Chapter 4
Production Techniques, Mechanism, and Application of Biochar in Remediating Soil Contaminated with Heavy Metals: A Review

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Abstract The ultimate goal of heavy metal contaminated soil remediation is to increase crop yields on the premise of ensuring food production safety. Soil contaminated by heavy metals threatens the quality of agricultural products and human health. Hence, it is necessary to choose appropriate economic and effective remediation techniques to control the deterioration and revive the land quality. Among the methods available, biochar application for adsorption and remediation of heavy metal contaminated soil is emerging to be a sustainable approach. Biochar introduction to the soil provides organic matter and essential macro and micronutrients like C, N, P, K, Ca, Mg, etc., which enhances soil enzyme and microbial activities. Additionally, the plant root environment, soil water retention, and saturated hydrau-

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J. Aravind et al. (eds.), *Strategies and Tools for Pollutant Mitigation*,
https://doi.org/10.1007/978-3-030-98241-6_4

lic conductivity can be improved in the presence of biochar. This chapter is intended to present an overview of the production techniques of biochar, its properties, and characteristics required for effective heavy metal removal and the corresponding process conditions, mechanisms involved in the interaction of biochar with heavy metals, and the benefits as well as bottlenecks of biochar application in soil.

Keywords Biochar · Heavy metals · Remediation · Soil contamination · Mechanism

4.1 Introduction

Soil contamination with heavy metals is a matter of global concern due to the impending damage of the natural ecosystem and human health hazards through bioaccumulation in the food chain. Some of the soil contaminants include heavy metals (cadmium (Cd), zinc (Zn), copper (Cu), nickel (Ni), lead (Pb), arsenic (As), etc.), pesticides, and polycyclic aromatic hydrocarbons (PAHs). Though minuscules of heavy metals are naturally present in the soil, the concentration rises beyond admissible limits (10–1000 times) due to anthropogenic activities such as mining, solid waste disposal, and wastewater irrigation (Gao et al. 2020). Scientific research articles reported the average concentration of heavy metals in soil (worldwide data) to be 20 mg/kg Cu, 0.06 mg/kg Cd, 20–200 mg/kg Cr, 10–150 mg/kg Pb, 40 mg/kg Ni, and 10–300 mg/kg Zn. National soil surveys revealed that out of the 19.4% contaminated arable land, more than 80% was polluted with inorganic compounds. The potential risk of heavy metal leaching to surface or ground waters should also be taken into consideration. It is claimed that millions of people from India, China, and Bangladesh are facing health-related threats due to the negative impacts of metal contamination (Sonone et al. 2020).

Globally, all developed and developing nations require new technology to renew nature and negative emissions technologies for greenhouse gases. Soil amendments are being developed to carry out in situ metal stabilization and avoid the risk of soil and groundwater ecosystems. Of the many strategies employed to remediate heavy metal contaminated soil like phytoremediation, soil dressing, soil washing, etc., chemical immobilization proved to be the most efficient, in terms of its economic feasibility and simplicity. Chemical immobilization includes the addition of amendments to the soil to help retain contaminants. Tons of crop residues are produced worldwide which are neither effectively used nor recycled (Wang et al. 2018; Maji et al. 2020; Pathy et al. 2020b). The raw materials for adsorbent production include waste products of humans, animals, and plants. So, this technology also helps to improve the waste management of the nations and give more potential economy of the nation. China is one of the most populated countries that produce 2.5–3 billion tons of animal wastes, 1.2 billion tons of vegetable and fruit wastes, 2 billion tons of municipal waste (Chen et al. 2020a), 0.5–0.7 billion tons of domestic garbage wastes, and 0.17–0.3 billion tons of domestic meat wastes per year. These are fundamental raw materials of the large-scale production of biochar (Wang et al. 2013).

Biochar production technology is proving to be the best method to treat soil contamination by heavy metals. Biochar production is a currently developing technology to enhance the soil nutrients retention capacity, water holding capacity, reduction of greenhouse gas emission, and stabilizes the carbon (Kamali et al. 2021). Biochar is a product of the thermochemical conversion of biomass to carbon-rich materials, under limited oxygen conditions, which is used for environmental management. This carbon-negative or carbon-neutral material can be used as a soil ameliorant, adsorbent, and in several climate mitigation approaches. The process greatly reduces the volume of the residues while eliminating the pathogens and improving the nutrient utilization efficiency. Their specific activities include high cation exchange capacity (CEC), high pH, moisture content, and total nitrogen and phosphorus ions of soil, promoting root development and decreasing soil erosion (Abhijeet et al. 2020; Mandal et al. 2021). Due to the aromatic nature of biochar, it can effectively adsorb both organic and inorganic contaminants. Application of biochar to soil is reported to effectively immobilize heavy metals due to their high surface area, pore volume, and sufficient adsorption sites. The high porous structure of biochar can be attributed to the presence of tubular arrangement of plant cells. Being a slow-release organic material, biochar releases the adsorbed metal ions at a slower rate, fulfilling the requirements of the plants (Wang et al. 2018; Pathy et al. 2021). Table 4.1 shows various sources of biochar that have been used for removing heavy metals in soil and Table 4.2 includes information on remediation of other contaminants using biochar.

Table 4.1 Sources of biochar, their production conditions, and heavy metals remediated from soil

Source of biochar	Pyrolytic temperature (°C)	Residence time (min)	Removal of pollutants	References
Bamboo	750	180	Cd, Cu, Pb, and Zn	Lu et al. (2014)
Rice straw	500	30	Cd, Cu, Pb, and Zn	Lu et al. (2014)
Diary manure	350	240	Pb, Cd, and Zn	Liang et al. (2014)
Sugarcane straw	700	60	Cd, Pb, and Zn	Puga et al. (2015)
Corn straw	600	120	As	Yu et al. (2015)
Olive mill waste	400–450	30	Zn, Pb, and Cd	Hmid et al. (2015)
Bamboo	750	180	Pb and Cd	Xu et al. (2016)
Sludge	400	120	Cr and As	Tsang et al. (2016)
Soybean stover	300 and 700	180	Pb and As	Ahmad et al. (2016)
Pine needle	300 and 700	180	Pb and As	Ahmad et al. (2016)

Table 4.1 (continued)

Source of biochar	Pyrolytic temperature (°C)	Residence time (min)	Removal of pollutants	References
Bamboo	750	180	Cd, Cu, Pb, and Zn	Lu et al. (2017)
Rice straw	500	30	Cd, Cu, Pb, and Zn	Lu et al. (2017)
Pine cone	200 and 500	120	Pb	Igalavithana et al. (2017)
Vegetable waste	200 and 500	120	Pb	Igalavithana et al. (2017)
Switchgrass	400	30	Pb, Ni, and Co	Mohamed et al. (2017)
Wheat straw	450	120	Cd	Liu et al. (2018)
Sugarcane bagasse	450	240	Cd, Cu and Pb	Nie et al. (2018)
Rice husk	550	120	Hg	O'Connor et al. (2018)
Bamboo hardwood	550	300	Cd	Wu et al. (2019)
Rice straw	500	180	As, Cd, Cu, and Zn	Tang et al. (2020)
Sewage sludge	500	120	Zn	Penido et al. (2019)
Silver grass	500–600	60	As and Pb	El-Naggar et al. (2020)
Rice straw	500–600	60	As and Pb	El-Naggar et al. (2020)
Umbrella tree wood	500–600	60	As and Pb	El-Naggar et al. (2020)
Rice straw	500	300	Cd and Pb	Fan et al. (2020)
Maize straw	400	480	Cd and Cu	Tu et al. (2020)
Wood	550	120	Cu, Cd, and As	Zhang et al. (2020)
Bamboo	550	120	Cu, Cd, and As	Zhang et al. (2020)
Cornstalk	550	120	Cu, Cd, and As	Zhang et al. (2020)
Rice husk	550	120	Cu, Cd, and As	Zhang et al. (2020)
Corn straw	350, 500, and 700	120	Zn	Song et al. (2020)
Seweage sludge	300 and 500	30	Cu, Mn, Pb, and Zn	de Figueiredo et al. (2019)
Rice hull	450	120	Cd and Cu	Wang et al. (2021b)
Oriental plane	650	120	As, Cd and Pb	Wen et al. (2021)
Pig carcass	650	120	As and Pb	Pan et al. (2021)
Green waste	650	120	As and Pb	Pan et al. (2021)
Wheat straw	600–900	120	Pb, Zn, and Cd	Li et al. (2022)
Switchgrass	300	30 min	U(VI)	Kumar et al. (2011)
Sugar beet tailing	300	~2 h	Cr(VI)	Dong et al. (2011)

(continued)

Table 4.1 (continued)

Source of biochar	Pyrolytic temperature (°C)	Residence time (min)	Removal of pollutants	References
Spartina alterniflora	400	2 h	Cu(II)	Li et al. (2013)
Soybean straw	400	3.75 h	Cu(II)	Tong et al. (2011)
Sludge	400	2 h	Cr(VI) and Pb(II)	Zhang et al. (2013a)
Sludge	550	2 h	Pb(II)	Lu et al. (2012)
Rice straw	700, 400, and 100	6 h	Al	Qian and Chen (2013)
Rice husk and pinewood	300	20 min	Pb(II)	Liu and Zhang (2009)
Pine needles	200	16 h	U(VI)	Zhang et al. (2013b)
Miscanthus sacchariflorus	300, 400, 500, and 600	1 h	Cd(II)	Kim et al. (2013)
Hardwood	450	<5 s	Zn(II) and Cu(II)	Chen et al. (2011)
Corn straw	600	2 h	Zn(II) and Cu(II)	Chen et al. (2011)
Cattle manure	100, 400, and 700	6 h	Al	Qian and Chen (2013)
Canola straw	400	3.75 h	Cu(II)	Tong et al. (2011)
Spartina alterniflora	400	2 h	Cu(II)	Li et al. (2013)
Sludge	400–700	2 h	Fluoride	Oh et al. (2012)
Rice straw	100–700	6 h	Aluminum	Qian and Chen (2013)
Rice husk	350	4 h	Pb, Cu, Zn, and Cd	Xu et al. (2013)
Rice husk and pinewood	300	20 min	Lead	Liu and Zhang (2009)
Orange peel	400–700	2 h	Fluoride	Oh et al. (2012)
Miscanthus sacchariflorus	300–600	1 h	Cadmium	Kim et al. (2013)

This chapter investigates the application of biochar for remediating soil contaminated with heavy metals. It elucidates various techniques available for biochar production and the optimum process parameters required for synthesizing biochar with characteristics suitable for removing heavy metals efficiently. The mechanisms involved during the interaction of biochar with heavy metals are discussed. In addition, the advantages and disadvantages of biochar application in soil and the future perspectives in this research area.

Table 4.2 Sources of biochar, their production conditions, and other contaminants remediated from soil

Source of biochar	Pyrolytic temperature (°C)	Residence time (min)	Removal of pollutants	References
Swine manure	400	1 h	Herbicide paraquat	Tsai and Chen (2013)
Wood	200–600	1 h	Fluorinated herbicides	Sun et al. (2011)
Sugarcane bagasse	300 and 700	6 h	Hydrophobic organic compounds (HOCs)	Chen et al. (2012a)
Sugarcane bagasse	450 and 600	–	Sulfamethoxazole	Yao et al. (2012)
Soybean stover	300 and 700	3 h	Trichloroethylene	Ahmad et al. (2012)
Pinewood shavings	150–700	6 h	Naphthalene	Chen et al. (2012b)
Pine needle litters	100–700	6 h	Naphthalene (NAPH), nitrobenzene (NB), and m-dinitrobenzene (m-DNB)	Chen et al. (2008)
Pine needle	300 and 700	6 h	Hydrophobic organic compounds (HOCs)	Chen et al. (2012c)
Pine needle	300–700	3 h	Trichloroethylene	Ahmad et al. (2013)
Peanut shells	300 and 700	3 h	Trichloroethylene	Ahmad et al. (2012)
Palm bark	400	30 min	Methylene blue dye	Sun et al. (2013)
Orange peel	150–700	6 h	Naphthalene and 1-naphthol	Chen and Chen (2009)
Orange peel	300 and 700	6 h	Hydrophobic organic compounds (HOCs)	Chen et al. (2012c)

4.2 Techniques for Production of Biochar

The application of biochar in wastewater treatment and water purification is due to their inheriting characters including porous structure, high specific surface area, large pore volume, acid and alkali corrosion resistance, and rich functional groups. The preparatory conditions of biochar are crucial and should be chosen wisely depending on the type of biomass and intended properties and application. The characteristics of biochar and byproducts formed during the production depend on the process conditions such as temperature, heating rate, residence time, etc. These features influence the surface properties and porous structure of biochar (Wang et al. 2017).

In general, biochar production involved three processes including simultaneous carbonization, magnetization, and activation. Biochar has carbon-rich molecules depending on the organic content of the biomass and some specific characters including cation exchange capacity, large specific surface area, stable structure, and a large number of carbon sources. More than 200 scientific research articles were published about the production and application of biochar in the last decade (Wang and Wang 2019). There are several techniques for biochar production including pyrolysis, torrefaction, hydrothermal carbonization (HTC), gasification, and microwave carbonization. Among these methods, pyrolysis, HTC, and microwave carbonization are reported to be better due to ease of process controls, no requirement for drying steps, no hysteresis, rapid heating, and energy efficiency.

Pyrolysis is the most common method for the production of biochar. In this method, the organic materials are burned under high temperatures in inert atmospheric conditions and oxygen-free conditions (Selvam and Paramasivan 2021b; Selvam et al. 2021; Pathy et al. 2020a). This thermochemical process can be used to convert biomass into biochar, bio-oil, and syngas, whose composition depends on the range of operational conditions (Swagathnath et al. 2019b). Pyrolysis can be categorized as slow and fast pyrolysis corresponding to the heating rate. In slow pyrolysis (1–20 °C/min), the biochar is produced with high fixed carbon content and low minerals, making them suitable for carbon sequestration in soil. In addition, the composition of biochar produced in slow pyrolysis (35%) is much higher compared to fast pyrolysis (10%), where the bio-oil composition is considerably large (70%). The slow pyrolysis biochars are very stable in soil and contribute more to carbon sequestration. Decomposition of biomass during pyrolysis generally takes place between 200 and 500 °C and the carbon content increases with an increase in temperature. However, elements other than carbon like sulfur, nitrogen, oxygen, and hydrogen diminish at high temperatures (Vithanage et al. 2017).

Hydrothermal carbonization is another method of biochar production that uses low temperature to produce the biochar than pyrolysis. In this method, waste materials are converted into biochar under temperatures ranging from 150 to 375 °C with a residence time of 30 min. The operating conditions and product compositions are shown in Table 4.3. Mostly, hemicellulose and cellulose degrade at temperatures below 250 °C temperature (confirmed through FT-IR and ^{13}C NMR) and lignin

Table 4.3 Various techniques for biochar production and its process conditions (Tahir et al. 2020; Vithanage et al. 2017; Wang et al. 2020)

Production technique	Process conditions				Product composition (%)		
	Temperature (°C)	Oxygen	Heating rate	Residence time	Biochar	Bio-oil	Syngas
Fast pyrolysis	300–1000	Absent	High	Seconds	10	70	20
Slow pyrolysis	Low—350–550 High—600–900	Absent	Low	Seconds to hours	35	30	35
Hydrothermal carbonization	150–375	Presence	Low	Minutes to hours	60	30	10
Torrefaction	200–300	Absent	Low	Minutes to hours	85	10	5
Gasification	700–1200	Present	Moderate/high	Hours	10	5	85

degrades at high temperatures during hydrothermal carbonization (Ornaghi et al. 2020). Agricultural wastes are mostly used in hydrothermal carbonization to produce solid fuel (brown coal) and achieve maximum fuel (16.3 L CH_4/kg FM) (Oliveira et al. 2013). The biochar produced through HTC have high O-containing groups and render efficient cation exchange capacity. Though this method utilizes unconventional wet biomass, the energy consumption is very high as the carbonization depends on the moisture content of the biomass (Vithanage et al. 2017).

Microwave carbonization is also known as low-temperature pyrolysis that has a temperature ranging from 245 to 390 °C to burn waste materials (Selvam and Paramasivan 2021a) is an emerging technology where the carbonization efficiency is increased by combining with microwaves. Torrefaction is a form of slow pyrolysis technique, where the biomass is decomposed at relatively low temperatures (200–300 °C) for a high residence time. Biochar is obtained as a by-product in the first step of torrefaction, where the hemicellulose is decomposed into an unsaturated solid product. Gasification involves the production of high composition of syngas comprising of hydrogen, nitrogen, carbon dioxide, carbon monoxide, etc., at the expense of biochar and bio-oil. This technique is adopted mostly in energy sectors (Vithanage et al. 2017).

4.3 Biochar Properties for Potential Soil Amendment

Biochar possesses a large specific surface area, microporous structure, water, and nutrient retention capacity, high pH, and oxygen-containing surface functional groups that benefit the stabilization of heavy metals. Their properties solely regulate the mechanism and hence should be thoroughly analyzed before identifying the research needs. It is reported in the literature that biochar produced at higher pyrolytic temperatures has shown better adsorption capacities for Cd and Zn (Chatterjee et al. 2020). However, at very high temperatures, there is a loss of oxygenated functional groups which can reduce the cation exchange capacity of the biochar. Though its agronomic value is determined by the nutrient concentration of biomass, temperature >750 °C has a significant undesirable effect on the adsorption capacity of biochar (Domingues et al. 2017).

Ultimate and proximate analyses assist in evaluating the agronomical potential of biochar. The high ash content of biochar can be used to predict the presence of alkaline compounds such as $CaCO_3$ and $KHCO_3$ which can act as liming agents for improving the soil condition (especially acidic soils) and improve nutrient availability, irrespective of its pH. This characteristic has to be considered when correction of soil acidity is attempted. High ash content can be positively correlated with the chemical and nutrient composition of biomass. In addition, such biochars exhibit the high cation exchange capacity necessary for enhancing the nutrient and water retention capacity in soil (Domingues et al. 2017; Pathy et al. 2020a).

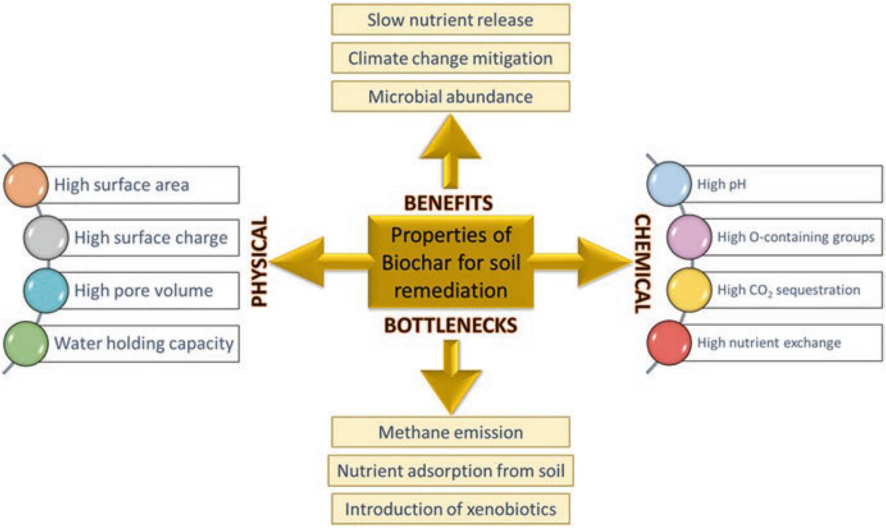

Fig. 4.1 Physical and chemical properties of biochar for potential soil amendment

Biochar produced at higher temperatures gets mineralized at a higher rate when applied to the soil. The carbon fraction of the biochar stimulates the decomposition of organic matter due to the presence of volatile materials. The magnitude of these materials helps in the evaluation of nitrogen cycling and carbon bioavailability in biochar. Conversely, biochar synthesized at low temperatures (300–450 °C) contains high aliphatic character making them susceptible to degradation by microbes in the soil. As a result of this, the duration of metal immobility decreases (Li et al. 2019; Rodriguez et al. 2020). Some of the inherent physical and chemical properties of biochar for efficient heavy metal remediation are depicted in Fig. 4.1.

4.4 Interaction of Biochar and Heavy Metals

Biochar is an organic substance that can uptake heavy metals and reduce their harmful effect in the contaminated soil environment. The functional groups of biochar responsible for this effect depend on the type of feedstock used and influence the surface charge to determine the adsorption of transition and non-transition metals. Biochar can interact with heavy metals and transform them from natural species to stable species in soil. The mechanism of action involves adsorption, ion exchange, redox reactions, volatilization, methylation/demethylation, precipitation, and complexation to abate the mobility of contaminants and ensure the bioavailability of metals. If the pH of biochar is greater than that of the soil, then there are higher chances of metal immobilization. This condition is more suitable for acidic soils where the solubility is comparatively higher (Gao et al. 2020; Yu et al. 2020).

In general, heavy metal remediation by biochar occurs through two different mechanisms: direct mechanism and indirect mechanism. In direct mechanism, biochar immobilizes the heavy metal components through chemisorption, physisorption, electrostatic attraction, complex formation, and precipitation. In indirect mechanisms, the application of biochar contributes to the soil environment by increasing soil pH, microbial biomass, organic carbon, water holding capacity, and nutrient use efficiency (Beesley et al. 2015).

4.4.1 Direct Mechanism

Biochar removes heavy metals from the contaminated soil environment through several types of mechanisms. In physisorption, the heavy metals are absorbed through the large surface area, porosity, and diffusion movements of biochar. Biochar has a large surface area with well-distributed pores such as micropores (<2 nm), mesopores (2–50 nm), and macropores (>50 nm) to adsorb the heavy metals. On the other hand, biochar can also adsorb via chemisorption (electrostatic attraction, ion exchange reaction, complex formation, and precipitation). Biochar has a negative surface charge due to the presence of a functional group. The electronegativity of biochar helps in attracting positive heavy metal ions due to the electrostatic attraction. The surface charge becomes more negative at higher pH and could facilitate more interaction between biochar and heavy metals (He et al. 2019). Biochar can release cations, such as Ca(II) and Mg (II), which got to exchange with the positive metal ions, and in this manner, metal got adsorbed onto biochar surface. The cation exchange capacity (CEC) determines the amount of cation being exchanged (the corresponding amount of HMs will get adsorbed), and hence biochar having a higher CEC value is desirable for maximum heavy metal adsorption. It was observed that biochar derived from animal biomass have a higher amount of Ca and hence they have a higher CEC value as compared to plant biomasses (Lei et al. 2019). Complexation is one of the important mechanisms that form the multiatom structures (complexes) with specific metal–ligand interactions. Biochar has a diverse function group on them which can immobilize the heavy metals by forming metal complexes. Some of the groups that drive the complex formation on biochar surface are –OH, –COOH, –C=O, and –C=N. Moreover, higher content of Fe(II), Mn(II), and carbonate in biochar helps in an increased amount of complex formations. Similarly, inorganic components such as Si, S, and Cl also play an important role in forming complexes with metal ions (Tan et al. 2017). Biochar has mineral elements in them, these elements interact with biochar and got precipitated on the surface. This is another mechanism via which the biochar immobilizes the heavy metals onto them (Xiao et al. 2020).

4.4.2 Indirect Mechanism

Instead of interacting directly with the heavy metals biochar can impact the soil's chemical properties which consequently enhance the heavy metal immobilization. When biochar is amended in the soil it increases the soil's pH. This leads to several reactions such as hydrolysis of HM, increased HM complex formation, and oxidation of residual fraction of HMs (Duan et al. 2017). These reactions help in metal immobilization. Similarly, biochar application in the soil increases its CEC, and that consequently enhances its metal adsorption capacity. It was also reported that minerals present in the biochar get transferred to soil, these minerals interact with metal ions and form complexes, and reduce their bioavailability (Rees et al. 2014). Biochar application in the soil also improves soil organic carbon content, this results in complex formation between metals and an oxygen-containing group of biochar. In this way, the heavy metals get converted to a less mobile fraction (organically bound fraction) in the soil and become unavailable for plant uptake (Abdelhafez et al. 2014). The most prominent mechanisms by which biochar removes heavy metals are shown in Fig. 4.2.

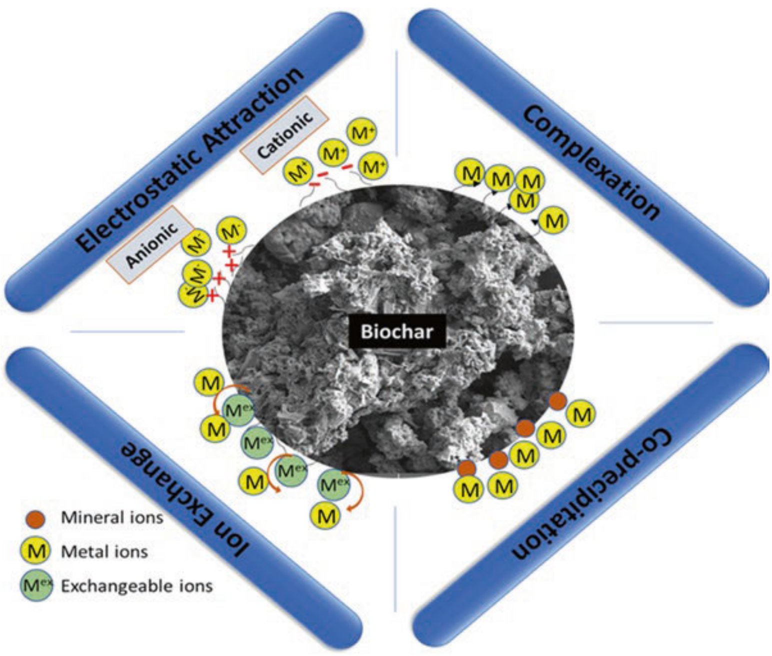

Fig. 4.2 Mechanisms of action behind heavy metal remediation by biochar

4.5 Modifications of Biochar for Enhanced Heavy Metal Removal

Biochar produced from different feedstocks exhibits different physicochemical properties, which also intend to change with respect to operational conditions such as the method of biochar production, temperature, heating rate, and time. The functional groups present on the surface of biochar that are solely responsible for adsorption and remediation of heavy metals from contaminated soils are highly influenced by the temperature at which the biochar is produced. For example, C–O–C, –OH, C=O, and $–CH_2$ were prevalent at moderate temperatures, whereas, only C=O and C=C were preserved at higher temperatures (Wang et al. 2021a). Also, at higher temperatures, the presence of oxygen-containing groups on the surface decreases corresponding to a decrease in adsorption of heavy metals ions (Ambaye et al. 2020). Biochar produced at lower temperatures has lower pH and high cation exchange capacity, making them suitable for soil with high pH and poor fertility (Tahir et al. 2020; Domingues et al. 2017). There are several other factors that determine the adsorption capacity of heavy metals on biochar, leading to decreased efficiency of remediation. In adverse cases, the biochar produced might not be functional enough to remove heavy metals from soil (Wang et al. 2021a). These scenarios call for the development of pretreatment modifications to improve the surface properties of biochar for enhanced remediation.

The modifications rendered on biochar can be physical (choice of feedstock, temperature, time, etc.) or chemical (acid/base treatments, steam, magnetization, impregnation of minerals, etc.). It can also be pre- or post-preparation of biochar. Magnetic biochar produced by Wang et al. (2021) with iron-based modification was found to be effective for simultaneous removal of As, Pb, and Cd. Magnetization was also induced by coprecipitation of Fe^{2+}/Fe^{3+} on orange peel powder prior to pyrolyzing the biomass (Tang et al. 2013). It was also confirmed that sulfur-based modifications can offer long-term and stable remediation of Hg in soil. The sulfur medium can be thiols, sulfur dioxide, or carbon disulfide and the immobilization takes place formation of hydrogen sulfide on the surface. However, this condition holds only in aerobic conditions, other than which the hydrogen sulfide molecules will be assimilated by sulfate-reducing bacteria (O'Connor et al. 2018). Oxidization of biochar with agents like sulfuric acid or hydrochloric acid rendered more carboxylic groups on the surface demonstrating higher entrapment of Cu, Pb, and Zn (Tang et al. 2013). Almost 100% remediation of copper and cadmium was achieved when biochar produced from switchgrass by HTC was treated with alkali. In advanced cases, a combined modification strategy was applied to enhance the surface area of biochar, followed by heavy metal immobilization. Treatment with sodium hydroxide has been reported to improve the surface area of produced biochar, after which the latter was modified with hematite for incorporating good adsorption capacity of heavy metals (Pan et al. 2021).

4.6 Applications of Biochar

Biochar is one of the best materials that are derived from woody biomass and crops residues for the removal of pollutants from the contaminated environment (Cheng et al. 2020). They have some unique features including large specific surface area, porous structure, and surface functional groups to remove the pollutants from the contaminated environment (Swagathnath et al. 2019a). Scientific research literatures on biochar focused on the removal of pollutants from the contaminated environment such as heavy metal removal (46%), removal of organic pollutants (39%), removal of nitrogen and phosphorous (13%), and other pollutants (2%) (Tan et al. 2015). The biochar production was mainly used to improve soil properties, crop production, and remediation enhancement of polluted environment (including remediation of heavy metals, remediation of organic pollutants, pesticide removal from soil environment, and remediation of other pollutants) (Chen et al. 2020b; Lebrun et al. 2021). The biochars have been widely used in various fields of soil environment including soil physical health alternation, soil acidity management, crop yield and production enhancement, soil micronutrients mineralization, soil quality and fertility restoration, nutrient retention and sorption, sequester soil carbon, soil chemical properties modifications, influence plant physiological parameters, and increased water availability. It can enhance the properties of the soil including soil microbial biomass carbon, phosphorus, nitrogen, carbon mineralization, and various enzymatic activities (Das et al. 2020). The biochar technology has been used in wastewater management to remove the pollutants from water due to its benefits including cost-effectiveness, high specific surface area, and surface reactive groups (Wei et al. 2018).

4.7 Advantages and Disadvantages of Biochar

Biochar production has a lot of advantages including recovery of components, water, and energy and efficiency enhancement strategies for resource recovery and removal of pollutants from the contaminated environment (Ye et al. 2020). Biochar production is a carbon-negative process that has additional benefits including nutrient retention, high stability against decay, the high adsorption capacity of carbon-oxygen complexes, and high capacity to adsorb cation per unit of carbon. At the same time, some of the issues were found in biochar technology including limiting nutrients and amount of C in soil, soil acidity, microbial activity, and low NPK compared to commercial fertilizers. The biochar production from wastes was beneficial for a few fields including clean water and sanitation, industry innovation and infrastructure, responsible consumption and production, climate action, and land on life. Biochars are also effective in removing organic contaminants (phenol, pesticides, and dyes) and inorganic contaminants (As, Pb, and Cd) from contaminated environments.

4.8 Toxic Compounds Present in Biochar

However, there exist certain risks associated with biochar amendments in the soil. For instance, the thermal degradation of biomass could lead to the generation of harmful compounds such as perfluorochemicals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/F), and volatile organic compounds (VOCs) (Godlewska et al. 2021). Although the presence of these chemicals in biochar is not common and primarily depends on the feedstock selections and pyrolytic conditions, the potentially harmful effect cannot be avoided completely. When the biochar is amended into the soil, these compounds can leach into the soil from biochar, subsequently entering into the food chain. The harmful effect on humans includes disruption of the endocrine system, which results in oxidative stress, apoptosis, and many of them are carcinogenic in nature (Weidemann et al. 2018). Hence, it becomes highly crucial to check the presence of these harmful chemical compounds in biochar before applying them in the field. Hence, it becomes highly crucial to understand the reason behind the toxicity of the biochar to choose biochar that will not contaminate the land on its application.

For PAHs, both the choice of biomass and the experimental conditions determine its concentration in biochar. For instance gasification results in more PAHs than any other thermos chemical technique. Moreover, in pyrolysis itself, a faster heating rate (Fast pyrolysis) produces more PAHs than that of a slower heating rate (slow pyrolysis). It was also observed that when N2 is used as a carrier gas instead of CO_2, it results in a higher amount of PAHs in the biochar. Biochar having a lower surface area could have higher bioavailable PAHs, as it will be limited adsorption sites that bind with the generated PAHs (Visioli et al. 2016). Similarly, it has been also observed that biochar produced from green garden waste contains more PAHs as compared to other biomasses. PCDD/F in biochar presents in an insignificant quantity; however, their presence becomes significant in the biomasses having higher chlorine content (i.e., food wastes). Hydrochar was observed to have higher PCDD/F content as compared to biochar because the former was produced at a lower temperature, which was not sufficient to degrade the generated PCDD/F (Hilber et al. 2017). On a similar note to reduce the amount of VOCs biomass needs to be highly carbonized and a slightly aerobic condition will reduce the concentration of VOCs in the biochar. And lastly, the presence of certain heavy metals (such as Pb, Cd, Hg) could also posses a challenge. It was reported that biochar produced from sewage sludge has a higher heavy metal concentration. Moreover, biomass collected from heavy metal contaminated sites could also result in a higher concentration of heavy metal in the biochar (Godlewska et al. 2021). It is also important to note that most of the toxic pollutants present in the biochar are not immediately bioavailable; however, a cautious approach needs to be adopted to evaluate biochar before applying it in the field.

4.9 Conclusion and Future Prospects

The use of biochar as a soil amendment is emerging considering its beneficial characteristics like surface area, pore volume, high pH, nutrient, and water retention capacities. This chapter provides an overview of the production methodologies, properties, and mechanisms involved in the adsorption of heavy metals. Soil remediation with biomass is a fast-growing field with the introduction of novel techniques to improve removal efficiency in a sustainable way. Some of the further perspectives of this research are given below:

- Co-pyrolyzed biochar from biomass and orthophosphate has been shown to be very effective against the adsorption of heavy metals such as Pb, Cu, and Cd. The biochar was able to complex, immobilize, and precipitate the metals due to the presence of phosphate and hydroxyl groups on their surface. Further research is needed to evaluate the role of surface carboxyl groups on the enhanced complexation of heavy metals.
- Biochar is being used as microbial immobilized carriers for abating PAHs using immobilized microorganism technology (IMT). This technology can couple bioremediation and bioaugmentation for complexing and degrading such high molecular weight compounds. Hence, attention should be paid to this emerging technology.
- Once biochar is applied to soil, they interact with heavy metals, organic and inorganic compounds in soil and hence it is important to understand the mechanism and changes in biochar properties with time. This would enable the utilization of biochar in crop productivity for a prolonged duration. The properties of biochar play a chief role in defining the environmental effect and delineating the direction for future use.
- Based on the selection of biomass and the experimental conditions biochar's properties can vary widely, and hence it becomes crucial in determining biochar's interaction with heavy metals. For instance, pH, CEC, and the presence of diverse functional groups affect the mechanism and potential of biochar in immobilizing the heavy metals from soil.
- Biochar's interaction with heavy metals can be broadly classified into two mechanisms; direct and indirect. In direct mechanism, biochar immobilizes the pollutants via electrostatic force, ion exchange reactions, complex formation, and precipitations. Whereas, in the case of indirect mechanism the biochar impacts the soil properties such as pH, soil CEC, mineralization of heavy metals, and soil organic carbon content thus affecting biochar's heavy metals uptake potential.
- To achieve the desired physicochemical characteristics necessary to remove heavy metals, biochar is being modified/engineered through various methods. Biochar can be modified chemically by treating it with various chemicals (based upon the requirement). A large number of current research is being focused on developing novel treatment methods for improving biochar metal removing properties. However, in certain cases, the modification techniques become either

chemical-intensive or economically costlier. Hence, future studies should address this challenge while developing various modification techniques.

- Most of the studies have been carried out on the laboratory scale and a limited number of studies have been undertaken in the field. Hence, more studies need to be done at the field level to understand the difficulties faced in scaling up the process. Moreover, attention should be given to carrying out the techno-economic assessments for the overall process, and thus it could be acceptable at an industrial level.

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