Engineered biochar as adsorbent for the removal of contaminants from aqueous medium

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ABSTRACT

Biochar is a relatively low cost, sustainable product which can be utilised in the removal of both inorganic and organic contaminants from aqueous media. This chapter outlines the mechanisms of immobilisation for both inorganic and organic contaminants and summarises the key properties that underpin these processes. Immobilisation as a result of cation exchange, complexation, electrostatic interactions, Cation- π bonding, precipitation and reduction is discussed for inorganic contaminants and immobilisation due to H-bonding and charge assisted H-bonding (CAHB), π-π Electron Donor Acceptor (EDA) interaction, electrostatic interaction and steric effect is discussed for organic contaminants. The properties examined include the role of functional groups, cation exchange capacity, specific surface area and pH for inorganic contaminants and specific surface area, aromaticity and polarity for organic contaminants. The effect of raw materials and pyrolysis conditions on these properties is reviewed. Future research needs to bridge the knowledge gained from laboratory work and field work to support the effective use of biochar in real world environments.

Key words: biochar, contaminated water, mechanisms, properties, heavy metal, inorganic contaminants, organic contaminants, immobilisation, sorption

Introduction

Biochar is defined as a porous, carbonaceous material that is produced by biomass pyrolysis at temperatures ranging from 350 - 1000°C under limited oxygen conditions (European Biochar Foundation, 2016). During pyrolysis highly aromatic clusters are formed which are responsible for several key features of biochar, specifically it´s high chemical stability and high porosity. Biochar is reported to have several functions such as the ability to sequester carbon, enhance soil fertility and remediate environmental contaminants including the removal of contaminants from aqueous media (Inyang *et al.*, 2016; Kätterer *et al.*, 2019). The use of biochar in the remediation of inorganic and organic pollutants has been highlighted for various aqueous media such as road runoff (Cairns *et al.*, 2020), mine waters (Bandara *et al.*, 2020), stormwater (Boehm *et al.*, 2020) drinking water (Hu *et al.*, 2019) and biologically treated wastewater (Hagemann *et al.*, 2020). Its attractiveness is further enhanced due to its relatively low cost, simple production process and versatility in utilizing renewable raw material , including biomass waste materials (Ahmad *et al.*, 2014; Zhang *et al.*, 2015; European Biochar Foundation , 2016; Wang *et al.*, 2018b; Xiao *et al.*, 2018).

Biochar itself is a reasonably broad term which covers production from a vast number of different biomass raw materials produced at different pyrolytic temperatures yielding biochar with different characteristics. Essentially raw material, pyrolysis and modification such as the addition of minerals, activation or magnetisation alter the efficacy and the mechanisms of the biochar to remediate contaminants in aqueous media. Comparative studies primarily review either raw material, pyrolysis temperature or modified vs unmodified biochar to review

sorption capacity or mechanisms (Table 1).

Raw material category	Biochar raw materials	Pyrolysis temperature (°C)	Maximum sorption capacity mg/g	Contaminant(s)	Major removal mechanisms	Author
Plant Biomass	Oak bark	400 and 450		As, Cd, Pb	ion exchange	Mohan *et al.* , 2007
	Pine bark			As, Cd, Pb		
	Oak wood			As, Cd, Pb		
	Pine wood			As, Cd, Pb		
	lucerne shoot	550		Cd, Cu	precipitation, complexation and electrostatic interaction	Bandara et al, 2020
	Norway spruce	450-500		Cd, Cu, Pb, Zn	electrostatic attraction	Cairns et al., 2020
	Norway spruce	450-500		Cd, Cu, Pb, Zn	electrostatic attraction and precipiation	
	Norway spruce	450-500		Cd, Cu, Pb, Zn	electrostatic attraction and precipiation	
	Tobacco stem	300-700		Cd	cation-p interaction, precipitation	Zhou et al., 2018
				Cu	complexation	
				Pb	Precipitation	
	Canna indica	500	125.8	Cd	precipitates, cation exchange, binding to oxygen-containing groups	Cui et al., 2016
	Pennisetum purpureum Schum	500	119.3	Cd	precipitates, cation exchange and binding to oxygen-containing groups	
	KMnO4 modified	600	28.1	Cd	surface adsorption	Wang *et al.* , 2015
			34.2	Cu	surface adsorption	
			153.1	Pb	surface adsorption	
	Miscanthus	300	11.4	Cd	surface sorption, precipitation	Kim et al, 2013
		400	11.99	Cd	surface sorption, precipitation	
		500	13.24	Cd	surface sorption, precipitation	
		600	12.96	Cd	surface sorption, precipitation	
	honey mesquite	200, 300, 350,		Cd, K	ion exchange, cation-pi bond	Harvey et al,. 2011
	cord- grass	200, 300, 350,		Cd, K	ion exchange, cation-pi bond	
	loblolly pine	200, 300, 350,		Cd, K	ion exchange, cation-pi bond	
	Anaerobically	600		Cd, Cu, Pb, Ni	precipitation and surface adsorption	Inyang *et al.* , 2011
	Sugarcane bagasse	600		Cd, Cu, Pb, Ni	surface adsorption	
	Hardwood mix	450	12.52	Cu	H bonding	Chen *et al.* , 2011
			11	Zn	H bonding	
	Straw	600	6.79	Cu	H bonding	
			4.54	Zn	H bonding	
	Celery	500 and 350	288 - 304	Pb	precipitation, cation exchange and surface complexation	Zhang *et al.* , 2017
	Wheat straw pellets	550		Ni	cation exchange, electro- static adsorption and surface precipitation	Shen et al, 2017
	Acacia wood chip	550	4.02	Zn	precipitation, chelation (complexation)	Van Hien et al, 2020
Sewage / Manure	Dairy manure	350	7.28-15.68	Cd	complexation, precipitation	Xu, Cao and Zhao, 2013
			4.16-8.96	Cu	complexation, precipitation	
			13.45-	Pb	complexation, precipitation	
			4.23-9.1	Zn	complexation, precipitation	
	Broiler litter	350 and 700		Cd, Cu, Ni, Pb	coordination by π electrons (CdC) of carbon and precipitation.	Uchimiya *et al.* , 2010
	Magnetised Sewage sludge	400	249	Pb	electrostatic attraction, ion exchange, complexation, precipitation	Ifthikar *et al.* , 2017
	Sewage sludge	550	30.88	Pb	coordination with organic hydroxyl and carboxyl functional groups, coprecipitation and complexation	Lu *et al.* , 2012
	Dairy manure	500	140.76	Pb	precipitation	Cao *et al.* , 2009
Food Waste	Nut shells	600		Cd, Pb	ion exchange	Trakal *et al.* , 2014
	Plum stones			Cd, Pb	ion exchange	
	Wheat straws			Cd, Pb	ion exchange	
	Grape stalks			Cd, Pb	ion exchange	
	Grape husks			Cd, Pb	ion exchange	
	Rice husk	350	>54.432	Cd	complexation, precipitation	Xu, Cao and Zhao, 2013
			>31.104	Cu	complexation, precipitation	
			>100.602	Pb	complexation, precipitation	
			>31.59	Zn	complexation, precipitation	
	peanut	400		Cr (III)	complexation	Pan et al., 2013
	soybean	400		Cr (III)		
	canola	400		Cr (III)		
	rice straw	400		Cr (III)		
	Sugar Beet Tailing	300	123	Cr (VI)	electrostatic attraction, reduction and complexation	Dong et al., 2011
Other	Sediment	400 and 500		Cd, Cu, Pb	cation–pi bond	Dong *et al.* , 2014

Table1. Immobilisation mechanisms of inorganic contaminants by biochar produced from different raw materials

Immobilisation of inorganic contaminants

The key immobilization mechanisms for inorganic contaminants in aqueous media by biochar are: cation exchange, complexation, electrostatic attraction, cation π bonding, reduction and subsequent sorption, and precipitation (Figure 1). It is worth noting that these mechanisms do not work in isolation and often several mechanisms are relevant at the same time (Ramola et al 2020a).

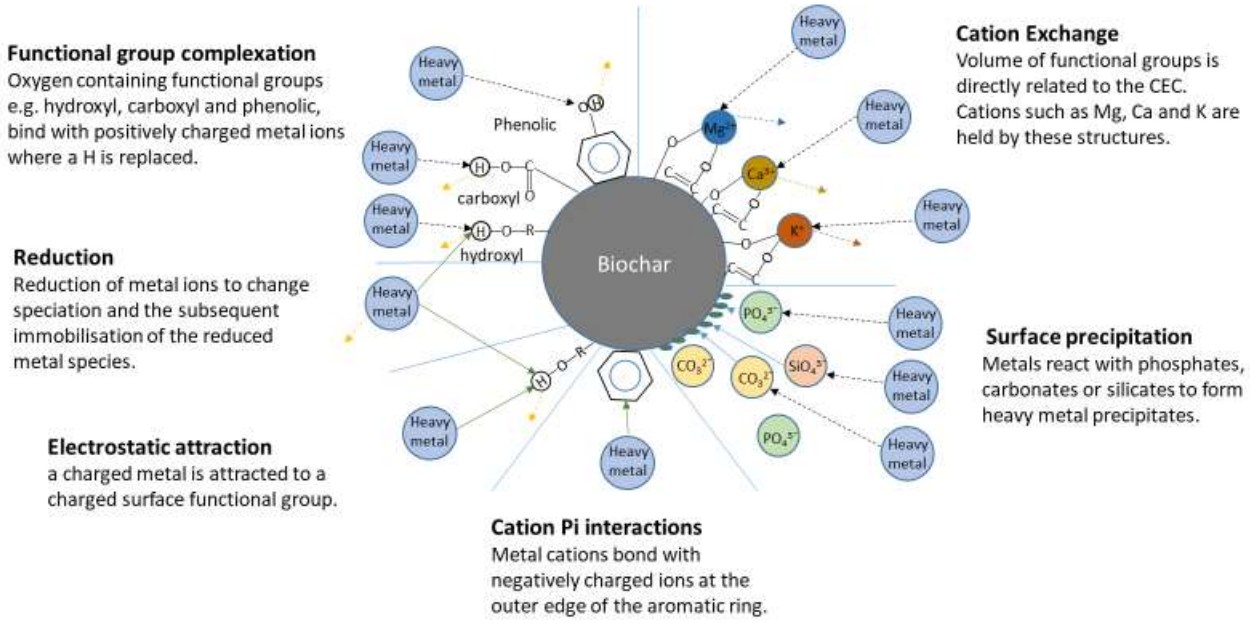

Figure 1. The six major mechanisms of heavy metal immobilization by biochar

Cation exchange

Cation exchange occurs most notably at early stage adsorption (Mohan *et al.*, 2007; Uchimiya *et al.*, 2010; Ifthikar *et al.*, 2017; Shen *et al.*, 2017) . During cation exchange the biochar releases exchangeable cations such as alkali and alkaline earths, typically Mg, Na, K

and Ca (Kumar *et al.*, 2016). These cations are effectively replaced by heavier metal cations found in the aqueous media which bind to the biochar in their stead. Immobilisation mechanisms often do not work in isolation but rather work simultaneously or are intrinsically linked. Studies, such as Mohan *et al.* (2007), cite several other mechanisms working alongside cation exchange in the remediation of inorganic contaminants i.e. precipitation and physical adsorption. In a similar vein cation exchange capacity (CEC) is recognised as being controlled by surface oxygen related functional groups (Trakal, Šigut, *et al.*, 2014; Ding *et al.*, 2016), these functional groups also being of great importance in the remediation of inorganic contaminants through complexation.

Complexation

Several authors cite functional group complexation as a major mechanism of immobilization specifically of transition metals such as Cr, Cu and Cd and post transition metals such as Pb (Lu *et al.*, 2012; Pan, Jiang and Xu, 2013; Cui *et al.*, 2016; Peng *et al.*, 2017). Complexation occurs when a H ion is replaced in functional groups such as phenolic, carboxy or hydroxyl (Figure 1) (Xu, Cao and Zhao, 2013; Dong *et al.*, 2014). Complexation is cited in studies with a variety of raw materials including sewage / manure (Weiwen Zhang *et al.*, 2020), food waste such as millet bran (Qiu *et al.*, 2019) and plant biomass (Wang *et al.*, 2018) (Table 1). Again, complexation is often described as working in conjunction with other mechanisms. Lv *et al.* (2018) reported complexation working alongside electrostatic interaction to remove Pb and Cu from aqueous solution.

Electrostatic interactions

Electrostatic interaction occurs between positively charged metals, such as Pb^{2+}, and the negatively charged surface of the biochar, particularly with a proliferation of oxygenated functional groups such as -COOH or -OH (Cui *et al.*, 2015; Lv *et al.*, 2018). Electrostatic attraction is a weaker process than precipitation or complexation and as a result metals immobilised via this mechanism are more susceptible to desorption (Bandara *et al.*, 2020). During their study Bandara *et al.* (2020) described the major mechanisms of Cd and Cu removal as electrostatic interaction with O-containing functional groups, surface complexation and precipitation. Ifthikar *et al.* (2017) also saw electrostatic attraction as being involved in the immobilisation of Pb alongside ion exchange, complexation and precipitation; electrostatic attraction was linked specifically to carboxyl groups. Cui *et al.* (2016) proposed

that electrostatic interactions are likely the primary driving force for Cd sorption on wetland plant derived biochar, however even here it is indicated that electrostatic interaction is not the sole mechanism of Cd sorption with complexation playing a role. Ramola et al. (2020 b) found electrostatic interaction to be one of the important mechanisms between Pb ions and mineral groups i.e. bentonite and calcite present in biochar-bentonite composite and biochar-calcite composite respectively prepared at 700ºC.

Cation- π bonding

Cation- π bonding is a stabilizing electrostatic interaction of a cation with the polarizable π electron cloud of an aromatic ring. During the pyrolysis of biochar graphene sheets are formed with aromatic structures (Wang *et al.*, 2020). Within these aromatic structures are electron rich domains on the edge of the aromatic structure which have been seen to attract inorganic contaminants such as Cd (Harvey *et al.*, 2011a). Uchimiya *et al.* (2010) recognised the sorptive interactions between d-electrons of metals and aromatic π-electrons of the biochar as one of the primary mechanisms for the retention of Ni and Cd by broiler litter biochar. Xu, Cao, Zhao, *et al.* (2013) also found interactions between d-electrons of metals and aromatic π-electrons when using dairy manure derived biochar, however their study reported that this was important for Zn and Cd remediation but less so for Cu. Kim *et al.* (2013), Yuan *et al.* (2020) and Qiu *et al.* (2019) also recognised the positive impact of aromaticity on adsorption of Cd.

Precipitation

In dependence of pH, metals can react with anions including CO_3^{2-}, PO_4^{3-} and SiO_4^{3-} to form solid precipitates (Šráček and Zeman, 2004). Again raw material is critical to this process being the main driver of the availability of these mineral components (Lu *et al.*, 2012; Xu, Cao and Zhao, 2013). Ifthikar et al. (2017) found silica co-precipitation to be of importance in the remediation of Pb by sewage sludge biochar due to the abundance of silica in the sewage sludge raw material. Precipitation was also significant in Zhang et al.'s (2017) study of celery derived biochar, however due to the characteristics of the raw material carbonate rather than silica co-precipitation was evident. The importance of raw material is further highlighted by Arán *et al.* (2017) who reiterated that the formation of metal carbonates and phosphate precipitates is favoured in biochar from mineral-rich raw material. Several studies assert that precipitation is the primary mechanism for immobilization (Cao and Harris, 2010;

Inyang *et al.*, 2012; Lu *et al.*, 2012; Xu, Cao and Zhao, 2013). These studies typically use a raw material of sewage sludge / manure or an amended raw material which provides a high pH and high levels of phosphate and carbonate to be released to precipitate with metals (Inyang *et al.*, 2012). However, precipitation is usually not the sole immobilization mechanism even when such mineral rich raw materials are used. In Xu, Cao and Zhao's (2013) study where P rich dairy manure was used as a raw material, electrostatic attraction and precipitation were both seen to be the governing mechanisms for the removal of Pb, Cu, Zn and Cd. Similarly , Van Hien *et al.*'s study (2020) illustrated the importance of precipitation alongside complexation in the immobilization of Zn.

Reduction

Metals can be reduced by biochar enabling the reduced metal species to be immobilised. Dong *et al.* (2011) reported that due to its high redox potential, Cr(VI) is easily reduced to Cr(III) under acidic conditions in the presence of organic matter. In Dong et al's study, the immobilisation of Cr occurred by electrostatic attraction of the negatively charged Cr(VI) to positively charged surface sections of a sugar beet biochar and reduction of Cr(VI) to Cr(III) facilitating complexation with functional groups. Cr(VI) reduction to Cr(III) was also reported by Mohan *et al.* (2011) in their study of oak biochar; by products of lignin pyrolysis such as catechol were seen to act as reducing agents as well as being important constituents of units that chelate Cr allowing the biochar to both reduce and bind Cr cations. Klüpfel *et al.* (2014) also highlight the importance of the pyrolysis process by demonstrating that new redox active moieties can be formed in the charring process. Bogusz, Oleszczuk and Dobrowolski, (2015) assert that this reduction can happen in metals with a positive normal potential such as Cu but not with metals such as Cd and Zn that have a negative normal potential.

Key material properties for inorganic contaminant immobilization

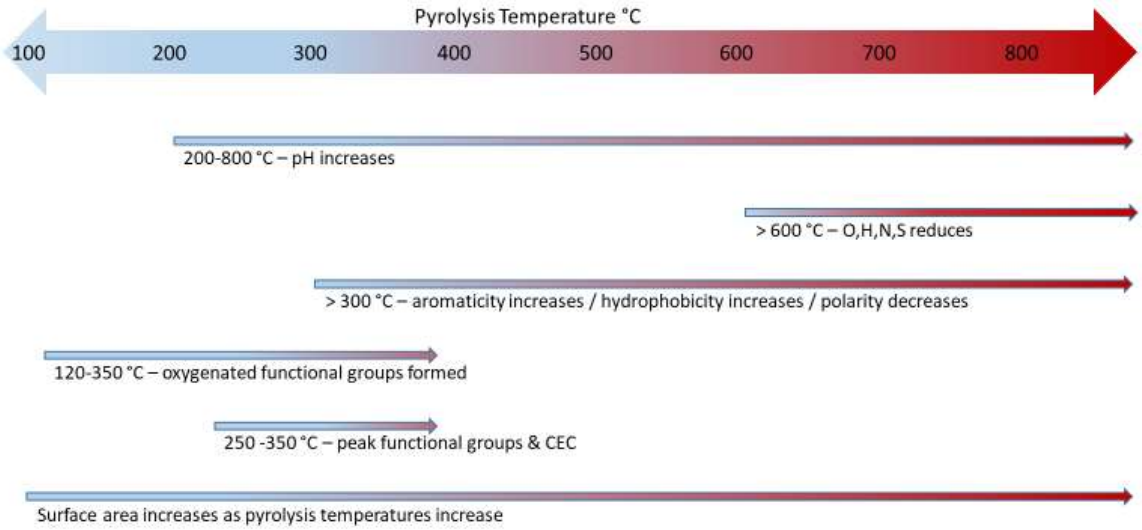

FIGURE 2. Biochar property changes as a result of pyrolysis temperature

Functional Groups

Surface functional groups of biochar are essential to several immobilisation mechanisms including cation exchange, electrostatic attraction and complexation. Ding *et al.* (2016) discuss the increase in cation exchange of the modified biochar as being resultant from the increase of oxygenated functional groups most notably carboxyl and hydroxyl groups. Other studies, such as Kharel *et al.* (2019) and Huff *et al.* (2018) acknowledge the role of functional groups in cation exchange and have specifically tried to increase carbonyl, carboxyl and hydroxyl groups to increase CEC. Functional groups such as carboxyl and phenolic groups also underpin electrostatic interactions as a charged surface to interact with a given contaminant (Cui *et al.*, 2015). Hydroxyl, carboxyl and phenolic groups also enable complexation to take place when a H ion is replaced by a metal (Trakal, Bingöl, *et al.*, 2014; Wang *et al.*, 2018b). The formation of these functional groups depends on raw material properties and pyrolysis temperature.

Trakal et al. (2014) suggests that differences in the relevance placed on functional groups can be explained by differences in pyrolysis temperature with studies around 350°C giving greater importance to functional groups and studies around 550-600°C attributing less

significance to functional groups as the levels of O reduce. Oxygenated functional groups, such as carboxyl, carbonyl and hydroxyl, start to form at ~120°C in the first stages of pyrolysis where oxygen is more abundant and continue until around 350°C (figure 2) beyond which the O / C ratio is lowered (Lehmann and Joseph, 2009). Studies such as Gray *et al.* (2014) and Wei Zhang *et al.* (2020) have recorded a decrease in these oxygenated functional groups as pyrolysis temperatures rose, with Gray recording a decrease from 370 to 500°C and a further decrease to elimination from 500 °C to 620 °C. Similarly in a comparative study Chen et al. (2011) saw that pyrolysis of hardwood at 450 °C resulted in a larger number of functional groups and a higher O/C ratio than straw pyrolyzed at 600 °C. Although temperatures below 450 °C appear to be the best conditions for oxygenated functional groups, at pyrolysis temperatures as high as 600°C the adsorption by hickory wood biochar was still seen to be primarily driven by functional groups (Wang et al., 2015). Whilst raw material and pyrolysis temperature are the primary drivers of the abundance of functional groups they can also increase as a result of oxidation; such oxidation can be a due to natural aging or by chemical oxidation such as with HNO_3-H_2SO_4 or NaOH-H_2O_2 (Fan *et al.*, 2018)

Cation Exchange Capacity

CEC is the key property for sorption through cation exchange. Raw material and pyrolysis temperature are key drivers of CEC (Trakal *et al.*, 2014). Studies show peak CEC to occur at pyrolysis temperatures of 250 – 350°C where functional groups are most abundant, and a diminishing of CEC as pyrolysis temperatures rise past this level (Figure 2), (Harvey *et al.*, 2011b). Mohanty *et al.* (2018) concur with the paradigm that low pyrolysis temperature (250–350 °C) lead to high CEC and suggest that this is as a result of the considerable volatile organic matter remaining on biochar rather than it being lost at higher temperatures. If a raw material has high levels of alkali and / or alkaline earths it has the potential for these elements to be available in the biochar for cation exchange. Ifthikar *et al.* (2017) used sewage sludge as a biochar raw material which contained high levels of Ca and Mg, as a result the exchange of these alkaline earth metals was shown to be involved in the early stage adsorption of Pb. Similarly the use of celery biomass as a raw material, which is rich in alkali and alkaline earth metals, resulted in cation exchange playing a significant role in adsorption (T. Zhang *et al.*, 2017). Conversely, in studies such as Mantonanaki *et al.* (2016) or Van Hien *et al.* (2020) where the raw material, such as coffee grounds or bamboo, have low levels of Ca, K or Mg, cation exchange is either not highlighted or is described as neither a driver nor a good predictor of adsorption.

Specific Surface Area

Specific surface area (SSA) is a property of biochar that is very often cited by authors due to its importance in the immobilisation of contaminants in aqueous media; the higher the SSA the more sites are available for sorption to occur. Ifthikar *et al.* (2017) in their study of magnetic sewage sludge biochar, described surface area as critical in the adsorption of Pb. When they compared magnetised and unmagnetised sewage sludge biochar an increase in surface area allowed access to a large number of active sites for remediation to take place increasing removal rates. In their study of oak bark and pine wood biochar, Mohan *et al.* (2007) also suggest that higher adsorption levels were at least partially due to the higher surface area of the oak bark biochar. It is worth noting that a higher surface area does not always result in higher rates of immobilisation particularly if chemisorption rather than physisorption is the driving factor. In studies where precipitation is the major immobilisation mechanism such as Cao and Harris, (2010) and Xu, Cao and Zhao,(2013) surface area is not a major factor. Xu, Cao and Zhao's study (2013) demonstrated that dairy manure biochar had lower surface areas than rice husk biochar (5.61m^2g^{-1} vs 27.8 m^2g^{-1}) but higher sorption (486 mmol kg^{-1} vs 65.5-140 mmol kg^{-1}) as a result of precipitation being the driving mechanism.

As with functional groups, surface area is primarily driven by raw material and pyrolysis temperature (figure 2). Wei Zhang *et al.* (2020) describe a surface area increase as a result of temperature increase with rice straw biochar pyrolysed at 400°C having a surface area 0.367 m^2g^{-1} which increased to 51.105 m^2g^{-1} at 700°C. The largest surface area increase occurred between 600 to 700°C with an increase from 8.598 m^2g^{-1} to 51.105 m^2g^{-1}. Ahmad *et al.* (2012) report a surface area increase from 6m^2g^{-1} to 448m^2g^{-1} when temperatures increased from 300 to 700°C. Chen *et al.* (2018) demonstrate an increase from 1.26 m^2g^{-1} to 351 m^2g^{-1} with an increase in temperature from 300 to 900°C. As explained by Kercher and Nagle, (2003) SSA increases due to the condensation of biomass to graphene like carbon structures forming pyrogenic micro- and mesopores. Hale *et al.* (2016) describe the increase in SSA at high temperatures as a result of amorphous components arranging into turboclastic chrystallites. Chen *et al.* (2011) and Ippolito *et al.* (2020) assert that it is raw material rather than pyrolysis temperatures play the major role in the SSA of biochar.

pH

The pH of biochar is usually alkaline (Lehmann and Joseph, 2015) and as a result it increases and buffers its environments pH. These increases are dependent on raw material and pyrolysis temperatures (figure 2), (Fidel *et al.*, 2017). Studies have shown that the solution pH which effects the metal speciation can be influenced by the pH of the biochar (Cairns *et al.*, 2020), the increase in aqueous media pH can induce changes in metal speciation that are favourable for cationic metals such as Pb or Cd and unfavourable for anionic metalloids such as As. The pH of the aqueous solution is cited as one of the main variables affecting the sorption process influencing both the speciation of the metals and the surface charge of the sorbent (Kilic *et al.*, 2013). pH is a key determinant of metal solubility and bioavailability; the more bioavailable a metal is, the more toxic it is to the surrounding ecosystem (Charters, Cochrane and O'Sullivan, 2016). Metals such as Pb and Cd are more mobile at low pH whereas metalloids such as As are more mobile at high pH and as a result the maximum sorption of these metals is seen at different pH (Mohan *et al.*, 2007). Metals that are more mobile at low pH such as Cd, Co, Ni, Pb and Zn are removed best at pH of ~5-6, above pH levels where the metals are mobile (Chen *et al.*, 2011; Lu *et al.*, 2012; Kilic *et al.*, 2013; Trakal, Bingöl, *et al.*, 2014). In contrast, the removal of metalloids that are more mobile at higher pH, such as As, fall when pH is above 8 and the metalloid is more mobile (Navarathna *et al.*, 2019). In terms of cationic heavy metals Lu *et al.* (2012) cited surface charge as being the primary mechanism for Pb sorption and that higher surface charge was driven by increasing pH from 2 to 5. Increasing adsorption was attributed to deprotonation as pH increased. Chen *et al.* (2011) also saw an increase in adsorption until a pH of 5 due to competition between protons and metal cations for sorption sites, with a decrease over pH 5 due to the formation of hydroxide complexes. Despite pH 5 being suggested as the pH of maximum sorption by Lu *et al.* (2012) and Chen *et al.* (2011) most studies cite a pH of 6 as being ideal. In their study of activated maple wood biochar Wang *et al.* (2018) saw that with an increasing pH there was an increasing surface charge due to the deprotonation of functional groups up to a pH of 6, above which soluble hydroxyl complexes or surface precipitation formed. Kilic *et al.* (2013) reported similar findings in their study where they saw an increase in electrostatic charge from pH 2 to 6, improving Ni and Co interaction with binding sites. At above pH 6, formation of hydroxylated complexes which compete for active sites were again found. Tran *et al.* (2017) were also in agreement in their study where they investigated the effect of solution pH on the adsorption process of Cu(II) in solutions with pH values from 2.0 to 6.0. They found that up to pH 6 the negative charge of carboxyl groups increased improving adsorption of Cu. Studies also show pH to have an impact on co-

precipitation with pH influencing the speciation of metals (Kilic *et al.*, 2013). Inyang *et al.* (2011) suggests that the co-precipitation of Pb and CO_3^{2-} forming hydrocerrusite and cerrusite was as a result of high pH. Similarly Cao and Harris, (2010) note that high pH (~pH 10) allows Pb co-precipitation with both phosphate and carbonate. Biochar pH is effected by pyrolysis temperatures with increases of pH demonstrated from 370 to 600°C (Gray *et al.*, 2014), 350 to 750°C (Domingues *et al.*, 2020) and 300 to 700°C (Yuan, Xu and Zhang, 2011; Ahmad *et al.*, 2012). Ramola et al. (2020b) found a significant increase in adsorption capacity of biochar-calcite composite prepared at 700 ºC, with increase in pH from 3 to 9. This may be because calcite form stronger bond with Pb under alkaline conditions.

Modification

A number of papers study the effect of modifying biochar to enhance adsorption mechanisms of inorganic contaminants in aqueous media. These modifications generally take the form of activation (creating activated carbon / activated biochar), addition of minerals, or magnetisation.

Several studies look to activate the pristine biochar, increasing sorption through an increase in specific surface area (SSA) and modifying surface chemistry, creating activated carbon from biomass sometimes referred to as activated biochar. Methods to chemically activate biochar include the addition of chemicals such as hydrogen peroxide (Wang *et al.*, 2018), sodium hydroxide (Ding *et al.*, 2016) or zinc chloride (Ifthikar *et al.*, 2017). Each of these studies demonstrated an increase in functional groups and surface area leading to an increase in sorption capacity. However, these methods do increase production costs and produce contaminated effluents during production (Hagemann *et al.*, 2020). Physical rather than chemical methods using steam, oxygen or carbon dioxide are also used to increase SSA and remove contaminants (Uchimiya, Isabel M. Lima, *et al.*, 2010; Grycová, Koutník and Pryszcz, 2016; Hagemann *et al.*, 2020)

The addition of minerals to modify biochar commonly takes place pre pyrolysis such as in Wang *et al's*, (2015) study where potassium permanganate ($KMnO_4$) was added to increase oxygen functional groups. Under high temperature, $KMnO_4$ was converted to MnO_x particles

306 onto the surface of the biochar which resulted in an increase in hydroxyl and carboxyl
307 functional groups due to oxidising effect of $KMnO_4$. These modifications increased the
308 sorption capacities of biochar by 2.1 times for Pb, 2.8 times for Cu and 5.9 times for Cd. Gan
309 *et al.* (2015) used ZnO modification to adsorb Cr (VI) ions. Again, the raw material was pre-
310 treated with ZnO prior to pyrolysis. The sorption of the modified biochar was 1.2-2 times
311 greater than the sorption of the pristine biochar.

312 Magnetising biochar is a further direction investigated by Yuan *et al.*(2020) Mohan et al.
313 (2014) and Chang et al. (2006), who introduced Fe^{3+} and / or Fe^{2+} to the pristine biochar to
314 increase the sorption of metals. Magnetisation was carried out with a variety of raw materials
315 including sewage sludge (Ifthikar et al., 2017), oak wood and bark (Mohan et al., 2014) and
316 chitosan (Chang, Chang and Chen, 2006). Each of these studies introduce Fe via solution that
317 is mixed with the biochar and then oven dried to bind the Fe to the surface of the biochar.
318 SSA has been reported to increase with magnetisation in some studies (Chang, Chang and
319 Chen, 2006; Mohan *et al.*, 2014; Ifthikar *et al.*, 2017), however in Mohan et al.'s study (2014)
320 this was dependant on raw material with oak bark SSA decreasing with magnetisation but
321 SSA increasing with oak wood magnetisation. Biochar loaded with Fe^{3+} increased the
322 oxygen-containing functional groups and enhanced the ability of complexing Cd (Yuan *et al.*,
323 2020). Ramola et al. (2014) observed that iron impregnated tyre biochar (FeTy) was able to
324 remove Pb better than its pristine biochar. The maximum removal of Pb by FeTy was 95%
325 that followed Temkin adsorption isotherm.

326

327 **Immobilization of organic contaminants**

328

329 As with inorganic contaminants in aqueous media several mechanisms have been
330 documented in the removal of organic contaminants primarily H-bonding and charge assisted
331 H-bonding (CAHB), π-π Electron Donor Acceptor (EDA) interaction, electrostatic interaction
332 and steric effect. These are driven by the structure and properties of the biochar, in particular
333 specific surface area (SSA), aromaticity which can be approximated by the molar H/C ratio
334 and polarity which can be approximated by the molar O/C ratio. Sorption behaviour differs
335 strongly between aromatic and aliphatic compounds, as well as neutral, polar, anionic,
336 cationic and zwitterionic compounds (Hale *et al.*, 2016; Sigmund *et al.*, 2020). The types of

organic contaminants found in aqueous media that have attracted the most concern and attention include pesticides, herbicides, polycyclic aromatic hydrocarbons, dyes, and antibiotics which are structurally diverse (Qiu et al., 2009, Beesley et al., 2010, Zheng et al., 2010, Teixidó et al., 2011, Xu et al., 2012).

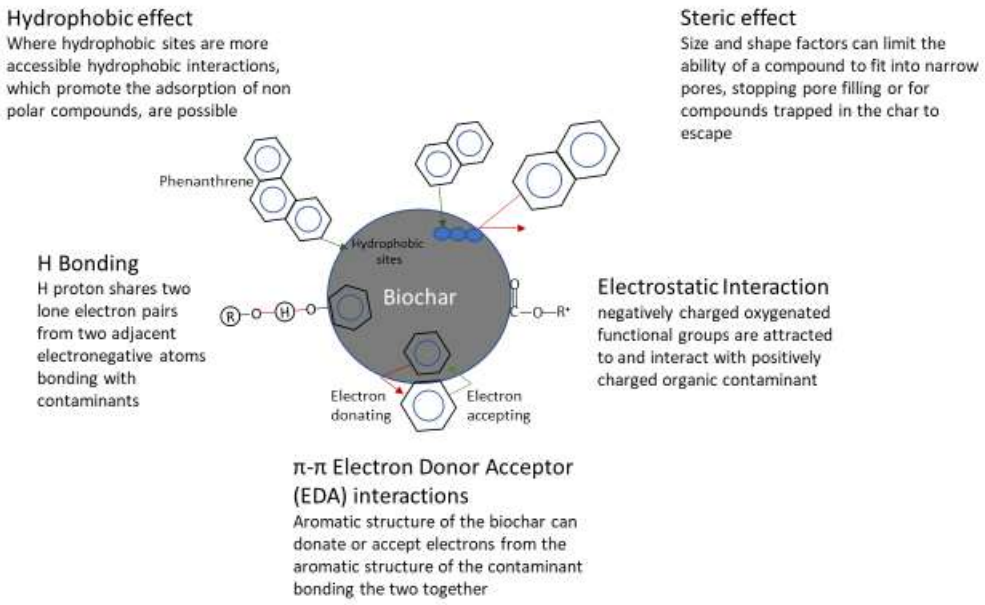

Figure 3. The major mechanisms of organic contaminant immobilization by biochar

π-π Electron Donor Acceptor Interactions

π-π Electron Donor Acceptor (EDA) has been highlighted as one of the most important interactions in the adsorption of aromatic organic compounds to biochar in aqueous media. π-π EDA can occur between π-electron accepting moieties in the centre of the aromatic cluster within the biochar structure and π-electron donating compounds such as phenols or polyaromatic hydrocarbons (PAHs) (Zhu and Pignatello, 2005). The π-π EDA mechanism has been reported as the major mechanism in organic contaminant removal for contaminants including PAHs such as phenanthrene, dibutyl phthalate, sulphides (sulfamethoxazole and

sulfapyridine), carbaryl and atrazine (Zhang et al., 2013; Jin et al., 2014; Xie et al., 2014). A study by Ahmed et al (2018) also determined that functionalized biochar can act both as π-electron-donor (sorbing phenanthrene) and π-electron-acceptors (sorbing dinitrobenzene). Therein the π-electron donating sites are located at the outer edges of the graphene like structures within the biochar. For polar contaminants π-π EDA is often reported in conjunction with H-bonding such as in the adsorption of tetracycline, estrone, 17β-estradiol, estriol, 17α-ethynylestradiol, bisphenol A and acetate (Saquing, Yu and Chiu, 2016; Zhou *et al.*, 2017; Ahmed *et al.*, 2018). The strength of π bonds is in the realm of weak interactions comparable to H-bonds (Pignatello *et al.*, 2017).

H-bonding

H-bonding occurs between a single proton covalently bound to more electronegative atoms and another electronegative atom bearing a lone pair of electrons. Such electronegative atoms can be found on the biochar surface (e.g. O-containing functional groups) (Gilli and Gilli, 2010). Studies have highlighted the importance of H-bonding in the removal of several polar organic contaminants such as tetracycline (Jing *et al.*, 2014; Tang *et al.*, 2018), norflurazon and fluridone (Sun *et al.*, 2011) and florfenicol (Zhao and Lang, 2018). Charge assisted H bonding (CAHB) is a special type of H-bonding that occurs when the dissociation constant of the H donor and H acceptor groups are very similar (Δ pKa approaches 0) creating an exceptionally strong H-bond (Li *et al.*, 2013). The formation of negative charge-assisted H bonds have also been reported by Ahmed *et al.* (2017) in the sorption of negative species (sulfonamide antibiotics) form aqueous media. Similarly at a pH of ~8 where deprotonation of the amino group and sulfamido were enhanced, sulfadimine (an antibiotic contaminant) converted to an anion state enabling a strong negative CAHB between sulfadimine and the carboxylate or phenolate functional groups on the biochar (Wan *et al.*, 2020).

Electrostatic interactions

Electrostatic interactions refer to the attraction of oppositely charged groups. For example, negatively charged oxygenated functional groups can bind positively charged organic contaminants, such as methyl violet or methyl blue (Xu *et al.*, 2011; Dawood, Sen and Phan, 2017). The charge of the biochar is heavily pH dependant, at pH below the point of zero charge (PZC) the surface charge is positive causing electrostatic repulsion of positively charged contaminants such as sulfadimidine (SMT^+)(Wan *et al.*, 2020; Ramola et al. 2020a);

as the pH of the biochar increases the ionization shifts depending on functional group and compound dissociation constants and the effect of the electrostatic repulsion declines.

Steric effects

Steric effects can influence sorption behaviour of organic compounds. Size and conformational factors may limit the ability of a molecule to fit into narrow pores (pore exclusion), or limit a molecule's approach to sorption sites on the surface (Pignatello, Mitch and Xu, 2017). Removal of organic contaminants from aqueous media by biochar must be considered in conjunction with the pore size of the biochar, the size of the organic contaminant and the shape of the organic contaminant.

Size exclusion was reported by

K. Yang et al. (2018) in their study of wood chips, rice straw, bamboo chips, cellulose, lignin and chitin biochar. Organic molecules were seen to be restricted and could not access biochar pores smaller than the molecule diameter. Tang et al. (2018) also reported size exclusion in their study of the removal of tetracycline by sewage sludge biochar suggesting that adsorbent shows its best adsorption property when pore diameter is 1.7 – 3 times larger than that of the adsorbate molecule. Schreiter et al. (2018) attributed the higher max sorption capacity for trichloroethylene (TCE) over tetrachloroethylene (PCE) to size exclusion with the smaller TCE molecules able to access a bigger portion of the pore volume of the biochar. Zhang et al. (2013) also conducted a bi-solute study about the removal of carbaryl and atrazine by pig manure biochar. In a similar manner to Schreiter et al. (2018) the higher removal of atrazine was attributed to the smaller molecular size of atrazine compared to carbaryl (0.61 nm versus 0.71 nm). Kah *et al.* (2016) also highlighted size exclusion as a phenomenon in their study of a diverse series of sorbents pyrolyzed at different temperatures. Size exclusion was significant for plant derived materials but not so for biochar derived from sewage sludge or pig manure raw materials. These raw materials did not have a microporous structure and as a result did not develop the porosity associated with size exclusion when pyrolyzed. For small molecules, pore filling can occur which is dependent on pore geometry, pore volume and pore size distribution. When these factors are favourable for contaminant condensation in these pores, pore filling can play a dominant role in the immobilisation of organic contaminants (Nguyen *et al.*, 2007; Zhu *et al.*, 2014; Zhao and Lang, 2018). Wang and Xing, (2007) studied the sorption of the hydrophobic compounds phenanthrene and naphthalene and noted that at low solute concentrations, sorption of phenanthrene and naphthalene by biopolymer biochar was dominated by the micropore-filling mechanism; however, with an

increase in the solute concentration, immobilisation of these two compounds shifted to a surface-sorption-dominant process.

Key material properties for inorganic immobilization

Specific Surface area

Specific surface area (SSA) is a property of biochar that, as with inorganic immobilisation, is often cited as important for the sorption of organic contaminants as a larger SSA means access to more sorption sites. The larger the SSA, the more opportunity the contaminant has to be removed by the biochar from aqueous media (Prévoteau et al., 2016). SSA is cited as being a primary property in the removal of organic contaminants in aqueous media by many papers (Zhang et al., 2013; Lattao et al., 2014; Wang et al., 2016; Zhao and Lang, 2018). SSA is driven by pyrolysis temperature and raw material (figure 2). The role of raw material is discussed by Kah et al. (2016) who demonstrate that plant based raw materials can develop micropores, increasing SSA and pore filling potential, but animal waste or sewage based raw materials do not show evidence of such micropore structures. Similarly Wang et al. (2016) highlight that the SSA of plant based biochar was significantly higher than animal based biochar with the result that there were positive correlations between SSA and removal of organic contaminants by wood dust biochar but no such correlations were apparent for swine manure biochar. In their meta data analysis review Ippolito *et al.*(2020) assert that although pyrolysis temperature is important in determining SSA, raw material has the largest influence on SSA with SSA being greatest in wood based biochar. None the less pyrolysis temperatures are still an important tool to control SSA: at higher pyrolysis temperatures amorphous carbons condense to crystalline structures, more pores are formed and volatiles are removed causing a higher SSA (Chen et al., 2012; Zhang et al., 2013; Wang et al., 2016) .

Aromaticity

The molar H/C ratio is widely recognised as an index for the degree of aromaticity / carbonisation of biochar which is essential for π-π EDA and hydrophobic interactions. As pyrolysis temperatures increase and aromaticity increases stacks of graphene grow enabling the π-π mechanism to dominate in the removal of contaminants from aqueous media (Jin et al., 2014). Hydrophobic interactions which promote the immobilisation of non-polar /

hydrophobic compounds, such as phenanthrene, are also possible where aromatic groups are more accessible (Sun *et al.*, 2013). The hydrophobicity of a contaminant is generally described by the octanol water partition co-efficient (K_{ow}). The aromaticity of biochar is affected by pyrolysis temperature, above ~300°C an increase in pyrolysis temperature leads to greater carbonisation and an increase in aromatic compounds (figure 2) (Uchimiya, Isabel M Lima, *et al.*, 2010; Mukherjee, Zimmerman and Harris, 2011; Lehmann and Joseph, 2015; Lou *et al.*, 2016). However, the degree of carbonisation in the biochar is also relevant to partitioning with the partitioning of organic contaminants occurring in the uncarbonized fraction of the biochar (Chen *et al.*, 2018; Schreiter *et al.*, 2018). At lower temperature pyrolysis (<400°C) removal of organic pollutants by biochar is dominated by partitioning due to the amorphous structure of the biochar making them effective media for the partitioning of more polar organic compounds (Chen, Zhou and Zhu, 2008; Sun *et al.*, 2012).

Polarity

The O/C ratio is commonly accepted as an index for polarity and is intrinsically linked to the abundance of oxygenated functional groups. The higher the polarity, and therefore the higher the O/C ratio, the more negatively charged the biochar surface is with the associated benefits for the removal of cations / polar contaminants via H-bonding and electrostatic attraction (Xu *et al.*, 2011; Qiao *et al.*, 2018; Schreiter *et al.*, 2018; Zhao and Lang, 2018). However a high O/C ratio and resultant negative charge can also cause the electrostatic repulsion of anions and can cause water clusters to form around the O-groups repulsing non-polar / hydrophobic contaminants, further demonstrating the importance of the relationship between contaminant structure and properties with the biochar structure and properties (Zhu, Kwon and Pignatello, 2005; Rajapaksha *et al.*, 2015; Chen and Ni, 2017; Schreiter *et al.*, 2018). Zhang et al. (2017) also discussed the link between partitioning and the polarity of the contaminant with acetone, cyclohexane and toluene partition rates relating directly to polarity; hydrophilic / polar contaminants were adsorbed more easily by biochar that was less polar as the low pyrolysis temperatures lent themselves to the presence of noncarbonized organic matter where partitioning takes place. Polarity, indexed by the O/C ratio, is determined in the main by pyrolysis temperatures; at lower temperatures O is more abundant, and as such the biochar is more polar (figure 2), (Chen and Chen, 2009; X. Zhang *et al.*, 2017).

Limitations

Whilst there is extensive literature on biochar and the removal of organic and inorganic pollutants more research should be conducted to bridge the gap between laboratory results and field work. The majority of research continues to revolve around laboratory findings rather than the use of biochar in the field or in simulated field conditions. Maximum sorption capacity is an important metric however, it represents sorption in perfect conditions such as ideal temperatures, pH, contaminant concentrations and flow. Single contaminant environments are often studied in laboratory batch experiments, yet these conditions are unlikely to be seen in the field where multiple contaminants exist together with dissolved organic matter affecting contaminant mobility, bioavailability and toxicity. The impact of changes in temperature, pH and contaminant concentrations have been studied providing useful insights but very rarely use the parameters as seen in aqueous media where biochar could potentially be deployed such as rivers, runoff or mine waters. Such laboratory findings are not fully transferrable to field conditions which limit their value when attempts are made to use these findings in practice. Whilst the use of simulated field conditions such as storm water, synthetic mine water or even collected mine water has been used to undertake studies in a laboratory setting this approach is far from prevalent.

Conclusion and future prospects

This chapter highlights the successful use of biochar as an adsorbent for the removal of contaminants from aqueous media. Biochar is a relatively low cost, sustainable product which has been demonstrated to be effective in the removal of both organic and inorganic contaminants. This has led to the study of biochar in relation to aqueous environments such as road runoff (Cairns *et al.*, 2020), mine waters (Bandara *et al.*, 2020), stormwater (Boehm *et al.*, 2020) drinking water (Hu *et al.*, 2019) and biologically treated wastewater (Hagemann *et al.*, 2020). This chapter reviews the key immobilisation mechanisms and underpinning material properties for both inorganic and organic contaminants.

The key immobilization mechanisms for inorganic contaminants in aqueous media by biochar are: cation exchange, complexation, electrostatic attraction, cation π bonding, reduction and subsequent sorption, and precipitation. These mechanisms do not work in isolation and it is common for several mechanisms to be relevant simultaneously. Key material properties for

inorganic contaminant immobilization include surface functional groups, cation exchange capacity, specific surface area and pH. These material properties are primarily controlled by raw materials and / or pyrolysis temperatures. Surface functional groups of biochar are essential to cation exchange, electrostatic attraction and complexation and are affected by both raw material and pyrolysis temperature. Functional groups start to form at ~120°C in the first stages of pyrolysis where oxygen is more abundant and continue until around 350°C. CEC is the key property for sorption through cation exchange. Raw material and pyrolysis temperature are primary drivers of CEC with the lower pyrolysis temperatures allowing more functional groups and as such greater CEC. Specific surface area (SSA) is a further important property of biochar; the higher the SSA the more sites are available for sorption to occur. As opposed to functional groups and CEC, SSA is seen to increase as a result of an increase in pyrolysis temperature. Solution pH, which can be affected by the biochar, is also cited as one of the main variables affecting the sorption process influencing both the speciation of the metals and the surface charge of the sorbent.

Several mechanisms have been documented in the removal of organic contaminants from aqueous media, primarily: H-bonding and charge assisted H-bonding (CAHB), π-π Electron Donor Acceptor (EDA) interaction, electrostatic interaction and steric effect. These are driven by the structure and properties of the biochar, in particular specific surface area (SSA), aromaticity which can be approximated by the molar H/C ratio and polarity which can be approximated by the molar O/C ratio. Again, these material properties are primarily controlled by raw materials and / or pyrolysis temperatures. As with inorganic contaminants specific surface area (SSA) is an important property of biochar in relation to the immobilisation of organic contaminants. The molar H/C ratio is an index aromaticity / carbonisation of biochar which is essential for π-π EDA and hydrophobic interactions. Aromaticity increases with pyrolysis temperatures enabling the π-π mechanism to dominate in the removal of contaminants from aqueous media. Hydrophobic interactions which promote the immobilisation of non-polar / hydrophobic compounds are also possible where aromatic groups are more accessible. The O/C ratio, which is commonly accepted as an index for polarity is intrinsically linked to the abundance of oxygenated functional groups. The higher the O/C ratio, the more negatively charged the biochar surface is with the associated benefits for the removal of cations / polar contaminants via H-bonding and electrostatic attraction. However, a high O/C ratio and resultant negative charge can also cause the electrostatic repulsion of anions and can cause water clusters to form around the O-groups

repulsing non-polar / hydrophobic contaminants. This highlights the importance of the relationship between contaminant structure and properties with the biochar structure and properties.

Studies reviewing the removal of contaminants from aqueous media by biochar in the field are scarce and as a result biochar onsite use in aqueous media necessitates further studies to systematically investigate the interplay of different environmental factors such as pH, dissolved organic matter (DOM) and the mix of contaminants seen in various real world sites. Fouling as a result of these environmental factors could lead to "caking" and the subsequent blocking of biochar surface and pores; such fouling is discussed in the activated carbon community but less so by biochar researchers. A transfer of knowledge between these research communities would help drive meaningful further developments in the field. Furthermore, key material properties of biochar relevant to field conditions are often not reported, including the previously discussed point of zero charge. Understanding the impact of the environmental pH on the charge of the biochar underpins a number of key immobilisation mechanisms and as such arguably should become standard to report bringing laboratory work and field study closer together.

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