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Review

Application of biochar for the remediation of polluted sediments



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ABSTRACT

Polluted sediments pose potential threats to environmental and human health and challenges to water management. Biochar is a carbon-rich material produced through pyrolysis of biomass waste, which performs well in soil amendment, climate improvement, and water treatment. Unlike soil and aqueous solutions, sediments are both the sink and source of water pollutants. Regarding in-situ sediment remediation, biochar also shows unique advantages in removing or immobilizing inorganic and organic pollutants (OPs). This paper provides a comprehensive review of the current methods of in-situ biochar amendments specific to polluted sediments. Physicochemical properties (pore structure, surface functional groups, pH and surface charge, mineral components) were influenced by the pyrolysis conditions, feedstock types, and modification of biochar. Furthermore, the remediation mechanisms and efficiency of pollutants (heavy metals [HMs] and OPs) vary with the biochar properties. Biochar influences microbial compositions and benthic organisms in sediments. Depending on the location or flow rate of polluted sediments, potential utilization methods of biochar alone or coupled with other materials are discussed. Finally, future practical challenges of biochar as a sediment amendment are addressed. This review provides an overview and outlook for sediment remediation using biochar, which will be valuable for further scientific research and engineering applications.

1. Introduction

With the expansion of industry, high concentrations of HMs and OPs are detected in sediments due to various inputs including those from sewage infiltration and atmospheric deposition (Harris et al., 2013). Sediments are basic environmental components that provide nutrients for many organisms and serve as repositories of organic and inorganic pollutants from aquatic ecosystems, which may have negative influences on environment and ecology (Zhang et al., 2014). Nowadays, serious adverse impacts of polluted sediments, such as toxicity to aquatic flora and fauna, have occurred in many countries due to mining or industrial processes, which has aggravated water pollution since the 1980s (Álvarez et al., 2014; Wang et al., 2019). Therefore, we must explore executable methods to achieve sediment remediation and maintain its ecological function.

Remediation strategies for polluted sediments include in-situ and exsitu actions (Akcil et al., 2015). Conventional ex-situ sediment remediation mainly relies on relocating polluted sediments, and in-situ

remediation involves natural recovery without human intervention or capping contaminants with special barrier materials to isolate pollutants (Gomes et al., 2013; Rakowska et al., 2012). Nowadays, sediment remediation technology mainly involves dredging (ex-situ) and capping (in-situ) (Fig. 1). Mildly polluted sediments are relocated to maintain ditches and lakes after dredging; nevertheless, heavily polluted sediments may cause secondary pollution if they are reused prior to detoxification (Chen et al., 2017; Wang et al., 2019). The large investments required for large-scale, ex-situ clean-up projects, and the detoxification of transported sediments in dredging work are also crucial problems (Chen et al., 2019). Hence, lower cost and more efficient in-situ sediment remediation technologies are increasing in popularity (Patmont et al., 2015; Lofrano et al., 2017).

Numerous laboratory experiments and full-scale field sediment treatments have shown that sequestration and immobilization of pollutants using a sorbent material has progressed to an innovative in-situ sediment remediation approach (Dong et al., 2018; Wang et al., 2019). Various carbonaceous materials are available for in-situ sediment

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remediation, including activated carbon, biochar, and carbon nanotubes (Patmont et al., 2015). As a potential surrogate, biochar has shown superior qualities (relative abundance and comparative sorptive abilities) compared with other carbonaceous materials and provides new material for polluted sediment remediation (Ameloot et al., 2013). For example, the cost of activated carbon is approximately 10 USD/m², whereas the cost of biochar is approximately 2 USD/m² (Cornelissen et al., 2011). Biochar is prepared through the pyrolysis of biomass (agricultural waste, forestry waste, and sewage sludge) under insufficient or zero oxygen conditions. Biochar has been successfully applied as an amendment to reduce contaminant bioavailability, or as an active capping material, to reduce contaminant mobility in a laboratory and pilot-scale sediment remediation (Zhang et al., 2020; Jia et al., 2020). The effectiveness of sorbent amendment for sediment remediation was presented by Ghosh et al. (2011). Several groups in the U.S. and Europe found that biochar placed on polluted sediments was physically stable for carbon sequestration and metal sorption in pilot studies (Ghosh et al., 2011). Thus, biochar has potential for sediment remediation and ecological engineering via contaminant isolation, and immobilization (Zhu et al., 2019)

The objective of this review was to methodically summarize and analyze the amendment of sediment using biochar. Sediments are generated from soil after natural weathering and transportation processes, and ultimately accumulate on the substrate as a critical compartment of aquatic ecosystems (Zhang et al., 2014). Biochar, as an outstanding remediation agent, has been widely used in wastewater decontamination to remove OPs, HMs, and other inorganic contaminants $(NH_4^+, PO_4^{3-}, and NO_3^-)$, and as a soil amendment to immobilize or insulate HMs and OPs (Ye et al., 2017; Wang and Wang, 2019; Wang et al., 2018; Yin et al., 2017). Moreover, many studies have focused on the performance of biochar in sediment remediation (Chen et al., 2017; Que et al., 2018). The application of biochar for polluted soil and water remediation has been comprehensively reviewed (Yuan et al., 2019; Ahmad et al., 2014). However, previous reviews have mainly focused on the application of carbonaceous materials (mainly activated carbon) in sediment remediation from technical and ecological perspectives, and there is a lack of detailed information regarding in-situ sediment remediation mechanisms and the potential risks posed by biochar

applications (Lofrano et al., 2017; Yin and Zhu, 2016; Li et al., 2020). To the best of our knowledge, this is the first comprehensive review that concentrates on the application mechanisms, methods, and risk of biochar for polluted sediment remediation and presents an overview of the following: (I) the effects of physicochemical properties (pore structure, functional groups [FGs], pH, and surface charge) of biochar on sediment remediation; (II) analysis of the mechanism of biochar for sediment remediation of HMs and OPs; (III) the risks of biochar additions to biological systems; (IV) the engineering application approaches of biochar in sediments; and (V) prospects and challenges for applying biochar in sediment remediation.

2. Effects of physicochemical properties of biochar on sediments remediation

In addition to sediment characteristics, the physicochemical properties of biochar significantly affect its ability to adsorb or immobilize pollutants from sediments, which also provides avenues for breakthroughs in improving the effectiveness of biochar (Suliman et al., 2016). The characteristics and components of polluted sediments impact long-term and accumulated toxicity due to the transportation and sedimentation of pollutants from other media. However, there is still a gap in our understanding of the effects of the physicochemical properties of biochar on sediment remediation. This study reviews the effects of biochar properties, including pore structure, pH, surface charge, FGs, and modification, on sediment remediation.

2.1. Pore structure

Pore structure, including surface area, porosity, and pore diameter, is an important physical property of biochar (Suliman et al., 2016). Surface area and porosity vary with the pyrolysis temperature used during biochar production. Therefore, it is of interest to summarize and determine the relationship between pyrolysis temperature and the physical properties of biochar to identify the optimal preparation temperature for polluted sediment remediation. The movability of pollutants in sediments is more active than in soil as sediments contain both water and solids. Biochar is used as a capping material to minimize the

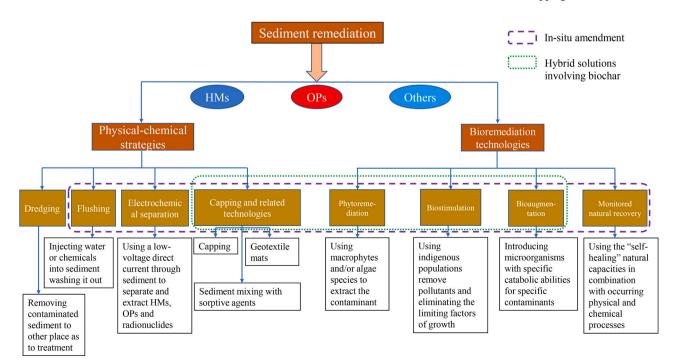


Fig. 1. The remediation strategies and bioremediation technologies of contaminated sediment remediation.

release of pollutants from sediments; therefore, an appropriate pore structure of biochar could maximize the immobilization of pollutants by biochar. For example, Liu et al. (2018) selected switchgrass biochar (pyrolysis at 300 °C [switchgrass biochar-300] or 600 °C [switchgrass biochar-600]) to compare the effect of biochar on Hg stabilization in sediment and reported that the surface areas of switchgrass biochar-300 and switchgrass biochar-600 were 2.6 and 230 m²/g, respectively. Biochar obtained at 600 °C with a larger surface area and higher S content was conducive to stabilizing Hg through precipitation of Hg-sulfide minerals (Liu et al., 2018). An assessment of the use of wheat straw biochar (pyrolysis at 400 °C [wheat straw biochar-400] or 700 °C [wheat straw biochar-700]) as an adsorbent, aiming to dissipate phenanthrene and pyrene in polluted sediments, was conducted by Chi and Liu (2016). Wheat straw biochar-700 manifested stronger immobilization of polycyclic aromatic hydrocarbon (PAHs) in sediments than wheat straw biochar-400 (Chi and Liu, 2016). For sediment remediation, production of biochar at 600-700 °C usually resulted in superior performance because a high pyrolysis temperature improved the pore structure and promoted a high surface area (Table 1).

In addition to the pyrolysis temperature, biochar feedstock is also an important factor. The raw biomass containing organic (cellulose, fats, and hemi-cellulous) and inorganic (N, P, S, K, and minerals) substances may affect the physical properties and remediation efficiency of the biochar. For example, Wang et al. (2018) applied three types of biochar produced from crofton weed, macadamia, and wheat straw (BC-1, BC-2, and BC-3) to adsorb flubendiamide in sediments and showed that the surface areas of BC-1, BC-2, and BC-3 varied considerably, at 382.21, 0.55, and $24.73 \text{ m}^2/\text{g}$, respectively. The addition of BC-1 to sediments was the most effective material in reducing freely dissolved flubendiamide in sorption studies due to its microporous surface texture, high surface area, and a higher fraction of non-carbonized organic matter (OM) than other biochars (Wang et al., 2018). According to presently reported research, the feedstock of biochar with ideal components (such as N, S, P) and high pyrolysis temperatures are beneficial for sediment remediation. However, more relevant research should be conducted to support this inference.

2.2. Functional groups

FGs, such as carboxylic group (-COOH), hydroxyl group (-OH), amino group (-NH₄), and aromatic compounds (-C=C-), in biochar determine the mechanisms between biochar and pollutants in sediment (Hung et al., 2020). Pyrolysis temperature and the raw biomass of biochar are the main factors related to FGs of biochar (Leng and Huang, 2018). In general, low pyrolysis temperatures are beneficial for forming FGs, which may improve the contact between the FGs and pollutants and enable a higher immobilization ability of biochar in sediments. When the pyrolysis temperature is increased, the carbonization degree of biomass is higher, but the abundance of FGs decreases (Suliman et al., 2016). Using different types of biomass, the FGs in biochar produced at low temperatures (< 300 °C) were unchanged, whereas there were multiple FGs in biochar produced at a relatively high pyrolysis temperature (> 400 °C) (Suliman et al., 2016). However, the opposite result was reported by Hung et al. (2020). The same FGs were present in red algae-based biochar (RAB) produced at 300 °C or 500 °C; but an increased content of oxygen-containing functional groups (OFGs) was reported for RAB-900 °C as the pyrolysis temperature increased from 700 °C to 900 °C (Hung et al., 2020). Thus, the abundance of -COOH and -COH groups in RAB-900 °C achieve the highest 4-nonylphenol reactions with H2O2 to generate reactive radicals under alkaline conditions from marine sediments (Hung et al., 2020). Hence, it is necessary to obtain biochar with ideal FGs for sediment remediation by appropriately balancing the feedstock and pyrolysis temperatures.

2.3. pH and surface charge

The pH and surface charge of biochar also vary with different feedstocks and pyrolysis temperatures and are closely related to the efficiency of sediment remediation (Liu et al., 2018). The alkaline matter in biochar caused by base cations (Ca, Mg, K, and Na) in raw biomass are transformed into oxides, hydroxides, and carbonates (e.g., ash) during pyrolysis (Que et al., 2018; Liu et al., 2018; Gong et al., 2019). The biochar feedstock influences all the properties related to the alkalinity. Previous studies had proved that the pH of sediment increased following the addition of biochar due to the alkaline materials in biochar (Que et al., 2018; Wang et al., 2018). The pH of biochar is related to the pyrolysis temperature, which significantly increases the pH of sediments (Yuan et al., 2011). With an increasing pyrolysis temperature, the enrichment of the ash content contributes to the increased pH of biochar (Leng and Huang, 2018). HMs and OPs vary in their sensitivity to sediment pH; in general, a higher sediment pH increases the stability of HMs but is less suitable for adsorption or degradation of OPs (Wang et al., 2019, 2018; Que et al., 2018; Lou et al., 2011). The surface charge of biochar is strongly influenced by the FGs that are present. Electrostatic attraction is a form of adsorption between biochar and pollutants controlled by the surface charge of biochar. Dong et al. (2020) prepared Fe-Ce/water caltrop shell biochar (WCSB) composite and applied for the degradation of phthalate esters (PAEs) in real marine sediments by persulfate. The results suggested that electrostatic attraction between PAEs and OFGs facilitated the degradation of PAEs on Fe-Ce/WCSB. As for HM ions, biochar with a surface charge can bind to pollutants with an opposite charge.

2.4. Modification

In comparison with modified biochar, pristine biochar has inappropriate physicochemical properties, making it difficult to achieve the optimal remediation capacity in polluted sediments. Hence, modification technologies of biochar have attracted the interest of researchers. Common biochar modification methods are physical modification, chemical modification, and synthesis of biochar-supported nanocomposites (Li et al., 2020). Physical modification includes steam activation and gas activation; however, few studies have investigated the use of physically modified biochar for sediment remediation, and further study is required. Chemical additive (e.g. HCl, H2SO4, H3PO4, KOH, NaOH, and MgCl₂) activation can increase the specific surface area and ameliorate the undesirable pore properties and oxygen-FGs of biochar (Qian and Chen, 2014; Tan et al., 2017; Wang et al., 2018), which contributes to improving the performance of biochar in reducing contaminants for sediment remediation. For example, Liu et al. (2018) found that activations using H2O2, ZnCl2, HNO3, H3PO4, and H2SO4 increased the specific surface area of rice husk biochar to varying degrees. Moreover, activation of biochar by HNO₃ significantly improved the amount of OFGs compared to other activated biochar (Liu et al., 2018). Furthermore, the decreased Cd content in overlying water of sediment indicated that the ability of biochar to adsorb HMs was increased by chemical activation (Liu et al., 2018).

Currently, more researchers are directing attention toward biocharbased nanocomposites because of the high efficiency in reducing environmental contaminants (Wang and Wang, 2018; Li et al., 2020). Biochar-based nano-materials have a higher carbon content, larger surface area, and higher porosity than those of raw biochar (Dong et al., 2017). For example, biochar-supported nano-chlorapatite (BC-nClAP) improved Pb immobilization in polluted sediments compared to pristine biochar and nano-chlorapatite, as shown by Huang et al. (2018). Biochar pores can also adsorb excessive phosphorus released by chlorapatite and reduce the agglomeration of chlorapatite (Huang et al., 2018). BC-nClAP performed high conglutination efficiency of Pb and increased the OM content in a sediment-nano-composite system (Huang et al., 2018). Many biochar-based nano-composites have been used in recent years

 Table 1

 Properties of biochar used for sediment remediation.

Feedstock	Pyrolysis temperature (°C)	Pyrolysis time	рН	Particle diameter (mm)	C (%)	O (%)	H (%)	N (%)	O/C (molar ratio)	H/C (molar ratio)	N/C (molar ratio)	BET surface area (m²/g)	Reference
Corn stover	600	20 min	8.7	_	41.57	8.05	1.5	0.42	0.194	0.036	_	6.3	Jośko
Corn stover	600	20 min	8.6	_	39.33	_	1.82	0.56	_	0.046	_	3.9	et al.
Corn stover	600	20 min	8.5	_	15.81	-	1.83	0.6	_	0.116	_	7.3	(2013)
Corn stover	600	20 min	8.6		7.91	-	1.64	0.71	_	0.207	-	10	
Straw	700	20 min	9.9	-	53.85	6.14	2	0.92	0.114	0.037	-	8.6	
				-		0.14			0.114		-		Oharra
Rice straw	600	3 h	-	-	37.87	-	1.21	0.33	-	0.032	-	234.9	Cheng
													et al.
													(2017)
Rice-straw	_	_	-	_	18.49	-	0.71	0.69	_	0.038	0.037	72.1	Lou
													et al.
													(2011)
Rice straw	500	2 h	10.77	2									Chen
					_	_	_	=	_	_	_	_	et al.
													(2017)
Rice-straw	500	3 h	4.75	< 0.18	80.91	15.17	2.679	1.242	0.1406	0.397		36.35	Lou
Rice straw	500	3 h	4.36	₹ 0.10	79.67	16.39	2.694	1.243	0.1543	0.405	-	31.49	et al.
ace straw	300	3 11	4.30	-	79.07	10.39	2.094	1.243	0.1343	0.403	-	31.49	
													(2013)
Rice straw	600	3 h	10.45	0.154	-	-	-	-	-	-	-	285.33	Huang
													et al.
													(2017
Rice straw	600	3 h	_	_	18.49	_	_	_	_	_	_	72.1	Lou
													et al.
													(2012
Switchgrass	300	$\sim 3 \text{ h}$			70.2								Liu et
Switchgrass	600	2–3 h	-	-	94.5	-	-	-	-	-	-	-	(2017
-	300	2–3 h	- 0 1	-	70.2	-	-	-	-	-	-	2.6	Liu et
Switchgrass			8.4	-		-	-	-	-	-	-		
witchgrass	600	2–3 h	9.9	-	94.5	-		-	-	-	-	230	(2018
Rice husk ^a	500	-	-	0.15	52.99	15.08	3.59	0.52	0.21	0.81	-	1.726	Que
													et al.
													(2018
Rice husk ^a	500	5–10 s	6	0.3	52.99	15.08	3.59	0.52	0.21	0.81	0.01	1.72	Liu et
													(2018
Rice husk ^a	500	5–10 s			46.6	22.23	3.97	0.45	0.36	1.02	0.01	22.73	Liu et
Rice husk ^a	500	5–10 s	-	-	47.06	21.48	3.85	0.52	0.34	0.98	0.01	45.16	(2018
Rice husk ^a	500	5–10 s	-	-	44.46	22.92	3.66		0.39	0.99	0.01	31.3	(2010
			-	-				0.56					
Rice husk ^a	500	5–10 s	-	=-	41.75	20.57	3.31	1.91	0.37	1	0.04	66	
Rice husk ^a	500	5–10 s	-	-	44.8	25.73	3.66	0.57	0.43	0.98	0.01	11.5	
Vheat straw	400	4 h	8.24	80	77.38	14.89	3.99	3.74	0.19	0.05	-	93.84	Chi ar
													Liu
													(2016
Wheat straw	550	_	8.86	2	81.83	4.76	0.32	0.52	0.04	0.05	_	24.73	Wang
													et al.
													(2018
Wheat straw	700	4 h	8.57	80	82.55	14.14	2	1.31	0.17	0.02		256.04	Chi ar
viicut straw	700	1 11	0.07	00	02.00	1	-	1.01	0.17	0.02	-	200.01	Liu
. 1	600	0.1		0.1.40								006.05	(2016
Bamboo	600	2 h	-	0.149	-	-	-	-	-	-	-	396.05	Huang
sawdust													et al.
Bamboo	600	2 h	-	0.149	-	-	-	-	-	-	-	306.18	(2018
sawdust													
Apple wood	400	6 h	_	_	74.7	_	8.97	2.14	_	_	_	356	Gong
charcoal													et al.
Rice straw					58.1		2.14	0.38				218	(2016
Bamboo	600	- 2 h	-	0.250	67.48	-		0.77	-	-	-	332	Luo ai
Daniiboo	000	2 11	-	0.230	07.40	-	-	0.77	-	-	-	332	
													Gu
			_										(2016
Poultry	400	-	7	-	53.45	15	3.71	2.8	0.21	0.83	-	6.7	Sun
litter													et al.
Wheat straw	400	_	7	_	65.79	20.4	3.43	0.21	0.23	0.63	_	2	(2012
olid swine	250	20 h	_	_	47.46	20.7	5.72	1.25	0.33	1.45	_	4	
Poultry	250	20 h	-	=-	40.2	22.1	3.86	1.67	0.41	1.15	-	8.7	
litter			-	-						-	-	-	
Mushroom	500	4 h	9.65	0.250								53.33	Chen
110311100111	300	7 11	2.03	0.230	-	-	-	-	-	-	-	55.55	
													et al.
													(2018
ine chips	400	-	_	0.149	-	_	-	_	_	-	_	35.9	Jia an
Charcoal	400	_	_	0.149	_	_	_	_	_	_	_	-	Gan
													(2014
Poultry	600	2-3 h	11		18.5							5.2	Liu et
manure				-		-	-	-	-	-	-		(2018
ut shells ^b	500	1 h		0.5-1.0	77.5		3.69						(2010
141 3110113	300	1 11	-	0.5-1.0	//.3	-	3.05	-	-	-	-	-	

(continued on next page)

Table 1 (continued)

Feedstock	Pyrolysis temperature (°C)	Pyrolysis time	pН	Particle diameter (mm)	C (%)	O (%)	H (%)	N (%)	O/C (molar ratio)	H/C (molar ratio)	N/C (molar ratio)	BET surface area (m ² /g)	Reference
													Yang et al. (2018)
Peanut shells	400	-	-	2	61	-		-	-	-	-	31	Li et al. (2018)
Crofton weed	~ 500	-	10.53	2	86.48	11.7	1.1	0.72	0.01	0.01	-	382.21	Wang et al.
Macadamia	550-660	_	6.2	2	93.16	1.68	2.56	0.67	0.01	0.33	_	0.55	(2018)
Wood chips	700	-	-	-	-	16.7	-	-	-	-	-	712	Xiao et al. (2011)
Pine wood	850	-	-	-	78	-	-	-	-	-	-	343 ± 2	Silvani et al. (2017)

Note: : not found.

due to their unique physical and chemical properties for removing contaminants (Xu et al., 2012), such as graphene-coated biochar (Zhang et al., 2012), MgO-biochar nanocomposites (Jung and Ahn, 2016), and carbon nanotube-coated biochar (Inyang et al., 2015; Xiong et al., 2018); however, only a few have been applied in sediments (Liu et al., 2018). Metal-based biochars have been applied to activate oxidants for OP degradation, among which iron-based catalysts have outstanding advantages, such as being environmentally friendly, non-toxic, and highly efficient (Dong et al., 2017, 2018). Dong et al. (2018) found that Fe₃O₄−RHB accelerated SO₄ • formation and exhibited high efficiency in PAE degradation in marine sediments, and that magnetic Fe₃O₄−RHB can facilitate the achievement of environmental sustainability. In addition to iron-based biochar as catalysts, copper, cobalt, mixed metals, and heteroatom-based biochars have been widely employed to remove pollutants in Fenton-like systems (Wang et al., 2019). Thus, the

application of biochar-based nano-composites in sediment remediation has considerable prospects. Overall, biochar modification or activation provides opportunities to improve the physicochemical properties of biochar and verify the feasibility for practical applications in sediment remediation. To obtain desirable biochar with suitable properties for pollutant sequestration or immobilization in sediment, a comprehensive understanding of the interaction mechanisms between biochar and pollutants is imperative.

3. Remediation of HM-polluted sediments by biochar

HMs can enter aquatic systems due to natural or anthropogenic causes, and industrial effluents are considered the main source (Zhang et al., 2016). It has been reported that 90% of HMs eventually accumulate and settle into sediments, resulting in much higher HM

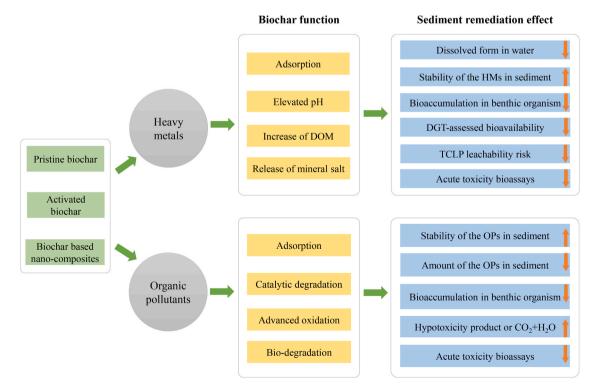


Fig. 2. The remediation effects of biochar for sediments polluted by heavy metals and organic pollutants (DOM: Dissolved organic matter, BCR: Community Bureau of Reference, DGT: Diffusive gradients in thin films, TCLP: Toxicity characteristic leaching procedure).

a Chemical activated.

 $^{^{\}rm b}$ Biochar-supported nano-composite.

concentrations in sediments than in the overlying water (Perrodin et al., 2012). HMs cannot be biologically/chemically degraded naturally; therefore, they are infinitely persistent in sediments, ultimately affecting the quality of the water and sediments. Therefore, HMs in sediments are the main focus of pollutant monitoring (Zhang et al., 2014; Yin and Zhu, 2016). Multiple biochars have been used to promote stabilization and reduce the bioavailability of HMs (Cu $^{2+}$, Pb $^{2+}$, Cd $^{2+}$, Zn $^{2+}$, and Hg $^{2+}$) in sediment (Chen et al., 2017; Liu et al., 2019). HMs bound onto biochar are dependent on the biochar characteristics, as discussed previously. In this section, studies on the mechanisms, distribution, and toxicity analysis of HM stabilization in biochar-sediment systems are reviewed (Fig. 2).

3.1. Adsorption of HMs in sediments

Metal cations (Cu²⁺, Pb²⁺, Zn²⁺, and Cd²⁺) are common pollutants in soil, water, and sediments, present as divalent ions or compounds, which exhibit similar characteristics and behaviors in sediments (Wang et al., 2018). The valences of metal anion species vary in different sediments (Wang et al., 2018). Biochar can immobilize and diminish the bioavailability of metal cations and oxy-anion compounds due to several different mechanisms, such as physical adsorption, cation exchange, surface complexation, precipitation, and electrostatic interactions for metal cations, reduction, and complexation of metal oxy-anion compounds (Fig. 3) (Liu et al., 2018; Huang et al., 2018; Uchimiya et al., 2012; Wang et al., 2019). Biochar, as an immobilization agent, can enhance the stability of Cu and Pb in sediments by surface precipitation (Wang et al., 2019). However, the distributions of metal fractions were not changed because only minimal soluble and carbonate metals in sediments could be captured by biochar (Zhang et al., 2020).

Moreover, the mineral components of biochar function as additional sorption sites for metals through electrostatic reaction and ion exchange, surface complexation, and induce the precipitation of metals by releasing soluble ions, such as PO_4^{3-} , CO_3^{2-} , and SO_4^{2-} (Li et al., 2017). In addition, the pH of a biochar-sediment system has a significant effect on HM immobilization, and the addition of biochar may change the sediment pH (Ojeda et al., 2016). In highly acidic conditions, the competition between H^+ and Cu^{2+} for active FGs on the biochar intensifies.

weakening Cu²⁺ adsorption (Zhang et al., 2017). Dong et al. (2014) showed that ion exchange processes between HMs and hydrogen were related to OFGs on biochar, which led to the changes in pH of the sediment. In addition, a higher pH enhanced the precipitation of HM ions with ligands (CO₃²⁻, SO₄²⁻, Cl⁻, OH⁻, etc.) (Shaheen et al., 2013). Liu et al. (2019) investigated the distribution and speciation of Hg in biochar-amended sediment during 1030 days. synchrotron-related methods, it was reported that the stabilization of Hg resulted from Hg-sulfide minerals and precipitation on or within biochar particles, which could co-exist with S, Fe, Cu, and Zn after switchgrass biochar remediation (Liu et al., 2018). In fact, metals could gradually stabilize in sediments because of natural attenuation (Yin and Zhu, 2016). Biochar accelerated this process and redistributed the metal fraction in sediments as long-term incubations due to the formation of stable compounds. Therefore, sediment particles with high OM content. which is an additional source for biochar production, could also be used as the biochar feedstock to remove contaminants. Some laboratory experiments had proven the feasibility of applying biochar derived from sediment to environmental remediation (Dong et al., 2014). Dong et al. (2014) prepared biochar derived from sediments to adsorb HM, and this biochar showed higher fixation capacities for Cu²⁺, Cd²⁺, and Pb²⁺ through complexation, ion exchange, and pore-filling. Hence, HMs could be effectively retained by biochar through adsorption.

3.2. Distribution of HMs in aqueous phase

The distribution of HMs includes two portions: the fractions in porewater and in the overlying water of the water-sediment phase (Que et al., 2018). Biochar can reduce metal concentrations in surface water, thereby lowering the pollution risk (Li et al., 2017). Organisms in sediments can slightly reduce the amount of HMs in porewater and overlying water by feeding; however, this method cannot completely remove HMs (Huang et al., 2018). The distribution of HMs in the aqueous phase will be influenced by different environmental conditions during the process of sediment remediation with biochar (Zhang et al., 2018). In the sediment-aqueous phase, for instance, the pyrolysis temperature of biochar is negatively correlated with the HM-removal rate in sediment porewater, as reported by Zhang et al. (2018). When biochar is prepared

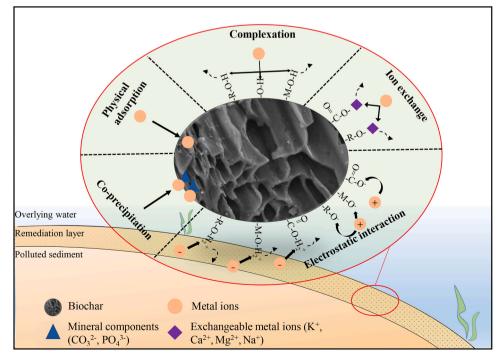


Fig. 3. Proposed mechanism of biochar for heavy metals in sediment.

at temperatures > 600 °C, the removal efficiency of HMs (Cd, Cu, Ni, Pb, and Zn) remained constant in sediment porewater (Zhang et al., 2018). The Cu concentrations in surface water and interstitial water after in-situ rice husk biochar remediation were investigated by Que et al. (2018). The Cu reduction rates in surface water and interstitial water with RHB amendment were increased by 8-60% and 11.1-48.1%, respectively. Furthermore, the stable Cu fraction in interstitial water increased due to the increased pH of sediments and bonding with FGs on the surface of biochar to capture the acid-extractable Cu (Que et al., 2018). Biochar-based composites also exhibit high sorption performances. Wang et al. (2019) prepared a composite with improved properties and well-dispersed attapulgite on biochar and showed that it significantly lowered the As and Cd concentrations by approximately 79-82% and 36-44% in the overlying water, respectively, and by approximately 68-82% and 38-48% in the sediment porewater, respectively. HM morphology is highly correlated with its content in surface water and porewater (Zhang et al., 2018). Besides the chemical properties, the particle size and dosage of biochar have influence on the adsorption of metals. In general, powdered biochar has a larger external surface area and shorter diffusive path lengths of pollutants than those of granular biochar. For example, at equal dosages, biochar with an increased particle size (< 380 µm) did not affect the adsorption efficiency of HM (Cu, Pb, Ni, Zn, Cd, and Cr) in sediment porewater, however, reduction of HMs slightly decreased when using biochar with an increase in particle size (> 380 µm) (Zhang et al., 2018). When sediment conditions change or human and natural disturbances occur, HMs may be released into the overlying water from sediments and cause re-pollution, and biochar could sever the circulation of HMs in sediment-aqueous systems (Zhang et al., 2014). Hence, research on the distribution of metals in the aqueous phase is of great significance for appraising the effect of in-situ sediment remediation by biochar.

3.3. Change of HMs species in solid sediments

The bioavailability and biotoxicity of HMs are affected by the addition of biochar in sediment and are closely related to their speciation fractions and binding states (Yu et al., 2010). Therefore, the HM concentrations and species in sediment that require amendment should be comprehensively considered. A risk assessment of HMs in lake sediment was conducted by Yang et al. (2014), and intensive human activities inputs and speciation distribution analysis showed that four metals (Cd, Cu, Pb, and Zn) were dominated by non-residual fractions in highly urbanized areas. This study revealed that the pH and total organic carbon (TOC) concentration of sediment are closely related to the chemical fractions of HMs (Yang et al., 2014). Consideration of the HM species in sediment is beneficial for assessing the bioavailability and toxicity of HMs following the biochar amendment. Huang et al. (2018) investigated the speciation of Pb2+ in solid-phase sediments, consisting of the acid-soluble fraction (F1), reducible fraction (F2), oxidative fraction (F3), and residual fraction (F4). The potentially available fraction of metals (F1 + F2 + F3) usually decreased with the addition of biochar to sediments and different chemical forms of HMs pose varying ecological risks (Yang et al., 2014). The acid-soluble and reducible fractions were regarded as the weakest bound fractions and caused direct toxicity to organisms. The basis of sediment remediation is to transform the active chemical forms of HMs (F1, F2 and F3) into the stable fraction (F4) due to the low bioavailability of F4 (Zhang et al., 2014; Yin et al., 2014). Wang et al. (2019) applied biochar/attapulgite composites for As and Cd immobilization in sediment; they showed that, after 60 days of treatment, the F1 values of As and Cd were reduced approximately by 43% and 11%, respectively, while F2 increased to different degrees, and F4 increased in sediment (Wang et al., 2019). Therefore, the use of a biochar/attapulgite composite as a sorbent could effectively enhance As and Cd immobilization in sediment. The chemical fractions of HMs are correlated with sediment properties (total organic carbon, pH, and clay content). When biochar is added to polluted sediments, HM stability

enhances due to the change in sediment properties. Activated biochar and biochar-supported nanocomposites lower the percentages of F1 and F2 of HMs in sediments (Han et al., 2019). The bioaccumulation and acute toxicity of HMs in sediments decreased after biochar remediation, and accordingly, the stability was increased. Chemical fractions of HMs are prone to transform among each other if environmental conditions change. For example, the presence of humic acid (HA) in sediments was conducive for the conversion of Cd due to the formation of ternary biochar-HA-Cd surface complexes (Gong et al., 2019).

3.4. Influence on HMs toxicity in sediment

HMs in sediments may be released into the water when the concentration is higher than the maximum sorption capacity of sediments or if the surrounding environment changes. In turn, released HMs can be taken up and accumulated by organisms in food chains, causing human health or environmental risks. Hence, toxicity assessments of HMs in biochar-amended sediments is imperative for measuring remediation efficiency.

Toxicity bioassays can elucidate the adverse impacts of in-situ sediment remediation. The influences of the OM content in sediments have been proved, i.e., to control the concentration of HMs and reduce their bioavailability and toxicity (Shaheen and Rinklebe, 2015). The toxicity characteristic leaching procedure (TCLP) method is used to assess the potential leaching toxicity of HMs in sediments under acidic conditions and could be used to evaluate the performance of biochar for amended sediments. Liu et al. (2018) discovered that several activated biochars improved the effects on Cd immobilization in sediment, as evidenced by the decreased concentration of TCLP-extractable Cd (by approximately 13-23%). Biochar, as a remediation agent, has a high solid OM content, which increases the OM content in sediments. BC-nClAP with a higher OM content could decompose organic acids; thus, more phosphate is released from BC-nClAP to immobilize Pb by precipitation and reduce TCLP-leachable Pb (Huang et al., 2018). With increased dosages of biochar in sediments, the stability of HMs generally increased and HM concentrations in the TCLP leachate correspondingly decreased (Wang et al., 2019).

Biological tests have also been an important element of appraising the detoxification feasibility of biochar for sediments, and an increasing number of researchers are conducting toxicity tests. A phytotoxicity test of sediments polluted by organic compounds and HMs with the addition of biochar, activated carbon, and multiwalled carbon nanotubes were assessed by Jośko et al. (2013). It was reported that the reduction in phytotoxicity of sediment after the application of biochar and other carbonaceous materials (activated carbon and multiwalled carbon nanotubes) was 27.5% and 17.7–28.9% (reduction of root growth inhibition) and 70% and 30–40% (reduction of seed germination inhibition), respectively. In addition, the reduction in sediment toxicity was positively correlated to the biochar diameter (Jośko et al., 2013). Other factors (nutrient binding and water availability) must be considered in the analysis of phytotoxicity in biochar-amend sediments (Jośko et al., 2013).

To summarize, biochar can alter the physicochemical properties of sediments and reduce the toxicity of HMs to aquatic organisms in sediments. Through toxicity analysis, researchers could estimate whether pure biochar and modified biochar have positive effects on sediments or the side-effects of remediation are better than detoxification. In fact, the toxicological risk of sediments may result from not only metals but also other highly toxic OPs, such as pyrethroids or cypermethrin (Li et al., 2018). Toxicity analyses to determine the effects of biochar in polluted sediment require further research.

4. Remediation of OP-polluted sediments by biochar

As a remediation agent, biochar exhibits a high efficiency for adsorbing or removing OPs, mainly by decreasing their bioavailability

and mobility through adsorption and degradation processes (Table 2). Pristine biochar, chemically modified biochar, and biochar-based nanocomposites are used to remove OPs. The effects of biochar may be correlated with interactions between microorganisms, biochar, and pollutants in the system, in which adsorption—desorption of pollutants, microbial growth and metabolism, biodegradation of pollutants, and chemical degradation processes occur simultaneously (Lou et al., 2015). The effects of biochar on the detoxication of OPs include increasing the stability of OPs in sediment, decreasing the concentration of OPs, bioaccumulation in benthic organisms, formation of hypotoxicity products, and acute toxicity, as evaluated by bioassays (Fig. 2). As for OP removal from sediments, the roles of biochar mainly involve adsorption, catalytic degradation, and bio-degradation, which are summarized in the following section.

4.1. Adsorption of OPs

A significant source of organic contaminants in surface water may be heavily polluted sediments, commonly polychlorinated biphenyls (PCBs), PAHs, pesticides, and herbicides. It has been reported that biochar has a superior capacity to adsorb OPs, due to its high surface areas, microporosity, special FGs (e.g., carbonyl, hydroxyl, and phenolic groups), and charge characteristics (Ahmad et al., 2014; Luo and Gu, 2016). Biochar in sediments may adsorb OPs mainly via H-bonding, $\pi - \pi$ interaction, electrostatic interaction, and pore filling (Fig. 4). The adsorption mechanisms depend on the characteristics of OPs, the physicochemical properties of biochar, and the sediment properties. For example, Wang et al. (2018) assessed the bioavailability of flubendiamide in the presence of biochar. Through sorption studies, partitioning into the noncarbonized OM of biochar and π - π electron donor-receptor action were the dominant mechanisms between biochar and flubendiamide. Sun et al. (2012) found that the hydrogen bonds of fluridone and norflurazon could interact with N-containing FGs of biochar. H-bonding between herbicides and FGs on biochar surface most likely plays an important role in their interactions (Wang et al., 2011). The sorption of OPs occurs through hydrophobic partitioning, as reported by

Xiao et al. (2011).

Pristine biochar consists of carbonized and non-carbonized fractions and has a high affinity to organic compounds. The sorptive ability of biochar in sediment system is higher than that of sediments alone, although the aging effect is enhanced over time (Lou et al., 2012). Biochar can increase the free sorption sites, so that movement of OPs is prevented by adsorption process within biochar, affecting their bioavailability in sediments. Typical OPs such as pesticides, antibiotics, PAHs, and dyes have been detected in sediments (Maletic et al., 2019; Jia et al., 2014); however, further research is essential to evaluate the applicability of adsorption for remediation of various types of OPs.

4.2. Catalytic degradation of OPs

Besides sorption, reactive removal is also a method of OP removal because biochar, as an efficient electron transfer medium, can motivate electron conduction and facilitate redox reactions. In natural sediments, reducing agents are omnipresent and abundant, such as aqueous Fe(II) and reduced sulfur species (bisulfide, HS⁻, and polysulfides) (Li et al., 2020). For instance, Gong et al. (2016) investigated the abiotic reductions of trifluralin and pendimethalin by sulfides in anoxic sediments using three types of black carbon. The result suggested that adding biochar as sufficient reductants could significantly accelerate the abiotic reduction of dinitroaniline herbicides. Moreover, Fe(II)-mediated (abiotic) reactions are conducive to the reductive transformation of halogenated OPs (Kappler et al., 2014). Adding biochar to sediments contributes to sulfide reduction, which results in high-toxicity OPs being degraded to hypotoxicity products by effective catalytic action, thereby reducing the environmental risk (Yang et al., 2018). Chen et al. (2018) found that biochar amendment significantly enhanced bacterial iron-reducing process. The electron flow during iron cycling was considered as a "mediator" to generate electrons, and high Fe(II) levels in biochar-amended sediments may result in high reductive reactivity, ultimately facilitating the reductive debromination of 2,2,4,4-tetrabromodiphenyl ether, as shown in anaerobic mangrove sediment slurries (Kappler et al., 2014).

Table 2Mechanism of biochar for sediment remediation.

Biochar	Feedstock	Pollutant in sediments	Mechanism of biochar	Reference
Pristine	Rice straw	Pentachlorophenol (PCP)	Adsorption	Lou et al. (2011)
	Rice straw	Nonylphenol	Degradation	Cheng et al. (2017)
	switchgrass	Hg	Adsorption	Liu et al. (2017)
	Rice straw	PCP	Sorption	Lou et al. (2012)
	Rice straw	PCP	Sorption	Lou et al. (2013)
	Wood chips	Tributyltin (TBT)	Adsorption	Xiao et al. (2011)
	Rice straw	Trifluralin and pendimethalin	Degradation and adsorption	Gong et al. (2016)
	Pinewood	Mercury	Adsorption	Bussan et al. (2016)
	Pine chips	Polybrominated diphenyl ethers (PBDEs)	Sequestration	Jia and Gan (2014)
	Switchgrass	Hg	Adsorption	Liu et al. (2018)
	Poultry manure		•	
	Oak			
	Pinewood	PCBs, PAHs and Cd	Adsorption	Gomez-Eyles and Ghosh (2018)
	Crofton weed	Flubendiamide	Sorption	Wang et al. (2018)
	Macadamia		•	
	Wheat straw			
	Rice husk	Cu	Adsorption	Que et al. (2018)
	Straw chip and pig manure	As(V) and Fe(III)	Adsorption	Chen et al. (2016)
Chemical modification	1 10		•	
Nitrate	Nut shells	PAHs	Degradation	Yang et al. (2018)
H ₃ PO ₄	Rice husk	Cd	Adsorption	Liu et al. (2018)
HNO ₃			•	
H ₂ SO ₄				
H_2O_2				
ZnCl ₂				
Coupling with nano-composite				
Chlorapatite	Bamboo	Pb	Adsorption	Huang et al. (2018)
Fe ₃ O ₄	Rice husk	PAEs	Degradation	Dong et al. (2018)
Fe ₃ O ₄	Bamboo	PAHs	Degradation	Dong et al. (2017)
Fe ₃ O ₄	Wood	PAHs	Degradation	Dong et al. (2018)

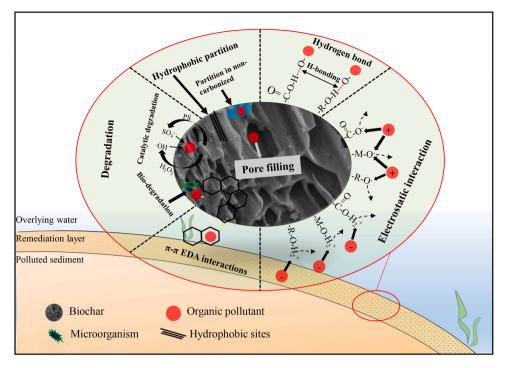


Fig. 4. Proposed mechanism of biochar for organic pollutants in sediment.

Biochar with reactive free radicals contributes to OP removal, mainly the combination of biochar with hydrogen peroxide (H2O2) or peroxydisulfate (PDS). Fenton (activated H2O2) and sulfate radical-based methods (activated $S_2O_8^{2-}$) are presently the most popular methods to degrade OPs (Wang et al., 2019). A biochar-based catalyst took part in H₂O₂-based chemical oxidation to generate •OH to efficiently degrade 2-chlorobiphenyl because biochar containing persistent free radicals could activate H₂O₂ (Fang et al., 2014). Redox-based advanced oxidation processes (AOPs) involving PDS and peroxymonosulfate (PMS) activations have attracted increasing interest due to the low cost, ease of operation, and versatility (Wang and Wang, 2018). For example, a Fe₃O₄ and bamboo biochar (BB) composite was used as a catalytic material to activate $S_2O_8^{2-}$ for degrading PAHs in SO_4^{-} •-based AOPs, in which the presence of BB promoted electron transfer and accelerated the formation of Fe²⁺ to generate SO₄• (Dong et al., 2017). In addition, catalytic testing showed that the Fe₃O₄-BB composite achieved the highest activity toward PDS after 24 h treatment (Dong et al., 2017), which was in agreement with the findings reported by Dong et al. (2018). Fe₃O₄-RHB can be used as an activator for the PDS oxidation process to rapidly facilitate the removal of PAEs in marine sediments (Dong et al., 2018). Biochar-based catalysts facilitate electron transfer, simultaneously expediate the formation of active radical (SO4•, •OH), and thus, accelerate OP degradation.

4.3. Biodegradation of OPs

Biodegradation refers to the living microorganisms on biochar degrading OPs in sediment. Biochar with a high surface area could supply habitat and nutrients for microbial communities (bacteria, algae, and fungi), which is beneficial for pollutant biodegradation by immobilized microorganisms (Yang et al., 2018; Wu et al., 2016). Some microorganisms are known to generate enzymes to degrade various OPs (Huang et al., 2017). Microbial degradation is a natural attenuation process controlling the OP content in polluted sediments. Yang et al. (2018) enhanced the efficiency of removing phenanthrene in sediments using a combination of biochar and nitrate, and showed that PAH-degraders (*Thiobacillus* and *Stenotrophomonas*) settling in the biochar surface pores could utilize phenanthrene as a carbon source. Then,

the added nitrate was captured by biochar and served as an electron acceptor to stimulate phenanthrene degraders. Microbial community structures vary with different OP concentrations and biochar dosages (Lou et al., 2015). There has been minimal research regarding the utilization of biochar for OP removal through bio-degradation in sediment; however, this approach is promising based on the capability of other carbonaceous materials (Cheng et al., 2017; Lou et al., 2015). For example, Jin et al. (2017) found that *Pseudomonas* sp. isolated from Jiaozhou Bay wetland sediment, with preeminent environmental adaptability, was immobilized in coal cinder and chitosan beads for benzopyrene degradation. Therefore, coal cinder with a larger specific surface area and pore size, and a greater amount of OFGs as a degrading bacteria carrier, is the optimal choice for benzopyrene degradation (Jin et al., 2017). Through a similar means, biochar may also be used as a bacteria carrier material for OP biodegradation in further experiments.

5. Potential risks of biochar to biological systems in sediment

Using capping technology with biochar for in-situ sediment remediation should consider not only the binding and isolation performance, but also the potential risks posed to biological systems. Previous studies on the toxicological effects of carbonaceous materials have focused on analyses at the microbial community, fauna, and indigenous plant levels (Rakowska et al., 2012; Wang et al., 2018), and the potentials risk of biochar to plants in sediment have not been investigated. The effects of biochar on microbial communities and enzyme activity could indirectly change the efficiency of sediment remediation. Thus, the potential risks of biochar were concluded at indigenous microbial composition and benthic organism levels in this section.

5.1. Effect of biochar on indigenous microbial composition

Sediment remediation focuses on whether biochar causes changes in the microbial community and enzyme activity in sediment ecosystems (Luo and Gu, 2016; Chen et al., 2018). Microbial dynamics are an indicator for the remediation process, which is related to the stability of the sediment structure, nutrient cycling and respiration, water content, disease resistance, and carbon storage capacity (Cheng et al., 2017; Luo

and Gu, 2016). Additionally, enzyme activity is used to appraise microbial activity due to its direct relationship with sediment functionality (Huang et al., 2017). Researchers are increasingly concentrating on the effect of remediation techniques on microbial communities and enzyme activity in sediments (Que et al., 2018; Liu et al., 2018).

Biochar alters the structure and abundance of microbial communities and the micronutrient content in sediments. Biochar may also increase the microbial community abundance of sediments on account of its porous structure, which provides habitat and nutrients (Chen et al., 2017). For example, Chen et al. (2016) showed that biochar derived from fresh biogas slurry residue exerted a positive effect on the microbial community by either promoting an increase in abundance or reducing the magnitude of loss via mediating reductions of As⁵⁺ and Fe³⁺. By contrast, biochar was perceived to have a negative effect on the abundance of organisms in Desulfosporosinus and Pedobacter genera (Chen et al., 2016). Microbial community abundance often (directly or indirectly) reflects the physical-chemical properties of sediments (Deng et al., 2015). Bacterial abundance and diversity in control sediment groups were higher than those in sediments treated by activated biochar (Huang et al., 2017). The reported results suggested that the application of biochar affects microbial community abundance and diversity in polluted sediments.

Moreover, enzyme activity in sediments is susceptible to biochar. Some studies have proved that enzyme activity in sediments was influenced by the biochar content (Huang et al., 2017). A high biochar concentration in sediments caused decreases in invertase and alkaline phosphatase activity, and extractable Zn and Cd fractions declined, whereas the pH and OM content increased in biochar-amended sediments (Huang et al., 2017; Han et al., 2019). Biochar addition promoted N and P recycling, thereby affecting enzyme activity (Huang et al., 2017). However, phenol oxidase activity was positively correlated with the biochar content in sediments (Luo and Gu, 2016). Meanwhile, biochar also poses a risk of increasing the number of harmful microorganisms in sediments, competing with beneficial microorganisms for nutrients and habitats, which would render sediment remediation much less effective. To facilitate biochar technology to achieve better remediation effects and reduce the risks of biochar application to sediments, further research regarding the mechanisms between various biochars and microbial communities and enzymes are needed.

5.2. Effect of biochar on benthic organisms

Various benthic organisms dwelling in sediment are exposed to biochar and pollutants, which have impacts on the water-sediment layer. Benthic organism behaviors such as digging, feeding, and excreting (recognized as bioturbation) can be an indicator for toxicity of biochar and pollutants, such as worm, tubificid (Tian et al., 2020). Bioturbation causes the movement of capping material (sediment, biochar particles) and the release of pollutants from sediment to water (Tian et al., 2020). The available reports have proved that carbonaceous materials (activated carbon, charcoal) did not have significant negative effects on fish embryos and molluscs (Rakowska et al., 2012). Thus, biochar may cause negative effects on aquatic organisms, due to feeding on biochar particles or pollutants and habitat changes resulting from the presence of biochar. When tubifex worms were exposed to sediment containing biochar (produced at 700 °C), the bioaccumulated concentrations of As and Cd in tissue decreased and the abundance and biodiversity of microbial community increased (Zhang et al., 2020). To the best of our knowledge, toxicity experiments of biochar on aquatic organisms in sediment are currently inadequate and further studies are needed.

6. Engineering applications of biochar in polluted sediments

Polluted sediment treatment technologies mainly aim to reduce or immobilize pollutants, thereby reducing the risk posed by pollutants to

organisms or humans. Nowadays, common sediment remediation strategies include dredging and capping. Dredging treatments can maximize the removal of pollutants from aquatic environments (Chen et al., 2019). The benefits of dredging engineering for dislodging Cu, Cd, and Pb from lake sediments after six years was proved by Chen et al. (2019). Dredging reduces the labile fractions of metals, increasing the metal-binding capacity of available sediment solids and retarding the leaching of metals from solids (Chen et al., 2019). Nevertheless, disadvantages of dredging technology cannot be ignored, including: (I) dredging cannot fully remove all contaminants; (II) new pollutants will migrate downward and again cause pollution owing to the short maintenance time after sediment relocation; (III) the cost of this technique is high; and (IV) original benthic communities in sediments may be destroyed (Akcil et al., 2015). Considering the above disadvantages of dredging, the application of low-cost biochar in in-situ capping to immobilize contaminants is feasible and has become a current research hotspot. Capping technology for a mature sediment remediation method has already been successfully used by the US Environmental Protection Agency (Förstner and Apitz, 2007). Forming a capping layer with biochar and other materials (calcite, zeolite, and apatite), or mixing biochar with sediments as a capping, are two commonly used methods (Zhang et al., 2016). Three engineering methods are commonly used for biochar application in polluted sediments (Fig. 5): (a) A capping layer combining biochar with other material (gravel, quartz sand, or zeolite) is used for low-flow water or closed lakes; (b) two permeable geotextile layers containing the capping material is suitable for high-flow water; and, (c) biochar mixing sediments as a capping layer is appropriate for shallow water or small-scale water bodies.

6.1. Coupling biochar with other capping materials

The majority of pollutants in sediment come from sewage (Yang et al., 2014). Establishing an isolation barrier between sediment and sewage would effectively reduce the risk of sediment contamination and prevent the release of pollutants from polluted sediment into the water (Ghosh et al., 2011). Biochar is very useful as a sorbent for active capping due to its potentiality to limit the interactive diffusion of pollutants between sediment and water (Silvani et al., 2017). Biochar as capping material must combine other materials that contribute to biochar deposition (Fig. 5a). Traditional materials such as sand and natural zeolite have been applied for capping with biochar, which is suitable for low-flow water or closed lakes. Capping treatment, an developing technology, employs inert materials to effectively prevent contaminants exposure risk from sediments by binding and adsorption, which can create a protective barrier against contaminants (Zhang et al., 2017). By isolating sediments from water, the pollutant concentrations in the overlaying water are maintained at safe levels (Gomes et al., 2013; Ghosh et al., 2011). Zhang et al. (2017) incorporated RHB into the sediments, aided by covering with a quartz sand layer to prevent the biochar floating, to reduce the concentrations of Cu²⁺ and 4-chlorophenol. The results indicated that a certain thickness of RHB could limit the release of Cu^{2+} and 4-chlorophenol from sediments through adsorption, flocculation, or ingestion by microorganisms. Besides, it has been demonstrated that the biochar layer could adsorb more NH₄-N from water than soil layer and inhibit its endogenous release from sediment in capping systems (Zhu et al., 2019). To improve the stability of these clean materials and prevent the formation of a biochar-sediment mixture, two permeable geotextile layers could fasten the reactive core, as shown in Fig. 5b. With geotextile layers, these capping materials can resist high-flow water and extreme weather (Wang et al., 2018). Thus, a dissolvable or biodegradable geotextile is needed when using biochar as a capping amendment.

6.2. Mixing biochar with polluted sediments

Instead of capping with clean amendment materials, mixing biochar

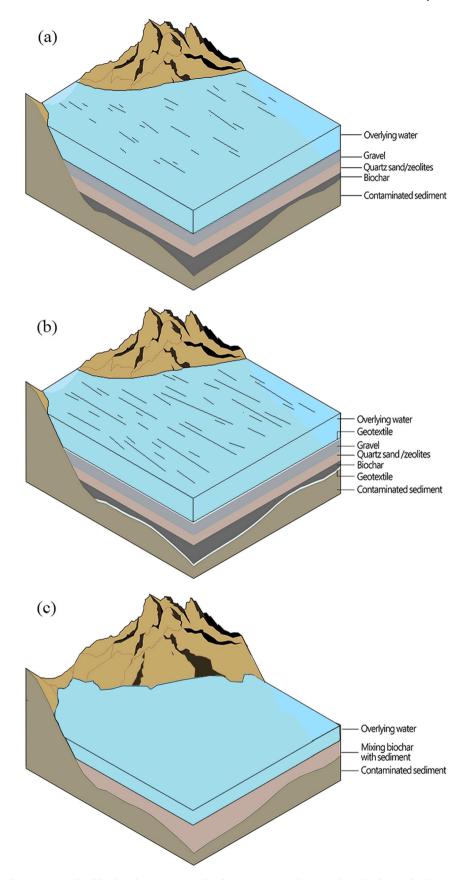


Fig. 5. The engineering application methods of biochar for contaminated sediments. Capping layer combine biochar with other material (gravel, quartz sand or zeolite) (a); two permeable geotextile layers containing the capping material (b); biochar mixing sediments as capping layer (c).

with sediment is another method used to immobilize contaminants and reduce their bioavailability and accumulation in food chains (Fig. 5c). The capping treatment can potentially couple with in-situ bioremediation and provide feasibility for field long-term capping treatment technology (Wang et al., 2019; Silvani et al., 2017). However, long-term capping treatment may weaken the remediation capacity of biochar due to the lack of adsorption sites (Lou et al., 2012). Mechanical mixing is feasible only in shallow water or small-scale sediments. For large-scale sediment remediation, however, the direct mixing of the capping material is not feasible. Mixing biochar with polluted sediments to allow full interaction could reduce contaminant mobility, toxicity, and bioavailability in sediments (Liu et al., 2018; Lou et al., 2012), and this method is commonly used in laboratory experiments for adsorption or binding contaminants from sediments (Lou et al., 2011; Wang et al., 2019). Many laboratory experiments have been conducted with continuous shaking to intensively mix biochar and polluted sediment (Dong et al., 2014). Sediment remediation methods using biochar can reduce costs and labor.

7. Conclusion and future perspectives

Biochar exhibits a high efficiency for treating polluted sediments, which is in line with the principles of environmentally sustainable development. In capping technology, the low-cost of biochar provides a nonnegligible advantage as a capping material to adsorb and degrade pollutants, and biochar could perform comprehensive functions in sediment remediation (Fig. 6). Despite biochar being considered a promising material for pollutants immobilization or sequestration in sediment remediation, some research gaps and uncertainties remain that require further investigation and development.

(1) Optimizing biochar properties and enhancing its ability to immobilize target pollutants for sediment remediation. The physicochemical properties of biochar are greatly influenced by the biomass feedstock and production conditions. Pre-treatment of biomass and post-modification of biochar could be designed to improve its properties, which must be environmentally friendly and low-cost. Moreover, the commercialized preparation of biochar is currently retarded and rough; therefore, the technical procedures and equipment should be improved for delicacy structure biochar. The physicochemical properties of biochar produced from various waste biomasses and pyrolysis conditions

- are entirely different in contaminant management; thus, a database of biochar feedstock, preparation conditions, physicochemical properties, and function could be built for further utilization.
- (2) Improving the utilization patterns of biochar could save labor and costs. Lake, river, and marine sediment deposits are very different, which influences pollutant behavior. The expenditure of capping mainly contains three aspects: 1) cost of biochar; 2) efficiency of biochar; 3) capping layer design and establishment. Activated biochar amendment could reduce the thickness of traditional capping technology but may increase the immobility of pollutants. New and innovative technologies for capping or mixing should be invented to remediate polluted sediments. In addition, the optimal layer thickness of biochar in capping should effectively isolate pollutants from sediments to the overlying water, for decades to centuries under extreme weather conditions. Long-term monitoring of different layers at polluted sites could provide a valuable database for sediment remediation.
- (3) Microbial communities and enzyme activity are easily affected by biochar in sediments. Further studies are needed to ascertain whether other aquatic organisms are sensitive to biochar. Toxicity experiments are necessary to determine the practicality of different biochars and synthesis methods for large-scale applications. Effects of biochar-amendment on the eco-function and health of sediments and food chains are critical issues that require further attention. The complex physical and chemical parameters of actual sediment is a challenge that requires further field experiments.
- (4) Increasing attention has been paid to the application of biochar for emerging contaminants in sediment, such as endocrine disrupters, medicines, and personal care products. The potential application of biochar for metals that are present in trace amounts but exhibit persistent accumulation in the natural storage system, and many other anthropogenic contaminants should be also considered, such as Ni²⁺, Co²⁺, Sb⁵⁺, and Sb³⁺ as well as radionuclide ions such as Sr²⁺, Cs⁺. Therefore, the synergistic treatment of different pollutants should be investigated in natural sediments with various coexisting pollutants.
- (5) Biochar as an amendment for sediments polluted by organic or inorganic contaminants generally has complex mechanisms that require further exploration. Variations in the properties of sediments caused by biochar, types of biochar (pristine or modified),

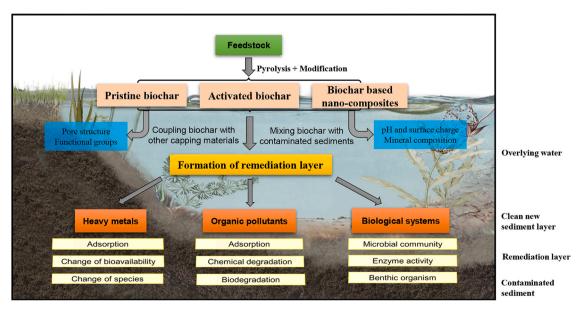


Fig. 6. The comprehensive functions of biochar in sediments.

- time of treatment, and environmental conditions (pH, temperature, etc.) may all influence the remediation efficiency. A deep understanding of these parameters is important for further applications of biochar.
- (6) Capping technology has the potential for cost-effective and longlasting sediment remediation. However, most capping experiments with biochar have been confined to laboratory- or pilotscales. Amendments have been conducted in laboratories without consideration of field conditions; therefore, additional field data and pilot-scale experiments representing the reliable practicability of biochar in the environment are essential. For improvement, other clean materials coupling biochar in caps, which conform to the principles of ease of availability, low-cost, and negligible toxicity, should be selected.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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