017a)
Cr (VI)	Comp. - C materials	Graphene oxide / Hyancith	Pre-pyrolisis	+	Wang et al., (2014)
	Comp. - Organics	Ployethylenimine-methanol / Rice husk	Post-pyrolysis	+	Shang et al., (2016)
	Comp. - Organics	Chitosan / Fe-treated *Eichhornia crassipes*	Post-pyrolysis	+	Ma et al., (2014)
	Comp. - Organics	Chitosan + ZVI particles / Bamboo	Post-pyrolysis	+	Zhang et al., (2015)
					Zhou et al., (2014)

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5.1. Activation

The activation of biochar involves the use of steam or acidic or alkaline solutions to create a network of interconnecting micropores that ultimately increases the surface area upon which metal cations can chemically or physically adsorb. Physical activation methods force high temperature steam through the pores of the biochar, which increases the surface area, while chemical activation methods expose the biochar to acidic or alkaline solutions which oxidise the surface and create oxygen-containing functional groups (Figure 3).

5.1.1. Physical activation

5.1.1.1. **Steam**

Steam activation is a common modification method used to increase the structural porosity of the biochar and remove impurities such as products of incomplete combustion. This treatment serves to increase the surface area upon which sorption can occur. Lima and Marchall (2005) produced activated biochars from poultry manure feedstocks by pyrolysing at 700 ˚C followed by steam activation at 800 ˚C with a range of water flow rates and durations. Higher flow rates and longer activation times increased the sorption of Cd, Cu and Zn on the surface of the biochar.

Although steam activation increases the surface area and porosity of biochar, Shim et al. (2015) found that the Cu^{2+} sorption capacity of biochar produced by slow pyrolysis of *Miscanthus* at 500 °C was not significantly changed by activation with steam at 800˚C. They found that although steam activation of the biochar increased the surface area, the abundance of functional groups decreased, alongside an increase in aromaticity. Similarly, Lou et al. (2016) observed that steam activation of biochar prepared with pine sawdust increased the surface area but had little effect on the characteristics of surface functional groups. The steam treatment did not affect adsorption capacity for phosphate due to electrostatic repulsion by the negatively charged surface of biochar. Therefore, in the context of inorganic pollutant

sorption, steam activation seems to be more effective when applied prior to a second activation/modification step that creates functional groups, as the steam only increases the surface area of biochar.

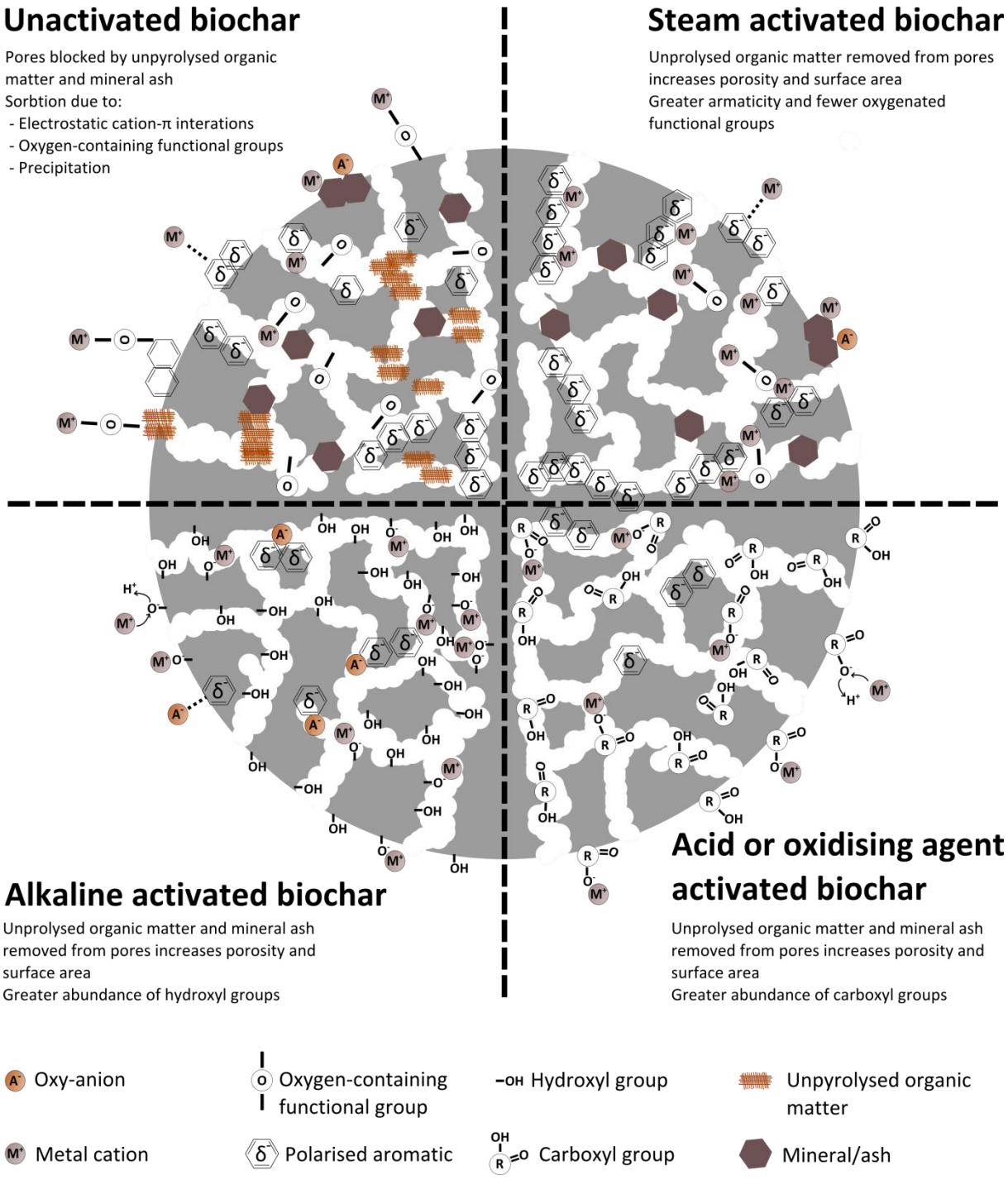

Figure 3. Conceptual model identifying the mechanisms of metal cation (e.g. Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}) and oxyanion (e.g. PO_4^{3-}, AsO_4^{3-}) sorption to unactivated biochar and biochar physically activated with steam or chemically activated with acids, oxidising agents, or alkaline solutions

5.1.2. Chemical activation

5.1.2.1. **Acids and oxidising agents**

Biochar surfaces contain several functional groups (e.g. carboxyl, hydroxyl, phenol) that can chemically bond with metal cations and remove them from solution. Acid treatments provide more oxygenated functional groups on biochar surfaces and increase the potential for biochar to chemically bind positively charged pollutants through specific adsorption. The modification of biochar by exposing the surface to acidic solutions forms carboxylic groups on the biochar surface (Hadjittofi et al., 2014; Qian et al., 2013) and develops micropores that lead to an increase in the surface area (Iriarte-Velasco et al., 2016).

Hadjittofi et al. (2014) activated a biochar derived from cactus fibres with HNO_3 to increase the abundance of carboxylic groups on the surface since these groups act as strong Cu^{2+} binding sites. Adsorption was shown to be pH dependent since the sorption capacity of the resulting biochar was an order of magnitude greater at pH 6.5, compared to pH 3, indicating chemical sorption on oxygen-containing functional groups on the biochar surface. Oxygen-containing functional groups were also shown to be incorporated into structure of a rice straw biochar upon post-pyrolysis treatment with a mixture of H_2SO_4 and HNO_3, evidenced by higher O/C ratios in the final product (Qian et al., 2013).

Acid-treatment increased the surface area, the total pore volume and volume of micropores after treatment of pine tree sawdust with diluted H_3PO_4 prior to pyrolysis (Zhao et al., 2017). The incorporation of P-O-P bonds into the C structure increased the Pb sorption capacity of the phosphoric acid-treated biochar by >20% compared to a non-treated sample due to phosphate precipitation and surface adsorption (Zhao et al., 2017).

Activation of biochar with strong acids can be expensive at large scale and present environmental issues during the disposal of the activation media, so activation with H_2O_2, a less-expensive and cleaner product has been proposed as an alternative biochar activation

316 medium to increase sorption capacity. Huff et al. (2016) reported an increase in oxygen-
317 containing functional groups in a pinewood biochar treated with H_2O_2. The cation exchange
318 capacity of the biochar treated with 30% H_2O_2 almost doubled that of an untreated biochar
319 since the oxygen-containing functional groups in the surface of biochar, which were more
320 abundant in the activated biochars, exchanged with cations in solution. Xue et al. (2012)
321 found that treating a hydrochar with a 10% H_2O_2 solution increased Pb sorption capacity
322 compared to the unmodified hydrochar and attributed the increase to a greater abundance of
323 carboxyl functional groups that can form complexes with Pb. Although Xue et al. (2012)
324 observed similar mineral compositions in activated and unactivated biochars, the introduction
325 of acid or oxidising agents dissolves mineral components from within the biochar structure
326 and removes them from the biochar matrix. These minerals (e.g. P, Ca, Mg, K, Na,) are
327 particularly important for the removal of metal cations from water by some biochars due to
328 precipitation (Xu et al., 2013), so some acid treatments may reduce sorption by precipitation.

329 5.1.2.2. **Alkaline solutions**

330 The most common alkali treatment of biochar is with Group I metal hydroxides (KOH or
331 NaOH). Activation of biochars with metal hydroxides increases adsorption by increasing
332 porosity and surface area and by creating of a greater number of oxygenated functional groups
333 on the surface of the biochar. These oxygenated functional groups provide proton donating
334 exchange sites upon which metal cations such as Pb^{2+} chemically adsorb (Petrović et al.,
335 2016). Goswami et al. (2016) demonstrated that activation of biochar with KOH, followed by
336 pyrolysing to 350-550 ˚C opened up the partially blocked pores and enlarged the diameters of
337 smaller ones. The KOH and pyrolysis increased the surface area and increased adsorption of
338 Cd from aqueous solution by surface complexation. Hamid et al. (2014) provided further
339 evidence that Cu sorption on KOH activated biochar was due to chemical adsorption, as the
340 kinetics of sorption fitted a pseudo second order model and thermodynamic studies indicated

a spontaneous endothermic process. The increase in surface area resulting from modification of biochar with KOH also increases the adsorption of oxyanions from solution. Jin et al. (2014) also reported that maximum adsorption capacity of As(V) by biochar produced from municipal solid wastes was increased 1.3 times from 24 mg/g to 31 mg/g after activation with 2M KOH, due to an increase in surface area and the abundance of functional groups on the biochar surface. Pietrzak et al. (2014) compared two activation methods using NaOH, which comprised either pre- or post-pyrolysis activation of feedstock or biochar by physical mixing or by impregnation with a NaOH solution. The authors reported greater surface area and a higher iodine sorption capacity when activation was conducted by physical mixing of both the feedstock and the biochar with solid NaOH.

5.2.Biochar-based composites

Biochar based composites are produced by impregnating biochar with metal oxides, clays, organic compounds or carbonaceous materials, such as graphene oxide or carbon nanotubes, or by inoculation with microorganisms, to alter the surface properties of the biochar (Figure 4). Here the biochar is essentially used as a high-surface-area scaffold to support the materials being deposited. Composites are distinguished from chemical activation because they involve the creation of completely new functional groups on surfaces that did not previously exist on the biochar or feedstock surface.

5.2.1. Metal oxides

Biochars generally have a high surface area but a negative surface charge and high pH. These properties make biochars excellent sorbents for metal cations due to specific adsorption on oxygenated functional groups, electrostatic attraction to aromatic groups and precipitation on the mineral ash components of the biochar (Beesley et al., 2015), but poor sorbents for oxyanion contaminants (e.g. NO_3^-, PO_4^{3-} and AsO_4^{3-}). By exploiting the high surface area of biochars as a platform to embed a metal oxide with contrasting chemical properties (and

usually a positive charge), biochar-based composites are capable of removing negatively charged oxyanions from aqueous solutions. The objective of most methodologies to create metal oxide biochar-based composites is to ensure a homogenous spread of the metal over the biochar surface. The biochar is essentially used as a porous carbon scaffold upon which metal oxides precipitated to increase the surface area of the metal oxide.

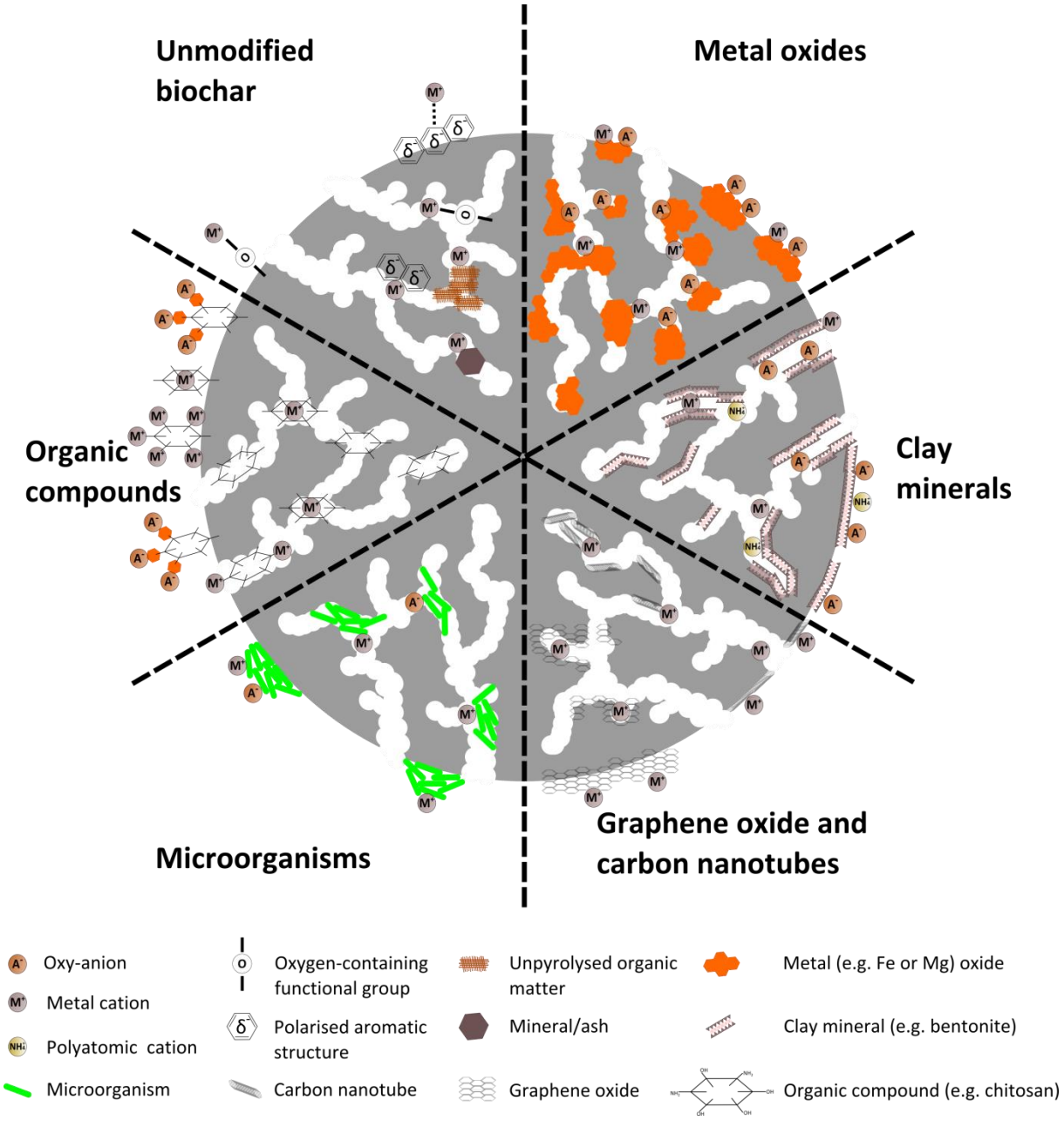

Figure 4. Conceptual model identifying the mechanisms of metal cation (e.g. Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}), oxyanion (e.g. PO_4^{3-}, AsO_4^{3-}) and polyatomic cation (e.g. NH_4^+) sorption to unmodified biochar and biochar modified with metal oxides, clay minerals, carbonaceous materials (graphene oxide and carbon nanotubes), microorganisms, and organic compounds.

Generally, impregnation of biochar with metal oxides is performed by soaking biochars or their feedstocks in solutions of metal nitrate or chloride salt solutions (Figure 5). The most frequently used impregnation agents in the literature are $FeCl_3$, Fe^0, $Fe(NO_3)_3$ and $MgCl_2$. After soaking biochar with metal salt solutions, the biochar is heated under atmospheric conditions (i.e. not low-oxygen conditions) at temperatures 50-300 °C to allow nitrates or chlorides to be driven off as NO_2 and Cl_2 gases and convert the metal ions to metal oxides.

Agrafioti et al. (2014) demonstrated that soaking rice husk and municipal waste biomass biochars in CaO, iron powder and $FeCl_3$ prior to pyrolysis created Ca, Fe^0 and Fe^{3+} modified biochars, respectively. These modifications increased the capability of the biochars to remove As(V), but not Cr(VI), from aqueous solution. This observation is supported by Fristak et al. (2017) who revealed a 20-fold increase in the sorption of As when corncob biochar was modified with $Fe(NO_3)_3$ after pyrolysis, but that the modification had negligible effect on sorption of the cationic lanthanide Eu.

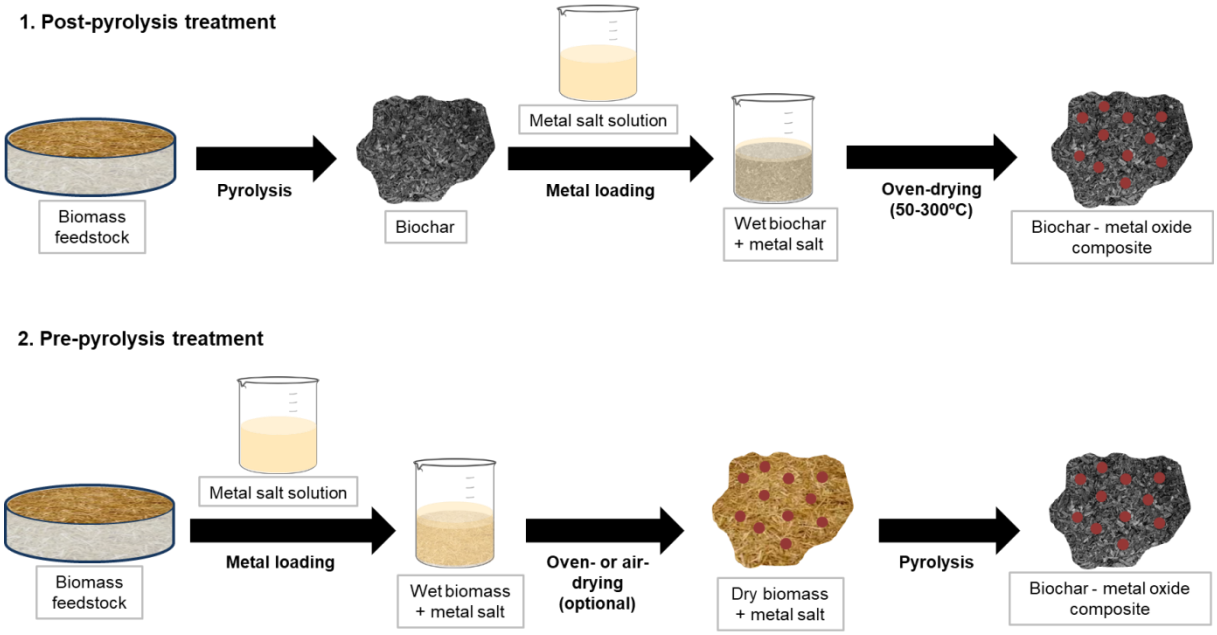

Figure 5. Diagram outlining the pre-pyrolysis and post-pyrolysis procedures used to modify biochars with metal salts to create metal oxide biochar-based composites.

Most metal oxide modifications result in a reduction in the surface area of the biochar due to clogging of pores with metal oxide precipitates (Rajapaksha et al., 2016; Zhou et al., 2017a). Michálešková-Richveisová et al. (2017) used the same method as Fristak et al. (2017) to modify biochars made from garden wood waste and wood chips as well as corncob, which resulted in a decrease in the surface area of the biochar due to the filling of micro- and mesopores with Fe. However, despite the lower surface area, modification increased PO_4^{3-} sorption capacity by a factor of 12 to 50 due to pH-dependent binding to positively charged functional groups on the biochar surface.

Several attempts have been made to exploit the magnetic properties of Fe to create magnetic biochars that are capable of removing both metal cation (Mohan et al., 2014) and oxyanion pollutants (Zhou et al., 2014) from contaminated media. The magnetic property of modified biochars enables the pollutant-loaded biochar to be removed from the media using a magnet. Wang et al. (2015b) created a magnetic biochar by pyrolysing pinewood biomass with hematite, a natural iron-oxide mineral, resulting in an As sorption capacity almost double that of the unmodified biochar. The modification of biochar to improve magnetic properties was developed further by Zhou et al. (2017b) by coating with a magnetised gelatin. The authors observed a 2.6 times increase in the maximum adsorption of As(V) from solution after biochar modification, attributed to the high electrostatic affinity of As(V) to iron-oxide particles and protonated oxygen-containing functional groups present on the biochar surface.

Biochar-based composites have also been produced by embedding oxides of Al, Mn and Mg on biochars and improving the sorption of both oxyanions (primarily As and P) and metal cations (particularly Pb). Zhang and Gao (2013) produced a biochar with high adsorption capacity for As and P from solution by modification with $AlCl_3$ to create a biochar-AlOOH nanocomposite, Wang et al. (2015a) modified biochar using $MnCl_2$ and found that, compared to the control, the manganese oxide-modified biochar displayed significantly improved

sorption capacitiy for As and Pb. Zhang et al. (2012) compared the modification of biochar produced from 5 different feedstocks by soaking the biochar in $MgCl_2$ and applying further thermal treatment at 600˚C. The MgO content in the modified biochars ranged from 8.3% to 26.1%, and the increased adsorption capacity for PO_4^{3-} and NO_3^- was attributed to the positive charge of the MgO that precipitated on the biochar surfaces. The potential of Mg-modification to increase the adsorption potential of biochar for metal cations was further explored by Jellali et al. (2016), who compared the adsorption of lead from solution by a biochar treated with $MgCl_2$ prior to pyrolysis to that of unpyrolysed cypress sawdust. The maximum adsorption capacity of the Mg-modified biochar was approximately 7.4 times higher than that of the sawdust.

Generally the sorption of oxyanions (PO_4^{3-} and AsO_4^{3-}) on the surface of metal oxide biochar-based composites is due to chemical adsorption or electrostatic attraction to the positively charged metal oxide embedded on the surface (Ren et al., 2015; Zhou et al., 2014), whereas sorption of cationic metals is due to chemical adsorption on oxygenated functional groups on parts of the biochar that remain unmodified (Tan et al., 2015), or co-precipitation within the metal oxide lattice (Zhou et al., 2017a).

5.2.1.1. **Modification of living feedstock biomass**

Yao et al. (2013) demonstrated an innovative method of biochar modification by irrigating tomato plants with Mg solution and subsequently pyrolysing the biomass to yield a Mg-rich biochar with an improved adsorption capacity for PO_4^{3-}, compared to the control. The results showed a strong correlation between the removal rate of P and the concentration of Mg in the biochar. While interesting, this modification methodology is time consuming, and may be prohibitively expensive.

442 5.2.1.2.**Electro-modification**

443 The efficiency and homogeneity of metal oxide deposition on the surface of biochar can be
444 improved by using an electric field to evenly deposit metal ions from the electrodes and the
445 electrolyte on the surface of the biochar. The application of an electrical field, using an Al
446 electrode to a solution containing a NaCl electrolyte deposited nano-sized aluminium crystals
447 of beochemite (AlOOH) on the surface of a marine macroalgae feedstock prior to pyrolysis
448 (Jung et al., 2015a). The resulting electro-modified biochar had a 45 times greater surface
449 area, and a well developed microporous structure, most likely due to the generation of strong
450 oxidising agents (HOCl and OCl^-) from the NaCl electrolyte. Maximum PO_4^{3-} sorption
451 capacity trebled, compared to the unmodified biochar. The optimum preparation parameters
452 were later identified for this electro-modification method as a current density of 39 mA/cm^2, a
453 pyrolysis temperature of 584 C˚, at a heating rate of 6.91 °C/min (Jung et al., 2016a). Electro-
454 modification was further exploited by Jung et al. (2015b) to prepare Mg/Al-biochar based
455 nanocomposites by using an Al electrode and $MgCl_2$ as an electrolyte, which increased the
456 PO_4^{3-} sorption capacity by a factor of ~28, compared to the previous paper. The use of electro-
457 modification not only results in a more homogenous distribution of metal oxides over the
458 surface of the biochar, but also considerably decreases the time required to create metal oxide
459 biochar based composites from a few hours to a few minutes.

460 **5.2.2. Clay minerals**

461 Impregnation of biochars with clay minerals, such as kaolinite, montmorillonite or bentonite,
462 can modify biochar composition and physical properties, resulting in enhanced sorption
463 capacity for oxyanions (e.g. PO_4^{3-}) and polyatomic cations (e.g. NH_4^+). To prepare clay
464 mineral biochar-based composites, the feedstock is generally mixed with a suspension of the
465 clay mineral prior to pyrolysis (Chen et al., 2017; Ismadji et al., 2016; Rawal et al., 2016; Yao
466 et al., 2014). Pre-pyrolysis mixing of bamboo with clay minerals (bentonite and kaolinite)

mixed with iron sulphate resulted in the incorporation of mineral phases into the biochar structure, revealed by high contents of Al, Fe and S in the modified biochar (Rawal et al., 2016). Similarly, Yao et al. (2014) reported increased contents of Al, Fe and Na in montmorillonite and kaolinite biochar composites produced from plant biomass feedstocks (bamboo, bagasse and hickory chips), indicating successful incorporation of both clay minerals into the biochar structure. X-ray diffraction analysis of a bentonite biochar-based composite produced by pyrolysis of cassava peel and bentonite revealed the typical basal spacing of the crystalline structure of the bentonite along with the amorphous structure of the biochar, indicating that bentonite structure remained after pyrolysis (Ismadji et al., 2016).

Chen et al. (2017) observed that mixing bamboo powder with montmorillonite prior to pyrolysis increased the surface area and the pore volume and diameter, partly due to the presence of layered montmorillonite. Layered surfaces have been observed by Scanning Electron Microscope imaging of clay modified biochar, resembling common clay structure morphology (Yao et al., 2014). However, high pyrolysis temperatures can lead to loss of structural water from the clay mineral, reducing the interlayer space of montmorillonite and ultimately reducing the pore diameter and volume of the modified biochar (Chen et al., 2017; Ismadji et al., 2016; Rawal et al., 2016).

The increased surface area of a montmorillonite modified biochar resulted in a greater adsorption capacity for NH_4^+ and PO_4^{3-}, compared to an unmodified biochar, but showed a stronger affinity for PO_4^{3-} than for NH_4^+ (Chen et al., 2017). NH_4^+ was mainly controlled by Van der Waals forces and partially by cation exchange, whereas phosphate was adsorbed through electrostatic interaction and ionic bonding between PO_4^{3-} and cations present in the montmorillonite (Chen et al., 2017). The maximum adsorption capacity was 12.5 mg/g for NH_4^+ and 105 mg/g for PO_4^{3-} and slow-release behaviours were exhibited for both these

nutrients, indicating a potential market for the saturated biochar-composite as a slow-release fertiliser.

A bentonite-biochar composite produced from cassava peel and activated with CO_2 at the final pyrolysis stage, presented ~150% greater sorption capacity for NH_4^+ than an unmodified biochar (Ismadji et al., 2016). This increase is ascribed to enhanced physical adsorption of NH_4^+ onto the surface of bentonite-biochar composite, together with its exchange with cations present in the interlayer of bentonite and a more developed microporosity due to activation with CO_2.

Deposition of MgAl-layered double hydroxides (LDH), as anionic clay minerals, within the biochar matrix increased the PO_4^{3-} sorption capacity of the resulting biochar-based composite with respect to unmodified biochars and other LDHs used as adsorbents. The enhanced phosphate adsorption was due to successful deposition and separation of the LDH nanosized particles on the biochar surface and increased sorption capacity either through anion exchange or surface adsorption (Zhang et al., 2013b).

5.2.3. Coating with carbonaceous materials (graphene oxide and carbon nanotubes)

Graphene oxide is a widely used precursor for the production of graphene and has shown great sorption capacity for metals, such as Cd^{2+}, Co^{2+} , Cu^{2+}, Pb^{2+} and Zn^{2+}, which chemically bind with the oxygen-containing groups present on the graphene oxide surface (Ren et al., 2012; Sitko et al., 2013; Zhao et al., 2011). Graphene oxide-biochar composites have been used to improve biochar sorption capacity (Shang et al., 2016; Tang et al., 2015). These composites are prepared by impregnation of the feedstock in a graphene oxide suspension before pyrolysis, which generally increases the surface area and creates more oxygen-containing functional groups than the unmodified biochar due to the incorporation of the graphene structure in the composite after pyrolysis (Shang et al., 2016; Tang et al., 2015).

Shang et al. (2016) found that Cr(VI) removal efficiency from aqueous solution by graphene oxide biochar-based composite prepared from hyacinth biomass was considerably higher than that of an unmodified biochar. The authors suggested that Cr(VI) sorption onto the composite was likely via electrostatic attraction of Cr(VI) coupled with Cr(VI) reduction to Cr(III) and Cr(III) complexation (Shang et al., 2016). Tang et al. (2015) mixed wheat straw with a suspension of graphene oxide at different biomass:graphene oxide ratios (0.1%, 0.5% and 1%) prior to slow pyrolysis at 600 ºC and studied the graphene oxide-biochar composite sorption characteristics for Hg^{2+} in aqueous solution. The Hg^{2+} removal efficiency increased with increasing the proportions of graphene oxide in the composite, with the highest load of graphene oxide (1%) removing 8.7% more Hg^{2+} from solution than the unmodified biochar. Fourier transform infrared spectroscopy indicated that mercury was primarily bound by oxygen-containing functional groups on the graphene oxide-biochar composite.

Biochar coated with carbon nanotubes (CNT) has been also synthesized and evaluated for its metal cation sorption capacity (Inyang et al., 2014; Inyang et al., 2015). For the CNT-biochar composites preparation, the biomass feedstock (sugarcane bagasse or hickory chips) was mixed with a CNT suspension, stirred, and oven-dried prior to pyrolysis. CNT were successfully incorporated to the biochar structure, resulting in higher surface area and pore volume and increasingly negatively charged surface with increasing CNT loading (Inyang et al., 2014). Improvement of Pb^{2+} sorption capacity with the CNT coating treatment was only observed when hickory was used as a feedstock, whereas no effect was found for the sugarcane biochar (Inyang et al., 2015). However, mixing the CNT with a surfactant (sodium dodecyl benzene sulfonate) prior to biomass impregnation improved the Pb^{2+} removal efficiency of both CNT-biochar composites (Inyang et al., 2015). Pb^{2+} was likely adsorbed through interaction (chemical binding or electrostatic attraction) with oxygen-containing groups in CNT-biochar composite surface (Inyang et al., 2015).

5.2.4. Microorganisms

Biochar provides a high surface area inert material to support the colonisation and growth of biofilms with desirable properties. The inoculation of microorganisms onto the surface of biochars has primarily been attempted to facilitate the biodegradation of organic contaminants, which is beyond the scope of this review. However, alongside biodegradation of naphthenic acids, Frankel et al. (2016) observed biosorption of metals from solution by biofilms on biochars colonised by microorganisms isolated from oil sands process water. Sorption of P and As was up to 6 and 7 times greater than uncolonised biochar, respectively, and up to 4 or 5 times greater than colonised and sterilised biochar.

5.2.5. Organic compounds

Biochars can be modified post-pyrolysis with organic compounds with functional groups that are capable of creating strong bonds with both the surface of the biochar and also pollutants from solution. Incorporation of amino groups onto the surface of biochar can enhance the pollutant sorption capacity by inducing strong complexation with the amino moieties. This modification can be achieved either by simple chemical reactions (Yang & Jiang, 2014) or by mixing biochars with polymers rich in amino groups, such as polyethylenimine or chitosan (Ma et al., 2014; Zhang et al., 2015; Zhou et al., 2014; Zhou et al., 2013).

Yang and Jiang (2014) prepared an amino-modified biochar with a commercial saw dust biochar by nitrification through electrophilic substitution reaction, using HNO_3 and H_2SO_4, followed by reduction with $Na_2S_2O_4$. Although no significant differences in the physical structure were found between the modified and unmodified biochar, the surface of the modified biochar had more functional groups, especially those associated to the amino moieties. The amino-modification resulted in 5 times greater Cu^{2+}sorption capacity which was strongly complexed by the amino groups present on the modified biochar surface (Yang & Jiang, 2014).

A rice-husk biochar, pre-treated with acid or alkali solutions, modified by mixing with polyethylenimine (PEI)/methanol solution, had a greater abundance of functional groups on its surface and was richer in N and O, confirming the incorporation of PEI to the structure (Ma et al., 2014). The presence of more amine functional groups enhanced the sorption capacity of the modified biochar for Cr(VI), which was partially reduced to Cr(III) during adsorption (Ma et al., 2014).

Zhou et al. (2013) prepared chitosan-biochar composites by mixing biochars produced from bamboo, sugarcane bagasse, hickory wood and peanut hull feedstocks with an acid chitosan solution. The composites had a smaller surface area than the unmodified biochars, probably due to the pore blockage by the incorporation of chitosan in the biochar structure, which was confirmed by higher N, H and O contents. Generally, modification with chitosan increased the metal cation sorption capacity of biochars, although some exceptions were found probably related to the lower surface area. Pb adsorption isotherms of chitosan modified bamboo biochar and characterisation Pb-laden composites suggested that Pb was adsorbed primarily due to an interaction with amine functional groups of chitosan (Zhou et al., 2013).

Chitosan has been also applied to improve the impregnation of biochars with metal oxides to produce magnetic biochars (Zhang et al., 2015; Zhou et al., 2014). When mixed with a γ-Fe_2O_3-biochar composite, more functional groups were incorporated into the chitosan- γ-Fe_2O_3-biochar composite, which showed promising results concerning Cr(VI) sorption from aqueous solution (Zhang et al., 2015). Similarly, a modified biochar produced using bamboo biochar, chitosan and zero valent iron (ZVI) particles at various ratios, showed much higher removal efficiency for Pb^{+2}, Cr(VI), As(V) and P than the unmodified biochar (Zhou et al., 2014). Coating biochar with chitosan alone (with no ZVI addition) enhanced the removal efficiency of Pb^{+2} and Cr(VI) due to the complexation capacity of the amine functional groups of chitosan, but the presence of ZVI further improved the removal of these metals. Whereas

590 the chitosan-only modified BC showed no sorption capacity for As(V) and P, the presence of
591 ZVI in the composite greatly increased the removal efficiency of As(V) and P, likely
592 adsorbed by electrostatic interactions with ZVI particles (Zhou et al., 2014).

593 **6. Future work**

594 Further development work will mainly optimise the choice of feedstock, pyrolysis
595 temperature, and conditions under which biochars are modified (e.g. temperature, rate,
596 concentration and choice of chemical compound, solid:solution ratio, mixing) in order to
597 obtain a versatile suite of enhanced biochars with highly predictable properties that can be
598 applied to multiple remediation scenarios. New developments should seek to find
599 compromises between the biochar feedstock, modification method and sorption performance
600 that minimises costs and maximises the breadth of technical applicability, while maintaining
601 long-term performance.

602 Biochar modification will inevitably raise the production costs, thus the profitability of using
603 modified biochars compared to other materials, such as activated carbons, as adsorbents
604 should be analysed for each specific case. The production and application costs of biochar as
605 adsorbent for pollutants in aqueous solutions depends on multiple factors that present some
606 uncertainties and can vary considerably. These include the origin and availability of the
607 feedstock; preparation of the raw material (cleaning, drying); costs of biochar production,
608 which will depend largely on pyrolysis conditions (slow *vs* fast, temperature); distribution
609 costs; the environmental impact and lifetime and regeneration after use (Alhashimi & Aktas,
610 2017). The economical assessment of using any adsorbent should also consider its efficiency
611 for a given contaminant or material. Physical activation of biochar would increase the energy
612 consumption costs, whereas chemical activation and production of biochar-based composites
613 would also include the price of reagents (Banerjee et al., 2016). In these cases, a particularly
614 challenging aspect of future optimisation is to decrease the quantity of chemicals required to

activate or modify the biochar produced to minimise costs of production while maintaining maximum sorption capacity by optimising the biochar:modifying agent ratio .

There is a considerable opportunity to develop biochars that act as scaffolds for nano-adsorbents which have received increasing research attention recently (Kyzas & Matis, 2015). Creating biochar-based nano-adsorbents would offer a huge potential to develop adsorbent nano-materials with a high surface area and a specific surface functionality while using as little materials as possible.

The stability of biochar-based composite modifications over time should be monitored in future experiments as some of the materials imbibed in the biochar matrix (e.g. metal compounds, C nanotubes, organic compounds) can leach away from the biochar if they are not well fixed. To address this issue, leaching tests are required. One scenario worthy of investigation is the stability of metal-biochar composites in acidic solutions (pH 4-5), to determine whether metals are released from the biochar matrix.

Another gap is the ecotoxicology of these new biochar formulations. Biochar itself has been shown to be good for environmental applications, but sometimes has been shown to contain toxic compounds (Soudek et al., 2016). Modifying or activating the biochar leads to chemical and physical changes that could potentially increase the toxicity (reactivity, presence of nanoparticles, metals, etc). For example, Shim et al. (2015) pointed out that activated biochars can induce toxicity to *Daphnia magna*. To ensure environmental protection, the toxicity of modified biochars needs to be evaluated to avoid undesirable impacts to aquatic organisms (Gonçalves et al., 2016).

Also important is the sustainability of modified biochars and how they may contribute to the circular economy. A considerable challenge facing the designers of biochars and activated or modified biochars is to enable the regeneration and re-use of the sorbent so that the ‘pollutant’

639 can be desorbed from the biochar surface and recovered. The biochar may then be used to
640 adsorb more pollutants from water. This is particularly important when considering disposal
641 of biochar after it has been used to remediate water. If the saturated biochar is considered
642 hazardous waste then disposal may be costly and so a re-usable sorbent offers environmental
643 and economic advantages. If the inorganic pollutant loaded on the biochar cannot be
644 efficiently desorbed and recovered then the saturated biochar may still be used as a resource.
645 For example, P and N saturated modified biochars could be of potential use in agriculture
646 (cropping) or ecological restoration (revegetation) as a slow release fertiliser when applied to
647 soils (Ismail & Hameed, 2016; Roy, 2016). Accordingly, biochars containing Cu or Zn may
648 be useful as micronutrient fertilisers.

649 **7. Conclusions**

650 The development of methods to modify biochars to enhance their inorganic pollutant sorption
651 capacity or to expand the breadth pollutants that they can be removed from aqueous solution
652 is in its infancy. Physical and chemical activation of biochar can increase the surface area and
653 increase the abundance of oxygenated functional groups to increase cation adsorption.
654 Embedding materials on the surface of biochar can alter the properties of the surface by
655 creating biochar-based composites, enabling the adsorption of different pollutants. Research
656 into biochar-based composites have primarily been progressed by embedding iron or
657 manganese oxides to increase oxyanion sorption capacity.

658 The E-supplement contains a table which classifies the inorganic contaminants of primary
659 concern classified by their chemical behavior and includes citations to peer reviewed articles
660 that identify their sources in water.

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