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Review

Plenty of room for carbon on the ground: Potential applications of biochar for stormwater treatment

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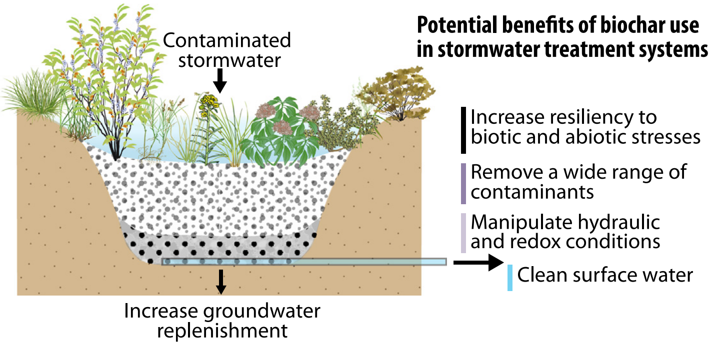
HIGHLIGHTS

- Critical review of biochar used in low impact development (LID).
- Benefits and limitations of biochar use are discussed.
- Biochar removes a wide range of stormwater pollutants.
- Biochar can manipulate hydraulic and ecological functions of LID.
- Biochar could increase resiliency of LID.

GRAPHICAL ABSTRACT



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ABSTRACT

Low impact development (LID) systems are increasingly used to manage stormwater, but they have limited capacity to treat stormwater—a resource to supplement existing water supply in water-stressed urban areas. To enhance their pollutant removal capacity, infiltration-based LID systems can be augmented with natural or engineered geomedia that meet the following criteria: they should be economical, readily available, and have capacity to remove a wide range of stormwater pollutants in conditions expected during intermittent infiltration of stormwater. Biochar, a carbonaceous porous co-product of waste biomass pyrolysis/gasification, meets all these criteria. Biochar can adsorb pollutants, improve water-retention capacity of soil, retain and slowly release nutrients for plant uptake, and help sustain microbiota in soil and plants atop; all these attributes could help improve removal of contaminants in stormwater treatment systems. This article discusses contaminant removal mechanisms by biochar, summarizes specific biochar properties that enhance targeted contaminants removal from stormwater, and identifies challenges and opportunities to retrofit biochar in LID to optimize stormwater treatment.

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Contents

1. Introduction

Water scarcity is one of the biggest challenges of this century (Liu et al., 2017). Nearly one fifth of the world's population lives in water-stressed areas, and nearly one fourth of the world's population face water shortage at least one month in a year (United Nations, 2014a). Although there is sufficient amount of fresh water on Earth, it is not often available where it is needed the most: urban areas (McDonald et al., 2014). Urban areas are home to nearly 50% of the world's population, which is projected to increase to 70% by 2050 (United Nations, 2014b), indicating the water scarcity issue in urban areas could get worse unless alternative water resources are utilized (Oppenheimer et al., 2017). Urban stormwater, a traditional waste, is one such alternative.

To manage stormwater, developers typically use low impact development (LID) systems, whose primary goal is to reduce flooding by reinstating natural stormwater infiltration in the developed area to its pre-developmental capacity. LID systems such as bioinfiltration systems, bioswales, green roofs, and dry/wet ponds reduce the volume of overland flow during a storm event, but they are not designed to remove most stormwater contaminants (US NRC, 2009). One of the challenges for treatment of stormwater is that a single filter medium may not efficiently remove different types of stormwater contaminants with contrasting properties (Grebel et al., 2013). To increase removal, filtration media in LID, typically sand and compost, can be augmented with materials of greater contaminant removal capacity. However, to make the design modification economically feasible, the augmented geomedia should be readily available, produced at a low cost, and have the capacity to remove a wide range of contaminants simultaneously during conditions relevant to passive stormwater treatment systems. Biochar, a carbonaceous porous adsorbent, meets all the criteria and has demonstrated to improve contaminant removal from contaminated waters (Ahmad et al., 2014; Inyang and Dickenson, 2015; Rajapaksha et al., 2016). Biochar is produced typically as a co-product from waste biomass and expected to last for decades in the environment, as carbon in biochar is recalcitrant with an average half-life of over 100 years (Spokas, 2010).

Many review papers have summarized different benefits of biochar; biochar can increase fertility of soil by improving nutrients utilization capacity (Sohi et al., 2009; Xu et al., 2012), sequester carbon (Brassard et al., 2016; Sohi et al., 2009), remove pollutants from wastewater (Ahmed et al., 2016; Mohan et al., 2014; Tan et al., 2015), and remediate or treat contaminated soil/water (Rajapaksha et al., 2016). In contrast, this review summarizes the utility of biochar to improve stormwater treatment. Although recent laboratory studies examined the potential of biochar to remove stormwater contaminants, field studies to confirm the positive impact of biochar are lacking. The review summarizes the results from laboratory studies, and makes recommendations to inform the use of biochar in stormwater treatment systems. These recommendations are based on our in-depth review that connects the links between recent advances in biochar applications in multiple disciplines including land management, agriculture, soil remediation, and wastewater treatment.

Unlike drinking water or wastewater treatment systems, the stormwater treatment systems are passive and subjected to intermittent infiltration of stormwater during wet season with a period of freezing or drying between infiltration events. Characteristics of an intermittent rainfall event such as rainfall intensity, duration, and antecedent drying period can affect the contaminant removal from stormwater (Li et al., 2012; Mohanty et al., 2014a; Mohanty et al., 2013). Biochar can be effective in removing contaminants under these complex conditions (Nabiul Afrooz and Boehm, 2016, 2017; Lau et al., 2017). Biochar can also, simultaneously remove different types of contaminants including metals/metalloids (Inyang et al., 2016) and microbial and organic contaminants (Inyang and Dickenson, 2015) in the presence of dissolved organic carbon (DOC). Thus biochar use in stormwater biofilter is more sustainable than the use of other geomedia (*e.g.*, zero-valent iron or iron oxide coated sand) that are more likely to get exhausted in the presence of DOC (Mohanty et al., 2013) and effectively remove only a few types of contaminants.

Removal of contaminants by biochar could vary based on several factors: characteristics of contaminants, biochar properties, and treatment conditions. Understanding the links between these factors will help optimize the design of LID that use biochar. This paper highlights these links and provides a critical review of the latest advances in biochar applications for pollutant removal from stormwater. We have identified key properties of biochar that aid contaminant removal, compared the similarity and differences between biochar and activated carbon—an extensively studied carbonaceous material used for contaminant removal, discussed the mechanisms of contaminant removal by biochar during stormwater infiltration, and suggested potential design modifications of different stormwater treatment units where biochar can be added to improve the treatment efficiency. At last, we summarized potential challenges and opportunities to optimize the treatment capacity of biochar-augmented LID.

2. Biochar production methods and properties

To improve the efficiency of biochar-augmented stormwater treatment systems, it is critical to enrich specific biochar properties that enhance contaminant removal (Fig. 1). Biochar properties can be controlled by selecting specific feedstock types and biochar production processes. Biochar is produced from biomass under thermochemical processes including pyrolysis, gasification, and hydrothermal

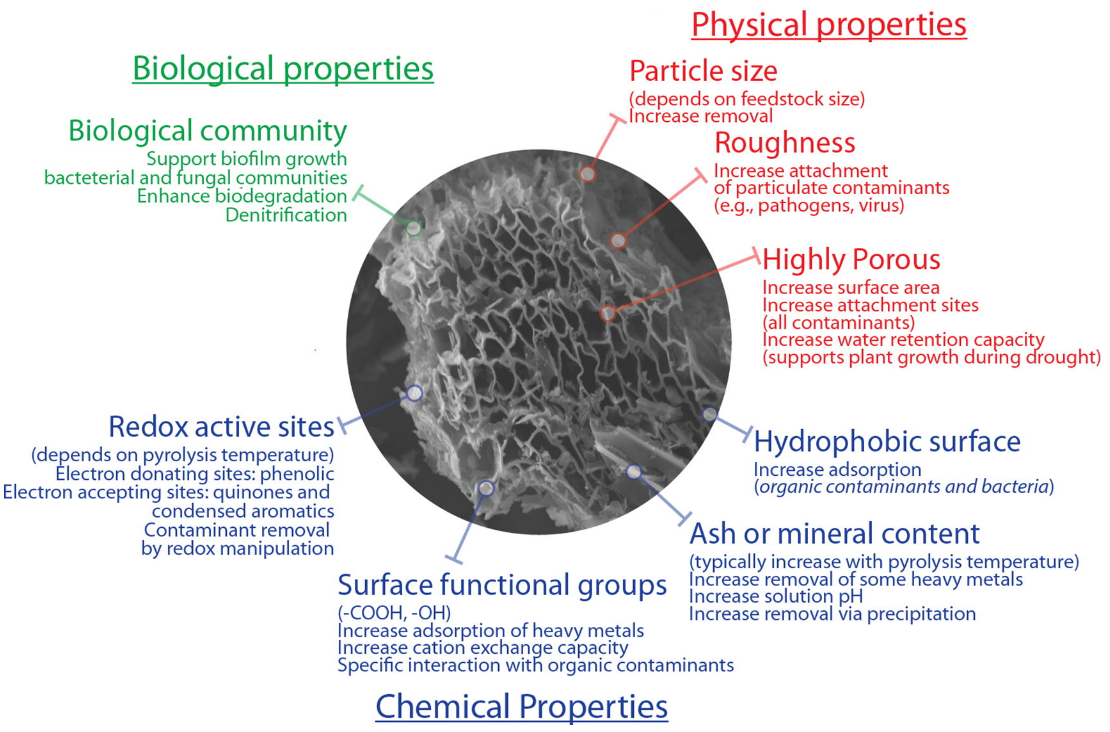

Fig. 1. Physical, chemical, and biological properties of biochar for removal of contaminants from stormwater.

carbonization. Pyrolysis, the most common method for biochar production, requires limited oxygen supply and high temperature of 300–800 °C. The quantity and quality of biochar produced vary with residence time of feedstock within the pyrolysis chamber. Slow pyrolysis, the conventional pyrolysis method, uses long vapor residence time (>1 h) and slow heating rate (5–7 °C/min) to produce biochar with high yield, a small volume of syngas (CO, CH_4, and H_2) and bio-oil with high energy density (Liu et al., 2015). In contrast, fast pyrolysis uses short residence time (>10 s) at high heating rate (>200 °C/min) to produce biochar with low yield due to the preferential formation of bio-oil (Qian et al., 2015). Gasification requires high temperature (>700 °C) in O_2 or steam as oxidants and produces syngas as the main product with biochar as the solid co-product. Comparatively, the less energy-intensive hydrothermal carbonization (180–250 °C) produces hydrochar, a biochar analogue, with little gas production (1–5%) (Libra et al., 2014). The details of these thermal processes are described in recent review articles (Libra et al., 2014; Liu et al., 2015; Qian et al., 2015; You et al., 2017).

Feedstock types and conditions used during biochar production affect biochar properties, which can ultimately affect its capacity to remove stormwater contaminants. Biochar retains the pore structure of the feedstock during pyrolysis; thus, porosity or pore size distribution in biochar depends on the feedstock types. For instance, softwood-derived biochar tends to have more pores and thus higher surface area than the hardwood-derived biochar, because less dense compositions of softwood are more susceptible to thermal decomposition (Mukome et al., 2013). Pyrolysis temperature affects the formation of pore structure, *i.e.*, with increases in pyrolysis temperature, the micropore volume and surface area of biochar increase due to release of volatiles and formation of internal pores as well as channel structures. To expose more pores and increase the surface area, biochars can be activated using acid/alkaline solutions and oxidants such as steam and CO_2/NH_3 (Rajapaksha et al., 2016; Xiong et al., 2017). It should be noted that activated biochar is functionally the same as activated carbon, and activation of biochar will increase the cost of biochar, thereby minimizing potential economic benefit of biochar over commercially available activated carbon.

Biochar production methods and feedstock types also affect biochar chemical properties including elemental composition, pH, cation or anion exchange capacity, functional groups, hydrophobicity, and ash content. High cation exchange capacity (CEC), *i.e.*, the parameter representing biochar's negative surface charge, favors the adsorption of cations such as metals. Comparatively, biochars with high anion exchange capacity (AEC) show strong affinity for anions such as phosphate and metalloids. Low pyrolysis temperature (*e.g.*, 250–350 °C) may lead to high CEC as a result of the considerable volatile organic matter remaining on biochar (Mukherjee et al., 2011; Suliman et al., 2017). These properties are also governed by the feedstock use for biochar production. For example, Mukherjee et al. (2011) showed that grass biochar had higher CEC than oak and pine wood biochar. Hydrophobicity, a measure of organic carbon content and property, can enhance adsorption of pollutants such as hydrophobic organic compounds and pathogens on biochar surfaces. Hydrophobicity increases with pyrolysis temperature as a result of high fixed carbon content and removal of oxygen (Ahmad et al., 2012). Hydrophobicity is also affected by the surface functional groups originated from the feedstock. Compared to wood-derived biochar, non-wood feedstock such as grass, sludge, and manure yields biochar with fewer aromatic but more aliphatic groups and higher ash content (Fang et al., 2016; Mukome et al., 2013). Post treatment can oxidize or reduce surface functional groups and change its hydrophobicity (Rajapaksha et al., 2016). Manure-based biochar contains higher concentration of nutrients than wood-based biochar (Mukome et al., 2013), which can affect biochar capacity to remove or release nutrients in stormwater. Thus, it is critical to select biochar based on the treatment needs.

3. Comparison between biochar and activated carbon

In contrast to biochar, activated carbon has been used for water purification for several decades. Both biochar and activated carbon are carbonaceous materials produced via similar process—pyrolysis of biomass—but differ by cost and post-processing / activation steps. In general, activated carbon can be up to 20 times more expensive than biochar, due to higher energy consumption and lower yield for production of activated carbon (Thompson et al., 2016). However, the economic benefits of biochar must take into account typically higher contaminant removal capacity of activated carbon and its consistency of properties and performance compared with biochars.

Either activated carbon or biochar can exhibit greater contaminant removal depending on the contaminant types and biochar or activated carbon properties (Table 1). In a field study, granular activated carbon was shown to adsorb 2–10% more polychlorinated biphenyls than two biochars produced by pyrolyzing shipping pallets at 700 °C for 30 min or softwood at 450 °C for 2.5 h (Denyes et al., 2013). Similarly, activated carbon appears to be more efficient than biochar in removing polychlorinated dibenzo-*p*-dioxin/dibenzofurans (Chai et al., 2012). Because of high surface area, activated carbon adsorbed more Hg(II) and atrazine than biochar (Tan et al., 2016). In contrast, another study (Xu et al., 2016) showed that biochar has greater capacity than activated carbon to remove Hg(II) because of the nature of the interaction with the types of sorption sites present on activated carbon and biochar. They showed that attachment of Hg on biochar occurs via bonding at C═O or C═C sites, whereas attachment on activated carbon occurs via bonding with —COOH or —OH sites.

Because of lower sorption capacity of biochar compared with activated carbon, biochar may not be effective in reducing the toxic effect of contaminants toward microorganism or plants. For instance, compared with biochar, activated carbon reduced soil toxicity toward *Vibrio fischeri* and *Folsomia candida* (Koltowski and Oleszczuk, 2016) and decreased the inhibitory effect of contaminated soil toward seed germination (Josko et al., 2013). These results indicate that contaminants removed by activated carbon may be less bioavailable than those removed by biochar possibly because of the difference in removal mechanisms such as the extent of sorption on biochar or activated carbon surfaces and DOC accumulated on the surfaces. Because of the same reason, addition of compost to biochar, which increases dissolved organic carbon accumulation on biochar surface, further enhanced biodegradation of the attached trace organic contaminants (Ulrich et al., 2017b). Consequently, contaminants immobilized by biochar can be mineralized by soil microorganisms, resulting in long-term removal of organic contaminants. For example, Shan et al. (2015) found that activated carbon reduced mineralization of C-14-catechol, while biochar had no effect on the mineralization rate. Biochar was more effective than activated carbon in mineralizing dichlorodiphenyltrichloroethane accumulation in contaminated soil (Denyes et al., 2016). Activated carbon reduced bioaccumulation of PAHs in plants by a factor of two compared with biochar and lowered the DOC concentration by 20% whereas biochar had no effect on DOC (Oleszczuk et al., 2017). This result indicates that plants in LID can more actively remove contaminants from biochar-amended soil than activated carbon-amended soil.

In some cases, biochar has been shown to remove more contaminants than activated carbon. Fine biochar particles adsorbed more trace organic contaminants than granular activated carbon (Ulrich et al., 2017a) partly because of smaller particle size of biochar compared with granular activated carbon. Despite significant cost difference, activated carbon and biochar removed similar amount of pyrene (Hale et al., 2011), suggesting that biochar is more cost effective option for removal of pyrene. From wastewater, biochar could remove nearly two times more total chemical oxygen demand than activated carbon (Huggins et al., 2016), because macropores in biochar are more effective in capturing the particulate matter without being clogged. Although removal of contaminants can vary between biochar and activated carbon, biochar exerts greater environmental benefits considering higher greenhouse gas emission and energy demand for activated carbon production (Alhashimi and Aktas, 2017; Thompson et al., 2016). Thus, overall benefits of biochar in stormwater treatment system can be comparable with activated carbon despite the low cost of biochar.

4. Effect of biochar on physical, chemical, and biological processes, and contaminant removal in stormwater treatment systems

4.1. Hydraulic and redox manipulation

Typical geomedia used in stormwater treatment systems are chosen based on two properties: a high hydraulic conductivity to minimize overland flooding and a high storage volume to reduce peak flow and enhance removal of many contaminants from stormwater. To maintain high hydraulic conductivity, medium to coarse sand has been used. However, sand does not contain internal pores, thereby limiting storage volume—a key factor for denitrification and removal of other contaminants from pore water (Erickson et al., 2016; Payne et al., 2014b). The addition of fine media such as clay can increase the storage volume but also lowers hydraulic conductivity. In contrast, biochar can offer both advantages simultaneously. Biochar, owing to its vast network of internal pore structures, can not only increase the storage but also increase hydraulic conductivity when there is adequate grain size distribution.

Table 1
Comparison between biochar and activated carbon for contaminant removal. + indicates better performance or higher capacity and − indicates the opposite trend.

Parameter	Biochar	Activated carbon	References
Cost (USD/metric ton)	350–1200	1100–1700	(Thompson et al., 2016)
Energy demand (MJ/kg)	6.1	97	(Alhashimi and Aktas, 2017; Thompson et al., 2016)
Greenhouse gas emission (kg CO_2 eq/kg)	6.6	−0.9	(Alhashimi and Aktas, 2017; Thompson et al., 2016)
Surface area	−	+	(Tan et al., 2016)
Biomass yield in amended soil	+	−	(Brendova et al., 2016)
Cd uptake in amended soil	+	−	(Brendova et al., 2016)
Bioaccumulation of PAHs in plants	+	−	(Oleszczuk et al., 2017)
Chromium and zinc removal	+	−	(Alhashimi and Aktas, 2017)
Polychlorinated dibenzo-p-dioxin/dibenzofurans removal	−	+	(Chai et al., 2012)
Polychlorinated biphenyl adsorption	−	+	(Denyes et al., 2013)
Dichloro-diphenyltrichloro-ethane (*DDT*) accumulation	−	+	(Denyes et al., 2016)
Pyrene removal	+	−	(Hale et al., 2011)
Lowered toxicity	+	−	(Hale et al., 2013b)
Chemical oxygen demand removal	+	−	(Huggins et al., 2016)
Inhibition of seed germination	+	−	(Josko et al., 2013)
Soil toxicity toward *Vibrio fischeri* and *Folsomia candida*	+	−	(Koltowski and Oleszczuk, 2016)
Dissolved organic carbon (DOC) removal	No effect	+	(Oleszczuk et al., 2017)
Mineralization of C-14-catechol	+	−	(Shan et al., 2015)
Hg(II) adsorption[a]	+	−	(Tan et al., 2016; Xu et al., 2016)
Trace organic contaminants removal	+[b]	−	(Ulrich et al., 2017a)
Atrazine adsorption	−	+	(Tan et al., 2016)

[a] Contradiction between results of both studies on biochar ability to adsorb Hg(II) in comparison with activated carbon.

[b] Particle size of biochar was smaller than that of activated carbon, resulting higher volume percentage of biochar (33%) than activated carbon (12.5%) in biofilter.

While some studies have demonstrated that biochar application significantly improved water retention and increased hydraulic conductivity of soils (Abel et al., 2013; Ibrahim et al., 2013), others reported a decrease in hydraulic conductivity with biochar addition (Barnes et al., 2014; Lim et al., 2016; Liu et al., 2016). The observed discrepancy is attributed to the difference in particle size between added biochar and soil (or sand) and hydrophobicity of biochar. One study reported a decrease in saturated hydraulic conductivity with an increase in hydrophobicity or water repellency of porous media (Fox et al., 2007), but a recent study observed no apparent effect of hydrophobicity on hydraulic conductivity (Eibisch et al., 2015). Based on a meta-analysis of literature data, Omondi et al. (2016) found that biochar addition significantly reduced soil bulk density by 7.6%, and increased soil porosity by 8.4%, aggregate stability by 8.2%, available water holding capacity by 15.1%, and saturated hydraulic conductivity by 25.2%. Bioretention media typically contain 70–85% medium to coarse sand, and addition of biochar, based on particle size and amount of fine particles, can increase or decrease saturated hydraulic conductivity and have variable impact on clogging. Thus, particle size of biochar can be used as important design criteria to ensure that stormwater treatment units maintain high hydraulic conductivity and become less susceptible to clogging (Ahmed et al., 2016).

LID with a submerged layer can lower redox potential and induce reducing conditions, which is beneficial for removal of many contaminants including nitrate (Dietz and Clausen, 2006). However, constructing a submerged layer is expensive. A cheaper alternative would be adding porous media such as biochar that can increase water storage and create isolated reducing zones. The pore water trapped in the internal pores of biochar can be anoxic. Furthermore, biochar surface functional groups such as electroactive quinoid functional groups and polycondensed aromatic sheets are redox active, which can play a critical role in oxidation and reduction of attached contaminants (Klupfel et al., 2014). Biochar can serve as a microbial electron acceptor or donor to facilitate microbial degradation of contaminants via redox cycling (Saquing et al., 2016). Thus, biochar can be added as a redox control to remove contaminants sensitive to reducing conditions in LID. This is particularly useful because it is challenging to achieve reducing condition in LID due to rapid infiltration of stormwater, which is typically saturated with oxygen.

Opportunities: Benefits of biochar application on hydraulic conductivity and water retention of soil have been verified in agricultural land, but the extent of changes in hydraulic conductivity and water retention in stormwater treatment systems, which typically contain sand or sandy soil, has not been quantified. Further studies should evaluate the impact of hydraulic manipulation of filter media by biochar on the removal of contaminants, so that the results can inform the engineering design of stormwater treatment system. This can be achieved by development of models that predict biochar amendment on water retention and hydraulic conductivity. Furthermore, leaching of biochar particles from LID is rarely investigated (Mohanty and Boehm, 2015). Biochar can be physically disintegrated (Spokas et al., 2014), transport through porous media based on solution chemistry of infiltrating water (Chen et al., 2017a; Wang et al., 2013; Zhang et al., 2010). Thus, it is critical to evaluate potential leaching of biochar particles and associated contaminants in stormwater treatment system.

4.2. Plants growth

In stormwater treatment systems, plants serve multiple functions in addition to their aesthetic use. Plants reduce stormwater runoff volume by intercepting rainwater in their canopy, removing water via evapotranspiration, and increasing infiltration via root structure (Berland et al., 2017). Plants remove nutrients from soil by assimilation (Read et al., 2008), help retain metals/metalloids (Chen et al., 2014; Rycewicz-Borecki et al., 2016; Vezzaro et al., 2012), degrade organic contaminants (Lefevre et al., 2012; LeFevre et al., 2015) and inactivate pathogens by releasing root exudates (Chandrasena et al., 2017). Thus, it is critical that geomedia used in stormwater treatment system can support plant growth throughout dry and wet seasons.

Biochar can mitigate abiotic stress to plants (Rizwan et al., 2016). Several studies showed that addition of biochar improved water retention (Abel et al., 2013; Ibrahim et al., 2013) and helped plants survive drought (Kammann et al., 2011) and biotic stress (Elad et al., 2011). Traditionally, compost or mulch is a preferred geomedia for plant growth. While compost can help plant growth and remove some contaminants, it has also been recognized as a source of contaminants such as nutrients and copper (Chahal et al., 2016) and leach high concentration of DOC, which has potential to decrease contaminant removal capacity of added geomedia (Mohanty and Boehm, 2014). To minimize the negative impact of compost, it can be replaced by biochar, which can support plant growth in sandy media and remove contaminants from stormwater. Due to its low bulk density, biochar can be used to support plants on green roof (Cao et al., 2014; Kuoppamaki et al., 2016; Kuoppamaki and Lehvavirta, 2016).

Opportunities: The benefits of biochar application on plants in stormwater treatment system have not been quantified systematically. In particular, it is not clear which properties of biochar (*e.g.*, particle size, hydrophobicity) are beneficial for plant growth in bioretention systems. Future studies should examine how the coupled interactions between biochar, plants, and rhizosphere microbial community affect the growth of plants with varying drying duration.

4.3. Removal of contaminants

4.3.1. Metals/metalloids

Metals/metalloids are typically removed from contaminated water by electrostatic interaction and cation exchange on geomedia such as compost and mulch, as well as specific sorption mechanisms such as inner-sphere surface complexation and surface (co-)precipitation (Gwenzi et al., 2017). Biochars that are rich in deprotonated carboxyl groups and sulfonic groups show strong affinity for metals/metalloids, while anions such as carbonate, phosphate, hydroxide released from biochar can help precipitate cationic metals. Biochar, particularly with high ash content, can increase the solution pH, which could decrease solubility of metals/metalloids and increase their removal (Zhou et al., 2016). These mechanisms are typically examined by batch experiments and summarized in the recent reviews on contaminated water remediation (Inyang et al., 2016; Gwenzi et al., 2017). The removal mechanisms are expected to be similar in LID.

In contrast to numerous batch studies which examined capacity of biochar to remove metals/metalloids (listed by Inyang et al., 2016), only a few column studies are reported that resemble water flow relevant to stormwater treatment (Table 2). Although the biochar applications in these studies cannot be quantitatively compared due to different performance indicators adopted (*e.g.*, removal efficiency, breakthrough time, and pore volume), their common findings can provide useful conceptual information for designing LID.

The previous studies indicate that biochar has varying capacity to remove metals/metalloids under the flow through conditions, depending on metal/metalloid types and biochar properties (Table 2). Typically, Pb and Cu preferentially adsorb on biochar in mixed metal/metalloid systems, of which the breakthrough time was 2–5 times longer than other metals (*e.g.*, Zn, Cd, and Ni) (Ding et al., 2016) because of high affinity of Pb and Cu for organic complexation. Design of the filter layer also determines the metal/metalloid removal efficiency. Flow rate was inversely proportional to the exhaustion time of biochar column for Cd adsorption, as observed from the breakthrough curves reported in Roh et al. (2015). Another study showed that as the flow rate decreased from 5 to 1 mL/min, the time for 50% Ni and Co breakthrough increased by a factor of two to approximately 4.5 h (Vilvanathan and Shanthakumar, 2017). The same study indicated high media depth as another important parameter that increased the breakthrough time considerably. Particle size of biochar possibly controls the metal uptake

Table 2
Removal of metals/metalloids in biochar-packed column studies.

Biochar type	Contaminants (initial concentration)	Removal or adsorption capacity[a]	Key findings	Reference
H_2O_2 activated peanut hull hydrochar	Ni^{2+}, Ca^{2+}, Cu^{2+}, Pb^{2+} (0.25 mmol L^{-1})	0–30%	• H_2O_2 activation significantly enhanced metal sorption capacity of hydrochar, which capacity followed the order: $Pb^{2+} > Cu^{2+} > Cd^{2+} > Ni^{2+}$.	(Xue et al., 2012)
Wood pellet biochar from gasification	Cd^{2+}, Cr^{6+}, Cu^{2+}, Pb^{2+}, Ni^{2+}, Zn^{2+} (0.5–120 mg/L)	18–75%	• Removal of metals/metalloids by biochar was correlated to the amount of oxygen functional groups, O/C ratio, pH, and acidity.	(Reddy et al., 2014)
Hickory wood biochar modified with NaOH	Pb^{2+}, Cd^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} (100 mg/L)	11–54 mg/g	• Biochar was less effective to remove Cd^{2+}, Zn^{2+} and Ni^{2+} in mixed metal system; complete breakthrough occurred within few hours of experiment.	(Ding et al., 2016)
Chicken bone biochar	Cd, Cu, Zn (50 mg/L)	92–210 mg/g	• Complete breakthrough (exhaustion) after few days of experiment. Competitive adsorption among co-existing metals was observed; Cu and Cd outcompeted Zn.	(Park et al., 2015a)
Buffalo weed biochar-alginate beads	Cd^{2+} (10–20 mg/L)	3.5–13.4 mg/g	• The breakthrough time and the adsorption efficiency were higher at lower loading rate.	(Roh et al., 2015)
Teak leaves biochar	Ni^{2+}, Co^{2+} (25–75 mg/L)	7–27 mg/g	• Greater filter media depth decreased the exhaustion time and increased bed adsorption capacity, whereas increasing loading rate accelerated exhaustion of biochar.	(Vilvanathan and Shanthakumar, 2017)

[a] Removal (%) is based on breakthrough curve ($1 - C / C_0$), where C and C_0 are effluent and influent concentrations, respectively. If 100% breakthrough (exhaustion of biochar) was achieved during experiment, the removal was reported as capacity (mg of contaminants per gram of biochar).

by interfering with the hydraulics, but it is seldom discussed in the literature. The rule of thumb for efficient metal removal is to increase the residence time, which can be achieved by manipulating the column parameters, for example, extending the media depth or decreasing the flow rate (Roh et al., 2015; Vilvanathan and Shanthakumar, 2017).

Metal/Metalloid removal capacity of biochar is correlated to the amount of oxygen-containing functional groups (*e.g.*, carboxyl and hydroxyl) present on biochar. Typically, an increase in pyrolysis temperature decreases oxygen-containing functional groups on biochar surfaces, which resulted in a decrease in metal/metalloid removal capacity of biochar (Dong et al., 2014). Thus, the removal capacity of biochar can be improved via surface modification or oxidation that would increase oxygen-containing functional groups on biochar surfaces. For instant, peanut hull hydrochar treated by H_2O_2 exhibited 20 times more sorption capacity for lead than the untreated hydrochar (Xue et al., 2012). This was ascribed to increased oxygen-containing functional groups from 16.4% to 22.3% oxygen content. However, it is unclear whether modified biochar in stormwater treatment system can sustain its removal capacity in the long term due to weathering and ageing of biochar.

Opportunities: As most studies used deionized water under controlled conditions such as pH to test biochar capacity for removing metals/metalloids, they may have overestimated the removal capacity of biochar in field application. The pH of stormwater that usually ranges from the value of 6 to 7 is highly site-specific, depending on local precipitation and urban settings (*e.g.*, roads, buildings, farmlands, residential areas). In general, developed cities tend to have more acidic runoff than rural areas (US EPA, 2009), in which metals/metalloids are more mobile. High concentrations of major cations such as Ca, Mg, and Na can be present in stormwater, partly due to road salt application in winter, but their impact on biochar potential to remove metals/metalloids remains uncertain. Co-existing contaminants such as organics, nutrients, and bacteria could compete for the sorption sites and complex with metals/metalloids and decrease their removal, or on the contrary, facilitate precipitation on biochar surface and increase their removal. Synergistic or antagonistic effects of co-existing constituents in stormwater under dynamic field conditions require further examination, to advise the desirable surface properties of biochar for effective removal of the diverse metals/metalloids in stormwater.

The life-span of LID depends on the adsorption capacity of biochar filter and biochar ageing: the natural degradation or alteration of biochar surfaces with time. The reported column studies seldom consider the ageing effect, which is unavoidable in LID. Many studies used artificial ageing methods such as oxidants and atmospheric exposure, and their findings demonstrated that oxidation could change adsorption capacity of some metals/metalloids including Cd (Fristak et al., 2015), Pb, and As(III) (Wang et al., 2017). Only metals that bound to the surface exchange active sites on biochar seem to be affected by ageing, whereas metals/metalloids that are associated with the organic matter and sulfides fractions are not altered (Fristak et al., 2015). However, ageing processes are more complex in natural conditions than that used in these laboratory studies. Dynamic conditions such as dry-wet cycles as well as physical, chemical, and microbial weathering should be taken into account in future studies. It should be noted that the LID life-span is site-specific and design-specific, varying with rainfall intensity, catchment area, and land uses in different locations.

4.3.2. Organic pollutants

Organic contaminants in stormwater runoff include herbicides, insecticides, motor oils, polyaromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), flame retardants, perfluorinated compounds, and plastic additives. Biochar has the potential to remove most of these contaminants from stormwater via several processes including sorption. The sorption mechanisms include the π-π electron donor acceptor (EDA) interaction, hydrogen bonding, and hydrophobic attraction for non-ionic organics, as well as electrostatic attraction for ionic organics, based on surface polarity of biochar (Rajapaksha et al., 2016; Sun et al., 2012).

Table 3 summarizes the column studies, where biochar was used to remove organic contaminants. These studies showed that biochar physicochemical properties such as surface area, particle size, and mesoporosity play a critical role in determining the removal rate of organic contaminants and the removal capacity of biochar under flow-through conditions. Removal in a flow-through system depends on the rate of transport of contaminant via advection and the rate of contaminant uptake by biochar or sorption kinetics. While depth of filter media and rainfall intensity affect residence time or transport rate, properties of biochar such as particle size, surface area and internal pore size distribution affect sorption kinetics. Thus, particle size and mesoporosity of biochar can be controlled to improve the removal of slowly-adsorbing organic contaminant (Kasozi et al., 2010). While decreasing the size of pores increases sorption capacity and rate, it may increase the risk of pore blockage by organic carbon. For instance, smaller mesopore volume resulted in slower sorption kinetics for organic contaminants, as the pores are more susceptible to blockage that limits the intra-particle mass transfer (Ulrich et al., 2015).

As these biochar properties can be affected by the production processes such as pyrolysis temperature, the removal of organic contaminants can vary based on biochar production methods (Kearns et al., 2014). For instance, gasification biochar (produced at >700 °C) retained atrazine, tris(3-chloro-2-propyl)phosphate, benzotriazole, and prometon more effectively than pyrolysis biochar (produced at 300–

800 °C) even at a lower biochar loading, possibly due to the high surface area of biochar produced by gasification (318 m^2/g) compared to pyrolysis (108 m^2/g) (Ulrich et al., 2015). High ash and labile organic carbon content associated with feedstock types and production conditions may also restrict biochar capacity to remove antibiotics as shown in a batch study (Shimabuku et al., 2016).

Biochar can also stimulate suitable microbial community for biodegradation (Kizito et al., 2017). Biochar-amended silty clay column enhanced adsorption of pentabromodiphenyl ether, an emerging contaminant, and facilitated biodegradation by promoting archaeal biodiversity (Yan et al., 2017). These studies suggest the synergistic effect of biofilm and biochar for enhancing the removal of organic contaminants, which may be applicable in biochar-augmented stormwater treatment systems.

The removal efficiency for organic contaminants varies as a function of stormwater constituents such as DOC and dissolved oxygen. Dissolved organic carbon, which is ubiquitous in stormwater, may block the micro- and nano-pores of biochar and compete with organic contaminants (Ulrich et al., 2015). Presence of DOC from compost can also stimulate the biodegradation of micropollutants in stormwater-augmented biofilter (Ulrich et al., 2017a). On the other hand, dissolved oxygen affects removal via biodegradation by altering the bacterial community structure (Yan et al., 2017).

Hydraulic characteristics of stormwater treatment systems can interfere with the removal of organic contaminants. When organic contaminant removal is kinetically limited, increasing the contact time via decrease in flow rate or increase in filter media height can improve adsorption and vice versa (Vilvanathan and Shanthakumar, 2017). In this case, the predominant removal mechanism evolves from adsorption to biodegradation due to the reduced availability of sorption sites and increased efficacy of the microbial community (Yan et al., 2017).

Unlike drinking water and wastewater treatment systems, stormwater treatment systems are naturally subjected to intermittent wetting events punctuated by drying periods. These conditions can affect the removal of organic contaminants by either influencing redox condition (or oxygen concentration) or enhancing the weathering and ageing of biochar surface (Mohanty and Boehm, 2015). Alternative flooding and drainage can enhance biodegradation due to the intermittent supplement of oxygen (Kizito et al., 2017). Biological, chemical, and physical weathering (freeze-thaw cycles) can change physicochemical properties of biochar to different extents (Hale et al., 2012). As a result, adsorption of organic pollutants on biochar will vary. For example, biochar ageing increased sorption of di-alkyl phthalate (Ghaffar et al., 2015) and decreased capacity for fomesafen (Khorram et al., 2015).

If the removal capacity of biochar is low, its surface can be modified or activated by chemical or physical means, although it will increase the overall cost of biochar similar to that of commercially available activated carbon. Chemical modifications can increase the surface area and/or alter the surface chemistry of biochar (Rajapaksha et al., 2016). For instance, the sawdust hydrochar activated by KOH improved adsorption of tetracycline as a result of the increased surface area and pore volume (Chen et al., 2017b). Another study demonstrated that the Fe-impregnated biochar removed 99.6% and 87.1% of injected naphthalene (NAPH) and p-nitrotoluene (p-NT), respectively (Chen et al., 2011). However, it is not clear if the use of iron-impregnated biochar is practical when stormwater has high amount of DOC, partly because DOC can quickly exhaust the adsorption capacity of iron and limit its utility in stormwater biofilter (Mohanty et al., 2013).

Opportunities: Most of the studies investigated the removal of a single or few organic contaminants in a less complicated matrix compared to stormwater. Research is needed to examine the effect of common co-contaminants in stormwater on removal capacity of biochar. It has been reported that removal of different PAHs from synthetic stormwater varied significantly (Reddy et al., 2014), possibly due to the competition among all contaminants for the biochar adsorption sites, which should be further investigated in the future. Furthermore, the long-term leaching of dissolved organic contaminants accumulated on biochars receives less attention than the removal of contaminants by biochar. For instance, depending on feedstock type and pyrolysis temperature, biochars contain organic compounds such as phenolics and bio oils, which may leach into infiltrating water (Lievens et al., 2015).

Removal of multiple contaminants of diverse nature may require biochar to be modified for multiple surface functionalities, or require addition of mixture of biochars with contrasting properties. For instance, addition of high temperature biochar can remove organic contaminants whereas addition of low temperature biochar can remove metals/metalloids. Further research is needed to evaluate the technical feasibility of different chemical modifications, as well as their cost-effectiveness to harness the economic merit of biochar, sustaining stormwater treatment in the long term. In addition, many studies showed that organic pollutants are removed mainly via adsorption on biochar, whereas limited studies evaluated the role of biodegradation

Table 3
Column studies examining the removal of organic contaminants by biochar.

Biochar	Contaminants	Removal[a]	Key findings	Reference
Buffalo weed biochar-alginate beads	2,4,6-Trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) (10–20 mg/L)	2.7–20.2 mg/g	• Adsorption of TNT, and RDX from wastewater highly depended on feed concentration. • Thomas model could be applied in designing of adsorption column.	(Roh et al., 2015)
Magnetic activated sawdust hydrochar	Tetracycline (100 mg/L)	423 mg/g	• Magnetic activated sawdust hydrochar achieved stable adsorption of tetracycline regardless of pH (5–9).	(Chen et al., 2017b)
Fe-impregnated biochar	Chlorpyrifos, endosulfan, fenvalerate, diuron (0.06–0.08 mg/L)	45–100%	• Integrated recirculating constructed wetlands comprising plants (*Cyperus alternifolius*) and Fe-impregnated biochar accomplished high removal efficiencies of the four pesticides by adsorption and microbial degradation.	(Tang et al., 2016)
Biochar-amended silty clay	Pentabromodiphenyl ether (BDE-99) (0.025 mg/L)	77.2–100%	• Biochar improved the biodiversity of the archeal community, which led to the anaerobic degradation of BDE-99. • As the recharge time and filter media depth increased, the dominating removal mechanism evolved from adsorption to biodegradation.	(Yan et al., 2017)
Soybean stover biochar (BC; pyrolyzed at 300 °C or 700 °C)	Trichloroethylene (TCE) 100 mg/L	36–515 mg/g	• The performance of BC700 was moderately lower than activated carbon but higher than BC300. • BC300 had lower TCE desorption rate due to its strong binding or partition to the non carbonized fraction of biochar.	(Zhang et al., 2015)
Biochar (0.5 wt%)	Several trace organic contaminants including atrazine and methylbenzotriazole. (10 μg/L)		• Biodegradation of trace organic contaminants in biochar-augmented biofilter increased in the presence of compost.	(Ulrich et al., 2017a)

[a] Removal (%) is based on breakthrough curve ($1 - C / C_0$), where C and C_0 are effluent and influent concentrations, respectively. If 100% breakthrough (exhaustion of biochar) was achieved during experiment, the removal was reported as capacity (mg of contaminants per gram of biochar).

in biochar-augmented contaminant removal. Biodegradation is equally important for maintaining steady adsorption capacity and long lifespan of the LID facility. Therefore, future studies should explore the possibilities of boosting specific microbial growth on biochar to increase biodegradation.

The long-term stability of the engineered/designer biochar against various conditions such as growth of microbes, weathering, inorganic/organic clogging needs to be evaluated. Moreover, the impact of intermittent flow conditions on LID performance should be considered. In particular, it is not clear whether or how the antecedent drying period affects biodegradation and release of organic contaminants. For instance, drying period is known to affect particulates released from subsurface soil (Mohanty and Boehm, 2015)—a process that can potentially release sequestered contaminants by mobilizing fine biochar particles (Chen et al., 2017a).

4.3.3. Nutrients

Nutrients can be removed from stormwater by biotic and abiotic processes. Abiotic processes include adsorption of nitrate, ammonium, and phosphate on geomedia as well as precipitation of phosphate, whereas biotic processes include assimilation of nutrients by plants and microbes, and denitrification by denitrifier microbial and fungal communities (Payne et al., 2014a). Capacity of biochar to remove nutrients has been tested using both batch and column experiments. While batch experiments are useful to estimate the sorption capacity of biochar and mechanism of nutrient removal, they are inadequate to simulate hydrological conditions such as flow through media in stormwater treatment systems. Table 4 summarizes the results of column studies where biochar was utilized to remove nutrients.

Biochar can remove nutrients by adsorbing them, altering hydraulic properties of soil, or affecting growth of bacteria and plants that are known to assimilate nutrients. For instance, biochar can help plant grow on sandy soil or increase plant resistance to biotic stresses (Elad et al., 2011), and a healthy plant community could increase nutrient uptake. The efficiency of denitrification depends on hydraulic residence time (Nordstrom and Herbert, 2017). Because the rate of biological transformation of nitrate decreases with a decrease in hydraulic retention time or storage volume, it is critical to add geomedia that can increase residence time and adsorb nitrate. In this case, biochar is a promising candidate to remove nutrients by enhancing attachment as well as increasing storage volume and residence time (Bock et al., 2015). Drying of geomedia, which can occur between rainfall events, can inhibit denitrification and lead to the release of nitrate (Tan et al., 2013). However, biochar can increase the water retention capacity of geomedia (Omondi et al., 2016), thereby potentially lowering the adverse impact of drying on plants or microbial communities that help assimilate nutrients. An increase in water retention capacity of soil or sand by addition of biochar helps maintaining anoxic condition, which can support diverse microorganisms responsible for denitrification (Chen et al., 2015). Addition of submerged layer can further improve nutrient removal, particularly nitrate (Nabiul Afrooz and Boehm, 2017). However, addition of a submerged layer in LID can increase its design cost. On the other hand, abiotic removal of nutrients by biochar can minimize the size of submerged zone required for denitrification, similar to how it was observed when activated carbon was used to enhance denitrification (Erickson et al., 2016).

Because biochar has negative surface charge and high cation exchange capacity, its capacity to remove NH_4^+ is typically more than that of NO_3^- (Yao et al., 2012). However, depending on water chemistry and biological activity, attached nutrients can be released back into infiltrating water (Sarkhot et al., 2013), causing effluent nutrient concentration to exceed influent concentration. Pyrolysis temperature appears to affect nutrient leaching. Biochar produced at high temperature was shown to increase net phosphate leaching (Park et al., 2015b), whereas an increase in pyrolysis temperature caused both increase and decrease of NH_4^+ leaching in two studies (Gai et al., 2014; Tian et al., 2016).

Phosphate removal capacity of biochar varied partly because biochar does not adsorb phosphate efficiently. To increase adsorption, biochar can be impregnated with cations such as Mg and Zn (Li et al., 2016; Park et al., 2015b; Yu et al., 2016), MgO-nanoparticles (Usman et al., 2016; Yao et al., 2011), or activated with acids (Chintala et al., 2013). For instance, activating sesame straw biochar with HCl, H_2SO_4, H_3PO_4, KOH, MgO, $ZnCl_2$, and K_2SO_4 (Park et al., 2015b), found that $ZnCl_2$–activated biochar removed maximum amount of phosphate. However, the activation will increase the overall cost of biochars and may make their application less economically competitive (Table 1).

It should be noted that biochar, based on the feedstock types, can become a sink or source of NO_3^- and PO_4^{3-} (Hale et al., 2013a; Kuoppamaki et al., 2016; Kuoppamaki and Lehvavirta, 2016). In particular, biochar derived from poultry litter (Tian et al., 2014) and pelletized digested

Table 4
Removal nutrients by biochar.

Biochar	Nutrient removal (%)	Key findings	Reference
Wood-based biochar and sand mixture (3:7) by volume.	29.2–64.8 (NO_3^-) 50–58 (NH_4^+)	• Submerged layer increased nitrate removal but did not have any impact on ammonium removal. • Addition of biochar improve removal capacity of biofilter from net leaching to net removal.	(Nabiul Afrooz and Boehm, 2017)
Poultry litter biochar Hardwood biochar 10% (w/w) biochar mixed with sand.	92–96 (NH_4^+)	• Biochar amended soil columns exhibited far greater ammonium removal capacity (>90%) compared to 1.7% removal in sand-only columns. • High-temperature pyrolyzed biochars exhibited limited release of organic and inorganic nutrient.	(Tian et al., 2016)
Biochar amended woodchips	32–100% (TN)	• Biochar improved TN removal capacity of biofilter when compared to woodchips alone. • N removal cost decreased by using biochar.	(DeBoe et al., 2017)
70.0% agricultural char & 30% char from passenger car tires 7% (w/w) biochar	−26–97 (NO_3^-) 1–43 (PO_4^{3-})	• Green roof soil amended with biochar can improve runoff water quality and retention	(Beck et al., 2011)
Biochar feedstock from birch wood (including bark) 7% (w/w) biochar	−5–24 (TN) −21–27 (TP)	• Green roofs can be a source of nutrients, dependent upon media and plant properties as well as fertilizer application • Lab and field scale studies showed contradictory removal efficiencies	(Kuoppamaki et al., 2016)
Pinewood (6.7 wt%, 33 vol%)	86 (TN) 68 (NO_3^-)	• Biochar-amended biofilters exhibited >60% removal of TOC, TN, NO_3^-, and TDP following 6 months of operation	(Ulrich et al., 2017a)
Bamboo charcoal 0.5% (w/w)	15.2 (NH_4^+–N)	• Bamboo charcoal slowed vertical mobility of NH^{4+}–N in soil column	(Ding et al., 2010)
Monterey pine-sawdust biochar; pine biochar; pine waste biochar	40–80 (NH_4^+–N)	• Leaching of NH_4^+–N significantly reduced with pine and pine waste biochars added to soil columns. • Addition of biochar did not significantly affect nitrate leaching	(Paramashivam et al., 2016)

sewage sludge (Shepherd et al., 2017) leach nutrients back into the system, and therefore should not be used in biofilter where nutrient removal is a priority.

Opportunities: The reported column and batch studies demonstrated the utility of biochar to remove nutrients in controlled laboratory conditions, which may not simulate complex natural conditions relevant to stormwater infiltration (*e.g.*, antecedent drying condition). Furthermore, previous studies that used modified biochar rarely used complex water matrix with DOC and co-contaminants, which can affect removal of nutrients. Ageing of biochar in stormwater systems can affect its removal capacity as anion exchange capacity of biochar is known to decrease with biochar age (Lawrinenko et al., 2016). Future studies should examine the best ways to apply biochar in stormwater treatment systems. In particular, it is not clear how the presence of other media could affect the performance of biochar. For instance, Iqbal et al. (2015) found that addition of biochar to compost or co-composting biochar did not significantly affect leaching of nitrate/nitrite, ortho-phosphorous, and DOC.

4.3.4. Biological contaminants

Biological contaminants such as pathogens, fecal indicator bacteria, and viruses are typically removed in stormwater biofilter by several mechanisms including physical filtration or straining, adsorption on geomedia, inactivation by chemical agents, predation, and die off during drying period (Rippy, 2015). Among all stormwater contaminants, biological contaminants are most difficult to remove because of their potentials to grow using nutrients in stormwater (Chudoba et al., 2013) and release from filter media during intermittent infiltration events (Mohanty et al., 2015a). Table 5 summarizes the results of column experiments with biochar to remove biological contaminants from contaminated water. These reported studies suggested that biochar may remove pathogenic bacteria more efficiently than non-pathogenic bacteria (Abit et al., 2014; Suliman et al., 2017), and the removal can vary among different strains of same bacterial species (Abit et al., 2012; Abit et al., 2014; Bolster and Abit, 2012). Although biochar addition mostly improves bacterial removal, it does not improve virus removal. Only one study evaluated biochar ability to remove virus and reported that addition of biochar in fact enhanced virus transport (Sasidharan et al., 2016), possibly because of electrostatic repulsion between virus and biochar surfaces. Biochar can also reduce the mobilization of bacteria during intermittent infiltration of stormwater. A low remobilization was attributed to increase in moisture content that limit detachment of bacteria during advancement of air-water interface and irreversible attachment of bacteria on biochar (Mohanty et al., 2014a).

Bacteria removal capacity of biochar depends on three main factors: biochar properties, indicator bacteria surface properties, and stormwater aqueous chemistry. Biochar properties such as particle size, pyrolysis temperature, and feedstock type affect bacteria removal.

Table 5
Removal of biological contaminants by biochar.

Biochar type	Contaminants (initial concentration)	Removal (%)	Key finding	Reference
Softwood/bark biochar 5% w/w sand	*E. coli* K12 (10^6 CFUs mL^{-1})	83–100	• Biochar weathered by intermittent infiltration of stormwater via dry-wet cycles removed more *E. coli* than biochar exposed to same amount of stormwater without drying cycle. • Removal of find biochar particles (<125 μm) substantially decreased *E. coli* removal.	(Mohanty and Boehm, 2015)
Poultry litter, pine chips (1 and 2% w/w soil)	*E. coli* (10^7 CFUs mL^{-1})	4–100	• Increase in pyrolysis temperature helped improve *E. coli* removal capacity of wood based biochar. • Poultry litter biochar was less effective than pine-chip biochar. • Removal was higher in unsaturated column than saturated column.	(Abit et al., 2012)
Poultry litter 2 and 10% w/w soil	*E. coli* (three isolates) (10^7 CFUs mL^{-1})	17–100	• High temperature pyrolyzed biochar at 10% biochar provided the greatest reduction in transport. • Low temperature pyrolyzed biochar enhanced transport for all but one isolate.	(Bolster and Abit, 2012)
Poultry litter, pine chips (2% w/w soil)	*E. coli* O157:H7 *Salmonella typhimurium* (10^7 CFUs mL^{-1})	−6 to 99	• Poultry liter biochar (350C) facilitated transport of bacteria. • Biochar produced at high pyrolysis temperature generally improved removal irrespective the feedstock. • Removal varies with pathogen species.	(Abit et al., 2014)
Raw hydrochar KOH activated-hydrochar (1.5% w/w sand)	*E. coli* (10^6 CFU mL^{-1})	72–93	• Activation of biochar with KOH increased removal efficiency and increased the strength of attachment (irreversible attachment). • Improved in removal due to activation was attributed to a decrease in net negative charge by activation.	(Chung et al., 2014)
Softwood/bark biochar 5% w/w sand	*E. coli* K12 (10^4–10^8 CFUs mL^{-1})	87–97	• Increase in flow rate and feed concentration of *E. coli* did not diminish removal potential of biochar. • Addition of compost countered the positive effect of biochar.	(Mohanty and Boehm, 2014)
Softwood/bark biochar; hardwood biochar 5% w/w sand	*E. coli* K12 (10^6 CFUs mL^{-1})	80–100	• Dissolved organic carbon decreased bacterial removal capacity of biochar. • Biochar decreased mobilization of attached *E. coli* during intermittent infiltration of stormwater.	(Mohanty et al., 2014a)
Waste wood biochar	*E. coli* (74 MPM/mL)	27	• Coarse biochar was inefficient at removing *E. coli* from stormwater	(Reddy et al., 2014)
Pine wood, pine bark 0–20% w/w sand	*E. coli* O157:H7 *E. coli* K12 (10^8 CFUs mL^{-1})	5–80	• Oxidation of biochar lowers removal capacity • Biochar more efficient at removing the pathogenic bacteria (*E. coli* O157:H7) than the nonpathogenic bacteria (*E. coli* K12).	(Suliman et al., 2017)
Mixed soft and hard wood biochar 30% v/v sand	*E. coli*, enterococci	75–100	• Biochar augmented biochars more efficiently removed *E. coli* than enterococci • Removal for both *E. coli* and enterococci decreases with repeated exposure to stormwater • Presence of saturation zone and length of antecedent dry period did not influence FIB removal	(Nabiul Afrooz and Boehm, 2017)
Wood derived low temperature biochar 30% v/v sand	*E. coli* (10^5 CFUs mL^{-1})	25–90	• *E. coli* removal decreased in the presence of biofilm. • Presence of natural organic matter in stormwater decreased *E. coli* removal.	(Nabiul Afrooz and Boehm, 2016)
Wood biochar modified with $H_2SO_4^-$, $H_3PO_4^-$, KOH^-	*E. coli* K12 (10^6 CFUs mL^{-1})	92–98	• H_2SO_4 activated biochar was most efficient at *E. coli* removal • Amino-modification resulted in less effective performance.	(Lau et al., 2017)
Biochar (10% w/w sand)	*E. coli* Bacteriophages (PRD1, MS2 and ΦX174)	5.3–67.8 (*E. coli*) 11.3–50 (virus)	• Biochar addition improved bacterial removal capacity of sand but diminished the attachment of virus. • Elimination of fine fraction (<60 μm) of biochar lowered it bacterial removal.	(Sasidharan et al., 2016)

In general, removal of fine biochar particles can lower the removal of bacteria (Mohanty and Boehm, 2014; Sasidharan et al., 2016), possibly because of decrease in surface area and decrease in porosity. Biochar produced by higher temperature pyrolysis exhibits better bacterial removal capacity (Abit et al., 2012; Suliman et al., 2017), because high temperature condition increases carbonization of biomass, which in turn enhances hydrophobic attachment of bacteria on biochar surface. Feedstock types affect bacterial removal because pyrolysis of biochar can produce other constituents such as nutrients, ash, and volatile organic carbon. For instance, poultry liter biochar contains excess phosphate and other nutrients that not only limit bacterial attachment but also decrease the removal of other anionic co-contaminants (Abit et al., 2012). Thus, wood-based biochar, not poultry liter biochar, should be used in stormwater treatment system for bacterial removal. High ash content could increase pore water pH and decrease the attachment of bacteria; thus, biochar with low ash content should be used for bacterial removal.

Bacterial removal also varies with stormwater composition. However, most studies estimated biochar capacity to remove indicator bacteria in deionized water without stormwater constituents, particularly natural organic matter (NOM). NOM is ubiquitous in stormwater and can lower adsorption capacity of many geomedia used for treatment of drinking water (Abudalo et al., 2010; Zhao et al., 2014) and stormwater (Mohanty et al., 2013). Although the presence of NOM in stormwater decreased bacterial removal capacity of biochar, it still performed better than sand, a traditional bioretention medium (Mohanty and Boehm, 2014; Mohanty et al., 2014a). However, when biochar is mixed with compost, biochar cannot remove any more indicator bacteria than conventional bioretention media (Mohanty and Boehm, 2014) due to overwhelming amount of compost-derived DOC in the pore water.

Stormwater treatment systems are subjected to typical weather conditions such as fluctuating temperature or drying environment, wetting, and freeze-thaw cycles. These conditions can affect biochar capacity to remove biological contaminants. Mohanty and Boehm (2015) found that biochar exposed to stormwater with NOM via dry-wet cycles removed more bacteria than biochar exposed to the same volume of stormwater without drying cycles. They attributed this result to removal or mineralization of NOM from biochar surface during drying periods. Thus, drying period between rainfall events can help regenerate adsorption capacity of biochar as adsorbed organic carbon are mineralized or diffused into internal pores. Other studies, however, found an opposite effect of weathering on bacterial removal capacity of biochar. For instance, oxidation of biochar surface at high temperature or in the presence of air can increase in negative surface charge (Wang et al., 2017), and consequently decrease bacterial attachment (Suliman et al., 2017). Similarly, biological ageing such as formation of biofilm on bacterial surface can decrease indicator bacteria removal in stormwater biofilter (Nabiul Afrooz and Boehm, 2016). Overall, these studies indicate that biochar performance can vary in nature due to weathering of biochar.

Opportunities: More studies should use actual pathogen and virus, not indicators, to test the removal capacity of biochar. While removal of virus by biochar was low, bacterial removal capacity of biochar varied by orders of magnitude, which adds uncertainty to the performance of biochar-augmented LID. Future studies should establish methods to tailor biochar properties to maximize its bacterial removal capacity. While biochar improved bacterial removal capacity of conventional bioretention media in laboratory studies, it has not been tested in pilot studies or field applications. Future studies should examine whether the laboratory performance of biochar can be demonstrated in field environment. The conditions are more complex due to exposure to dry-wet and freeze-thaw cycles, which can enhance the mobility of particles and particle-associated contaminants from soil (Mohanty et al., 2014b; Mohanty et al., 2015b). Most studies, with a few exceptions (Nabiul Afrooz and Boehm, 2017; Reddy et al., 2014), used high bacterial concentration—orders of magnitude greater than the typical concentration observed in stormwater. Increase in feed concentration can result in high bacterial removal; thus, future studies should use bacteria at low concentration (relevant to stormwater) to examine whether feed concentration has any impact on bacterial removal. To overcome inconsistency in bacterial removal, biochar can be activated or augmented with other antimicrobial agents. Activation would increase the cost of biochars and may deem their use less environmentally

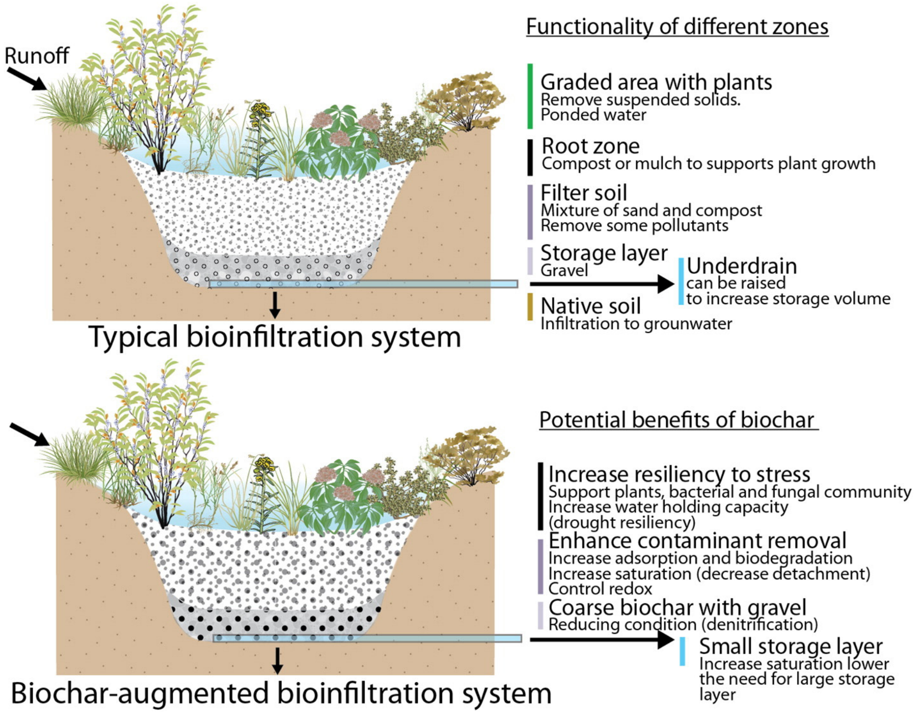

Fig. 2. Potential functions of biochar at different region of bioinfiltration system.

Table 6
Potential use of biochar in low impact development system to increase removal of stormwater contaminants.

Low impact development system	Advantages/disadvantages	Potential benefits of biochar use
Downspout filter boxes: a box packed with geomedia, including soil and compost, to support plants and to remove contaminants accumulated or deposited on the roof top. Roof gutters route stormwater from the surface of the roof into downspouts that feed into vegetated filter boxes, which are generally located at the ground level.	• Primarily remove metals/metalloids and TSS • Easier to install maintain and replace then other BMPs • Limited to stormwater on roofing • Limited capacity to remove nutrients leaching from planter boxes	• Help remove other contaminants including nutrients and organic chemicals. • Support plant growth in filter box by retaining water and slowly releasing nutrients
Tree boxes: a pre-manufactured concrete box buried underground filled with soil media and typically planted with a native tree or shrub. Stormwater from nearby impervious surfaces enters through curb cuts at the top of the BMP. Stormwater infiltrates through the media and feeds into storm drain system through a perforated pipe.	• Remove particulate contaminates (Maniquiz-Redillas and Kim, 2016) • Low installation and maintenance cost • Limited nutrient and pathogen removal (Schifman et al., 2016) • Above/below ground space limitations	• Augment the filter media with biochar, which could not only increase contaminant removal but also support the growth of plant by retaining water and nutrients from runoff.
Green roofs: vegetation layer on a building roof that serves to capture direct precipitation. Geomedia is chosen to be lightweight comprising of lightweight soils and additives such as pumice.	• Noise reduction (Berndtsson, 2010) • Reduction in urban heat island effect • Pollutant removal limited to deposited airborne contaminants. • Potential for nutrient release from green roof fertilizers and composts.	• Support plant growth on green roof by retaining water (Kuoppamaki et al., 2016)and slowly releasing nutrients • Increased nutrient removal (Kuoppamaki et al., 2016; Kuoppamaki and Lehvavirta, 2016) • Low weight geomedia (Beck et al., 2011)
Bioinfiltration/bioretention system: a depressed vegetated tack of land where the soil is replaced with filter media (typically sand and compost) to re-route stormwater to storm drain system (bioretention) or into underlying soil (bioinfiltration).	• Removal of wide variety of pollutants. • Increased potential for biodiversity and urban environmental education (Ahern, 2013) • Larger area demand (5% of the impervious watershed) (US EPA, 2009) • High installation and maintenance cost	• Support plant growth in bioretention system by retaining water and slowly releasing nutrients • Increase contaminant removal
Natural and constructed wetlands: a depressed, vegetated tract of land where the groundwater table is higher than the surface elevation of the BMP, facilitating the formation of a permanent shallow pond.	• Increased potential for biodiversity and urban environmental education (Ahern, 2013) • Removal of a wide variety of pollutants. • Operation and maintenance costs are variable and expensive. • Relatively land intensive	• Support plant growth in constructed wetland by retaining water and slowly releasing nutrients • Increase contaminant removal
Sand filters: it consists of an initial sedimentation chamber which removes large and heavy sediments. Stormwater then percolates through the sand filter, at a designed infiltration rate. Stormwater is ultimately captured by a perforated pipe in the underlying layer and feed into storm drain system.	• Primarily remove metals/metalloids and TSS (Hatt et al., 2008) • Minimal land requirement • Limited nutrient removal (Hatt et al., 2008) • High operation cost to prevent clogging	• Increased removal of hydrocarbons, metals, TSS, and toxic organics
Level spreader (**filter strips**): a densely vegetated area, on a mild slope, that promotes sheet flow of stormwater, reduces the velocity of stormwater and additionally facilitates infiltration and sedimentation over the vegetated surface.	• Low construction and maintenance cost • Removal of a wide variety of pollutants (Knight et al., 2013) • Erosion • Land intensive	• Support plant growth in level spreader by retaining water and slowly releasing nutrients • Increase contaminant removal
Swales: constructed trenches or canals with a dense vegetated surface. Their design allows for the conveyance of stormwater, velocity reduction, and infiltration.	• Groundwater recharge potential • Removal of a wide variety of pollutants. • Use restricted in flat and steep graded areas • Unable to handle high flow rates	• Support plant growth in swales by retaining water and slowly releasing nutrients • Increase contaminant removal
Infiltration trenches: an excavated trench that is then backfilled with course gravel and stone to create room for water storage in the void space.	• Groundwater recharge potential • Moderate land demand • Limited nutrient and pathogen removal	• Increase removal of hydrocarbons, metals, TSS, and toxic organics
Wet retention pond: wet ponds are depressed tacts of land that	• Groundwater recharge	• Increase contaminant removal

Table 6 (*continued*)

Low impact development system	Advantages/disadvantages	Potential benefits of biochar use
allow for the ponding of stormwater during hydrologic events.	potential • Increased potential for biodiversity • Minimal maintenance cost • Moderate land demand • Must maintain permanent pool	

friendly. While activation generally improved bacterial removal and decreased mobilization (Lau et al., 2017), its impact in the long term is unknown due to weathering of biochar in nature that may reverse the changes occurred during activation. Furthermore, introducing antimicrobial agents can adversely impact natural microbiome that helps degrade organic contaminants. Therefore, future study should account for both positive and negative impact of geomedia modification and the cost associated with modification.

5. Recommendations for biochar use in stormwater treatment systems

Although laboratory studies have demonstrated the potential benefits of biochar for stormwater treatment, its capacity in field conditions, particularly in different types of low impact development (LID), has not been reported. Based on the findings of laboratory studies, we surmise that biochar in stormwater treatment systems in field conditions can serve three main functions: (1) soil amendment for plant growth that may increase the remove of nutrients, (2) filter media for contaminant removal, and (3) hydraulic and redox manipulation of geomedia layer to further enhance contaminant removal (Fig. 2). Miles et al. (2016) summarized possible use of biochar in different stormwater treatment systems. In addition to providing a similar assessment in Table 6, we include the benefits and drawbacks of each type of LID, and the mechanistic reasons behind the use of biochar at different locations within LID.

6. Summary

Biochar has high potential to remove stormwater contaminants and maintain plant health in stormwater treatment systems. In comparison to activated carbon, use of biochar in stormwater biofilter is particularly viable because of its low cost and diverse environmental benefits. Based on biochar use at different sections of biofilters, biochar can serve multiple functions:

- Soil amendment for plant growth, which can substitute the use of other organic amendments such as compost that have negative impact on contaminant leaching.
- Filter media for contaminant attachment/removal. Biochar is particularly useful to remove organic contaminants from stormwater, whereas removal of metals/metalloids, nutrients, and pathogens varies by a wide range based on biochar surface properties, contaminant properties, and water chemistry.
- Storage media to increase water holding capacity. Increase in saturation by biochar addition can help increase denitrification.
- Redox control agent to further enhance contaminant removal via reduction/oxidation.

Many opportunities exist to examine the effectiveness of biochar in conditions relevant to stormwater treatment. A summary of future opportunities is listed below:

- Laboratory studies on biochar do not account for all complexities of stormwater biofilters, including unsteady/intermittent flow, changing weather conditions, and variable loading based on concentrations of contaminants and flow rate. Result from field application biochar to treat stormwater is lacking or rarely reported. Thus, future research should conduct pilot- or field-scale studies to validate the results of laboratory column experiments and identify possible causes of discrepancies, if any.
- It is unclear how weathering and ageing in field conditions and the presence of co-contaminants would affect the removal capacity of biochar in the long term.
- Future studies should evaluate methods to tailor specific biochar properties to increase the predictability of contaminant removal.
- Physical erosion of biochar particles from stormwater treatment systems needs further investigation.
- Future studies should examine the effect of biochar on manipulation of rhizosphere bacteria and fungi, which degrade the sequestered contaminants in stormwater LID.

Despite these challenges, biochar appears to be more viable and promising material than other available geomedia for stormwater treatment, because it is relatively less expensive, readily available, and has capacity to serve multiple beneficial functions in stormwater treatment systems.

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