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Biochar-Facilitated Soil Remediation: Mechanisms and Efficacy Variations

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Recent research suggests that biochar amendment is a promising approach to mitigate soil contamination *via* immobilizing heavy metals and organic pollutants. Through intensive literature review, this paper was aimed to better understand the processes, mechanisms, and effectiveness of biochar in immobilizing chemical contaminants in soil. The quality characteristics of biochar as a soil amendment varied greatly with the feedstock materials and the pyrolysis conditions. Biochar products from different sources demonstrated remarkably diversified capacities and efficiencies for stabilizing soil contaminants. Soil-incorporated biochar was able to stabilize Cd, Cu, Ni, Pb, and Zn and reduce their bioavailability through enhanced sorption (based on electrostatic attraction, ion exchange, and surface complexation) and chemical precipitation (incurred from soil pH elevation and ash addition of carbonates and phosphates). The stabilization efficacy was largely determined by cation exchange capacity, pH, and ash content of the biochar. Biochar amendment increased the mobility of anionic toxic elements [e.g., CrO_4^{2-}, AsO_3^-, and $Sb(OH)_6^-$] in soil. Soil-incorporated biochar was also able to adsorb non-polar organic compounds (through pore filling, partition, and hydrophobic effect) and polar organic compounds (via H-bonding, electrostatic attraction, specific interaction, and surface precipitation). The adsorption efficiency was controlled by the biochar surface properties specific surface area, microporosity, and hydrophobicity. Biochar may facilitate the mineralization of organic pollutants by enhancing soil microbial activities. The effectiveness of biochar-facilitated soil remediation was case specific, changing with the biochar source, amendment rate, placement, soil type, and pollutant species. More field studies are needed to evaluate the long-term effectiveness of biochar-facilitated soil remediation under practical circumstances.

Keywords: biochar, heavy metals, organic contaminants, adsorption, immobilization

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INTRODUCTION

Biochar is charcoal prepared by pyrolytic processing (i.e., O_2-absent heating at 300–700°C) of residual biomass materials and used as a soil amendment in agricultural and environmental applications (Lehmann and Joseph, 2012). The black carbonaceous solid is porous, environmentally recalcitrant, and abundant in surface functional groups (Guo et al., 2016). The relatively high porosity and surface functionality engender biochar with great specific surface area (SSA) and cation exchange capacity (CEC), enabling the material to retain water, nutrients, and pollutants in soil (Ahmad et al., 2014). In addition, biochar contains significant portions of labile organic carbon (OC) and possibly plant nutrients (e.g., N, P, K, Ca, Mg, and S) (Song and Guo, 2012). Intensive laboratory studies and field trials have demonstrated that appropriate biochar amendment is effective to ameliorate soil physical, chemical, and biological properties, increase crop productivity, and reduce the bioavailability of heavy metals and organic contaminants in soil (Chan et al., 2007; Park et al., 2011; Novak et al., 2016; Ghorbani et al., 2019). As a promising soil amendment, biochar has been explored in uses of soil health improvement, pollution alleviation, land reclamation, and climate change mitigation.

Soil contamination by heavy metal(loid)s (e.g., Cd, Cr, Hg, Pb, Cu, Zn, As, Co, Ni, and Se) and persistent organic pollutants [POPs, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-ρ-dioxin (PCDD), and polychlorinated dibenzofurans] is a worldwide problem that threatens environmental sustainability, food safety, and human health (Fabietti et al., 2009; Su et al., 2014; Sun et al., 2018). To control the hazardous effects and ideally restore the ecosystem services of contaminated soils, an array of *in situ* and *ex situ* remediation techniques have been developed, including surface capping, encapsulation, landfilling, soil flushing, soil washing, soil venting (air sparging), vacuum ventilation (vapor extraction), thermal extraction, electrokinetic extraction, chemical degradation, stabilization, solidification, vitrification, bioremediation, and phytoremediation (Zhu et al., 2010; Liu L. et al., 2018). These techniques employ physical, chemical, thermal, electrical, and biological methods and processes to contain, immobilize, and ultimately eliminate soil contaminants. In field practice, all the available techniques demonstrate particular advantages and disadvantages of remediation efficiency, cost effectiveness, and applicability (Liu L. et al., 2018).

Recently, biochar amendment has been investigated to alleviate soil contamination and facilitate soil remediation (Chai et al., 2012; Houben et al., 2013; Koltowski et al., 2016; Ippolito et al., 2017). Existing literature reviews suggest that biochar amendment immobilizes heavy metals and POPs in contaminated soils and reduces their bioavailability primarily through precipitation, electrostatic interaction, surface adsorption, structural sequestration, and facilitated decomposition; the decontamination efficacy varies with the biochar source, amendment rate, soil type, and pollutant species (Ahmad et al., 2014; O'Connor et al., 2018; Zama et al., 2018; Kumpiene et al., 2019; Yuan et al., 2019). Most of the reported research trials were in short-term laboratory experiments. The long-term (e.g., >5 years) effects of biochar amendment on contaminant mobility and bioactivity in field soils remain unclear. By comprehensively reviewing the literature, this paper was aimed to further understand the mechanisms and the processes through which biochar amendment mitigates soil contamination, with the ultimate goal to provide instructions of appropriate biochar utilization for effective soil remediation.

QUALITY VARIATIONS OF BIOCHAR AS A SOIL AMENDMENT

Biochar products from different sources vary widely in characteristics and function capacity as a soil amendment. Biochar is produced from biomass materials using the thermochemical technique pyrolysis, through which organic residues are heated in O_2-free or highly limited, ambient-pressure environments for a certain time to be carbonized into charcoal, with the generation of pyrolysis bio-oil and syngas as byproducts (Guo et al., 2016). Common biochar feedstocks extend to forest debris, crop residues, food processing waste, and manures including sewage sludge and biosolids (**Table 1**). These biomass materials are significantly different in organic and ash compositions, attributing to the notable quality variations of the resulting biochar products. The carbonization (pyrolysis) conditions further influence the quality characteristics of biochar. Three parameters are usually used to manipulate the carbonization conditions: pyrolysis (peak) temperature, solid residence time, and heating rate, each stretching over a wide range of values (Guo et al., 2020). The pyrolysis temperature for biochar production is mostly in the range of 300–700°C (**Table 1**). A higher temperature accelerates the carbonization process, allowing the pyrolytic transformation of biomass to reach a deeper level and be completed in a shorter time (Song and Guo, 2012; Chen et al., 2017). Complete pyrolysis is critically important to transform all feedstock OC into carbonized, pyrogenic OC (i.e., altered, amorphous C structure). The solid residence time for achieving complete pyrolysis is determined by the pyrolysis temperature and the heating rate, ranging from seconds to days. The heating rate may be as low as $<1°C\ s^{-1}$ and as high as $>200°C\ s^{-1}$, varying with the pyrolysis temperature, feed characteristics (particle size, moisture content, and density), and feed mass flow (Guo et al., 2020). Biochar products from incomplete pyrolysis also contain noticeable portions of uncarbonized C (i.e., with crystalline character of the precursor materials) (Chun et al., 2004; Keiluweit et al., 2010).

Biochar is porous, showing a rough morphological surface with honeycomb-like anatomical or other irregular structures under the microscope (**Figure 1**). The inherent micropores (diameter in the range of 0.8–235 µm and mostly <22 µm, with average at 10 µm; Hardie et al., 2014) engender the material a relatively high intrapore volume (e.g., 0.9–1 $cm^3\ g^{-1}$; Batista et al., 2018) and low envelope density (e.g., 0.2–0.6 $g\ cm^{-3}$; Joseph et al., 2019). Biochar is composed primarily of amorphous, aromatic carbon, and possesses abundant O-containing surface functional groups (e.g., –C=O, –COOH, and –OH). A disorderly stacked graphene sheet structure has been proposed for biochar (**Figure 1**). The aromaticity of biochar generally increases while the surface functionality decreases as the pyrolysis temperature is elevated (Song and Guo, 2012; Zhao et al., 2016). This is largely a result of the progressive losses of aliphatic C–H, olefinic C=C, carbonyl, carboxyl, and hydroxyl groups at a higher pyrolysis temperature (Fu et al., 2012; Tan et al., 2015).

Biochar is the major product of slow pyrolysis and yet the byproduct of fast pyrolysis (aiming at pyrolysis bio-oil) and

TABLE 1 | Quality characteristics of biochar as influenced by feedstock and carbonization conditions.

Feedstock	Pyrolysis conditions	pH	Ash %	Organic carbon %	Total N g kg^{-1}	Total P g kg^{-1}	Total K g kg^{-1}	Cation exchange capacity cmol$_c$ kg^{-1}	Specific surface area m^2 g^{-1}	References
Hard wood	400°C slow pyrolysis	7.5	3.2	79.0	2.5	0.18	3.0	7.9	15.4	Tian et al., 2016
Hard wood	500°C slow pyrolysis	8.2	4.2	84.8	3.0	0.34	3.6	7.5	26.6	Tian et al., 2016
Soft wood	400°C slow pyrolysis	7.3		74.6	2.5		2.5			Gezahegn et al., 2019
Soft wood	600°C slow pyrolysis	8.1		88.6	3.8		1.8			Gezahegn et al., 2019
Oak wood	400°C slow pyrolysis	8.3	11.0	72.0	3.0	0.72	9.7			Fryda and Visser, 2015
Beech wood	670°C gasification	11.9	23.8	72.3	4.0	0.7	13.0			Fryda and Visser, 2015
Poplar wood	400°C slow pyrolysis	9.0	3.5	67.3	7.8			144.0	3.0	Kloss et al., 2012
Poplar wood	525°C slow pyrolysis	8.7	6.8	77.9	10.7			107.7	55.7	Kloss et al., 2012
Spruce wood	400°C slow pyrolysis	6.9	1.9	63.5	10.2			73.5	1.8	Kloss et al., 2012
Spruce wood	525°C slow pyrolysis	8.6	4.7	78.3	11.7			52.2	40.4	Kloss et al., 2012
Tamarisk wood	Two-stage 300–550°C slow pyrolysis	10.4		79.6	13.7	2.3	16.3			Ippolito et al., 2017
Pine wood	Two-stage 300–550°C slow pyrolysis	9.1		87.8	4.3	0.3	2.2			Ippolito et al., 2017
Pine chips	400°C slow pyrolysis	7.6		73.9	2.55	0.15	1.4	7.3		Gaskin et al., 2008
Pine chips	500°C slow pyrolysis	8.3		81.7	2.23	0.14	1.5	5.0		Gaskin et al., 2008
Pine shaving	300°C slow pyrolysis		1.5	54.8	0.5				3.0	Keiluweit et al., 2010
Pine shaving	400°C slow pyrolysis		1.1	74.1	0.6				28.7	Keiluweit et al., 2010
Pine shaving	500°C slow pyrolysis		1.4	81.9	0.8				196.0	Keiluweit et al., 2010
Spruce wood and needle mix	400°C slow pyrolysis	6.9	1.9	63.5	10.2			73.5	1.8	Kloss et al., 2012
Spruce wood and needle mix	525°C slow pyrolysis	8.6	4.7	79.6	11.7			73.5	40.4	Kloss et al., 2012
Pine needle	300°C slow pyrolysis		1.9	68.9	10.8				19.9	Chen et al., 2008
Pine needle	400°C slow pyrolysis		2.3	77.8	11.6				112.4	Chen et al., 2008
Pine needle	500°C slow pyrolysis		2.8	81.7	11.1				236.4	Chen et al., 2008
Greenwaste	450°C slow pyrolysis		10.8	71.1	11.7			52.2	7.3	Zheng et al., 2010
Greenwaste	450°C slow pyrolysis	9.4		36.0	1.8			24.0		Chan et al., 2007
Switchgrass	250°C slow pyrolysis	5.4	2.6	55.3	4.3	1.0	4.9	119	0.4	Ippolito et al., 2012
Switchgrass	500°C slow pyrolysis	8.0	7.8	84.4	10.7	2.4	11.6	82	62.2	Ippolito et al., 2012
Miscanthus	600°C slow pyrolysis	10.2		53.3	3.1	2.9	12.2	29.5		Houben et al., 2013
Fescue straw	300°C slow pyrolysis		1.5	54.8	10.2				4.5	Keiluweit et al., 2010

(Continued)

TABLE 1 | Continued

Feedstock	Pyrolysis conditions	pH	Ash %	Organic carbon %	Total N g kg^{-1}	Total P g kg^{-1}	Total K g kg^{-1}	Cation exchange capacity $cmol_c$ kg^{-1}	Specific surface area m^2 g^{-1}	References
Fescue straw	500°C slow pyrolysis		2.1	81.9	10.9				50.0	Keiluweit et al., 2010
Fescue straw	700°C slow pyrolysis		1.7	92.3	7.0				139.0	Keiluweit et al., 2010
Corn cobs	550°C slow pyrolysis			81.4	12.2				56.4	Wijitkosum and Jiwnok, 2019
Corn cobs	500°C fast pyrolysis	7.8	13.3	77.6		4.36	43.4		<1.0	Mullen et al., 2010
Corn stover	500°C fast pyrolysis	7.2	32.8	57.3		12.9	23.5		3.1	Mullen et al., 2010
Corn stalk	300°C slow pyrolysis	7.2	8.2	53.2	26.1		29.0			Liu Z. et al., 2018
Corn stalk	400°C slow pyrolysis	8.6	14.0	58.1	26.9		43.5			Liu Z. et al., 2018
Corn stalk	500°C slow pyrolysis	10.0	16.3	59.7	24.3		50.0			Liu Z. et al., 2018
Corn stalk	600°C slow pyrolysis	9.8	17.3	61.8	17.3		50.5			Liu Z. et al., 2018
Cotton stalk	600°C slow pyrolysis	10.3	9.5	83.2	48.0				121	Windeatt et al., 2014
Soybean straw	300°C slow pyrolysis	7.3	10.4	68.8	18.0	3.25			5.6	Vithanage et al., 2017
Pepper straw	600°C slow pyrolysis	9.3	25.0	70.0	9.0	3.3	49.0			Fryda and Visser, 2015
Pepper straw	670°C gasification	11.0	33.5	59.0	8.0	3.1	44.0			Fryda and Visser, 2015
Rice straw	200°C slow pyrolysis		31.2	47.6	13.0			58.7	7.2	Jiang et al., 2015
Rice straw	400°C slow pyrolysis		34.1	46.3	12.6			60.7	19.7	Jiang et al., 2015
Rice straw	600°C slow pyrolysis		45.5	42.5	10.2			32.5	193.2	Jiang et al., 2015
Wheat straw	600°C slow pyrolysis	11.6	23.4	75.3	10.0				6.3	Windeatt et al., 2014
Wheat straw	500°C slow pyrolysis	9.6		45.3	24.9	1.0	7.9	27.5	51.5	Sun et al., 2019
Wheat straw	400°C slow pyrolysis	9.1	9.7	65.7	10.5			161.6	4.8	Kloss et al., 2012
Wheat straw	525°C slow pyrolysis	9.2	12.7	74.4	10.4			97.7	14.2	Kloss et al., 2012
Rapeseed straw	300°C slow pyrolysis	6.5	8.2	52.6	8.8	23.5				Liu Z. et al., 2018
Rapeseed straw	600°C slow pyrolysis	10.0	17.3	70.9	6.7	50.3				Liu Z. et al., 2018
Sugarcane bagasse	600°C slow pyrolysis	8.6	13.0	88.6	13.0				149.1	Windeatt et al., 2014
Sugarcane bagasse	350°C slow pyrolysis	7.8	11.0	69.3	6.0					Nwajiaku et al., 2018
Sugarcane bagasse	700°C slow pyrolysis	9.7	12.8	69.6	3.8					Nwajiaku et al., 2018
Rice husk	500°C slow pyrolysis	9.2		47.8				17.6		Ghorbani et al., 2019
Rice husk	600°C slow pyrolysis	9.9	47.0	54.5	11.0				114.9	Windeatt et al., 2014
Rice husk	400°C slow pyrolysis	8.6	27.5	54.1	4.9					Nwajiaku et al., 2018
Rice husk	700°C slow pyrolysis	10.7	35.6	54.5	3.6					Nwajiaku et al., 2018
Rice husk	750°C gasification		82.0	12.0	1.6	2.2	5.7			Fryda and Visser, 2015
Palm shell	600°C slow pyrolysis	6.1	6.7	90.6	9.0				220	Windeatt et al., 2014

(Continued)

TABLE 1 | Continued

Feedstock	Pyrolysis conditions	pH	Ash %	Organic carbon %	Total N g kg^{-1}	Total P g kg^{-1}	Total K g kg^{-1}	Cation exchange capacity cmol$_c$ kg^{-1}	Specific surface area m^2 g^{-1}	References
Coconut shell	600°C slow pyrolysis	8.5	4.1	93.9	4.0				222.5	Windeatt et al., 2014
Peanut hull	300°C slow pyrolysis	7.8	1.2	68.3	19.1				3.1	Ahmad et al., 2012a
Peanut hull	500°C slow pyrolysis	10.1		80.4	24.8	1.97		4.6		Gaskin et al., 2008
Peanut hull	400°C slow pyrolysis	7.9	8.2	74.8	27.0	2.6		13.6	0.52	Novak et al., 2009
Peanut hull	700°C slow pyrolysis	10.6	8.9	83.8	11.4				448.2	Ahmad et al., 2012a
Pecan shell	350°C slow pyrolysis	5.9		64.5	2.6	0.3		24.6	1.0	Novak et al., 2009
Pecan shell	700°C slow pyrolysis	7.2		91.2	5.1	0.5			222	Novak et al., 2009
Cottonseed hull	350°C slow pyrolysis	7.0	5.7	77.0	19.0				4.7	Uchimiya et al., 2011b
Cottonseed hull	650°C slow pyrolysis	9.9	8.3	91.0	16.0				34.0	Uchimiya et al., 2011b
Olive pomace	600°C slow pyrolysis	10.5	18.1	71.8	19.0				1.2	Windeatt et al., 2014
Coconut fiber	600°C slow pyrolysis	9.6	13.5	82.6	24.0				23.2	Windeatt et al., 2014
Orange peel	300°C slow pyrolysis		1.6	69.3	23.6				32.3	Chen and Chen, 2009
Orange peel	700°C slow pyrolysis		4.8	71.6	17.2				201	Chen and Chen, 2009
Poultry litter	300°C slow pyrolysis	9.5	47.9	38.0	41.7	22.7	69.3	51.1	2.7	Song and Guo, 2012
Poultry litter	400°C slow pyrolysis	10.3	56.6	36.1	26.3	26.3	81.2	41.7	3.9	Song and Guo, 2012
Poultry litter	500°C slow pyrolysis	10.7	60.6	34.5	12.1	27.9	87.9	35.8	4.8	Song and Guo, 2012
Poultry litter	600°C slow pyrolysis	11.5	60.8	32.5	12.1	27.9	91.5	35.8	4.8	Song and Guo, 2012
Poultry litter	700°C slow pyrolysis	10.3	46.2	45.9	20.7				50.9	Cantrell et al., 2012
Poultry litter	300°C slow pyrolysis	9.1		31.3	20.4	46.8	43.0			Sikder and Joardar, 2019
Pig manure solids	620°C slow pyrolysis		44.7	50.7	32.6	71.5	25.6			Ro et al., 2010
Pig manure solids	350°C slow pyrolysis	8.4	32.5	51.5	35.4				0.92	Cantrell et al., 2012
Pig manure solids	700°C slow pyrolysis	9.5	52.9	44.1	26.1				4.1	Cantrell et al., 2012
Pig manure solids	750°C gasification		77.0	21.0	3.0	23.8	30.5			Fryda and Visser, 2015
Cow manure	400°C slow pyrolysis	9.0	70.3	17.5	13.5	4.36	26.4			Singh et al., 2010
Cow manure	500°C slow pyrolysis	8.4		41.7	18.9	7.2	5.3		8.6	Kiran et al., 2017
Cattle manure	600°C slow pyrolysis	10.0			20.0	0.28				Gavili et al., 2018
Cow manure	300°C slow pyrolysis	8.5	42.7	34.3	25.5				3.5	Qin et al., 2019

(Continued)

TABLE 1 | Continued

Feedstock	Pyrolysis conditions	pH	Ash %	Organic carbon %	Total N g kg^{-1}	Total P g kg^{-1}	Total K g kg^{-1}	Cation exchange capacity cmol$_c$ kg^{-1}	Specific surface area m^2 g^{-1}	References
Cow manure	500°C slow pyrolysis	9.4	48.0	37.5	25.3				7.0	Qin et al., 2019
Cow manure	700°C slow pyrolysis	10.4	54.5	37.0	14.5				121.1	Qin et al., 2019
Sewage sludge	300°C slow pyrolysis	6.8	56.6	30.7	41.1				4.5	Ahmad et al., 2014
Sewage sludge	600°C slow pyrolysis	8.3	74.6	24.8	27.8				35.8	Ahmad et al., 2014
Sewage sludge	450°C slow pyrolysis		68.4	25.4	17.0	114.0	10.3			Roberts et al., 2017
Sewage sludge	750°C slow pyrolysis		80.6	24.9	6.0	119.0	11.7			Roberts et al., 2017
Sewage sludge	487°C fast pyrolysis	9.0	65.9	19.7	45.0					Arazo et al., 2017
Sewage sludge	600°C slow pyrolysis	9.7	59.1	46.3	33.0	198.0			79.6	Adhikari et al., 2019
Cattle carcass	450°C slow pyrolysis	9.4			39.5	108.0	30.8			Ma and Matsunaka, 2013
Bone meal	350°C slow pyrolysis	7.5		18.0	33.0	127.1	2.5			Zwetsloot et al., 2016
Range	200–750°C	5.4–12.4	1.1–82.0	12.0–93.9	0.5–48.0	0.1–198.0	1.4–91.5	4.6–161.6	0.4–444.8	
Mean		8.9	24.4	61.1	14.5	26.8	26.3	52.5	59.0	
Standard deviation		1.39	23.96	20.75	11.05	45.94	25.92	41.94	86.65	

gasification (pyrolysis combined with partial oxidation—aiming at syngas). Within each of the three thermochemical techniques, the carbonization conditions (i.e., temperature, solid residence time, and heating rate) can be adjusted to optimize major product generation. Even with the same feedstock, biochars from gasification and fast pyrolysis are evidently lower in OC content and higher in ash content than the products from slow pyrolysis. Overall, biochars from different sources demonstrated a pH value (in 1:5 solid/water extract) ranging from 5.4 to 12.4 and mineral ash content from 1.1 to 82.0% (**Table 1**). The pH is a comprehensive expression of the water-soluble base cations (e.g., Na^+, K^+, Ca^{2+}, and Mg^{2+}) and organic acids (e.g., formic acid, acetic acid, hydroxybutyric acid, and benzoic acid) in biochar. The base cations originate from the mineral ash components in the feedstock, whereas the organic acids are generated during biomass pyrolytic transformation. Biochar products from complete pyrolysis contain minimal organic acids and demonstrate a pH value typically >7.5 to reflect the presence of basic ash minerals. In general, the pH of biochar is related to its mineral ash content, with higher-ash-content products showing a higher pH value (**Table 1**). Biochars from higher-temperature pyrolysis are normally greater in ash content (**Figure 2**) and pH, and the products derived from manure and rice plant residues are higher in ash content and pH than those derived from wood and other plant residues. The OC content of biochar ranged from 12.0 to 93.9%, generally decreasing as the ash content increased. For low-ash feedstocks (e.g., wood and many other plant residues), the derived biochars showed an increasing trend in OC content as the pyrolysis temperature was elevated, whereas biochars derived from ash-rich feedstocks (e.g., manures, rice plant residues, and bones) illustrated an opposite trend (**Table 1**). Biochars also contain more or less the plant nutrients N, P, K, and others. The N, P, and K contents of the reported biochars are 0.5–48.0, 0.1–198.0, and 1.4–91.5 g kg^{-1}, respectively, being largely correlated with the products' ash contents. Most of the feedstock P and K would be recovered in biochar, yet the vast majority of feedstock N would be lost to pyrolysis vapors (bio-oil and syngas), especially at high pyrolysis temperatures (e.g., $>500°C$) (Song and Guo, 2012). The nutrients in biochar are slowly releasable (Wang et al., 2015), supplementing the nutrient supply of amended soils to support plant growth. Sewage sludge- and bone-derived biochars may contain P at >100 g kg^{-1} and therefore serve as an ideal source of P to crops. Moreover, biochars generated from specialty biomass like municipal organic solids and contaminated-soil-grown plant materials may contain toxic elements at above-threshold concentrations for use as a soil amendment (Buss et al., 2016).

Biochars demonstrate a CEC value of 5–162 cmol$_c$ kg^{-1} and a Brunauer–Emmett–Teller (BET)–SSA value of 0.4–448 m^2 g^{-1} (**Table 1**). The CEC indicates the capacity of biochar to adsorb cationic nutrients and metal contaminants, while the SSA implicate biochar's ability to retain water, gases, and organic molecules. Research has revealed that biochar is generally sorptive to polar gases (e.g., H_2S, NH_3, NO_x, and volatile organic compounds), water-soluble metal ions (e.g., Cu^{2+}, Pb^{2+}, Zn^{2+}, and Cd^{2+}), and various organic pollutants (e.g., agrochemicals, antibiotics, and PAHs) (Ahmad et al., 2014; Tan et al., 2015).

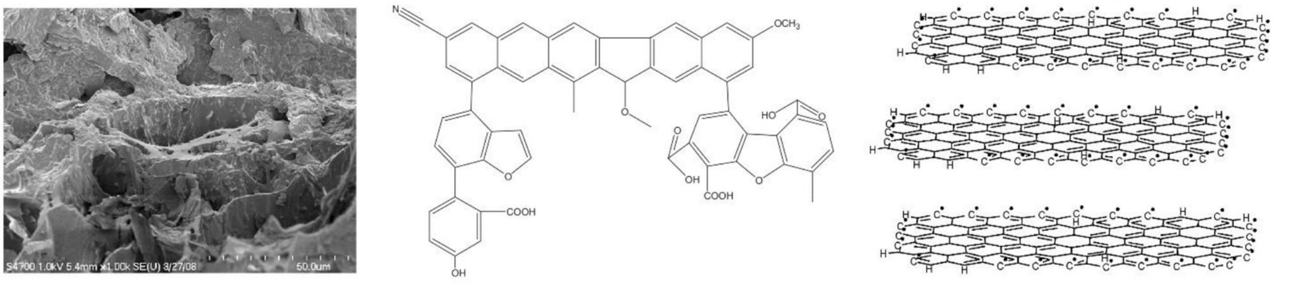

FIGURE 1 | A scanning electron micrograph of corn stover-derived biochar (left), an aromatic-C molecular biochar model (middle), and a disorderly stacked graphene sheet structure proposed for biochar (right) showing the high porosity, aromaticity, and surface functional group abundance of the material (Lehmann and Joseph, 2012; Chen et al., 2017; Zhao et al., 2017).

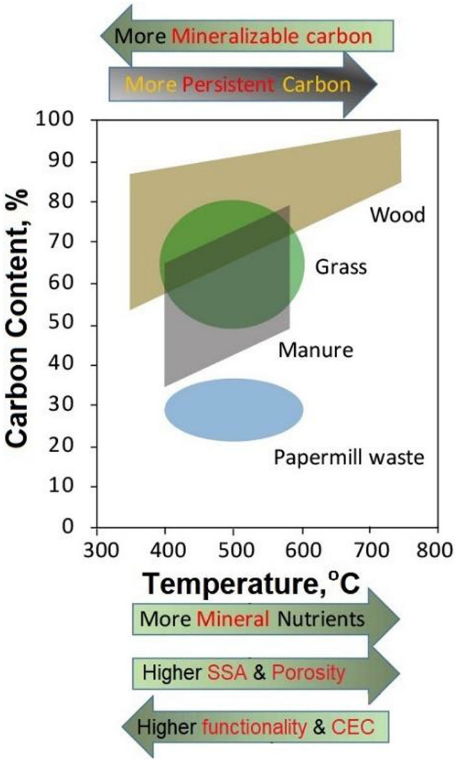

FIGURE 2 | General change trends of biochar's total carbon content, carbon stability, mineral ash content, porosity, specific surface area, abundance of surface functional groups, and cation exchange capacity in response to the feedstock and pyrolysis temperature. The graph was modified from Joseph et al. (2019).

The CEC of biochar is originated primarily from the surface functional groups, while SSA is related to biochar's porosity. A higher pyrolysis temperature in the range of 300–700°C favors micropore development while promoting O-containing functional group elimination, resulting in biochar products with increased SSA yet reduced CEC (**Figure 2**). Biochars with high ash contents, like those derived from manures, typically demonstrate low SSA values, likely due to ash blockage of the inherent micropores. After applying to soil, the SSA and CEC of biochar may gradually increase over time as a result of natural weathering (Steiner, 2016).

As a soil amendment, biochar has a vital advantage over compost and other raw bio-materials in its high environmental recalcitrance. The mean residence time of biochar in the natural soil environment was estimated at 90–1,600 years (Singh et al., 2012). The environmental stability of biochar originates from its condensed aromatic carbon. Biochars with higher aromaticity and greater C condensation are generally more recalcitrant (Lehmann et al., 2015). Biochar OC can be nominally divided into three fractions: labile, intermediate stable, and stable (Singh et al., 2012). Research suggests that >65% of the OC in biochars with H/OC molar ratio <0.7 would remain in natural soils 100 years after field application (Joseph et al., 2019). Biochars prepared at higher pyrolysis temperatures generally contain a greater proportion of stable OC (**Figure 2**).

The International Biochar Initiative recommends the following parameters for evaluating the quality of biochar as a soil amendment: pH, lime equivalence, EC, mineral ash content, OC content, SSA, H/OC molar ratio, particle size distribution, germination inhibition assay, total and available plant nutrients, and the presence of inorganic and organic pollutants. The OC content needs to exceed 10% and the H/OC molar ratio surrender 0.7 for a pyrogenic material to be qualified as biochar (IBI, 2015). The European Biochar Certificate (EBC) program suggested similar quality variables for biochar: pH, EC, volatile matter content, total ash content, total carbon (TC) content, SSA, H/OC molar ratio, O/C molar ratio, water content, bulk density, macronutrient (N, P, K, Ca, and Mg) contents, and contents of heavy metals and organic contaminants. A certified biochar product is required to contain $\geq$50% TC at $\leq$0.4 O/C and $\leq$0.7 H/OC molar ratios. The contents of Zn, Pb, Cu, Cr, Ni, Cd, and Hg are capped at 400, 150, 100, 1.5, 90, 50, 1.5, and 1 mg kg^{-1}, respectively, and PAHs, PCBs, and PCDD/Fs at 12, 0.2, and 0.00002 mg kg^{-1}, respectively (EBC, 2012). Considering the mechanisms and the processes through which biochar amendments facilitate soil remediation (as discussed below), biochars selected for soil remediation should be weighted more in pH, lime equivalence, SSA, CEC, and nutrient (especially P)

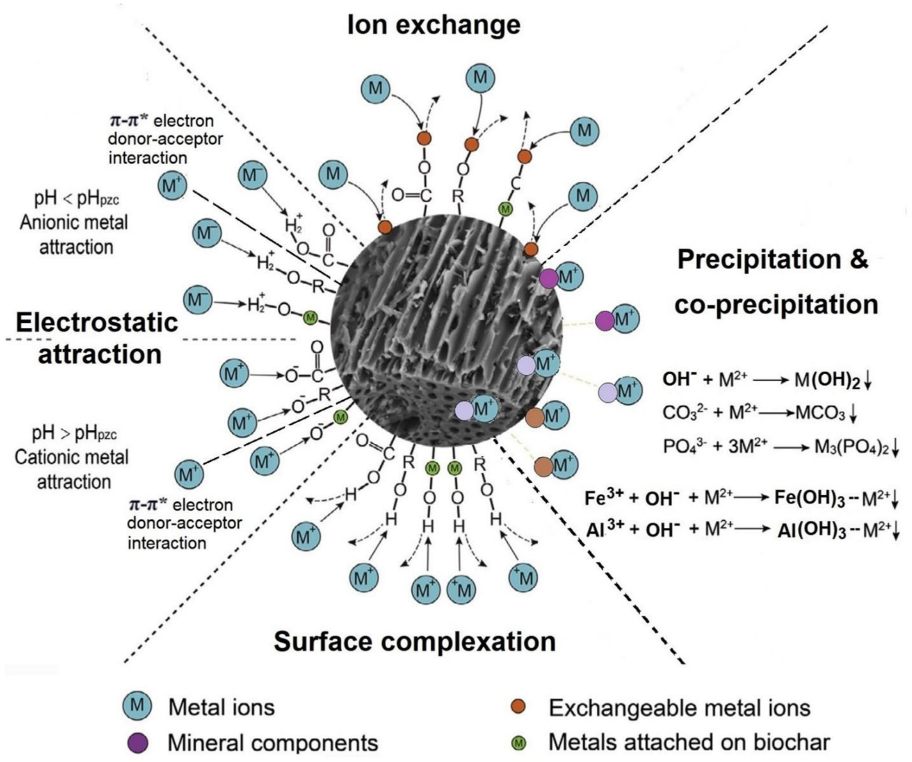

FIGURE 3 | Major mechanisms through which biochar stabilizes heavy metals in contaminated soils. The graph was modified from Tan et al. (2015).

content when the TC content and H/OC molar ratio criteria are met.

BIOCHAR FOR REMEDIATION OF HEAVY-METAL-CONTAMINATED SOILS

Biochar has been explored for mitigating soil heavy metal contamination. Reported research using laboratory vessel, greenhouse pot, and field plot experiments suggests that biochar is capable of effectively sorbing heavy metal cations from water and immobilizing heavy metal elements in soil and therefore serves as a promising amendment for reducing the ecotoxicity of heavy-metal-contaminated soils (Guo et al., 2010; Ahmad et al., 2014; Tan et al., 2015; O'Connor et al., 2018).

Mechanisms

Unlike soil washing, leaching, and extraction that ultimately remove heavy metals from contaminated soils (Liu L. et al., 2018), biochar amendment does not eradicate but stabilizes heavy metals in soil, transforming the toxic elements into less soluble and less bioaccessible forms. The overall process is rather similar to that of chemical stabilization in which treatment agents such as phosphate- and carbonate-containing chemicals are applied to contaminated soils to react with heavy metal contaminants and convert them into precipitates (Houben et al., 2013; Liu L. et al., 2018). The bioavailability and the ecotoxicity of heavy metals in the treated soils are consequently reduced to below the risky level, restoring the desirable soil function to grow safe crops. In biochar-facilitated soil remediation, selected biochar products are applied at appropriate rates to heavy-metal-polluted sites and thoroughly mixed with the contaminated soil. The applied biochar interacts with heavy metals in the soil, adsorbing heavy metal ions on the pore surfaces and potentially transforming them into hydroxide, carbonate, and phosphate precipitates. As the water-soluble, bioactive fraction of heavy metals in soil decreases, potential uptake and bioaccumulation of heavy metals by soil organisms (including plant roots) are minimized (Ahmad et al., 2014). Since heavy metals are not removed and the immobilization effect may diminish over time, biochar-amended soils need to be regularly monitored for heavy metal toxicity.

Biochar stabilizes cationic heavy metals primarily through sorption and chemical precipitation (**Figure 3**). Biochar possesses various surface functional groups such as hydroxyls, carbonyls, and carboxyls (Tan et al., 2015). Depending on the pH, dissociation or protonation of these functional groups entails biochar electrical charges. The zeta potential of canola-straw- and peanut-straw-derived biochars became more negative as the solution pH increased between 3.0 and 8.0, indicating a greater negative charge density on the biochar surface at a higher pH (Xu et al., 2011). Biochars derived from corn stover, red oak, cottonseed hull, pecan shell, and pure cellulose through 200–900°C slow pyrolysis showed pH_{ZNC} (pH at which biochar has zero net charge) in the range of 3.1–8.5, increasing as the pyrolysis temperature was raised (Uchimiya et al., 2011a; Banik et al., 2018). This corroborates that biochars produced at higher temperatures had a lower CEC value owing to further losses of surface functional groups (**Figure 2**), as a higher pH_{ZNC} indicates fewer negative charges on the surface. At pH $<pH_{ZNC}$, biochar may be positively charged and therefore able to adsorb anionic pollutants such as NO_3^-, AsO_3^-, and CrO_4^{2-} (Fidel et al., 2018). Both hydrolyzable non-bridging (degraded and negatively charged at high pH) and non-hydrolyzable bridging (positively charged even at high pH) oxonium groups (oxygen heterocycles) were detected in biochars produced at $>500°C$ pyrolysis temperature (Ippolito et al., 2017). The negatively charged surface functional groups enable biochar to adsorb heavy metal cations through electrostatic attraction. Furthermore, the aromatic biochar surface abundant in π electrons could exert electrostatic attraction to electron-deficient metal cations through π-π* donor–acceptor interactions (Vithanage et al., 2017). Cations adsorbed through electrostatic attraction remain in the diffusion layer of biochar particles (i.e., outer-sphere adsorption) and are subject to leaching losses (Tan et al., 2015). Heavy metal ions in the soil solution can be adsorbed to biochar via ion exchange by replacing those cations (e.g., Ca^{2+}, Mg^{2+}, Na+, K^+, and H^+) originally associated with the biochar surface functional groups (Fidel et al., 2018). This specific interaction (i.e., inner-sphere adsorption) is stronger than electrostatic attraction, yet the adsorbed metal cations are exchangeable, as influenced by the solution pH and ionic strength (Ding et al., 2014; Fidel et al., 2018). A lower pH and a higher solution ionic strength generally reduce the sorption of metal cations onto biochar through ion exchange, owing to the increased competition from other cations. Shim et al. (2015) reported that increasing the solution pH in the range of 3.0–6.0 significantly promoted the removal of Cu^{2+} by *Miscanthus* straw-derived biochar from water. Metal cations may also form complexes with the surface functional groups and be strongly sorbed. Using positive matrix factorization analysis, Uchimiya et al. (2011a) validated surface complexation as the major mechanism for biochar sorbing Cd^{2+}, Cu^{2+}, Ni^{2+}, and Pb^{2+} *via* the ligand-like surface functional groups (e.g., carboxylic, hydroxyl, and phenolic groups). With the formation of biochar–metal complexes, Na^+, K^+, Ca^{2+}, Mg^{2+}, and other cations were released into soil, causing soil pH changes (Uchimiya et al., 2011a). Formation of organo-metal complexes on biochar surface and in pores was further evidenced by spectroscopic analyses (Kumar et al., 2018). Uchimiya et al. (2010a) reported that the addition of dissolved organic matter (DOM) substantially reduced the sorption of Cu^{2+}, Cd^{2+}, and Ni^{2+} by biochars. Natural DOM contains surface ligands capable of complexing metal ions (Weng et al., 2002). The DOM released from biochar may reduce its sorption for heavy metal ions (Oustriere et al., 2016).

The abundance of surface functional groups as indicated by CEC is the most important trait that determines the capacity of biochar for stabilizing heavy metals through sorption-based interactions. Jiang et al. (2015) noticed that, among the biochars generated from rice straw through 200, 400, 500, and 600°C slow pyrolysis, the 400°C product had the highest CEC (60.65 $cmol_c\ kg^{-1}$) and demonstrated the greatest sorption capacity for aqueous Cu^{2+} in batch sorption trials. Activation improves the SSA, aromaticity, and hydrophobicity of biochar but decreases its CEC, surface functional groups, and polarity (Uchimiya et al., 2010a; Shim et al., 2015; Yuan et al., 2019). Steam or CO_2 activation of willow-wood-derived biochar, for instance, increased the biochar's SSA from 11.4 to $>510\ m^2\ g^{-1}$ but enhanced little its capability to reduce the ecotoxicity of a heavy-metal-contaminated soil (Zn, Pb, Cr, Cu, Ni, and Cd) at 5 wt% amendment rate (Kołtowski et al., 2017).

Precipitation is equally important as sorption in biochar stabilizing soil heavy metals. In most cases, biochar amendment elevates soil pH by introducing additional alkalinity (**Table 2**). Hydrolysis of heavy metals is promoted at higher pH, in which cationic metals react with hydroxyls in water to form metal hydroxide precipitates, reducing the concentration of water-soluble metal ions. Research has identified soil pH elevation as an important mechanism for biochar amendment to mitigate soil heavy metal contamination (**Table 2**). Ippolito et al. (2017) noticed that addition of wood-based biochars (pH >9.1) at 5–15 wt% elevated the pH levels of mine land soils (pH <5.4) by 0.5–3.5 units and evidently reduced the 0.01 M $CaCl_2$-extractable portions of the inherent Cu, Pb, Zn, and Cd. Other researchers observed similar soil pH elevation and soluble metal decreases when acidic soils were amended with pH 8.8–10.2 biochars (Park et al., 2011; Ahmad et al., 2012b; Houben et al., 2013; Zheng et al., 2015; Cui et al., 2016). In rice paddy soils, the elevated pH favored the formation of Fe/Al hydroxide precipitates; soluble metal ions could be encapsulated by co-precipitation in iron plaques deposited on rice roots (Zheng et al., 2012). Precipitation also occurs when cationic metal ions react with biochar-introduced carbonate, sulfate, and phosphate (Vithanage et al., 2017). Nearly all biochars contain carbonates (e.g., K_2CO_3, Na_2CO_3, $CaCO_3$, and $MgCO_3$) that contribute to alkalinity and high pH (Cao et al., 2011; Jiang et al., 2012). Biochars derived from manures and sewage sludge usually contain substantial phosphates (Song and Guo, 2012). Mixing poultry-litter-, dairy-manure-, and sewage-sludge-derived biochars at 2–5 wt% with Pb-contaminated soils resulted in substantial decreases of soil 0.01 M $CaCl_2$-extractable, physiologically based extraction test (PBET)-extractable, and toxicity characteristic leaching procedure (TCLP)-extractable Pb by forming pyromorphite $[Pb_5(PO_4)_3Cl]$, hydroxypyromorphite $[Pb_5(PO_4)_3(OH)]$, and Pb phosphate (Cao et al., 2011; Netherway et al., 2019). Sequential extraction analysis suggested that, in mining soils amended with wood-derived biochar that contained little P, precipitation of Cd^{2+} was chiefly through carbonate formation, Pb^{2+} through oxyhydroxide formation, and Cu^{2+} and Zn^{2+} through both carbonate and oxyhydroxide formation (Ippolito et al., 2017).

Clearly, biochar amendment facilitates the stabilization of heavy metals in contaminated soils through surface interactions (electrostatic attraction, ion exchange, and surface complexation) and (co-)precipitation (**Figure 3**). The carboxyl, hydroxyl, and phenolic groups on the biochar surface are particularly effective in binding cationic heavy metal contaminants (Uchimiya et al., 2011a).

TABLE 2 | Research trials of biochar-facilitated remediation of heavy-metal-contaminated soils.

Biochar source	Soil type	Metals	Experiment	Effect	Mechanisms	References
Hard wood pH 9.9 OC 89.0% P 0.43%	Sandy loam pH 7.1 OC 8.2%	As	20 vol% biochar mixing with soil; 8-month greenhouse pots with *Miscanthus*	Elevated soil pore water As; little effect on plant As uptake	Possibly DOC and HPO_4^{2-} increase in soil water	Hartley et al., 2009
Stinging nettle OC 52.1% N 2.1% SSA 3.5 m^2/g	Mine spoil Sand pH 3.2	As and Cu	Sunflower grown in polycyclic aromatic hydrocarbon-spiked, 1 wt% biochar-amended, 56-day laboratory-incubated soil microcosms	Reduced Cu leaching but affected little on As mobility; plant growth improved	Metal stabilization *via* biochar sorption	Sneath et al., 2013
Hard wood pH 9.9 OC 53%	Loam pH 5.4 OC 4.6%	As, Cu, Cd, Zn	50 vol% biochar mixing with soil; 60-day outdoor pot setting, ryegrass seed germination test	Decreased Cd and Zn while increased As and Cu in soil pore water; enhanced seed germination	Soil pH elevation by 2.1 units; As mobility enhanced additionally by soil DOC increase	Beesley et al., 2010
Hard wood pH 9.9 OC 53%	Loam pH 6.2 OC 11.0%	As, Cd, Zn	Water leaching soil columns in parallel with biochar columns	Reduced Cd and Zn concentrations but not As in soil leachate	Metal retention by biochar through sorption	Beesley and Marmiroli, 2011
Rice straw pH 10.5 CEC 32.1 $cmol_c/kg$ Bean stalk pH 9.2 CEC 27.5 $cmol_c/kg$	Rice paddy soil pH 6.1 CEC 12.5 $cmol_c/kg$	As, Cd, Pb, Zn	One-season rice grown in field plots with 0–20 cm soil amended with 20 t/ha biochar and basal fertilization	Biochar reduced Cd, Zn, and Pb but increased As in soil pore water and rice	Soil pH elevation and formation of iron plaque on root surface	Zheng et al., 2015
Orchard prunings	Mining soil OM 1.7%	As, Cd, Cu, Pb, Zn	Bioassay with bacteria and ryegrass of water extracts from 10 vol% biochar soil pots	Reduced free metals yet increased As and DOC-associated metals in soil pore water	Biochar enhanced soil As and metal mobility by altering soil pH, DOC, and P	Beesley et al., 2014
Sewage sludge pH 7.2 OC 28.0% N 2.6% P 5.8%	Loamy sand pH 4.0 OC 0.24%	As, Cd, Co, Cr, Cu, Ni, Pb, Zn	5 and 10 wt% biochar mixing with NP fertilized soil; flooded greenhouse pots with growing rice	Decreased soil EDTA-extractable and bioaccumulated As, Cr, Co, Ni, and Pb but increased the portions of others	Not discussed; soil flooding may be considered	Khan et al., 2013b
Eucalyptus wood pH 10.4 Poultry litter pH 10.0	pH 6.0 OC 1.98%	Cd	Greenhouse 60-day amaranth grown in 3 wt% biochar-amended soils	Biochar reduced 0.01 M $CaCl_2$-extractable soil Cd and plant Cd extraction efficiency	Biochar restricted soil Cd phytoextraction	Lu et al., 2014
Wheat straw pH 10.4 P 1.44% CEC 21.7 $cmol_c/kg$ SSA 8.9 m^2/g	Rice paddy soils Loam pH 4.9–6.1	Cd	1–5 years of rice and wheat grown in NPK-fertilized field plots with top 15-cm soil amended by biochar at 40 t/ha	Biochar elevated soil pH and reduced soil 0.01 M $CaCl_2$-extractable Cd and crop grain Cd. The effect decreased over time	Precipitation; surface functional group complexation; Fe/Al/P mineral encapsulation on biochar surface and in pores	Cui et al., 2011; Bian et al., 2014; Chen et al., 2016
Sewage sludge 500°C pyrolysis pH 7.2	Rice paddy soil pH 4.5	Cd	One-season rice in field plots with top 25-cm soil mixed with biochar at 3 t/ha	Biochar reduced soil NH_4NO_3-extractable Cd and rice grain Cd	Soil pH elevation and P precipitation	Zhang et al., 2016
Rice straw pH 9.5 CEC 64.8 $cmol_c/kg$	Greenhouse soil Loam pH 6.2–6.8 CEC 15–16.7 $cmol_c/kg$	Cd	Sequential extraction of soil from lettuce plots with 20 t/ha biochar amendment in top 15-cm soil	Lettuce Cd content reduced in lightly polluted but not in heavily polluted soil	Soil pH increased, exchangeable Cd decreased but Fe oxide- and OM-bound Cd increased	Zhang et al., 2017

(Continued)

TABLE 2 | Continued

Biochar source	Soil type	Metals	Experiment	Effect	Mechanisms	References
Partial pyrolysis Wood pH 3.2 Poultry litter pH 7.0	Ferrosol pH 6.1 OC 1.6% Dermosol pH 7.9 OC 7.9%	Cd	Batch sorption and desorption experiments with 5 wt% biochar-amended, 11-month incubated soils	Only poultry litter-based biochar increased Cd^{2+} sorption and retarded its desorption	Biochar stabilizes metals mainly through elevating soil pH and chemical precipitation	Qi et al., 2017
Commercial oak wood charcoal pH 10.0 SSA 1155 m^2/g	Abandoned land soil Loam pH 4.4 OC 1.8%	Cu, Cd	5-year ryegrass in field plots with top 17-cm soil amended by 67 t/ha charcoal and NPK fertilizers	Charcoal decreased soil available, leachable, and bioaccessible Cd and Cu	Soil pH increase	Cui et al., 2016
Poultry litter pH 8.8 CEC 238 cmol$_c$/kg Greenwaste pH 7.7 CEC 250 cmol$_c$/kg	Shooting range soil, copper mine soil, and metal-spiked soil pH 5.4–6.4 OM 0.8–7.1%	Cd, Cu, Pb	5 wt% biochar mixing with soil; 14-day lab incubation; 35-day greenhouse spiked-soil pots with Indian mustard	NH$_4$NO$_3$-extractable and pore water Cd, Pb decreased in spiked soil; Cu, Pb, and Zn in plant shoots and roots reduced	Precipitation; chemisorption; strengthened electrostatic interaction from soil pH rise	Park et al., 2011
Soybean straw 300°C pyrolysis pH 7.3 SSA 5.6 m^2/g	Shooting range soil Sandy loam pH 8.0 OM 5.2%	Cu, Pb, Sb	DTPA- and TCLP-extraction of 0.5–2.5 wt% biochar-amended, 30-day incubated soils	Biochar-immobilized Pb and Cu but mobilized Sb	Stabilization of Pb and Cu *via* precipitation and electrostatic and π-π electron shift-adsorption	Vithanage et al., 2017
Rice straw Field trench smoldering with soil cover	Rice paddy soil pH 7.0	Cd, Pb, Zn	Leafy vegetable grown in field plots with 5 wt% biochar amendment of top 20-cm soil	Biochar reduced soil bioavailable and vegetable metals and increased plant biomass yield	Biochar reduces Cd, Pb, Zn solubility by elevating soil pH	Niu et al., 2015
Miscanthus straw pH 10.2 CEC 29.5 cmol$_c$/kg	Sandy loam pH 6.6 OC 19.0% CEC 5.5 cmol$_c$/kg	Cd, Pb, Zn	12-week greenhouse rapeseed grown in 1–10 wt% biochar-amended, NPK-fertilized soil pots	Similar to liming, biochar reduced soil 0.01 M CaCl$_2$-extractable and plant accumulated metals	Soil pH rise-induced chemical precipitation	Houben et al., 2013
Cottonseed hull 350°C pyrolysis Acid washed pH 6.9 Poultry litter 700°C pyrolysis pH 9.7	Loamy sand pH 5.6 OC 0.6%	Cd, Cu, Ni, Pb	48-h metal sorption by unamended and 10 wt% biochar-amended soils from metal-spiked water in flasks	Greatly reduced the concentrations of all the metals in solution relative to unamended soil	Enhanced metal retention by biochar raising pH from 5.5 to 7.1; O-containing hydroxyl, carboxyl, and phenolic groups binding metals *via* complexation	Uchimiya et al., 2011a
Poultry litter 350°C pyrolysis pH 9.2 Pecan shell 450°C pyrolysis H$_3$PO$_4$ activated	San Joaquin NIST soil 50% clay pH 9.2 OC 0.89%	Cu, Cd, Ni	24-h metal sorption by unamended and 10 wt% biochar-amended soils from metal-spiked water in flasks	Biochar increased Cd and Ni but reduced Cu sorption by soil. DOM-removed biochar further enhanced all metal sorption	Carboxyl-rich biochar DOM can mobilize Cu^{2+} retained by alkaline soil; formation of metal phosphate precipitates	Uchimiya et al., 2010a
Willow wood SSA 11.4 m^2/g Activated SSA >510 m^2/g	Industrial site soils pH 4.3–7.1	Cd, Cr, Cu, Ni, Pb, Zn,	Bioassay of 5 wt% biochar-amended, 60-day incubated soils with garden cress, springtail, bacteria	Activation did not help biochar reduce soil eco-toxicity but helped reduce soil leachate ecotoxicity	Soil DOC weakens the biochar–metal interaction	Kołtowski et al., 2017

(Continued)

TABLE 2 | Continued

Biochar source	Soil type	Metals	Experiment	Effect	Mechanisms	References
Rice husk 500°C pyrolysis	Mining soil Loamy sand	Cd, Cu, Ni, Zn	16-day N_2 flushing of 5 wt% biochar-amended, 42-day incubated soil	Biochar increased dissolved Cu, Cd, Ni, and Zn under oxic conditions	Metal mobility was enhanced by biochar-introduced DOC	El-Naggar et al., 2018
Wood pH 9.1–10.4	Mining soils pH 4.0–5.4	Cd, Cu, Pb, Zn	Batch and sequential extraction of soil amended with biochar at 5–15 wt%	Increased soil pH, reduced 0.01 M $CaCl_2$-extractable metals and altered metal speciation	Biochar metal retention: Cd with carbonates, Pb with oxyhydroxides, Cu and Zn with both	Ippolito et al., 2017
Miscanthus straw pH 8.7	Former sewage field sandy loam pH 5.0 OC 2.6–4.9% P 0.3–0.5%	Cu, Pb, Zn, Cd	2-year orchard grass grown in field plots of top soil amended with 2.5–5.0 wt% biochar	Biochar reduced Cd and Zn but increased Cu and Pb in leachate	Soil pH elevation; biochar reduces soluble metals in soil but may increase colloidal transport in metal phosphates	Schweiker et al., 2014; Wagner and Kaupenjohann, 2015; Wagner et al., 2015
Hard wood	Texture unknown pH 5.4 OM 4.3%	Cu and Pb	20 vol% biochar mixing with soil; 4-month greenhouse pots with ryegrass	Greatly reduced soil pore water concentrations of Cu and Pb and their plant accumulation	Likely electrostatic sorption and metal–CO_3 precipitates; soil pH elevation by 0.2 units	Karami et al., 2011
Poultry litter pH 9.7 P 2.3% Biosolids pH 5.2 P 1.2%	Urban soil pH 4.9 CEC 16.1 $cmol_c/kg$	Pb	PBET and TCLP extraction of 3 wt% biochar-amended, 12-week incubated soil	Biochar reduced PBET-extractable Pb but not TCLP-extractable Pb, in particular by biosolid biochar	Formation of pyromorphite and Pb-phosphate in addition to soil pH increase	Netherway et al., 2019
Dairy manure pH 7.1 P 1.74% SSA 11.2 m^2/g	Shooting range soil Sand 92.3% pH 7.1 OC 0.79%	Pb	2.5 and 5 wt% biochar mixing with soil; 210-day lab incubation; afterwards 15-day earthworm exposure	Reduced 0.01 M $CaCl_2$- and TCLP-extractable Pb in soil; little effect on earthworm	Soil pH rise due to biochar calcite dissolution; $Pb_5(PO_4)_3(OH)$ formation	Cao et al., 2011
Oak wood 400°C pyrolysis pH 10.2 CEC 24.4 $cmol_c/kg$	Shooting range sandy loam pH 7.2 OM 2.0% CEC 2.4 $cmol_c/kg$	Pb	5 wt% biochar mixing with soil; 7-day lab incubation; afterwards 5-day lettuce seed germination test	Greatly reduced water-soluble, exchangeable, and PBET-extractable Pb in soil; increased seed germination	Mainly due to soil pH rise by 0.8 units. Biochar also contributed labile C	Ahmad et al., 2012b
Rice straw 300°C pyrolysis	Oxisols and utisols pH 4.7–5.2 OM 0.35–0.84%	Pb	Batch sorption of Pb^{2+} from aqueous solution by 3–5 wt% biochar-amended soils	Clear rises in soil CEC, pH, and Pb^{2+} sorption; detection of CO_3^{2-} and $-COO^-$ in biochar	Surface complexes between Pb^{2+} and biochar functional groups; electrostatic interaction	Jiang et al., 2012
Hard wood pH 7.0 SSA 5.3 m^2/g CEC 7.2 $cmol_c/kg$	Former industrial site	Ni, Zn	Leaching and extraction of soils from field plots amended with 2 wt% biochar for 3 years	Biochar reduced metal leaching by >80% and increased the residual portion in soil	Chemisorption; higher biochar rate to improve grass establishment	Shen et al., 2016
Grain husk pH 8.3 CEC 65.4 $cmol_c/kg$ Cattle manure pH 10.3 CEC 48.8 $cmol_c/kg$	Sand OM 0.78%	Zn	Spectroscopic examination of Zn-spiked, 1–5 wt% biochar-amended soils after 180-day plant growth	Aging increased biochar O, Si, Ca, Al, Mg, and Zn contents and reduced C, N, P, and K contents	Precipitation, surface sorption, and organo-mineral complexes on biochar surface and in pores	Kumar et al., 2018

DOC, dissolved organic carbon; OM, organic matter; CEC, cation exchange capacity; SSA, specific surface area; DTPA, diethylenetriaminepentaacetic acid; PBET, physiologically based extraction test (pH 2.2, 0.4 M glycine extraction); TCLP, toxicity characteristic leaching procedure (pH 4.9, 0.1 M HOAc extraction).

Efficacy Variations

The efficacy of biochar amendment on immobilizing soil heavy metals is influenced by an array of factors, including the biochar source, amendment rate, metal species, soil type, and placement in soil (Ahmad et al., 2014; O'Connor et al., 2018). Biochar products manufactured from various biomass feedstocks through different pyrolysis conditions demonstrate great variations in pH, mineral ash content and composition, surface functionality, and CEC (**Table 1**) and consequently possess varied capability and effectiveness for stabilizing soil heavy metals (**Table 2**). For example, Ding et al. (2014) reported that the maximum sorption capacity of sugarcane-bagasse-derived biochar for Pb^{2+} in water (as soluble Pb^{2+} in soil solution) decreased as the pyrolysis temperature of biochar production increased in the range of 250–600°C. When mixing with contaminated rice paddy soil in field plots at 20 Mg ha^{-1}, rice-straw-derived biochar (pH 10.5; CEC 32.1 $cmol_c$ kg^{-1}) reduced soil NH_4NO_3-extractable and rice-root-accumulated Cd, Pb, and Zn but increased As (arsenic) to significantly higher extents than soybean-straw-derived biochar (pH 9.2; CEC 27.5 $cmol_c$ kg^{-1}) prepared under the same carbonization conditions (Zheng et al., 2015); the concentration of As in rice shoot was more than tripled relative to the unamended control (Zheng et al., 2012). At 1, 5, and 10 wt% amendment rates, poultry-litter-based biochar reduced the Pb concentration of Indian mustard roots grown in pH 5.4 Australian soil from 3,243 to 1,276, 513, and 367 mg kg^{-1}, respectively, while greenwaste-based biochar reduced the level to 2,769, 2,299, and 1,196 mg kg^{-1}, respectively (Park et al., 2011), implicating the importance of biochar source and amendment dosage in developing biochar-facilitated soil remediation programs. A higher biochar amendment rate in the practical range (e.g., <5 wt%) typically yields greater results of heavy metal stabilization. Soil characteristics, in particular the clay and OC contents, and co-existing cations also affect the effectiveness of biochar amendment in stabilizing heavy metals. Uchimiya et al. (2011a) reported that addition of plant residues-derived 350°C pyrolysis biochars at 10 wt% significantly enhanced the sorption of loamy sand (pH 5.6; OC 0.6%) for Cu^{2+} and Pb^{2+} but not Cd^{2+} and Ni^{2+} from a mixed metal solution (each 300 μM), whereas the sorption for Cu^{2+} of clay soil (clay 50%, pH 9.2, OC 0.89%) from a mixed $Cu^{2+}/Cd^{2+}/Ni^{2+}$ solution (each 1.5 mM) was noticeably reduced with 10 wt% amendment of poultry-litter-derived 350°C pyrolysis biochar. The researchers believed that biochar products from low-temperature-pyrolysis could not compete with soil clay particles for sorbing Cu^{2+}. In the same tests, replacement with 700°C-pyrolysis poultry litter biochar resulted in evident increases of Cu^{2+} sorption by the clay soil (Uchimiya et al., 2010a). Biochar amendment affects plant growth. Lu et al. (2014) grew 60-day greenhouse amaranth (*Amaranthus tricolor* L.) in soil pots (pH 6.0; Cd 6.1 mg kg^{-1}) amended separately with poultry-litter- and wood-based biochars both at 3 wt%. Relative to the control without biochar amendment, the poultry litter biochar amendment tripled the amaranth biomass yield, while the wood biochar amendment decreased such by 50%. Meanwhile, the total amount of amaranth-absorbed Cd reduced from 35.0 to 17.3 and 7.7 mg, respectively. In soils without chemical fertilization, manure-derived biochar furnishes additional nutrients and promotes plant growth, whereas plant-residue-derived biochar may immobilize available N and restrict plant growth (Guo, 2020). Furthermore, the effect of biochar amendment on stabilizing heavy metals may be initially strong but diminishes over time. In a 5-year field plot study, Cui et al. (2016) noticed that the leachability (by TCLP extraction), availability (by 0.01 M $CaCl_2$ extraction), and bioaccessibility (by simplified bioaccessibility extraction test) of Cu and Cd in contaminated paddy soil (pH 4.2) were significantly reduced by 3 wt% wood-based biochar amendment, 1 wt% apatite incorporation, and 0.2 wt% lime addition, yet the effect decreased gradually as time progressed.

In general, soil amendment with biochar at >2.0 wt% helps stabilize cationic heavy metals (e.g., Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+}, and Zn^{2+}) and reduce the bioaccessible portion and the bioaccumulation of these toxic elements in soil. The efficacy is greater for biochar products possessing higher pH, CEC, and ash content levels, is more evident in acidic, coarse-textured, low OM soils, and becomes diminishing over time (**Table 2**). Manure-derived biochars are typically more efficient than wood-derived biochars in stabilizing soil heavy metals. Biochar amendment does not stabilize but helps mobilize anionic toxic elements [*e.g.*, Cr in $Cr_2O_7^{2-}$ and CrO_4^{2-}, As in AsO_3^{-} and AsO_3^{3-}, and Sb in $Sb(OH)_6^{-}$] in soil. In biochar application, thorough and uniform incorporation of the amendment into contaminated soil is necessary to allow the biochar to get into direct contact with heavy metal contaminants. In all the reported research studies, biochar in <2 mm particles (mostly <1 mm) was fully mixed with the treated soils to achieve the remediation effect (**Table 2**). The soil moisture content was controlled at $>60\%$ of the soil water holding capacity to secure efficient biochar–heavy metal interactions that only occur in the soil solution phase. In combination with chemical fertilization, biochar amendment normally stimulates plant growth by improving the overall soil health (Guo, 2020). Practically, biochar amendment may be employed to temporarily rectify soils with slight to moderate heavy metal contamination. It may also be used jointly with phytoremediation to facilitate the "cleanup" of Cr (VI)-, As-, and Sb-contaminated soils. Long-term (e.g., >5 years) field research trials are warranted to validate the method feasibility. To date, merely one such study (Cui et al., 2016) was reported.

By reviewing the literature, Ahmad et al. (2014) concluded that biochars with more O-containing functional groups were desirable to immobilize inorganic and polar organic pollutants in soil and water. Accordingly, manure-derived biochar products from low pyrolysis temperature (e.g., <500°C) may be more efficient in mitigating soil heavy metal contamination. Since biochar amendment does not remove heavy metals from soil, the method may only be applicable to slightly to moderately contaminated soils. In practice, appropriate biochar amendment rate and thorough soil incorporation have to be considered, with the remediation effect being regularly monitored.

TABLE 3 | Research trials of biochar-facilitated remediation of soil organic contamination.

Biochar source	Soil type	Pollutants	Experiment	Effect	Mechanisms	References
Dairy manure pH 7.1 P 1.74% SSA 11.2 m^2/g	Shooting range soil Sand 92.3% pH 7.1 OC 0.79%	Atrazine	15-day earthworm exposure to atrazine-spiked, 2.5–5 wt% biochar-amended, 210-day lab-incubated soil	Greatly reduced 0.01 M $CaCl_2$- and TCLP-extractable atrazine in soil and atrazine earthworm uptake	Soil pH increase from 7.1 to 7.6 due to biochar calcite dissolution; biochar adsorbed atrazine on surface	Cao et al., 2011
Wood chips 450°C pyrolysis SSA 27 m^2/g	Sandy loam OM 1.4% pH 6.8 CEC 9.3 cmol_c/kg	Chloropyrifos and carbofuran	35-day green onion grown in pesticide-spiked, 1 wt% biochar-amended soils	Increased residual pesticides in soil but reduced pesticide plant accumulation	Biochar sequestered pesticides in micropores *via* high SSA-induced surface adsorption	Yu et al., 2009
Sugarcane residue pH 8.6 SSA 58.9 m^2/g CEC 113.7 cmol_c/kg	Sandy loam pH 5.7 OC 0.59% Clay pH 5.8 OC 2.4%	Ethinylestradiol	Batch sorption and desorption trials with unamended and 5 wt% biochar-amended soils; 30-day lab incubation	Increased steroid sorption and desorption retardation in both soils; reduced steroid microbial mineralization	Biochar adsorbs estrogen hormones	Wei et al., 2019
Hard wood	Loam pH 5.4 OC 4.6%	PAHs and As, Cd, Cu, Zn	50 vol% biochar mixing with soil; 60-day outdoor pot setting, ryegrass germination test	Reduced both total and bioavailable PAHs in soil; enhanced seed germination	Likely strong sorption of PAHs by biochar and enhanced PAHs microbial degradation	Beesley et al., 2010
Sewage sludge pH 7.3 OC 27.1% N 3.4% S 4.6%	Texture unknown pH 6.8 OC 7.0%	PAHs	2, 5, and 10 mass% biochar mixing with soil; 8-week greenhouse pots with lettuce	Reduced PAHs bioaccumulation; enhanced plant growth	Likely strong sorption of PAHs by biochar through partition; stimulated soil microbial activity	Khan et al., 2013a
Willow, coconut, wheat straw Non-activated (pH 8.0–9.9; SSA 3.1–26.3 m^2/g) and steam activated (pH 7.2–8.8; SSA 246–841 m^2/g)	Industrial site soils	PAHs	Solvent extraction of 5 wt% biochar-amended, 60-day incubated soils and bioassay with garden cress, springtail, and bacteria	Activated biochar further reduce bioaccessible PAHs in soil. Biochar reduced soil toxicity to springtail and bacteria but not phytotoxicity	Both SSA and surface interaction are important for biochar to immobilize PAHs	Koltowski et al., 2016
Soft wood 450°C pyrolysis pH 10.0	Brownfield soil pH 7.7 CEC 9.5 cmol_c/g	PCBs	Bioassay of 2.8 wt% biochar- amended soils in field plots and greenhouse pots	Pumpkin root decreased PCB content by >60%; mixing affected biochar effects	With thorough mixing with soil, biochar reduces PCB bioavailability by strong sorption	Denyes et al., 2013
Bamboo pH 9.5 SSA 332 m^2/g	Loam pH 5.2 OM 4.7%	PCP	Column leaching of 14-day incubated, 2–5 wt% biochar-amended, PCP-spiked soil	Residual PCP in and PCP leaching losses from soil columns were decreased	Sorption of PCP by biochar mainly via partition.	Xu et al., 2012
Corn stover SSA 67.2 m^2/g Pine wood SSA 102 m^2/g	Industrial site soils	PCDD, PCDFs	24-day POM strip extraction of and 28-day earthworm exposure to soils amended with biochar at 0.2 × OC	Biochar greatly reduced soil POM-extractable and bioavailable PCDD and PCDFs	Not specified; clearly biochar immobilizes soil PCDD and PCDFs by sorption	Chai et al., 2012
Rice straw 500°C pyrolysis pH 8.9	Oil spill site Clay loam pH 6.5 OC 5.4%	Petroleum	180-day lab incubation of 2 wt% biochar-amended soils	Soil microbial degradation of petro-hydrocarbon improved by 20%	Biochar as a biostimulant to furnish C, N, P, and other nutrients to microbes	Qin et al., 2016

(Continued)

TABLE 3 | Continued

Biochar source	Soil type	Pollutants	Experiment	Effect	Mechanisms	References
Pine wood 350°C pyrolysis SSA 164 m^2/g 700°C pyrolysis SSA 187 m^2/g	Sand pH 9.2 OC 0.16% Silt loam pH 5.8 OC 1.2% Silt loam pH 5.1 OC 5.1%	Phe	Batch adsorption and desorption experiments with 0.5 wt% biochar-amended soils	The magnitude of biochar enhancing phenanthrene sorbed to soil depended on biochar source, soil OC, and biochar age in soil	Natural DOC and biochar surface functional groups influence biochar sorption for hydrophobic organics	Zhang et al., 2010
Stinging nettle OC 52.1% N 2.1% SSA 3.5 m^2/g	Mine spoil Sand pH 3.2 High As, Cu, Cd	Phe and As, Cu	Sunflower grown in PAHs-spiked, 1 wt% biochar-amended, 56-day lab-incubated soil pots	Biochar increased phenanthrene degradation by 44%; plant growth improved	Biochar supplies additional C, N, P, and other nutrients	Sneath et al., 2013
Pine wood pH 7.5 OC 85.2% Oliver pruning pH 9.3 OC 82.9% Rice husk pH 6.5 OC 43.1%	Washed sand pH 5.4 OC <0.1% Silt pH 6.6 OC 2.2% Silt loam pH 6.3 OC 2.6%	Phe	Batch adsorption and desorption experiments with 1 wt% biochar-amended soils	Phenanthrene sorption on wood-based biochar was less evident; sorption on biochar was more evident in low-OC soils and reduced mineralization	The source of biochar influenced its sorption performance	Jiménez et al., 2018
Hard wood 450 and 600°C pyrolysis pH 8.5–9.7 OC 76–78% SSA 4–39 m^2/g	Sandy clay loam (pH 6.2; OC 3.5%) and loamy sand (pH 4.8; OC 1.0%)	Simazine	Column leaching of simazine-spiked, 0.5–5 wt% biochar-amended, 21-day incubated soils; biochar-amended field microplots	Simazine biodegradation suppressed and leaching reduced; biochar effects lasted >2 years and correlated inversely to particle size	Strong sorption of simazine to biochar	Jones et al., 2011
Olive mill waste pH 10.2 SSA 2.5 m^2/g	Sandy loam pH 7.3	Tebuconazole, metalaxyl	Fungicide persistence and migration in 4 t/ha biochar-amended field plots	Biochar reduced leaching and degradation of fungicides in soil	Sorption of fungicide by biochar	Gamiz et al., 2016
Hard/soft woods Gasification pH 9.8–9.9 OC 28.7–55.3% SSA 159–242 cmol_c/g	Sandy loam (pH 4.3; OM 3.0%; CEC 2.3 cmol_c/g); silt (pH 7.8; OM 2.0%)	Tylosin	Batch adsorption and desorption with 1–10 wt% biochar-amended soils; column leaching with 5 wt% biochar-amended soils	Retarded tylosin transport in soil; increased tylosin adsorption at higher biochar rate; more tylosin was non-desorbable in higher pH soil	Strong sorption of tylosin to biochar	Jeong et al., 2012

OC, organic carbon content; DOC, dissolved organic carbon; PAHs, polycyclic aromatic hydrocarbons; PCP, pentachlorophenol; PCDD, polychlorinated dibenzo-ρ-dioxins; PCDFs, polychlorinated dibenzofurans; Phe, phenanthrene; SSA, BET-specific surface area; POM, polyoxymethylene passive uptake.

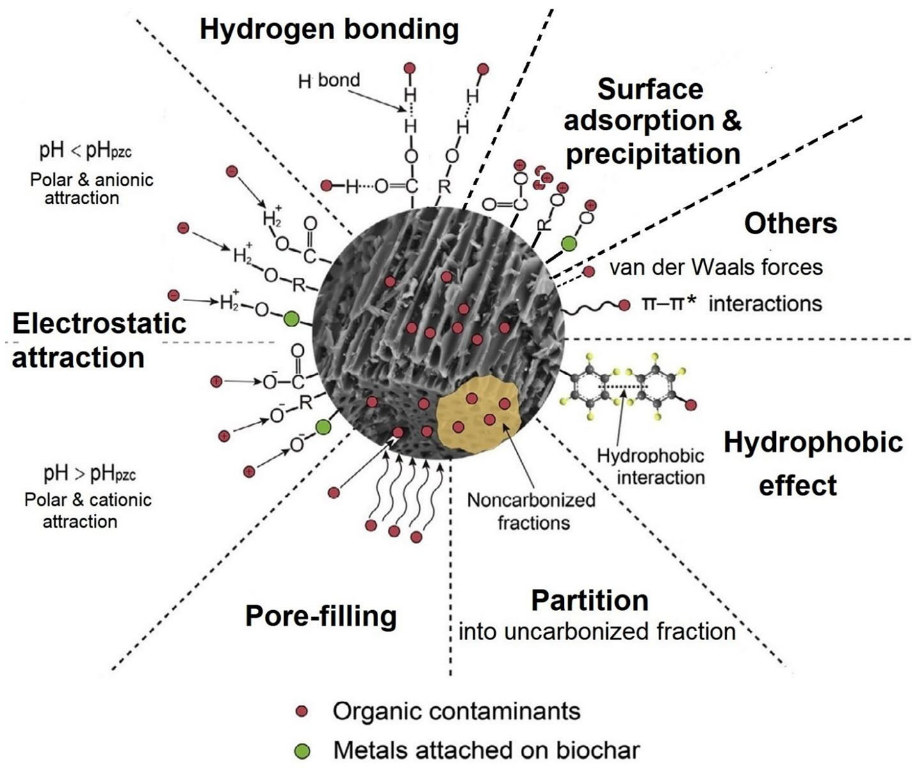

FIGURE 4 | Major mechanisms through which biochar stabilizes organic contaminants in soil. The graph was modified from Tan et al. (2015).

BIOCHAR FOR REMEDIATION OF ORGANIC-CONTAMINATED SOILS

Research has also demonstrated that biochar is capable of retaining and even promoting the decomposition of various organic contaminants in soils (**Table 3**). Biochar amendment may be a practical approach to mitigate soils polluted by pesticides, herbicides, antibiotics, PAHs, PCBs, petroleum hydrocarbons, and other POPs (Ahmad et al., 2014; Tan et al., 2015; Zama et al., 2018).

Mechanisms

After incorporation into contaminated soil with thorough mixing, biochar promptly interacts with organic contaminants and soil microorganisms. Organic contaminants are stabilized on the biochar surface and in pores and may be further decomposed by microbes as stimulated by biochar amendment. The porous, functional-group-abundant, and aromatic-C-condensed biochar surface is able to adsorb various organic compounds through different mechanisms. As organic pollutants are adsorbed by biochar, their concentrations in soil water are decreased, and bioaccessibility to soil organisms, including plant roots, is reduced. Meanwhile, biochar amendment enhances overall soil health by improving soil physical, chemical, and biological properties (Guo, 2020). In addition to furnishing mineral nutrients such as N, P, K, Ca, Mg, and S, biochar amendment introduces substantial amounts of biodegradable OC as soil microbial substrate. Following the initial perturbation period, biochar-amended soils generally demonstrate improved microbial community structure and promote microbial activity (indicated by soil respiration rate, soil enzyme activity, and soil microbial biomass) (Liao et al., 2016; Irfan et al., 2019). Consequently, the microbial mineralization of many organic pollutants in soil is accelerated.

Biochar is able to stabilize organic contaminants via a number of physical and chemical sorption mechanisms (**Figure 4**). Biochar interacts with organic molecules through van der Waals forces, the universal electrostatic attraction between non-polar molecules (London dispersion forces) and between polar molecules (dipole-dipole forces) (Petrucci et al., 2007). The van der Waals forces, though fairly weak, increase with the molecules' surface area (e.g., higher molecular weight) and can be dominant as the particle size of biochar decreases (Yang and Evans, 2007). Biochar consists of C, O, H, N, and other mineral elements (**Table 1**). It may interact with polar organic compounds by forming H bonds through the O-, N-, and H-containing functional groups (**Figure 4**). H-bonding is another form of electrostatic attraction stronger than van der Waals forces (Tan et al., 2015). The abundant functional groups in biochar become dissociated at $pH > pH_{ZNC}$ and protonated at $pH < pH_{ZNC}$, engendering biochar with negative charges and positive charges, respectively (Fidel et al., 2018). The surface charges enable biochar to electrically attract polar organic molecules and ionized organic pollutants with counter charges (e.g., many pesticides, hormones, and antibiotics). This type of electrostatic attraction, as conventionally referred to, is generally stronger than H-bonding and van der Waals interactions. Intensified electrostatic attraction may lead to inner-sphere adsorption (specific surface interaction), in which ionized organic compounds react chemically with the biochar surface functional groups and are retained (Xu et al., 2011). In addition, the aromatic C in biochar possesses excess π-electrons, while many organic molecules, especially those containing O, N, S, P, Cl, and Br, are electron-deficit; biochar may interact with these organic contaminants through π-π^* electron donor–acceptor interactions (Xie et al., 2014; Vithanage et al., 2017).

Biochar adsorbs non-ionic organic compounds through surface adsorption and/or partition. Smaller pores have higher surface energy, and therefore sorption of organic pollutants occurs first in biochar micropores (Uchimiya et al., 2010b). At low surface coverage [i.e., equilibrium solute concentration (Ce) to solute water solubility (Sw) ratio ≤ 0.2], non-linear, competitive adsorption of organic solutes into micropores in biochar's carbonized porous surface is dominant; at higher surface coverage (i.e., Ce/Sw >0.2), the adsorption shifts increasingly to linear, non-competitive partition into biochar's uncarbonized C moiety (Uchimiya et al., 2010b; Chiou et al., 2015; Zhao et al., 2019). Pore filling ("in-pore" surface adsorption) was suggested as an important mechanism for biochar adsorbing organic compounds (**Figure 4**). Research indicates that the extent of surface adsorption is proportionally related to biochar's SSA and surface porosity as well as aromaticity (Zhu et al., 2014), while the capacity of partition adsorption is dependent on biochar's OC content and mineral ash content (Chiou et al., 2015; Zhao et al., 2019). The hydrophobic effect (avoidance of non-polar molecules and hydrophobic molecular moieties from contacting water) also facilitates the sorption of hydrophobic organic pollutants by biochar (Tan et al., 2015).

In addition, biochar contains more or less multivalent metal elements such as Fe, Al, Ca, and Mg on the surface (Bian et al., 2014). Polar and ionized organic compounds may form complexes with the metal ions and be deposited on the biochar surface or precipitated in soil. The sorption kinetics of many organic molecules on biochar follow the pseudo-second-order pattern, suggesting the importance of "chemisorption" (surface precipitation, **Figure 4**) in biochar–organic interactions (Tan et al., 2015). Xu et al. (2011) investigated the removal of methyl violet from water by two crop-residue-derived biochars as influenced by the solution pH and ionic strength and concluded that sorption of methyl violet by biochar was mainly through electrostatic attraction, specific interaction, and surface precipitation.

The surface properties of biochar, in particular SSA, pore size, pore volume, polarity, aromaticity, and hydrophobicity, have a predominant effect on biochar–organic compound interactions (Tan et al., 2015). In general, biochars produced at higher pyrolysis temperatures are greater in SSA, aromaticity, and hydrophobicity and lower in surface polarity due to the loss of O- and H-containing functional groups. Jiang et al. (2015) reported that, as the pyrolysis temperature was elevated from 200 to 400, 500, and 600°C, the biochar products from rice straw increased in SSA from 7.2 to 19.7, 44.0, and 193.2 m^2 g^{-1}, respectively, and their sorption capacities for cyromazine in water also increased steadily, with the 600°C biochar showing the highest organic sorption capacity. The mineral ash in biochar, especially the manure-derived products, may block the surface micropores and alter the SSA, hydrophobicity, polarity, and other surface properties. Zhang et al. (2013) observed that de-ashing by HCl–HF treatment increased the SSA value of pig-manure-based 350°C (ash 45.3%) and 700°C (ash 66.8%) pyrolysis biochars from 23.8 and 32.6 to 67.1 and 218.1 m^2 g^{-1}, respectively, but decreased the CEC level from 96.8 and 112.5 $cmol_c$ kg^{-1} to 5.6 and 8.7 $cmol_c$ kg^{-1}, respectively. As a result, the sorption capacities for the pesticides carbaryl and atrazine of pig-manure-based biochars were greatly enhanced, indicating the importance of biochar surface properties (Zhang et al., 2013). Clearly, different biochar products have varied sorption capacities and primary sorption mechanisms for stabilizing soil organic contaminants. Non-polar, hydrophobic organic contaminants such as PAHs and petroleum hydrocarbons are adsorbed by biochar mainly through pore filling, partition, and hydrophobic effect, while polar and ionized organic pollutants, including most pesticides and antibiotics, are adsorbed via H-bonding, electrostatic attraction, specific interaction, and surface precipitation (**Figure 4**).

Efficacy Variations

The efficiency of biochar amendment to stabilize organic pollutants and facilitate their elimination from soil is case specific, varying with biochar source, particle size, amendment dosage, pollutant chemical nature, and soil type (**Table 3**). The biochars produced from canola straw, peanut straw char, soybean straw char, and rice hull through the same 350°C pyrolysis processing, for example, demonstrated evidently different sorption capacities for removing methyl violet from water (Xu et al., 2011). Using 30-day incubation experiments, Koltowski et al. (2016) noticed that, at 5 wt% amendment rate, willow-, coconut shell-, and wheat straw-derived biochars reduced the freely dissolved (extractable by POM strips) and bioaccessible (extractable by silicon rods) fractions of PAHs in soils collected from three different industrial sites by 28–87% relative to the unamended controls. Steam activation greatly increased the biochars' SSA and pore volume and subsequently the sorption capacity for PAHs (Koltowski et al., 2016). Biochar itself may contain PAHs (up to 65 mg kg−1; Keiluweit et al., 2012; Quilliam et al., 2013), but mostly at insignificant, low-environmental-risk levels (Li et al., 2016; Weidemann et al., 2018). Amending sandy loam (pH 5.7; OC 0.54%) and clay (pH 5.8; OC 2.4%) soils with sugarcane-residue-derived biochar (pH 8.6; SSA 58.9 m^2 g^{-1}; CEC 113.7 $cmol_c$ kg^{-1}) at 5 wt% improved the sorption of 17α-ethinylestradiol (EE2, an estrogen hormone) on both soils and reduced their microbial mineralization (Wei et al., 2019). Furthermore, the sandy loam soil demonstrated a remarkably higher sorption efficiency for EE2 than the clay soil; the biochar amendment decreased the adsorption coefficient Koc of the former but increased that of the latter (Wei et al., 2019). When a strongly acidic (pH 3.2) mine spoil soil with mixed heavy metal and phenanthrene contamination was treated with 1 wt% biochar (N 2.1%; SSA 3.5 m^2 g^{-1}) generated from stinging nettle (*Urtica dioica* L.), the phenanthrene degradation in soil microcosms was improved by 44% over a 56-day lab incubation period (Sneath et al., 2013). It was possible that the added biochar mainly functioned to stabilize the heavy metals and did not significantly adsorb phenanthrene. Nevertheless, the biochar amendment did ameliorate soil health and promoted microbial activity, as indicated by the stimulated sunflower (*Helianthus annuus*) grown in the amended soil pots (Sneath et al., 2013). Qin et al. (2016) reported that the enhanced microbial activity by biochar amendment was responsible for the 20% facilitation in petroleum hydrocarbon biodegradation in a petroleum spill site soil (clay loam; pH 6.5) amended with rice-straw-derived biochar (pH 8.9) at 2 wt% over a 180-day lab incubation period. In addition to absorbing non-polar, hydrophobic organic compounds, biochar also showed high affinity for polar, hydrophilic organic pollutants. Jones et al. (2011) examined the effect of biochar amendment on leaching and biodegradation of the herbicide simazine in different soils. Two particle size fractions of commercial-wood-derived biochar were tested: coarse (2–10 mm) and fine (<2 mm). With addition at 0.5 and 5 wt% to soil, both biochar fractions suppressed the biodegradation of simazine and reduced its leaching in loamy sand (pH 4.8; OC 1.0%) and sandy clay loam (pH 6.2; OC 3.5%) soils, with more significant effects at a higher amendment rate, in finer particle size, and in greater-OC soils (Jones et al., 2011). The particle size of biochar influences the amendment efficacy through affecting the uniformity of biochar distribution in the treated soil. Denyes et al. (2013) noticed that soil incorporation of biochar by mechanical mixing was much more effective than hand or shovel mixing to achieve even distribution of biochar in soil and consequently enhance the retention of PCBs in 2.8 wt% biochar-amended brownfield soil and reduce PCB bioaccumulation in pumpkin (*Cucurbita pepo*) roots by >60%. Adsorption of pesticides, such as atrazine and simazine, by biochar may reduce the pesticidal efficacy of field-applied agrochemicals. To most surface-sprayed pesticides, the impact should be marginal.

In practice, wood- and plant-residue-derived biochars from higher pyrolysis temperatures and steam-activated biochars usually possess high SSA, porosity, and aromaticity levels and therefore may be selected with preference over manure-derived biochars for sorption-based stabilization of organic contaminants. Over the long term, biochar amendment may facilitate the mineralization and the eventual elimination of organic contaminants in soil through improving soil microbial activities. The mechanisms through which biochar amendment improve soil health and soil microbial activities can be found elsewhere (Paz-Ferreiro et al., 2016; Guo, 2020).

CONCLUSIVE REMARKS

A notable number of studies have been conducted to investigate the feasibility of using biochar to remediate soils contaminated by heavy metals and various organic pollutants. The literature data indicate that biochar amendment is able to stabilize heavy metals and organic compounds in soil and mitigate soil contamination; the efficacy, however, is case specific, changing with biochar source, amendment dosage, soil type, pollutant species, and even biochar placement in soil. Differently sourced biochars vary significantly in physical and chemical quality properties and demonstrate diverse capacities and efficiencies for stabilizing soil heavy metals and organic contaminants. Biochar amendment does not remove heavy metals from soil; soil-incorporated biochar instead transforms the water-soluble and bioaccessible fractions of heavy metals into immobilized forms, reducing the bioavailability and the ecotoxicity of the toxic elements. This is achieved primarily through elevating the soil pH, introducing carbonates and phosphates, and enhancing surface sorption. Biochar stabilizes cationic heavy metals via electrostatic attraction, ion-exchange-based surface adsorption, surface complexation, and (co-)precipitation. For anionic forms of toxic elements, such as CrO_4^{2-}, $Cr_2O_7^{2-}$, AsO_3^-, AsO_3^{3-}, and $Sb(OH)_6^-$, biochar amendment generally improves their mobility in soil, suggesting that biochar may be used to facilitate phytoextraction-based remediation of Cr (VI)-, As-, and Sb-contaminated soils. The abundance of surface functional groups and the CEC of biochar determine its ability to adsorb heavy metals, while the pH/lime equivalence and the phosphate content control its capacity to precipitate heavy metal contaminants. This remark serves as a guideline for designing and selecting biochar products to mitigate soil heavy metal contamination. In general, manure-derived biochars at lower pyrolysis temperature were more efficient than plant-residue-derived biochars in stabilizing soil heavy metals. Soil-incorporated biochar also stabilizes non-polar and polar organic pollutants through adsorption and reduces their ecotoxicity and bioaccumulation. Biochar amendment may promote the mineralization of organic contaminants in soil by enhancing soil health and microbial activity. Adsorption of biochar for non-polar organic contaminants is chiefly via pore filling, partition, and hydrophobic effect and for polar organic pollutants via hydrogen bonding, electrostatic attraction, specific surface interaction, and surface precipitation (chemisorption). The surface properties of biochar including SSA, microporosity, polarity, and aromaticity influence its capability for adsorbing organic pollutants. Plant-residue-derived biochars at higher pyrolysis temperature mostly outperformed manure-derived biochars in adsorbing organic contaminants. Overall, biochar amendment serves as a promising approach to stabilize soil heavy metals and organic contaminants and mitigate the hazardous soil pollution effects. Though the stabilization efficiency may not be comparable to other agents such as lime, phosphate salts, and activated carbon, biochar is more economically available and can furnish other environmental benefits such as carbon sequestration and soil health improvement when appropriately applied. Biochar amendment may be implemented in slightly polluted cropland to secure safe food production, in mine land restoration efforts to promote vegetation, and in soil bioremediation and phytoextraction projects to facilitate the process. The pollutant stabilization effect of biochar in field soils, however, may diminish over time. Field studies at larger scales are clearly needed to examine the long-term effect of biochar amendment on mitigating soil contamination under practical circumstances.

The application of biochar for improving soil health, facilitating soil remediation, and enhancing carbon sequestration remains currently at the fledgling stage. An emerging biochar industry with profitable commercial production and wide field application is foreseen. The research community has been focusing on validating the agricultural and the environmental benefits of soil–biochar amendment programs and developing biochar quality standards. Though Japan enacted the Soil Productivity Improvement Act in 1987 to sanction the practice of conditioning agricultural soils with charcoal and pot ash (Ogawa and Okimori, 2010), the US and the European countries have not established any governmental policies to regulate biochar use as a soil amendment. Production and application of biochar as a soil amendment may be subject to legislative regulations such as fertilizer policy, soil remediation and protection policy, urban planning policy, and biodiversity policy (van Laer et al., 2015). A sustainable biochar industry warrants systems thinking of feedstock supply security, bio-oil and producer gas standards, and national policies of renewable energy, CO_2 emission tax, and carbon sequestration credits (van Laer et al., 2015).

AUTHOR CONTRIBUTIONS

MG reviewed the literature, synthesized the information, and prepared the manuscript. WS helped with literature data collection and manuscript development and reviewed the manuscript. JT initiated the topic, conducted preliminary experiments and literature review, and examined the draft. All authors contributed to the article and approved the submitted version.

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