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Application of biochar as an innovative soil ameliorant in bioretention system for stormwater treatment: A review of performance and its influencing factors

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ABSTRACT

As an emerging environment functional material, biochar has become a research hotspot in environmental fields because of its excellent ecological and environmental benefits. Recently, biochar has been used as an innovative soil ameliorant in bioretention systems (BRS) to effectively enhance pollutant removal efficiency for BRS. This paper summarizes and evaluates the performance and involved mechanisms of biochar amendment in BRS with respect to the removal of nutrients (TN (34–47.55%) and PO_4^{3-}-P (47–99.8%)), heavy metals (25–100%), pathogenic microorganisms (*Escherichia coli* (30–98%)), and organic contaminants (77.2–100%). For biochar adsorption, the pseudo-second-order and Langmuir models are the most suitable kinetic and isothermal adsorption models, respectively. Furthermore, we analyzed and elucidated some factors that influence the pollutant removal performance of biochar-amended BRS, such as the types of biochar, the preparation process and physicochemical properties of biochar, the aging of biochar, the chemical modification of biochar, and the hydraulic loading, inflow concentration and drying–rewetting alternation of biochar-amended BRS. The high potential for recycling spent biochar in BRS as a soil ameliorant is proposed. Collectively, biochar can be used as an improved medium in BRS. This review provides a foundation for biochar selection in biochar-amended BRS. Future research and practical applications of biochar-amended BRS should focus on the long-term stability of treatment performances under field conditions, chemical modification with co-impregnated nanomaterials in biochar surface, and the durability, aging, and possible negative effects of biochar.

Key words: biochar, bioretention, influencing factors, mechanism, pollutant removal, stormwater

HIGHLIGHTS

- Biochar as an innovative ameliorant in bioretention system (BRS) for stormwater treatment is reviewed.
- Biochar enhances pollutant removal, which benefits soil amendment, adsorbent, redox control agent and nutritional supplement.
- The application of biochar-amended BRS must be scaled up, emphasizing high performance and long-term stability.

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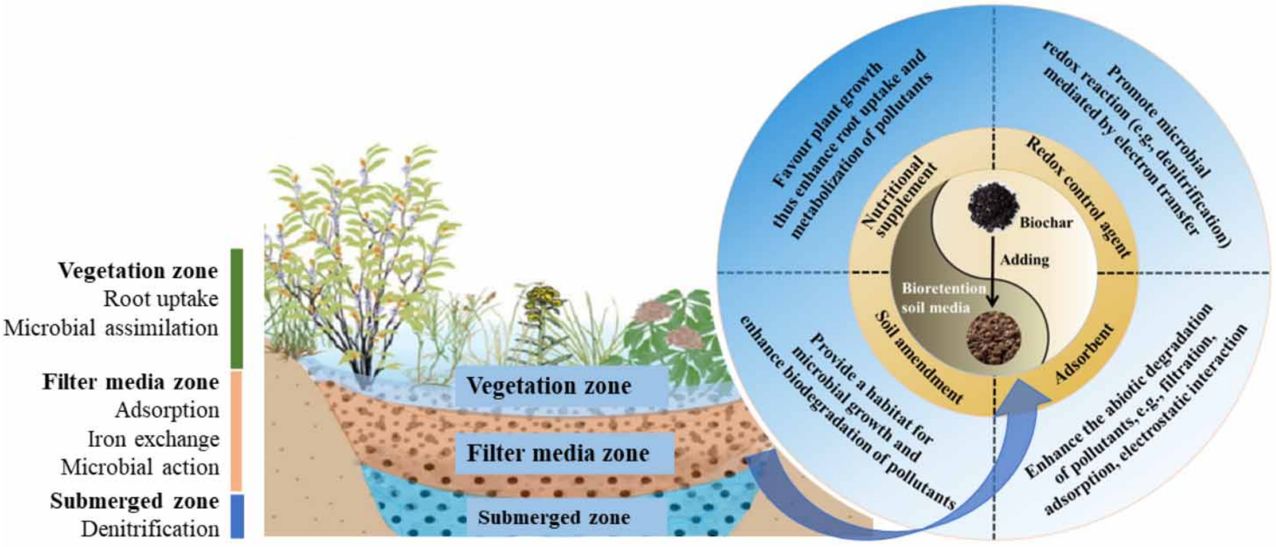
GRAPHICAL ABSTRACT



1. INTRODUCTION

With urbanization, many natural green spaces have been progressively replaced by impervious pavements, leading to increased stormwater runoff and peak flow and increased pollutants in runoff (Osman *et al.* 2019). Therefore, early urban stormwater runoff has become one of the main pollution sources of surface receiving water bodies (Jia *et al.* 2021). Many countries have proposed advanced stormwater management concepts; China recently proposed an innovative idea and new methodology called the Sponge City (SPC) to improve effective control of urban runoff and to temporarily store, recycle, and purify urban stormwater (Chan *et al.* 2018; Yin *et al.* 2021). The bioretention system (BRS) is a common type of low-impact development (LID), and it has become the widely used measure in SPC construction and the most preferred technical measure for stormwater reuse. It can remove pollutants from urban stormwater through the combined action of porous soil media, plants, and microorganisms (Lucke & Nichols 2015; Wang *et al.* 2017b; Mehmood *et al.* 2021). Treating stormwater for recycling as a fit-for-purpose water resource must meet the applicable water quality standards (Hong *et al.* 2022). Untreated urban stormwater usually contains some risk pollutants, such as pathogens, heavy (toxic) metals, and emerging organic pollutants, which pose high risk to receiving waters and human health. For instance, toxic metals in stormwater runoff resulting from the wear of motor vehicle parts, industrial or manufacturing activities, and metal-coated roofs (LeFevre *et al.* 2015) can cause cell deformation of organisms in the surrounding environments (Muthusaravanan *et al.* 2018). Organic pollutants in stormwater, such as phthalates, industrial phenols, benzene, bisphenol A and diethylstilbestrol, may interrupt genomic epigenetic factors, causing diseases and even causing human death (Sharavanan *et al.* 2019). Microbial pathogens in water runoff may cause skin diseases or infections (Xu *et al.* 2020).

The bioretention medium is crucial to the BRS's ability to remove pollutants. It not only removes pollutants through physical and chemical mechanisms but also provides habitats for microorganisms to support the biological removal process of pollutants (Hong *et al.* 2022; Xiong *et al.* 2022). However, the medium in traditional BRS is relatively simple, usually comprising a mixture of soil (or organic materials) and sand (Jiang *et al.* 2019). This can make it difficult for BRS to balance permeability and decontamination performance, and contaminant' leaching can occur (Chandrasena *et al.* 2014; Xiong *et al.* 2019). To solve this problem, scholars have extensively researched soil media improvements. Many studies (Zhang *et al.* 2008; Bjorklund & Li 2017; Poor & Kube 2019; Tian *et al.* 2019; Kong *et al.* 2021) have explored that adding iron chips (e.g., zero-valent iron, iron oxide), wood chips, industrial byproducts (e.g., coconut shell, high-carbon ash, activated carbon) and biochar prepared from solid wastes into the bioretention media can effectively improve the decontamination ability of BRS. Therefore, modifying the soil media of the traditional BRS is necessary to meet functional objectives, especially by seeking out new types of green and environmentally friendly materials to augment the physicochemical properties of soil medium to enhance the decontamination capacity of BRS.

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Biochar, a porous carbon-rich material derived from biomass pyrolysis under oxygen-free or oxygen-limited conditions, has emerged as an innovative and promising additive or adsorbent in pollution control systems. Numerous studies have been conducted on biochar-modified BRS, focusing on the effect of biochar on soil physicochemical properties and microbial communities, the effect of biochar on the carbon footprint (Xing *et al.* 2021), the effect of biochar on the transformation and migration of pollutants in soil, and the effect of biochar-augmented filler on purifying stormwater quality (Xiang *et al.* 2019; Yang *et al.* 2019). Made biochar as an alternative for bioretention modified media is attractive because it has controllable surface properties (Hong *et al.* 2022). For instance, biochar is an efficient adsorbent for removing phosphorus from stormwater due to its high specific surface area (Jung *et al.* 2015), and it has a strong binding ability for heavy metals such as Cu, Cr, and Pb due to its abundance of oxygen functional groups (e.g., hydroxyl and carboxyl groups) (Yang *et al.* 2019). Dry-derived biochar has high ash content and rich surface functional groups, exhibiting excellent adsorption performance for tetracycline in water (Jang & Kan 2019). Meanwhile biochar can be used as a carbon source in BRS to provide an electron donor for the denitrification process, thereby achieving simultaneous nitrification and denitrification and mitigating greenhouse gas (N_2O) emissions (Xu *et al.* 2014; Xia *et al.* 2022). However, there is no consistent evidence that biochar can enhance the decontamination ability, and the biochar's ability to remove pollutants under different conditions showed uncertainty and sometimes did not promote the removal of pollutants (Valenca *et al.* 2021b; Biswal *et al.* 2022; Xiong *et al.* 2022). The improper use of biochar may not promote the removal of nitrate, but it will reduce the denitrification rate of BRS, and the addition of an excessive amount of carbon source will result in nitrogen leaching and secondary pollution (Valenca *et al.* 2021b; Xiong *et al.* 2022). Schmidt *et al.* (2021) demonstrated that adding biochar increased soil porosity, thereby promoting hydraulic conductivity, whereas Jia *et al.* (2021) found no positive effect of biochar on hydraulic conductivity. Some peer-reviewed studies have focused on the decontamination mechanism and biochar application in BRS (Boehm *et al.* 2020; Deng *et al.* 2021; Biswal *et al.* 2022). However, to the best of our knowledge, a systematic review illustrating the removal mechanisms and various decontamination factors of biochar as an innovative soil ameliorant is still lacking in the scientific literature. For instance, the enhancement mechanism of biochar involved in the removal performance of biochar-amended BRS has not been reviewed. The potential influence of various factors such as application characteristics of biochar and operation environments of biochar-amended BRS on removal performance has not been thoroughly reviewed.

The objective was to identify gaps in the present literature and propose future biochar-amended BRS studies. In the present review, we present comprehensive research progress on the removal performance and involved biochar amendment mechanisms in BRS for removing nutrients, heavy metals, pathogenic microorganisms, and emerging organic pollutants. This review studied the kinetic and isotherm models of biochar adsorption and then summarized the benefits and underlying removal enhancing mechanisms of biochar in biochar-amended BRS to elucidate biochar's contribution to BRS. Furthermore, this review systematically evaluates the factors that influence the pollutant removal performance of biochar-amended BRS, such as the types of biochar, the preparation process and physicochemical properties of biochar, aging of biochar, chemical modification of biochar, hydraulic loading and inflow concentration, and drying–rewetting alternation of biochar-amended BRS. According to our knowledge, no comprehensive summary of the factors affecting the removal efficiency of biochar-amended BRS has been prepared so far. This work is novel enough to grasp the attention of researchers and policymakers, as it provides new and comprehensive insights into the design, establishment, operation, and management of biochar-amended BRS. This work will help in the decision-making process for a more appropriate and practical selection of biochar to optimize the design of biochar-amended BRS. This work ends with a discussion on future research and practical applications.

2. BIOCHAR ENHANCES THE REMOVAL PERFORMANCE OF BRS AND ITS RELATED MECHANISMS

2.1. Nitrogen and phosphorus removal

BRS eliminates nitrogen and phosphorus from stormwater through abiotic and biotic processes. Abiotic processes include medium adsorption of ammonium and phosphate, ammonia volatilization, and phosphate precipitation, whereas biotic processes include plant uptake and coupled microbial processes such as immobilization, nitrification, and denitrification (Payne *et al.* 2014). It has been confirmed that the nitrogen removal efficiency of conventional BRS is unstable, and nitrogen leaching occasionally occurs (Zhang *et al.* 2021a). Some studies have demonstrated that the removal rates of NH_4^+-N, NO_3^--N, and total nitrogen (TN) were significantly enhanced by adding biochar as an addition into the soil medium of bioretention facilities, but the removal rate of total phosphorus (TP) was low (Sang *et al.* 2019). Reddy *et al.* (2014) conducted a series of

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laboratory-scale soil column tests in which all columns were filled with biochar prepared with sawdust at 520 °C to simulate the rainfall infiltration process and investigated biochar's removal performance of pollutants. The results revealed that total suspended solids (TSS), NO_3^--N, and PO_4^{3-}-P in the outflow decreased by 86, 86, and 47%, respectively. Xu *et al.* (2016) revealed that adding 2, 4, and 8% biochar (mass ratio) can reduce the total accumulation of leaching nitrogen by 18.8, 19.5, and 20.2% ($P < 0.05$), respectively, and more than 90% of the total leaching nitrogen existed in the form of nitrates. The results indicated that nitrogen leaching decreases as biochar dosage increases. Meanwhile other studies have demonstrated that adding 30% (volume ratio) or 5% (mass ratio) of biochar in BRS can remove 99.42% of total ammonia nitrogen from stormwater sufficiently (Rahman *et al.* 2020a).

There are five main nitrogen removal pathways in the biochar-amended BRS (as displayed in Figure 1). First, biochar has a high cation exchange capacity and an abundance of negatively charged functional groups for NH_4^+-N adsorption, allowing it to improve nitrogen removal by enhancing adsorption. Second, adding biochar can significantly improve soil water retention and capillary soil force, which promotes the development of a micro-anoxic environment in capillary water (Ahern 2013; Liu *et al.* 2021). Under redox conditions, the anoxic state of soil promotes denitrification. Third, biochar can also serve as an electron donor for denitrifying bacteria, thereby enhancing denitrification (Tian *et al.* 2019). Fourth, the favorable porous structures and high specific surface area of biochar can also provide suitable environments for the growth of microbes such as nitrifiers, and the high porosity of biochar medium can facilitate atmospheric reaeration and oxygen filling within the bioretention soil matrix, which may lead to significantly higher soil microbial activity (Xu *et al.* 2014, 2016); thus, changes to biochar medium can stimulate suitable microbial communities to become dominant microflora and then accelerate nitrification and denitrification (Saquing *et al.* 2016; Kizito *et al.* 2017), which can effectively enhance NH_4^+-N, NO_3^--N and total nitrogen (TN) removal in biochar-modified BRS. Previous research has indicated that adding corn-straw biochar to soil columns may alter the microbial community structure related to the nitrogen cycle, highlighting the effect of biochar on the microbial transformation of nitrogen (Xu *et al.* 2016). The fifth enhancing pathway is that adding biochar as an addition bioretention soil medium can assist plant adaptation to adverse conditions such as drought (Kammann *et al.* 2011) and biological stress (Elad *et al.* 2011), indicating the positive effects of biochar on plant growth.

The main phosphorus removal pathways in BRS are substrate adsorption, plant uptake, and anion exchange. Lawrinenko & Laird (2015) discovered that some biochars have a good anion exchange capacity (AEC), which may reduce the leaching of PO_4^{3-}-P in soil. Several studies have documented that adding biochar can promote plant growth and the proliferation of phosphorus-accumulating organisms (PAOs) in soil, thereby enhancing biological phosphorus removal (Ji *et al.* 2020). However, this reinforcing effect is not obvious because phosphate is poorly adsorbed by negative-charged biochar with a low affinity for phosphate and other negative-charged compounds. Some chemical modification methods to improve the adsorption capacity of biochar have been adopted, such as the impregnation method with Mg and Fe cations (Park *et al.* 2015; Li *et al.* 2016; Yu *et al.* 2016) and acid modification (Chintala *et al.* 2013). Substantial studies have been conducted on the role of biochar in improving phosphorus removal in BRS. For instance, previous research has documented that the average removal rate of PO_4^{3-}-P was close to 90% when the bioretention cell incorporated Fe-biochar, while the bioretention cell modified with common biochar demonstrated a poor removal efficiency of PO_4^{3-}-P, and the average removal rate was less than 60% (Xiong *et al.* 2019).

2.2. Heavy metal removal

The heavy metals in stormwater runoff mainly exist in particulate and dissolved forms. Laboratory and field studies have demonstrated that BRS can remove heavy metals from stormwater, and the predominant removal mechanisms for a given metal are determined by its speciation and characteristics (LeFevre *et al.* 2015). The removal of heavy metals in particulate form complies with filtration or sedimentation, whereas dissolved metal ions are removed by the adsorption to the bioretention soil media or plant uptake. Among these, the process of dissolved metals sorption in bioretention soil media is mainly cation exchange, and the extent of metal adsorption depends on its combination ability with negatively charged surface sites, or absorption capacity through surface complexation with some polar functional groups and exchange dissociation of metal cations (Figure 1) (Jang *et al.* 2005; Hasany & Ahmad 2006). Studies have confirmed that the biochar-based bioretention soil medium can effectively enhance the removal of Ni, Cu, Cd, and Pb from stormwater runoff, and the removal rate was up to 80% (Ashoori *et al.* 2019), and the medium can achieve extensive removal efficiency for various metals from 18 to 75% (Reddy *et al.* 2014). Some chemical activation methods can be adapted to modify the surface characteristics of biochar, thereby enhancing its removal performances. The Al-impregnated biochar can effectively remove As, Pb, Zn, and Cu in

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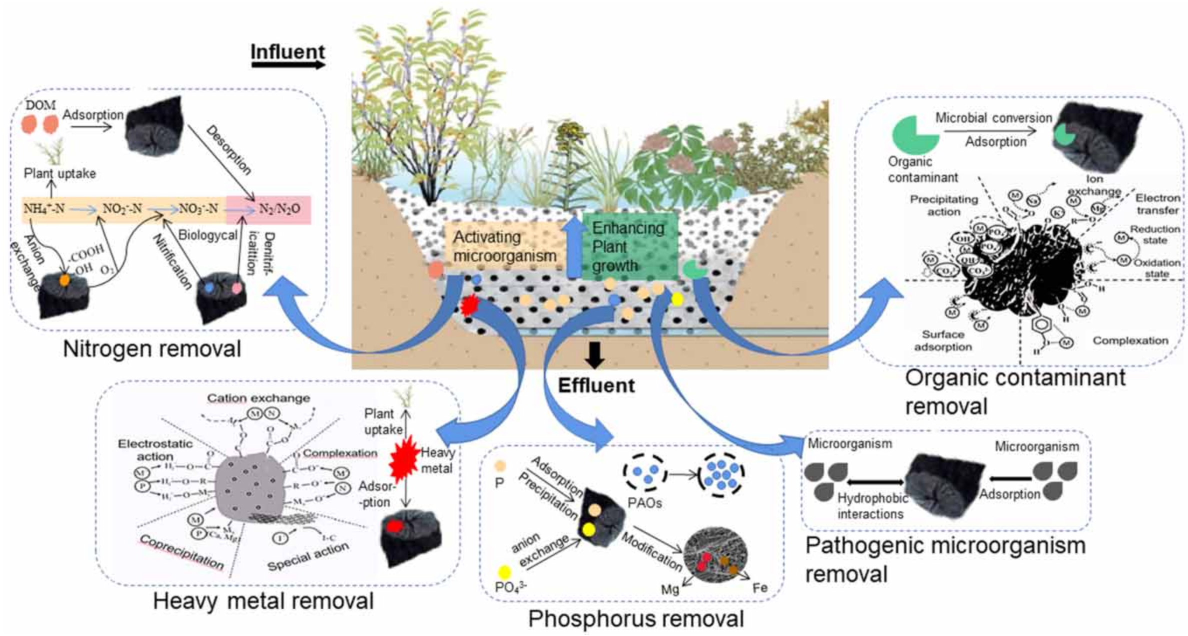

Figure 1 | Benefits of biochar as an amendment in BRS and the corresponding mechanisms involved in enhancing pollutant removal (modified from published papers (Mohanty *et al.* 2018; Deng *et al.* 2021), with permission). DOM: dissolved organic matter; PAOs: phosphorus accumulating organisms.

urban stormwater, and the impregnation of nanomaterials on biochar, which is a strong adsorbent, can enhance metals removal (Liu *et al.* 2019). Moreover, the removal rate of multicomponent metals in a nanoscale zero-valent iron-modified biochar-based sand column is higher than that of a biochar-based sand column, and the results suggest that the efficiency of a nanoscale zero-valent iron-modified biochar and unmodified biochar-amended infiltration columns was superior to the columns with the homogeneous sand medium in removing heavy metals from stormwater (Hasan *et al.* 2020).

The removal of heavy metals by BRS depends on the adsorption capacity of the soil medium and the bioaccumulation capacity of plant roots, whereas the characteristics of plant roots depend on the soil's water holding capacity and soil nutrient supply. Therefore, the application of biochar in BRS as an amendment to modify the soil medium can not only enhance the adsorption capacity of heavy metals but also strengthen the bioaccumulation and uptake capacity of heavy metals by plants, improve the physiological characterization of plant resistance to heavy metal stress, and ultimately promote the uptake of heavy metals by plant roots (Rees *et al.* 2015). Furthermore, metals can be adsorbed by ion exchange, chemical precipitation, and complexation of negatively charged functional groups on the surface of biochar (Figure 1), especially the chemical precipitation of cationic metals can be further enhanced with the presence of abundant anions released by biochar such as carbonate, phosphate, and hydroxide (Gwenzi *et al.* 2017). Biochar with high ash content increases the pH value of the solution, decreasing the solubility of metals and increasing their removal rate through precipitation (Zhou *et al.* 2016). Furthermore, as an electron shuttle agent and donor, biochar can reduce some metals by the redox activity, such as the reduction of Cr(VI) to Cr(III), Hg(II) to Hg(0), and then decrease the toxicity of metals (Chen *et al.* 2018). However, there may be competition for binding sites in systems with multiple metals, and those co-existing pollutants in stormwater, including pathogens and organic pollutants, may also compete for adsorption sites on biochar, thereby affecting the removal of heavy metals from systems.

2.3. Pathogenic microorganism removal

Pathogenic microorganisms are usually removed in BRS through physical filtration, adsorption, chemical inactivation, predation, and straining induced by exposure to droughty stressors (Rippy 2015). Pathogenic microorganisms are the most difficult pollutants to remove, with a significant difference between the removal of various pathogens (Figure 2). This is because they can use nutrients in stormwater to grow (Chudoba *et al.* 2013) and in multiple drying–rewetting conditions, the desorption of pathogenic bacteria such as *Escherichia coli* will be significantly higher than its adsorption, resulting in a decrease in the

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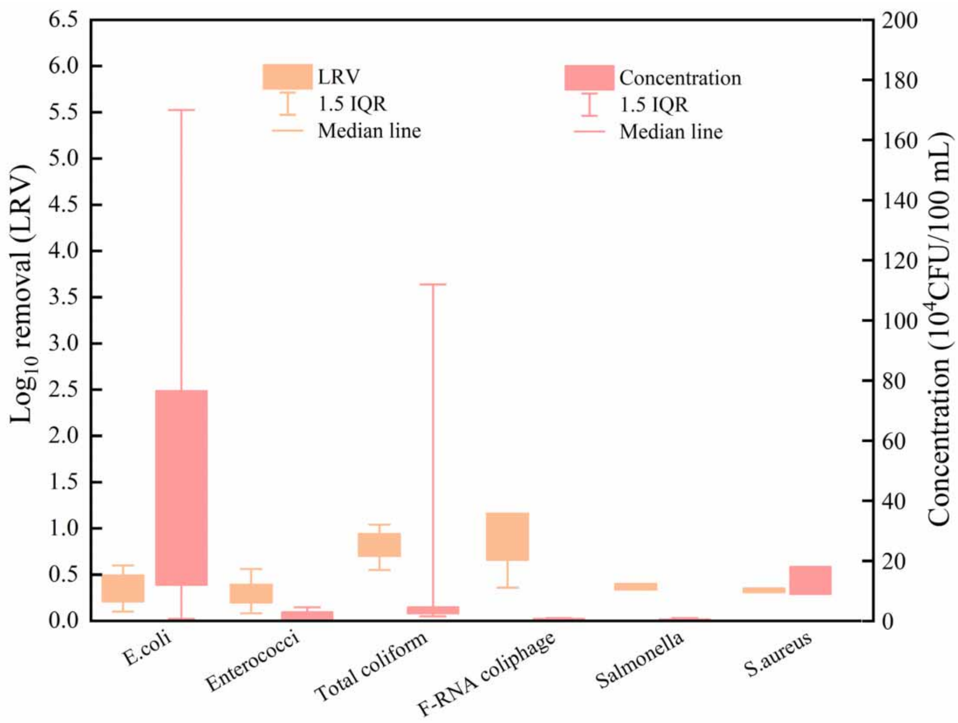

Figure 2 | Removal efficiency of bioretention on pathogens (data from previous publications (Thurston *et al.* 2001; Struck *et al.* 2008; Mohanty & Boehm 2014; Mohanty *et al.* 2014; de Rozari *et al.* 2015; Afrooz *et al.* 2018; Kranner *et al.* 2019; Rahman *et al*. (2020a).

pathogen removal rate. Studies have demonstrated that the removal rate of *E. coli* by the biochar-amended BRS is 96%, and it is not affected by a variety of stormwater infiltration rates and bacterial concentrations (Mohanty & Boehm 2014). When modified biochar was added to the bioretention soil media, the removal rate of *E. coli* increased significantly from 35% to approximately 92–98% (Lau *et al.* 2017). Although the nutrients present in stormwater for growth, Valenca *et al.* (2021a) discovered that *E. coli* in the pore water of the biofilter stop growing after rainfall, highlighting that biochar may continue to remove pathogens during inter-event periods.

Some characteristics of biochar, such as high porosity, many pores of different sizes, organic leaching, and hydrophobicity, may make it more suitable for pathogen removal than sand or gravel. Biochar can not only enhance the adsorption of pathogenic microorganisms (Figure 1) but also reduce pathogen mobilization during intermittent infiltration of stormwater (Mohanty & Boehm 2014). The statistical analysis is based on summary data from previous studies (Roy-Poirier *et al.* 2010; Abit *et al.* 2014; Mohanty & Boehm 2014; de Rozari *et al.* 2015; Afrooz & Boehm 2016; Afrooz & Boehm 2017; Lau *et al.* 2017; Suliman *et al.* 2017) demonstrating that a significant improvement in the removal rate of BRS on fecal indicator bacteria (FIB) (e.g., total coliform and *E. coli*) when adding biochar, and the removal ability is significantly affected by biochar addition ratio, indicating an enhancement in pathogen removal with the incremental addition of biochar (Figure 3). Compared with un-amended BRS, the maximum removal rate of total coliform and *E. coli* was improved by 11 and 34%, respectively. However, when biochar was mixed with compost, compared with traditional biological substrates, the removal of FIB was not enhanced significantly (Mohanty & Boehm 2014). The reason is that a large amount of dissolved organic carbon (DOC) is released from compost in pore water, and DOC may block pores and hinder adsorption. The biofilm formation on the surface of biochar may also inhibit the ability of biochar to remove pathogenic microorganisms (Afrooz & Boehm 2016). This may also result from the competition of organic matter on biochar adsorption sites (Figure 1) and the increase in electrostatic repulsion between biochar and cells after the adsorption of organic matter (Mohanty *et al.* 2014). Therefore, to reduce the possibility of biofilm formation or competition for adsorption sites on biochar surfaces, further research is required to explore the pathogen removal mechanism of biochar in the presence of organic pollutants.

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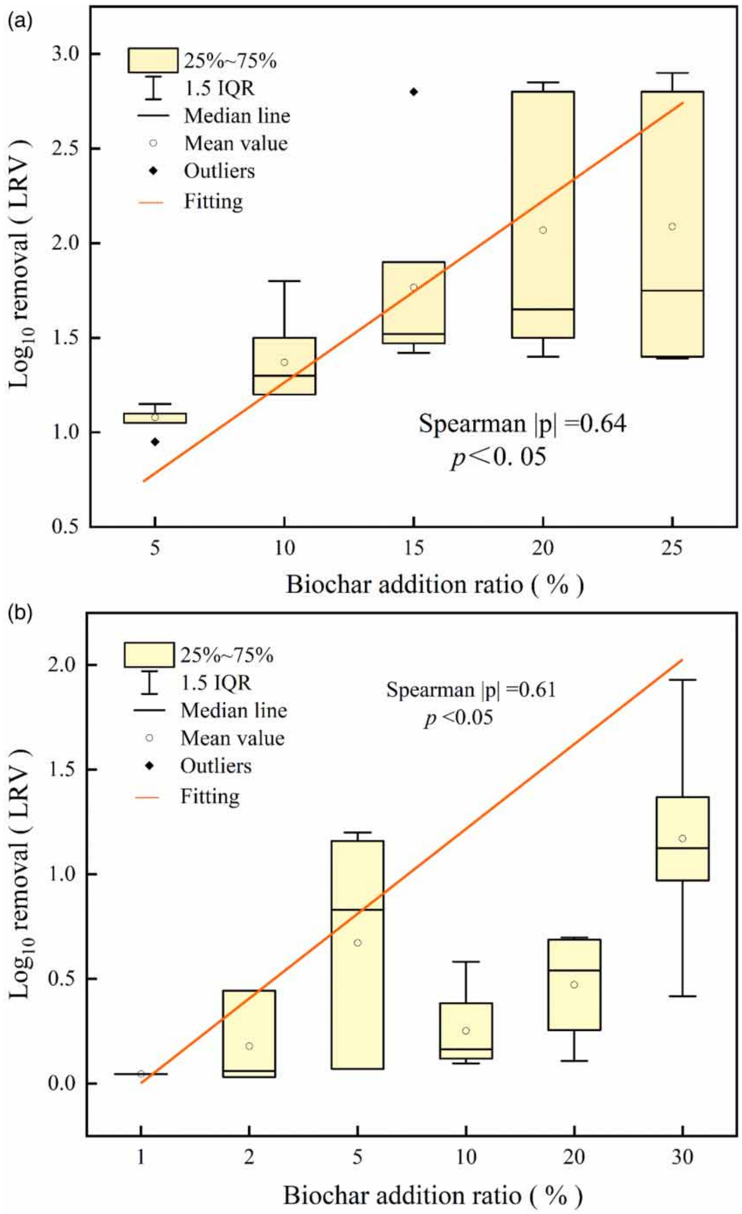

Figure 3 | Effect of biochar addition on (a) total coliform and (b) *Escherichia coli*.

2.4. Organic contaminants removal

Hazardous and/or emerging organic pollutants that are widely present in stormwater runoff at potentially harmful levels include herbicides, pesticides, vehicle fluids, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls, flame retardants, perfluorinated compounds, and plastic additives. Organic matter can be removed from stormwater via adsorption, filtration, chemical oxidation or reduction, hydrolysis, microbial degradation, etc., in BRS (Ulrich *et al.* 2017a). Some studies have demonstrated that adding biochar as an addition in BRS or wetland can enhance the removal of organics (Table 1). For instance, the removal rates of chlorpyrifos, endosulfan, fenvalerate, and diuron in the integrated circulating constructed wetland added with iron-impregnated biochar produced by *Cyperus alternifolius* can reach more than 99% (Tang *et al.* 2016). Yan *et al.* (2017) used biochar-modified silty clay to treat pentabromodiphenyl ether (BDE-99) from wastewater to reach a high removal rate of 77.2–100%, and the results indicated that the main removal mechanism shifted from adsorption to biodegradation with the increase in the hydraulic retention time and filtered medium depth.

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Table 1 | Removal efficiency for organics in biochar-amended BRS or control systems without biochar

Experimental scale	Stormwater type	Biochar feedstock	Organic parameters	Influent (μg/L)	RR-C (%)	RR-B (%)	References
Column	Synthetic	Pinewood	Fipronil	50	90.0	100	Ashoori *et al.* (2019)
			Diuron	50	0–99.0	100	
			1H-benzotriazole	50	−60.0–80.0	100	
			Atrazine	50	98.9	100	
			2,4-D	50	15.0–70.0	100	
			TCEP	50	−40.0–20.0	100	
Column	Real	Pinewood	Atrazine	NA	0–14.0*	>99	Ulrich *et al.* (2017b)
			Methylbenzotriazole	NA	50.0–56.5*	>99	
			Oryzalin	NA	60.0–75.0*	>99	
			2,4-D	NA	18.0–30.0*	>99	
			TCEP	NA	−10.0–36.0*	>99	
			TCPP	NA	64.0–78.0*	>99	
			Benzotriazole	NA	20.0–40.0*	>99	
			Diuron	NA	>85.0*	>99	
			Prometon	NA	−8.0–30.0*	>99	
			Simazine	NA	0–22.5*	>99	
			Fipronil	NA	23.5–32.5*	>99	
Microcosm	Real	Wood dust	Bisphenol A	200	0.7	98.4	Lu & Chen (2018)
Column	Synthetic	Dairy manure	2,4-DCP	6,000	50.3	86.2	Wang *et al.* (2020)
Column	Synthetic	Peanut shell	2,4-DCP	6,000	50.3	95.0	Wang *et al.* (2020)

RR-C, Removal rate of control systems; RR-B, Removal rate of biochar-amended systems; 2,4-D, 2,4-dichlorophenoxyacetic acid; TCEP, Tris(2-chloroethyl) phosphate; TCPP, Tris(3-chloro-2-propyl) phosphate; 2,4-DCP, 2,4-dichlorophenol; NA, Not available. The * indicates that the removal rate is sourced from the literature, in which the treating runoff volume is more than 0.7 year equivalents.

Organics can be adsorbed by biochar, predominantly via electrostatic attraction, hydrophobic effects, conjugation of aromatic π-donor and cationic π-acceptor, hydrogen bonding, and pore-filling (Figure 1) (Rajapaksha *et al.* 2016). Biochar also has redox-reactive and catalytic activities, allowing it to accept and/or donate electrons or promote electron conduction and produce reactive oxygen species (ROS), thus accelerating the non-biodegradation of adsorbed organics (Zhang *et al.* 2019). The larger specific surface area and pores of biochar also help to adsorb pollutants, reduce their concentration and fluidity, cut down the microenvironmental exposure levels to these pollutants, and provide suitable microbial culture habitat for the biodegradation process. Microbes combined with biochar can improve the removal efficiency of pollutants (e.g., nonylphenol, PAHs, atrazine, naphthenic acid) (Frankel *et al.* 2016; Ge *et al.* 2019) and then increase microbial biomass (Lou *et al.* 2019). Wang *et al.* (2020) reported that the removal rate of 2,4-dichlorophenol (2,4-DCP) in surface runoff could reach up to 80% using the combination treatment with biochar and microbes. The removal efficiency of organic pollutants varies with the change in stormwater composition (e.g., DOC and dissolved oxygen). DOC that is ubiquitous in stormwater can block biochar pores and compete with organic pollutants for active sites (Ulrich *et al.* 2015). Overall, biochar is a promising BRS ameliorant for treating stormwater containing organic contaminants (Table 1), despite the lack of research and practical applications of biochar on enhancing organic pollutant removal in biochar-amended BRS, especially the effect of biochar aging and DOC on the removal performance and its involved mechanisms.

2.5. Adsorption kinetics and adsorption isotherms

Researchers need to study the adsorption kinetics and adsorption isotherms models of biochar to explore the adsorption potential and to predict the adsorption capacities, which can help to understand the removal mechanism of different pollutants. The adsorption kinetics and isothermal adsorption model of various chemical pollutants and the fitting parameters are presented in Table 2. Most studies have demonstrated that the kinetic adsorption of biochar follows a pseudo-second-order kinetic model, implying that chemical adsorption would dominate the adsorption process (Thang *et al.* 2019). Adsorption of heavy metals (e.g., Cu, Cd, and Zn) follows a pseudo-second-order kinetic model, and the main removal mechanisms are chemical reduction and surface complexation (Hasan *et al.* 2020). Thang *et al.* (2019) investigated the adsorption kinetics

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Table 2 | Adsorption kinetic model and isotherm model of various chemical pollutants and the fitting parameters

Feedstock type	Pollutant	Kinetic model	Isotherm model	R^2 (Kin.)	R^2 (Iso.)	References
Waste wood	NH_3-N NO_2-N PO_4-P	PSO	Lang./Freun. Lang. Lang.	0.98 0.96 0.98	0.99/0.98 0.96 0.94	Alam & Anwar (2020)
Poultry litter	NH_3-N	NA	Lang./Freun.	NA	0.999/0.998	Tian *et al.* (2016)
Pine wood	Cu(II) Cd (II) Zn (II)	PSO	Lang.	0.99 0.91 0.91	0.97 0.91 0.97	Hasan *et al.* (2020)
Wheat straw	Cd(II) Cu(II) Zn(II)	PSO	Lang.	1.00 1.00 1.00	0.9893 0.9555 0.9974	Bogusz *et al.* (2015)
S. hermaphrodita	Cd(II) Cu(II) Zn(II)	PSO	Lang.	1.00 1.00 0.9997	0.9986 0.9983 0.9802	Bogusz *et al.* (2015)
Rice husk	As(V) Cr(III) Cr(VI)	PSO	Freun.	0.99 0.99 NA	0.983 0.894 0.842	Agrafioti *et al.* (2014)
Sewage sludge	As(V) Cr(III) Cr(VI)	PSO	Freun.	0.99 0.99 NA	0.747 0.70 0.914	Agrafioti *et al.* (2014)
Anaerobically digested sludge	Pb(II) Cd(II)	NA	Lang.	NA	0.99 0.99	Ni *et al.* (2019)
Wasted sludge	Tetracycline	PSO	Lang.	0.9659	0.9667	Ma *et al.* (2020)
Dairy manure	2,4-DCP	PFO	NA	0.982	NA	Wang *et al.* (2020)
Chicken manure	Phenol 2,4-DNP	PSO PSO	Lang. Lang.	0.99 0.96	≥0.98 ≥0.98	Thang *et al.* (2019)

Kin., kinetic model; Iso., isotherm model; 2,4-DCP, 2,4-dichlorophenol; 2,4-DNP, 2,4-dinitrophenol; PSO, pseudo-second-order kinetic model; Lang., Langmuir model; NA, Not available.; Freun., Freundlich model.

of phenol and 2,4-dinitrophenol; the results demonstrated that the removal process was well described by the pseudo-second-order kinetic model, which involves the role of the π–π bond and the hydrogen bond between functional groups of the adsorbent and the pollutants. The Langmuir and Freundlich models are two isotherm models widely used in biochar adsorption. Many studies have demonstrated that biochar adsorption isotherm conforms to the Langmuir model. However, Agrafioti *et al.* (2014)'s study indicated that the best fit model for heavy metals (i.e., As(V), Cr(III), and Cr(VI)) adsorption is the Freundlich model. This may be related to the types of pollutants and the surface properties of feedstocks. In the coexistence system of Pb(II) and Cd(II), Ni *et al.* (2019) discovered that the competitive adsorption between two metals could be described by the Langmuir–Freundlich model ($R^2 = 0.99$).

3. BENEFITS AND THE REMOVAL ENHANCING MECHANISMS OF BIOCHAR IN BIOCHAR-AMENDED BRS

3.1. Benefits of biochar as an innovative soil ameliorant in BRS

In the biochar-enhanced BRS, current studies have proven that various mechanisms are involved in enhancing pollutant removal by biochar, as in Figure 1. Overall, there are four benefits of biochar used as an innovative soil ameliorant in BRS (Figure 4): (1) as soil amendments, biochar can improve the physicochemical properties of soil, reduce the bioavailability of toxic substances in soil, and then improve the habitat environment of microbes in the soil. It can also be used as an alternative medium to replace the compost or other organic amendments without the negative effect of pollutant leaching; (2) as an adsorbent, biochar can remove pollutants through abiotic degradation processes such as filtration, adsorption, cation exchange, electrostatic interaction, precipitation, and oxidoreduction; (3) as a redox control agent, biochar can also be

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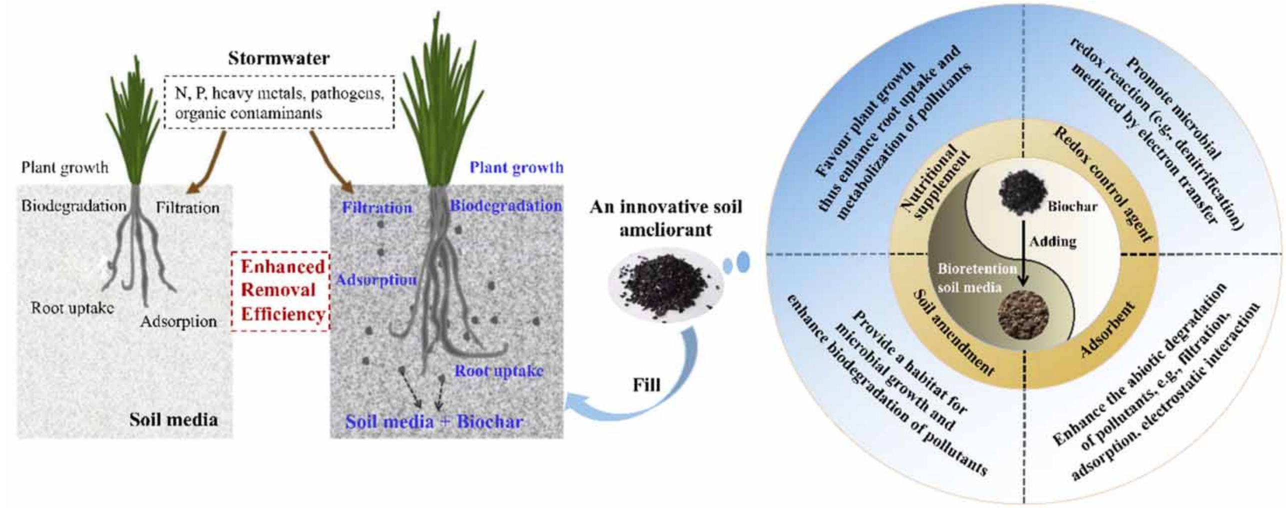

Figure 4 | Benefits of biochar as an addition to BRS for stormwater treatment.

used as an electron acceptor or donor of microorganisms to promote the microbial degradation of pollutants through redox cycles; and (4) as a nutritional supplement, biochar can release various nutrients, such as K, P, N, Mg and Ca and increase media porosity, leading to better oxygen conditions, which strongly favors plant growth (Mohanty *et al.* 2018; Deng *et al.* 2021). The improved plant growth in BRS is beneficial for nutrient and organics removal through plant uptake, oxygen release, organic exudate secretion, and the provision of more sites for microbial attachment on the plant rhizosphere (Tang *et al.* 2016), which then increases the microbial activity in the system and enhances the removal of pollutants via plant uptake and microbial degradation.

Furthermore, biochar improves the hydraulic performance of BRS. Compared with other soil ameliorants, biochar improves the water retention performance of the system in response to the early occurrence of flood peaks and increased runoff caused by short-term and intense storm events (Xiong *et al.* 2022). Biochar has a high specific surface area and porous structure, which increases the soil's total porosity (Joseph *et al.* 2021), thereby enhancing the soil's capillary force. Biochar has a complex porosity structure, increasing the flow path of stormwater runoff in BRS, thereby prolonging the hydraulic retention time (HRT) (Zhang *et al.* 2016). Yu *et al.* (2021) revealed that biochar could stabilize soil aggregates under the influence of Coulomb and van der Waals forces, forming a loose biochar–soil mixture, which not only increases soil water retention capacity but also reduces soil erosion. Some studies have proven that adding biochar increases the hydraulic conductivity of BRS (Tian & Liu 2017, 2018; Schmidt *et al.* 2021). However, most studies have indicated that biochar reduces the permeability of coarse-grained soils, which may be due to the various properties of fillers (Mohawesh & Durner 2019; Rahman *et al.* 2020a). For dense and fine-grained soil, adding biochar enhanced its hydraulic conductivity, and biochar with large-sized particles was more conducive to increasing hydraulic conductivity.

3.2. The removal enhancing mechanisms in biochar-amended BRS

The removal enhancing mechanisms for pollutants in biochar-amended BRS can be summarized as follows:

(1) For nitrogen, the key removal enhancing mechanisms are adsorption, biotic removal, ion exchange, and volatilization. The key removal enhancing mechanisms for phosphorus are precipitation, adsorption, plant uptake, and anion exchange. (2) The key removal enhancing mechanisms for heavy metals are chemical precipitation, reduction, complexation, adsorption, cation exchange, filtration, and plant uptake. Among them, adsorption, cation exchange, and complexation play important roles. (3) For pathogenic microorganisms, the key removal enhancing mechanisms are hydrophobicity and adsorption. High hydrophobic biochar reduces the interaction between biochar and microorganism, resulting in a lower removal rate (Mohanty & Boehm 2014). (4) The key removal enhancing mechanisms for organics contaminants in biochar-amended BRS can be concluded as adsorption, biodegradation, and hydrophobic interaction.

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4. INFLUENCING FACTORS OF DECONTAMINATION PERFORMANCE OF BIOCHAR-AMENDED BRS

4.1. Types of biochar

The removal efficiency of stormwater pollutants depends on the physicochemical properties of biochar, which are closely related to the types and preparation processes of biochar. Biochar can be divided into four types based on the feedstock: woody biochar, animal residues biochar, crop residues biochar, and sludge biochar (Thang *et al.* 2019; Ahmad *et al.* 2021). Biochar made from different types and sources of feedstocks may affect the surface area, porosity, and nutrient contents, thus affecting the removal efficiency of stormwater pollutants (see Table 3). For instance, woody biochar contains lower ash content and plant-available nutrients than other feedstocks (Ahmad *et al.* 2021). Hardwood biochar has a higher specific surface area than cork (Mohanty *et al.* 2018). However, animal residue biochar demonstrated the opposite trend (Shimabuku *et al.* 2016). The H/C ratios of biochar decreased in the following order: animal residues biochar > crop residues biochar > woody biochar, and their organic carbon (OC) contents are in the opposite order. Wood dust biochar pyrolyzed at a high temperature (≥600 °C) can effectively remove pathogens and indicator microorganisms in stormwater (Boehm *et al.* 2020). The results are consistent with that of Mohanty *et al.* (2014)'s column experiments, where infiltration columns incorporated with biochar prepared from wood dust can effectively remove *E. coli* from osmotic solutions. However, Sasidharan *et al.* (2016) found that biochar produced from various feedstocks such as *Macadamia shells*, *rice husks*, *Phragmites reeds*, and *wheat chaff* could not effectively remove *E. coli*. The removal ability of biochar to *E. coli* was positively correlated with the specific surface area and carbon contents of biochar, while it is negatively correlated with ash contents and volatile organic compounds (Valenca *et al.* 2021a). Woody biochar at high temperatures has a low O/C ratio (i.e., low surface polarity, high hydrophobicity) and low volatile substances, which can effectively eliminate pathogens and indicate organisms (Mohanty & Boehm 2014). Furthermore, woody biochar exhibited excellent removal efficiency for organic pollutants and nutrients.

Animal residue biochar contains excessive nutrients (e.g., N, P, and S) (Amoah-Antwi *et al.* 2020), which not only limits the attachment of pathogens but also reduces the removal efficiency of other anionic co-pollutants (Abit *et al.* 2012). When biochar is produced with animal residues or sludge, nutrients released from biochar will be fed back into the system; therefore, biochar cannot be applied to BRS with the priority target of nutrient removal. However, chicken manure biochar exhibited good phenol and 2,4-dinitrophenol removal ability due to hydrogen bond, electrostatic effect and π–π bond with adsorbate (Thang *et al.* 2019). Wang *et al.* (2020) demonstrated that the removal efficiency of 2,4-dichlorophenol by dairy manure biochar reached 86.2%. Crab shell biochar, with its high calcium content, has excellent removal performance for dyes because of its electrostatic adsorption, hydrogen bond, and π–π bond (Dai *et al.* 2018). Table 1 shows that woody biochar and crop residue biochar may have better removal efficiency, although animal residue biochar can effectively remove organic pollutants. This may result from the crop residue biochar, and woody biochar are more likely to form π–π bonds and hydrogen bonds with organic pollutants. The high content of dissolved organic matter provides a carbon source for microorganisms, promotes the synergistic effect of biochar adsorption and biodegradation, and improves the removal rate of organic pollutants (Jin *et al.* 2014; Wang *et al.* 2020).

Reddy *et al.* (2014) discovered that waste wood biochar has a low removal efficiency of heavy metals from urban stormwater, specifically 49.3, 2.5, and 41.9% for Cu(II), Cr(VI), and Zn(II), respectively. However, sewage sludge biochar has rich surface functional groups, low C, and high ash contents, which is conducive to removing metal ions (Ashoori *et al.* 2019; Jellali *et al.* 2021). Sewage sludge biochar has a high adsorption capacity for heavy metals (Cr(VI), Cr(III)) and can also effectively adsorb phenols; its ash high-Fe_2O_3 content contributes to the adsorption reaction (Agrafioti *et al.* 2014). The anions in stormwater can be combined with the binding sites provided by Ca, Mg, Fe, Na, and other metal ions in sludge biochar, thus promoting the removal of anions (Jellali *et al.* 2021). In summary, woody and crop residue biochar are the most comprehensive and widely used biochars. Sludge and poultry biochar also play an irreplaceable role in removing some pollutants.

4.2. Preparation process and physicochemical properties of biochar

There are many methods for preparing biochar, such as pyrolysis, gasification, and hydrothermal carbonization. Among these, pyrolysis is the most common method for producing biochar, which requires a limited oxygen supply and high temperatures between 300 and 800 °C. The quantity and quality of biochar vary with the residence time and temperature of feedstocks in the pyrolysis chamber. Biochar prepared at different temperatures will affect its structure and properties.

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Table 3 | Removal efficiency of pollutants in different biochar systems

Feedstock type	Pyrolysis conditions	Pollutant	Chemical modification	Removal efficiency (%)	References
Waste wood	T = 400 °C t = 10–min	NH_3-N NO_2-N PO_4^{3-}-P	–	98.2 99.4 99.8	Alam & Anwar (2020)
Rice husk	T = 500 °C G = 15 °C/min	PO_4^{3}-P NH_3-N	Mixed with $FeCl_3$	97.3 98.3	Xiong *et al.* (2019)
Wood	T = 900–1,000 °C	TAN DON TN DOC *E. coli*	–	99.52 50.19 47.55 86.28 Log 4.23	Rahman et al. (2020a)
Softwood	T = 815–1,315 °C t = 1–3 s	*E. coli*	–	96	Mohanty & Boehm (2014)
Wood pellets	T = 520 °C	*E. coli* NO_3^--N PO_4^{3-}-P Phenanthrene Naphthalene Cd(II) Cr(VI)	–	30 86 47 100 76 28 2.5	Reddy *et al.* (2014)
Pine wood	T ≥ 600 °C	Cu(II) Cd(II) Zn(II)	Modified with NZVI	96.7 95.8 76.8	Hasan *et al.* (2020)
Forestry wood	T = 700 °C t = 15 h	Cu(II) Ni(II) Cd(II) Zn(II)	Modified with H_2SO_4	96.8 51.7 60.7 80.3	Sun *et al.* (2020)
Oak tree	–	As(V)	Aluminum-impregnated	96.1	Liu *et al.* (2019)
S. hermaphrodita	T = 700 °C t = 4 h	Cd(II) Cu(II) Zn(II)	–	91 95 93	Bogusz *et al.* (2015)
Rice husk	T = 300 °C G = 17 °C/min t = 1 h	As(V) Cr(III) Cr(VI)	–	25 42 18	Agrafioti *et al.* (2014)
Corn straw	T = 600 °C G = 20 °C/min t = 2 h	NO_3^--N NH_{4-}-N TP	–	64 92 79	Li *et al.* (2021)
Peanut shell	T = 500 °C	2,4-DCP	–	95.0	Wang *et al.* (2020)
Sewage sludge	T = 300 °C G = 17 °C/min t = 1 h	As(V) Cr(III) Cr(VI)	–	53 >99 89	Agrafioti *et al.* (2014)
Solid waste	T = 300 °C G = 17 °C/min t = 1 h	As(V) Cr(III) Cr(VI)	–	55 >99 44	Agrafioti *et al.* (2014)
River sediment	T = 400 °C t = 4 h	COD TN TP	–	81 34 56	Sang *et al.* (2019)
Wasted sludge	T = 500 °C G = 10 °C/min t = 2 h	Tetracycline	$ZnCl_2$ activation and Fe/S decoration	174.06 mg/g	Ma *et al.* (2020)

(*Continued.*)

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Table 3 | Continued

Feedstock type	Pyrolysis conditions	Pollutant	Chemical modification	Removal efficiency (%)	References
Poultry litter	T = 500 °C G = 20 °C/min	NH_4^+-N	–	91.7	Tian *et al.* (2016)
Dairy manure	T = 500 °C	2,4-DCP	–	86.2	Wang *et al.* (2020)
Chicken manure	T = 200–600 °C G = 500 cc/min t = 2 h	Phenol 2,4-DNP	–	78.5 83.4	Thang *et al.* (2019)

T, pyrolysis temperature; G, pyrolysis gradient temperature; t, residence time; NZVI, nanoscale zero-valent iron; DBP, dibutyl phthalate; PHE, phenanthrene; 2,4-DCP, 2,4-dichlorophenol; 2,4-DNP, 2,4-dinitrophenol.

When the temperature increases, the total pore volume of biochar increases, the specific surface area increases first and then decreases, and the aromaticity increases. The temperature increases the total amount of acidic functional groups that are beneficial for adsorption on the biochar surface. Conversely, biochar with low-temperature pyrolysis is more suitable for removing inorganic pollutants because it usually contains more polar surface functional groups, which can interact with charged or polarized pollutants (e.g., metals) and promote chemical precipitation and electrostatic adsorption (Ahmad *et al.* 2014). Consequently, one of the most important aspects to consider when determining the feedstock and preparation method of biochar for removing specific pollutants is how to remove them effectively.

Due to differences in pyrolysis conditions, residence time, types of feedstocks, and moisture content, biochar exhibits diversity in structure and pore distribution, elemental composition, pH, specific surface area, cation exchange capacity, surface functional groups, and other physicochemical properties; consequently, this will affect the biochar's environmental benefits and application fields. By examining the relationship between the physicochemical properties of biochar and the removal performance of various pollutants, the biochar-based medium can be optimized, thus allowing the comprehensive removal of pollutants. Meanwhile, the main abiotic removal process of organic pollutants is adsorption, so the factors controlling the adsorption of organics, such as surface area, aromaticity, and internal pore size distribution, can improve the removal rate of organic pollutants via slow adsorption (Kasozi *et al.* 2010; Mohanty *et al.* 2018). The woody biochar prepared at high temperature has a low O/C ratio (i.e., low surface polarity and high hydrophobicity) and low volatile substances, which can effectively eliminate pathogens and indicate organisms (Mohanty *et al.* 2014). The woody biochar prepared by high-temperature pyrolysis has good bacterial removal ability (Abit *et al.* 2012; Suliman *et al.* 2017) because high temperature increases biomass carbonization, thus enhancing the hydrophobic adhesion of pathogenic microorganisms on biochar surfaces.

The particle size of biochar is important in determining pollutant removal efficiency. Fine particle biochar is more effective at removing nutrients and microorganisms. For instance, the removal efficiency of *E. coli* decreased from 95 to 62% when small particle biochar ($<$125 μm) was removed from the system (Mohanty & Boehm 2014). In column experiments, removing smaller biochar particles ($<$60 μm) enhances bacterial migration, which is detrimental to bacteria removal. The effect of biochar particle size on microbial removal efficiency is greater than other types of biochar (Sasidharan *et al.* 2016). McCrum (2017) discovered that when biochar particle size increased from 0.25–0.5 mm to 0.5–2.0 mm, the nitrate removal rate decreased from 98–99% to 70–75%. The change of removal efficiency caused by biochar particle size can result from the low specific surface area of large-size biochar. Biochar with a low surface area has high hydrophobicity and low volatile content, which is unfavorable for removing microorganisms and nutrients. Besides, the particle size of biochar will affect the system's hydraulic conductivity. Rahman *et al.* (2020a) demonstrated that the addition of biochar with a particle size of 0.15–0.25 mm decreased the hydraulic conductivity of the system, whereas Yu *et al.* (2021) demonstrated that the addition of large-pore biochar with a particle size of 0.25–1.0 mm increased the hydraulic conductivity of the system.

4.3. Biochar aging

Current research methods on biochar aging mainly include field natural and artificial simulation aging. Relatively mild aging methods (e.g., natural aging and freeze-thaw cycle aging) can generate new micropores on the surface of biochar, thereby increasing the specific surface area. However, strong chemical aging methods will cause the collapse of the pore structure

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of biochar, thereby reducing its specific surface area. The aging process increases the oxygen-containing functional groups on the surface of biochar, increases the proportion of elements O and C, enhances the polarity of biochar, and reduces the pH, according to the consistent findings of these aging methods (Baltrenas *et al.* 2015). Changes will also occur in the physicochemical properties of biochar and their interactions with soil–plant systems. These changes, in turn, lead to corresponding changes in the regulation of greenhouse gas. After biochar aging, the AEC of biochar decreases by 54% on average, which can be used as a parameter to reduce nutrient leaching in the soil environment or remove anionic pollutants in the water environment (Lawrinenko *et al.* 2016). The decline in AEC has the same beneficial effect on removing organic pollutants. For instance, due to aging, biochar adsorption of dialkyl phthalates increased significantly (Ghaffar *et al.* 2015).

However, the aging effects of biochar vary depending on the pollutants and environments present. With aging, biofilms are formed in the pores of the bioretention filter media, and extracellular polymeric substances (EPS) are simultaneously produced, thereby altering the performance of the biochar-amended BRS, such as hydrophobicity and electrokinetics. When biofilm forms on the filter media composed of sand and biochar and within their pore spaces, the removal rate of *E. coli* decreases (Afrooz & Boehm 2016). Biofilm weakens the hydrophobic interaction between biochar surface and pathogenic microorganisms by reducing the hydrophobicity of bare biochar surface. The biofilm deposited on biochar particles reduces the available adsorption sites attached to pathogens.

4.4. Chemical modification of biochar

The application of biochar in removing anion pollutants has some limitations because of the poor adsorption of anions, which is caused by the negative-charged functional groups surrounding the surface of biochar. To improve the performance of biochar, the surface properties of biochar have to be activated by a modification to obtain high-value-added modified biochar products so that they can be better used in stormwater treatment. Chemical or physical modification of biochar surface can functionalize biochar's surface properties, thus resulting in a larger surface area or functional groups to improve its adsorption capacity in aqueous solution, such as oxidation to obtain more acidic oxygen functional groups and alkalization to obtain larger surface area and adsorption capacity (Huff & Lee 2016). Because different pollutants are removed through different mechanisms, the selection of modification methods depends on specific target pollutants. Impregnating nanomaterials or metal oxides on biochar as strong adsorbents is conducive to removing pollutants in stormwater. For instance, under N_2 conditions at 600 °C, feedstock biomass was carbonized, and nanographene was added into the graphene suspension, achieving 98.1% Hg removal efficiency in wastewater (Tang *et al.* 2015). Fe-modified biochar can also promote the removal of bacteria because iron oxide-coated sand has a higher surface positive charge and greater roughness, so its removal efficiency of *E. coli* is significantly higher than that of conventional biological inhibition medium, and the removal rate increased from 82 to 99% (Zhang *et al.* 2010). Therefore, biochar impregnated with various nanomaterials had a high adsorption capacity for metals, organic pollutants, pathogenic bacteria, and nutrients (Xiong *et al.* 2019; Hasan *et al.* 2020). To remove co-existing pollutants in stormwater, further studies should focus on the feasibility of co-impregnation of multi-nanomaterials on biochar and the removal effectiveness of the nanomaterial-impregnated biochar in treating real or synthetic stormwater to maximize the removal of multiple pollutants in BRS (e.g., metal/metal oxides, organic pollutants, and nutrients). Additional research will be required to further investigate the long-term stability of modified biochar under various conditions (e.g., stormwater compositions and weather changes). Furthermore, factors such as the cost, practicability, and possible secondary pollution in the modification process of biochar should be carefully considered when evaluating the expected application benefits, especially when adding modified biochar into BRS to purify stormwater. Those factors may affect the economic and environmental competitiveness of biochar.

4.5. Hydraulic loading and inflow concentration

High hydraulic loading will cause most of the influent to pass through the BRS in the form of overflow or preferential flow, thereby reducing the contact time between biochar and stormwater (Kong *et al.* 2021) and significantly affecting the adsorption and biosorption of pollutants by biochar (Zhang *et al.* 2021a). Zhang *et al.* (2021b) demonstrated that high inflow volume would result in media saturation, and the improvement effect of adding biochar is no longer obvious, especially for nitrogen removal. For of a low hydraulic loading rate, longer HRT may lead to greater adsorption and mineralization of dissolved organic nitrogen (DON) on biochar and promote denitrification (Berger *et al.* 2019). With the increased hydraulic loading, HRT in the BRS decreased, and there may be competitive adsorption between DON and DOC on biochar (Rahman *et al.*

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2020a), resulting in a significant decrease in the removal of N and DOC. The concentration of pollutants in the inflow also affects the removal of pollutants by biochar. As the concentration of pollutants increases, the adsorption capacity of biochar gradually tends to be saturated (Hong *et al.* 2022). Li *et al.* (2021) conducted column experiments to investigate the effects of biochar on the removal of NO_3^--N, NH_4^+-N, and phosphorus in BRS at various influent concentrations. The authors found that, due to the limited adsorption capacity of biochar to NH_4^+-N and NO_3^--N, the high inflow concentration reduces the N removal rate, especially the removal rate of NH_4^+-N. When the inflow concentration of heavy metals was altered, the removal efficiency of low biochar application rate fluctuated greatly, which could be attributed to the adsorption–desorption characteristics of biochar (Hong *et al.* 2022). However, studies have demonstrated that hydraulic load, infiltration rate, and inflow concentration may not affect the removal of *E. coli* by biochar (Mohanty & Boehm 2014; Rahman *et al.* 2020b). The effect of hydraulic loading and inflow concentration on biochar's removal capacity may vary depending on the pollutant type.

4.6. Drying–rewetting alternation

Similar to other stormwater control measurements, BRS experiences typical weather conditions, such as temperature fluctuations or drought environment, wetting, and freeze–thaw cycles, which affect the removal ability of biochar in treating pollutants. Changes in the BRS's water status and climatic conditions, such as temperature, drying or freezing time, and humidity, may change the physicochemical properties of biochar. These dynamic conditions can also enhance the erosion of biochar particles and accelerate their aging rate. Mohanty & Boehm (2014) discovered that biochar exposed to stormwater through dry–wet cycles could remove more pathogenic bacteria than biochar exposed to the same volume of stormwater because of the removal or mineralization of oxide scales on biochar surface during drying. Therefore, with the adsorbed OC mineralized or diffused into pores, the intervening dry period contributed to the regeneration of biochar adsorption capacity. In contrast, other studies have proven that drying–rewetting alternation had opposite effects on the pathogens removal ability of biochar. For instance, the oxidation of biochar surfaces at high temperatures or in the presence of air can increase negative surface charges (Wang *et al.* 2017a), thus reducing bacterial attachment (Suliman *et al.* 2017). Similarly, biological aging, such as biofilm formation on the surface of biochar, can also reduce the removal of indicator bacteria in BRS (Afrooz & Boehm 2016). Rahman *et al.* (2020a) discovered that the removal effect of nitrogen oxides in biochar-amended columns significantly differed with the increase of the antecedent dry days (ADD). This may be due to the combined effect of medium saturation and nitrification–denitrification microbial activity during the ADD increase. Berger *et al.* (2019) discovered that increasing the duration of the pre-drying process increased nitrate removal rate from the biofilter, regardless of the amount of biochar.

5. CONCLUSION AND FUTURE PROSPECTIVE

The application of biochar as an innovative soil ameliorant in BRS for stormwater treatment has garnered the attention of scholars, and it has been demonstrated that biochar can significantly improve the operation performance of BRS.

- Biochar can be used as an adsorption medium to enhance the removal efficiencies of pollutants via abiotic processes such as filtration, adsorption, cation exchange, electrostatic interaction, precipitation, and chemical reduction. The pseudo-second-order and Langmuir models are the most suitable kinetic and isothermal adsorption models for biochar adsorption, respectively. Biochar improves the physicochemical properties of soil, decreases the bioavailability of toxic substances in soil, promotes plant growth, and increases microbial activity. Additionally, as an electron acceptor or donor of microbes, biochar can promote the microbial degradation of pollutants through redox cycles.
- Adding biochar to BRS has many benefits, but the use of biochar varies depending on the conditions. Woody biochar and crop residue biochar are the most comprehensive and widely used biochar. Animal residue biochar has good removal efficiency for organic pollutants. Some modified sludge biochar is effective at removing heavy metals (i.e., Cr(III) and Cr(VI)). Biochar prepared at high temperatures has a large total pore volume and specific surface area, thus making it suitable for removing organic pollutants and pathogenic bacteria, whereas biochar prepared at low temperatures is more suitable for removing inorganic pollutants. High hydraulic loading decreases the contact time between pollutants and biochar and reduces adsorption and nitrogen mineralization, leading to competitive adsorption. Chemical modification can enhance biochar's ability to remove anions, and the effect of wet and dry alternation on the performance of biochar requires further investigation.

Previous studies have some limitations that must be acknowledged, and future research must focus on the following issues regarding the application of biochar in BRS:

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- Increasing surface area and porosity through chemical activation is an important parameter to control the removal rate of biochar, and it will remain a hotspot for future research. Based on these findings, further studies should focus on the feasibility of co-impregnating various nanomaterials on biochar and the compatibility evaluation of chemical modification and nanomaterial impregnation to maximize the removal of various pollutants in BRS.
- BRS is a complex system. Water runoff contains a variety of organic pollutants, inorganic compounds, and suspended solids. To effectively remove a variety of pollutants simultaneously, future studies should investigate the combined effects of different biochar types, such as combining high-temperature pyrolysis biochar with low-temperature pyrolysis biochar and combining woody biochar with animal residue biochar.
- Current field experiments and engineering cases indicate that biochar has uncertainty in promoting the removal of pollutants. The complexity of stormwater BRS, including unstable/intermittent flow, various weather conditions, and high variant runoff quality of stormwater, is not considered in the current laboratory-scale studies of biochar. We should further investigate the long-term stability evaluation and the specific effects of various factors of biochar-amended BRS under field conditions and then answer the question regarding the service life of biochar in BRS.
- Under the condition of multiple pollutants co-existing in stormwater, the enhancement of biochar-amended BRS for removing pollutants will be reduced because of the competition of pollutants for adsorption sites. Consequently, studies should further explore the removal effect of pollutants in biochar-amended BRS under competitive adsorption and determine whether competitive adsorption accelerates biochar aging.

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DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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