

Bioremediation

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Bioremediation

Green Approaches for a Clean and Sustainable Environment

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Preface

Environmental issues have been at the forefront of sustainable development and have become a serious matter of concern in the twenty-first century. Environmental sustainability with rapid industrialization is one of the major challenges of the current scenario worldwide. Industries are the key drivers of the world economy, but they are also the major polluters of environment due to the discharge of partially treated/untreated toxic and hazardous wastes containing organic and inorganic pollutants, which cause severe environmental (soil and water) pollution and toxic effects in living beings. Among the different sources of environmental pollution, industrial wastes are considered as the major source of environmental pollution because industries use cheap and poorly or non-biodegradable chemicals to obtain products of good quality within a short period of time and in an economic way; however, their toxicity is usually ignored. The untreated/partially treated wastewaters discharged from various industries contain potentially toxic and hazardous organic and inorganic pollutants, which cause the pollution of soil and aquatic resources including groundwater and severe toxic effects in humans, animals and plants.

The governments around the globe are strictly advocating the development of efficient treatment technologies to mitigate the environmental pollution and health threats. Hence, the adequate treatment of industrial wastes to degrade/detoxify pollutants is of utmost importance for environmental safety and for promoting the sustainable development of our society with low environmental impacts. The removal of a wide range of pollutants from contaminated sites requires our increasing understanding of different degradation pathways and regulatory networks to carbon flux for their degradation and detoxification. Therefore, this book will provide a comprehensive knowledge about the fundamental, practical and purposeful utilization of different treatment technologies for the treatment/management of industrial wastes. This book will describe the microbiological, biotechnological, biochemical and molecular aspects of various treatment technologies, including the use of 'omics' for the development of effective treatment technologies for industrial wastes/pollutants to combat the forthcoming challenges.

This book is mainly focused on the various treatment technologies such as integrated treatment approaches, in situ/ex situ bioremediation, nano-bioremediation, biofilm formation, composting, microbe-assisted bioremediation, role of advanced biotechnological tools and techniques in bioremediation process and application of nanomaterials in the removal/treatment of organic/inorganic pollutants from industrial wastewaters/contaminated sites along with their ecotoxicological effects on the environment as well as human/animal health.

For this book, many relevant topics have been contributed by the experts from different universities, research laboratories and institutes across the globe in relevant fields. Researchers working in the field of waste treatment/management and related fields for a clean and green environment will find this compilation most useful for further study to learn about the subject matter.

This book will be of great value to researchers, environmental chemists and scientists, microbiologists and biotechnologists, ecotoxicologists, waste treatment engineers and managers, environmental science managers, administrators and policy makers, industry persons and students at bachelor's, master's and doctoral levels in the relevant field. Thus, in this book, readers will find the updated information as well as the future directions in the field of waste treatment/management for a clean and green environment.

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Lucknow, Uttar Pradesh, India

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5

Reducing Heavy Metal Toxicity using Biochar as a Naturally Derived Adsorbent

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5.1 Introduction

Heavy metals are highly hazardous, non-biodegradable elements which bioaccumulate in food webs. Their occurrence in waters or soils may cause threat to environmental and human well-being even at relatively low concentrations (Agrafioti et al. 2014). Growing industrialization and extensive agricultural activities have led to severe heavy metals incidences in recent years. Pb and Cd are non-essential elements for living organisms, which are carcinogenic even in low quantity, and are usually sourced in industrial wastewater from mining, smelting, electroplating and petrochemical production (Rai et al. 2019). The prescribed drinking water guidelines by the World Health Organization (WHO) and the American Water Works Association (AWWA) are 0.05 mg/L for Pb and 0.005 mg/L for Cd, respectively. Dumping of heavy metals directly or indirectly into soils and waters causes momentous risks to environmental sustainability.

Various methods have been adopted for the treatment of contaminated water, including electroplating, ion exchange, reverse osmosis, precipitation and membrane processes (Inyang et al. 2016). Adsorption is a commonly used technique for heavy metal remediation from wastewater. Biosorption using retro-applied organic materials is an ecologically friendly and cost-effective method, as biosorbents are environmentally safe and easily available in large quantities. Agricultural by-products with suitable changes may prove handy as active adsorbents for the removal of heavy metals from wastewater.

The accumulation of heavy metals is increasing, which affects water and soil quality and has emerged as a food safety risk. Several potent approaches have been suggested for heavy metal remediation from water and soil, which includes (i) phytoremediation, (ii) physical remediation, (iii) chemical remediation and (iv) bioremediation (Wang et al. 2015a). The residue obtained from biomass has been used for heavy metal remediation and has received worldwide attention because of its environment-friendly nature, low cost and easy availability. Biochar is a material with abundant prospective applications, but the properties of biochar can be altered by many factors.

5.2 Heavy Metals

Heavy metals are well defined as naturally occurring elements that are characterized by relatively high density compared to water (5 g/cm³ or five times greater than water) and high atomic mass. Heavy metals are also broadly classified as the elements that have an atomic number greater than 20 and atomic mass higher than 23. They are usually metallic elements found in the earth's crust and present in different environmental matrices in trace amount and thus are also called trace elements. Some physical phenomena such as temperature, phase association, adsorption and impounding influence the bioavailability of heavy metals.

Various chemical and biological factors such as thermodynamic equilibrium, complication mechanisms, lipid solubility, octanol/water partition coefficients, species characteristics, trophic interactions and biochemical/physiological variation also influence their bioavailability. The United States Environmental Protection Agency (USEPA) and the International Agency for Research on Cancer (IARC) also categorize them as possible human carcinogenesis promoter on the basis of epidemiological

and tentative studies that have displayed a link between cancer and heavy metals exposure in humans and animals. Various heavy metals such as Co, Se or Zn are essential trace elements and have an imperative role in the human and plant metabolism. They are components of numerous significant enzymes and play a vital role in several redox reactions (Stern 2010). Co is one of most common examples of essential trace elements present as an essential cofactor in some oxidative stress-related enzymes such as catalase, superoxide dismutase, peroxidase and cytochrome oxidases (Al-Fartusie and Mohssan 2017).

Similarly, other essential trace elements are also mandatory for different biological metabolisms; on the other hand, a higher concentration of metals is also involved in the cellular and tissue injury, leading to various diseases. Some other heavy metals do not show any biological significance and include non-essential heavy metals such as aluminium (Al), antimony (Sb), arsenic (As) and barium (Ba). Many heavy metals also possess very well hi-tech implications, such as iron (Fe), zinc (Zn), tin (Sn), lead (Pb), copper (Cu) and tungsten (W). Some are also a part of bioinorganic catalysis and play an important role in novel chemical transformations (Chellan and Sadler 2015). Additionally, some heavy metals are valuable and expensive, such as gold (Au), silver (Ag), iridium (Ir), rhodium (Rh) and platinum (Pt) (Seehra and Bristow 2018). Besides these, many such as mercury (Hg), cadmium (Cd), arsenic (As), chromium (Cr), thallium (Tl) and lead (Pb) are recognized as the dark side of chemistry. They show high toxicity even at lower concentration (Koller and Saleh 2018).

5.2.1 Sources of Heavy Metals

Heavy metals are widely spread contaminants found in terrestrial and freshwater ecosystems. They usually occur naturally in the earth's crust. Natural and anthropogenic activities are two probable routes that can derive heavy metals, including different environmental components such as air, water, soil and their interface. Unlike organic pollutants which ultimately break down to carbon dioxide and water, heavy metals persist in environment and assimilate in different environmental components such as air, water and soil. They can also be transported from one component to another. The concentration of heavy metals in environment is assessed by its source, adsorption or precipitation. The degree of adsorption depends upon the various physicochemical characteristics of the environment, such as water pH, hardness and redox potential as well as the presence of other such metals.

5.2.1.1 Natural Routes

Many natural sources of heavy metals have been recognized by different studies. Under the diverse environmental circumstances, natural emissions of heavy metals take place by rock weathering, volcanic eruptions, biogenic sources, forest fires, wind-borne soil particles and sea-salt sprays, out of which weathering is a well-known source of metals responsible for their widespread distribution to diverse environment components. Heavy metals exist in diverse forms such as oxides, sulphides, hydroxides, phosphates, sulphates, silicates and also as components of various organic compounds.

5.2.1.2 Anthropogenic Routes

Anthropogenic sources are associated with industrialization as atmospheric deposition, waste disposal, waste incineration, urban effluents, traffic emissions, fertilizer application and long-term application of wastewater in agricultural lands. Metals discharged in wind-blown dirt are frequently reported from industrial regions. Various key anthropogenic sources that considerably participate to heavy metal pollution of various environment sections include automobile emissions, which mainly emit Pb, smelting and insecticides processes, which mainly emit As, Cu and Zn, and combustion of fossil fuels, which emits Ni, V, Hg, Se and Sn. Many human activities also add significantly to environmental deterioration (He et al. 2005) (Figure 5.1).

5.2.2 Effects of Heavy Metals

Heavy metals can also cause cellular and tissue damage in various biological systems, mainly affecting nucleus, mitochondria, cell membrane, endoplasmic reticulum, lysosome and several enzymes

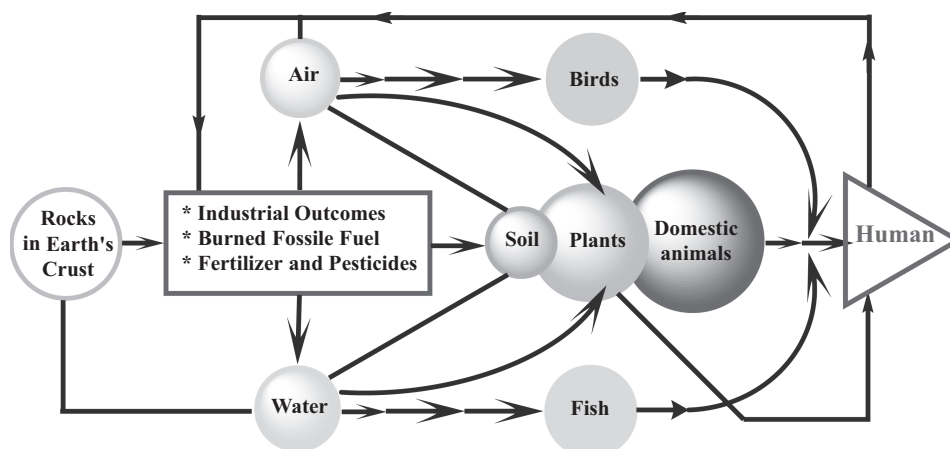


FIGURE 5.1 Sources and general environmental cycle of heavy metals.

responsible for detoxification, metabolism and damage restoration (Yedjou and Tchounwou, 2007). Metallic ions are believed to interact with DNA and nuclear proteins and lead to DNA damage and change the cell cycle inflection, carcinogenesis or apoptosis (Tchounwou et al. 2004). A number of studies have confirmed that the production of reactive oxygen species (ROS) as well as oxidative stress (OS) plays a vital role in the toxicity and carcinogenicity of heavy metals such as As, Cd, Cr, Pb and Hg. These five metals show high toxicity in low concentration; thus, EPA has categorized them as the most toxic heavy metals or priority pollutants (Figure 5.2).

5.2.2.1 Heavy Metal Pollution of Water

In water sources, heavy metals can be found in limited amounts, due to very high toxicity; still, they cause severe health problems in living organisms (Lawrence and Khan 2020). All heavy metals have their specific toxicity concentration that depends on the entities which are exposed to it. Water systems are polluted by various contaminants, but urbanization and industrialization are leading causes of the acceleration of heavy metal water pollution. Heavy metals are mainly transported through the run-off from urban, municipal and industrial areas. Surface and ground waters are mainly polluted by the direct release of untreated industrial wastes into the water system. Heavy metal contamination of sediments is a globally significant concern for aquatic animals as well as human health. In the aquatic system, sediments are the core site of metals and represent the extent of water pollution. In sediments, many physicochemical factors such as temperature, particle size, redox state, organic content, hydrodynamic state, microorganism and salinity affect the adsorption, desorption and consequent concentrations of heavy metals, and their distribution is also influenced by the chemical composition of the sediments, such as particle size and total organic content (TOC) (Ali et al. 2019). pH is another significant factor for the determination of bioavailability of heavy metals in sediments. Lower pH indicates higher risk of pollution.

5.2.3 Heavy Metals Toxicity

As, Cd, Pb, Cu, Hg, Cr and Zn are all included in the list of priority toxic pollutants and toxic trace metals, and these are the highest toxic heavy metals in the environment. They cause high toxicity in various environmental constituents, including water, air, soil, plants, animals and wildlife. Due to natural and anthropogenic activities, heavy metals are released and cause pollution in water system, sediments and soils. Various factors such as physicochemical and climatic properties affect the biogeochemical cycling and global dynamics of heavy metals in the environmental system. In toxicological investigation, the general mode of uptake of heavy metals is found to be inhalation, ingestion and dermal absorption.

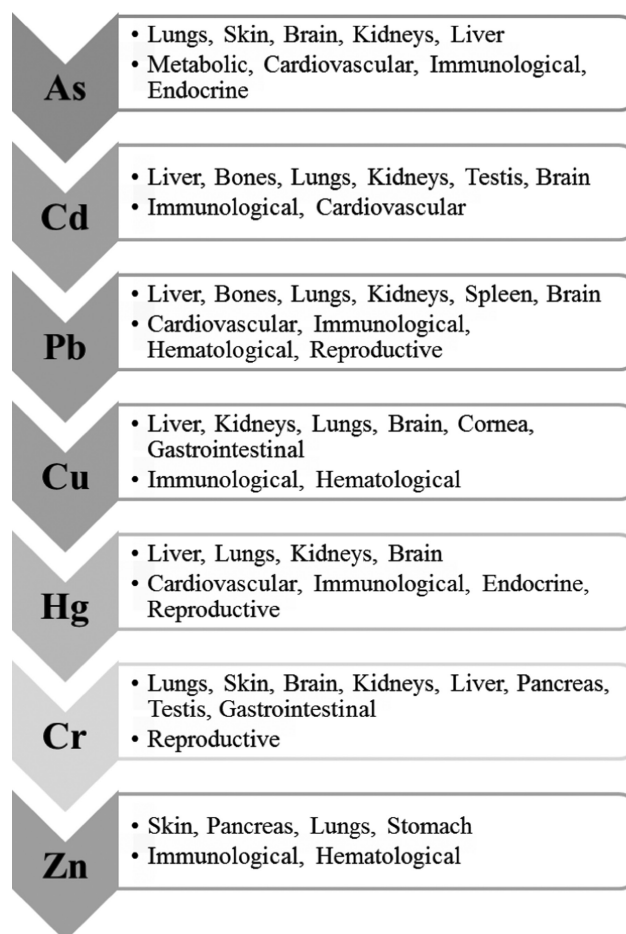


FIGURE 5.2 Impact of heavy metals on the biological system.

In the living organism, absorption occurs through active or passive diffusion (Tchounwou et al. 2012). Numerous factors such as gender, age, method of exposure, different susceptibilities and time interval of contact are used to determine the health risks posed by these heavy metals. The contaminated water affects every living being. Human beings are more susceptible to severe health hazards because of the greater uptake of heavy metals in the food chain (Jaishankar et al. 2014).

In general, source route of heavy metals in the body of an organism is directly from the environmental system including soil, sediments and water or enter through its food/prey, the entry route in the body of organism from water or sediments through the gills/skin and by alimentary canal. In the food chain, the concentration of heavy metals may vary with consecutive trophic levels. In the body of an entity, the accumulation of heavy metals relies on a lot of reasons such as the concentration of metals, physiological mechanisms involved in homeostasis, detoxification and regulation of the heavy metals.

5.3 Toxicity Mechanism of Heavy Metals

The exact mechanism through which heavy metals exert hazardous effects is not known; still, it has been found that metals cause oxidative stress, inflammation and changes in the immune response. In the earth, some heavy metals are known as essential heavy metals due to their noteworthy part

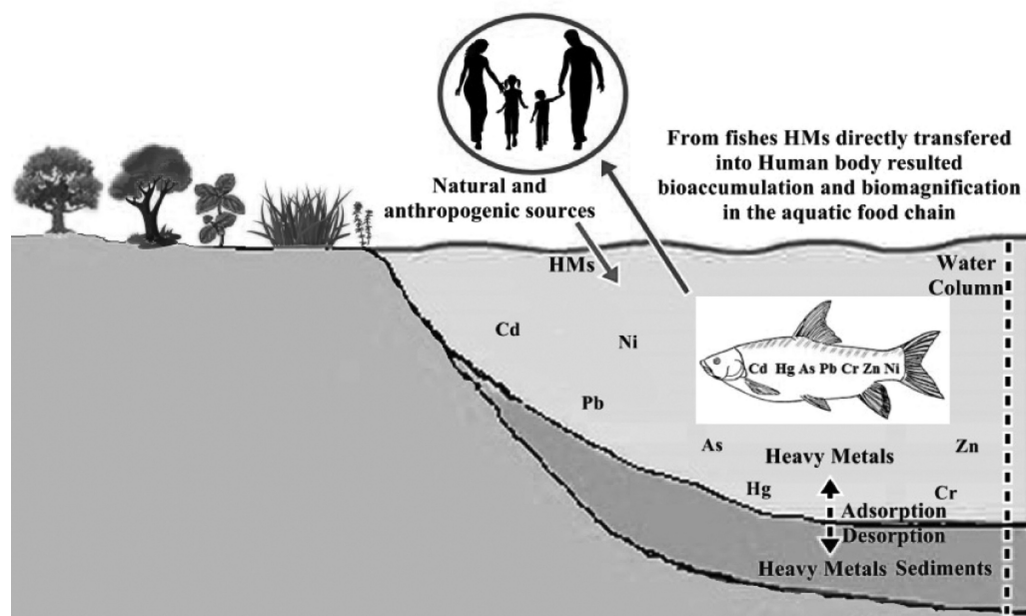
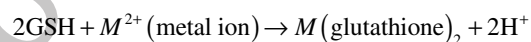


FIGURE 5.3 Transfer of heavy metals from freshwater fish to humans.

in the ecological systems, and the toxicity is based on duration and dose. Non-essential heavy metals such as Pb, Hg and Cd and metalloids such as As are highly toxic even at low exposure; on the contrary, in the development of the body, essential heavy metals are needed in trace amounts, but when their concentration crosses the threshold limits, they become toxic. For some heavy metals, a marginal difference is found between the essentiality and toxicity. Many heavy metals are tumorigenic, carcinogenic and mutagenic due to the formation of ROS that lead to the development of induced oxidative stress. Furthermore, they cause several diseases and abnormalities. Heavy metals are well known as metabolic poisons. The toxicity is mainly attributed to the primary interaction with sulphhydryl (SH) enzyme systems and its inhibition. Glutathione (GSH) is a significant antioxidant in the body and heavy metals interact with SH and replace H atoms on two adjacent GSH molecules that lead to the formation of a strong bond and thus GSH and heavy metals form an active complex (Figure 5.3).



5.4 Biochar: Composition and Sources

Pollutants can be removed effectively by adsorption, which is an effective physical phenomenon. Silica gel, activated carbon and aluminium oxide are some of the common adsorbents. Biochar is a black substance containing carbon. It is porous in nature, and because of the porosity and presence of several functional groups such as carboxyl, hydroxyl and phenolic groups, biochar has a robust binding potential for inorganic and organic compounds present in the environment (Park et al. 2011). Biochar is usually produced from the thermal degradation of cellulose-rich biomass waste from agriculture and forestry, such as plant residues, wood waste, peat, cattle manure, which are carbon rich. The steady carbon framework of the biochar supplements it with fascinating properties and capacity to trap water, air, metals and organic moieties. Temperature plays a pivotal role in the characterization of biochar. Biochars obtained by pyrolysis at high temperatures have a high surface area and microporosity and decreased molar H/C

and O/C ratios required for the sorption of organic contaminants. On the other hand, biochars obtained at low temperatures are energy-saving and suitable for the remediation of inorganic contaminants as they are rich in oxygen-containing functional groups (Zhang et al. 2015). Biochar has a tendency to act as a sorbent for metals such as Cd, Pb, Cr and Hg from soil as well as water through exchangeable ions or by complexation with functional groups. The metals can also be leached through physical adsorption and surface precipitation (Li et al. 2017). Wood biochar is a potent adsorbent because of its efficient porosity (from 10 to 3,000 μm) and specific area (from 5 to 600 m^2/g). Several factors including organic groups, inorganic materials and cations of biochar influence the metal sorption. Physical characteristics such as surface area are also responsible for the sorption of metals (Khan et al. 2016). As adsorbent, activated carbon has been used frequently, but biochar is a relatively cheap alternative for heavy metal remediation from the environment.

5.4.1 Synthesis of Biochar

Biochars are mainly produced by pyrolysis. During the process, some vital trace elements found in plants become part of the carbon structure; therefore, they are not leached and become accessible to plants via root exudates and microbial symbiosis. Because of the ability of biochars to serve as a carrier for plant nutrients, they may be used to synthesize organic fertilizers by mixing with molasses, ash, slurry, etc. Various organic chemicals are also formed during pyrolysis. Some of them get trapped in the pores and surfaces and may stimulate a plant's immune system, thereby increasing the resistance to pathogens. Some of the biochars have been obtained from plant roots. *Eichhornia crassipes* roots have proven as a source of biochars, which have been obtained by the pyrolysis of root powder in a muffle furnace under O_2 -limited conditions at 200°C–500°C (Li et al. 2018).

Pyrolysis depends upon the time, temperature of the pyrolytic material, pressure, size of adsorbent, heating rate and methods such as burning of fuel, electrical heating or by microwaves. In slow pyrolysis, oxygen-free feedstock biomass is transferred to a pre-heated kiln or furnace. Fast pyrolysis depends on fast heat transfer, at less than 650°C with a high heating rate (100–1,000°C/s). The characteristics of biochars are influenced by the extent of pyrolysis (pyrolytic temperature and residence pressure) and by biomass size and kiln or furnace residence time (Meyer et al. 2011). Residence time determines the rate at which volatile gases are removed from the furnace. Chances of secondary reactions on the biochar surface increase with the increase in residence time. Scots pine (*Pinus sylvestris* L.) among coniferous trees and silver birch (*Betula pendula*) among deciduous trees have been selected for their local availability and cost-effectiveness, and the prevalence has been obtained from potentially clean areas as wood biomass materials for biochar production. The tree selection had been done on the basis of similarity in age, and the materials are collected from low pollution concentration areas (Komkiene and Baltreinaite 2016).

Four types of biochars were produced upon pyrolysis on different temperatures, viz. 450°C \pm 5°C and 700°C \pm 5°C, for varying time periods. The four different biochars were: (i) Scots pine biochar produced at slow pyrolysis; (ii) Scots pine biochar produced at fast pyrolysis; (iii) silver birch biochar produced at slow pyrolysis; and (iv) silver birch biochar produced at fast pyrolysis. Some new biochars from the leaves of *Tectona* and *Lagerstroemia speciosa* have been obtained at 800°C, which have been used for the remediation of As(III) and As(V) from water solution. The biochar material was crystalline in nature and was identified by using scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, Brunauer–Emmet–Teller (BET) method, Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), zeta potential, particle size and X-ray photoelectron spectroscopy (XPS) (Verma and Singh 2019). Soil stabilization is one of the most efficient methods for the leaching of heavy metals from the soil. Soil stabilization is considered as a sustainable remediation approach (O'Connor et al. 2018) (Figure 5.4).

Usage of only biochar cannot compulsorily decrease heavy metal bioavailability as dependent on the soil texture and nature of contaminants due to limited adsorption mechanisms. Some modifications have been made to improve the adsorption capacity, including chemical, physical and magnetic modifications and impregnation with mineral sorbents (Rajapaksha et al. 2016). A MgO-coated corncob biochar was produced and used in a lead-laden soil. Magnesium oxide (MgO), having a high potential for soil stabilization (Shen et al. 2019), was anticipated to potentially increase the immobilization of

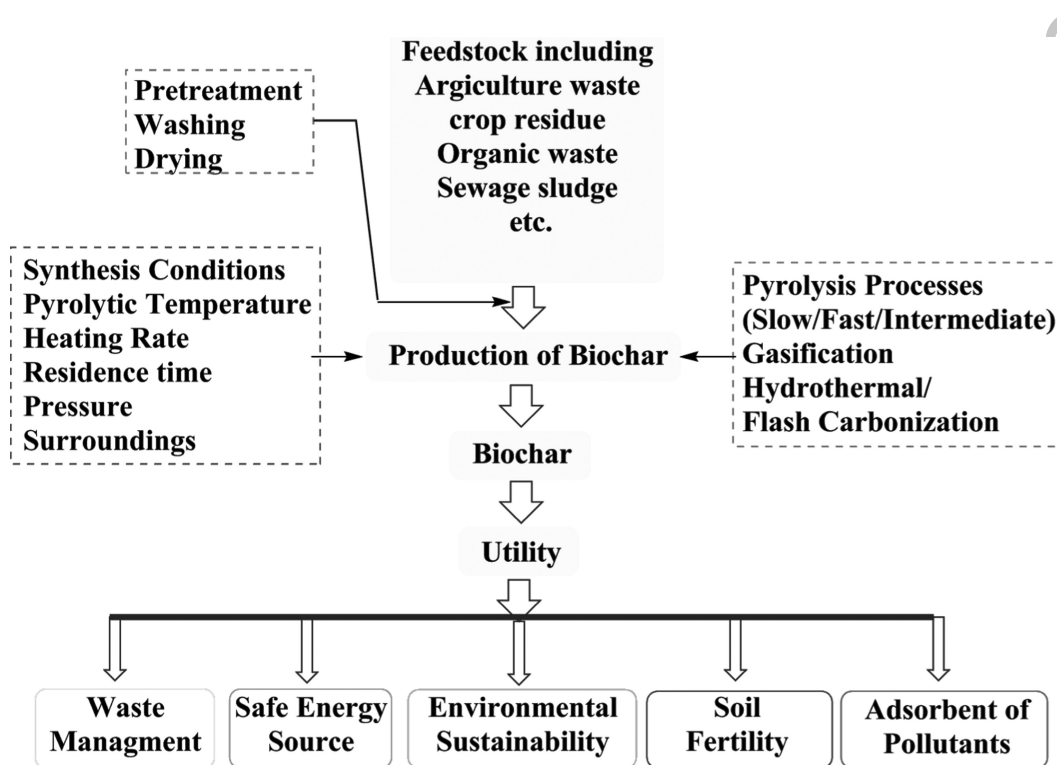


FIGURE 5.4 Production outline of biochar.

heavy metals by corncob biochar. Therefore, it was synthesized and characterized, and its performance in lead immobilization in soil was studied. The investigation revealed that the MgO-coated biochar adsorbed lead onto its surface through cation- π interaction and amplified surface adsorption owing to the greater surface area, and then the MgO coated on MCB's surface additionally boosted the adsorption via precipitation. The synergistic roles of biochar mineral composites make them favourable for soil remediation. The characteristics of biochar may vary upon changing pyrolytic conditions. It has been found that the biochar obtained by fast or slow pyrolysis had the same fused aromatic ring cluster, while the biochar obtained from gasification at high temperature had 17 rings per cluster and was much more condensed.

Fewer aromatic C-H functional groups were obtained from slow pyrolysis than from fast pyrolysis. The final product is usually more porous when obtained upon slow pyrolysis. The biomass and pyrolysis temperature are the vital factors that influence the characteristics of the biochar.

5.4.1.1 The Starting Biomass

Lignocellulosic biomass contains cellulose, hemicellulose and lignin. The percentage of these components in the starting biomass results in varying properties of the resultant biochar (Xiong et al. 2017). The pyrolysis of a high-lignin biomass obtained from pine wood and spruce wood produces a carbon-rich biochar (Antal and Gronli 2003).

5.4.1.2 Inorganic Species

The carbon content of the biochar varies from 45% to 60% by weight. A substantial amount of hydrogen and oxygen is found in biochar. Inorganic elements such as K, Na, Ca, Mg, Si, Al and Fe also occur frequently with biochar. The biochar derived from wood-based biomass has a lower inorganic content than

the biochar derived from herbaceous biomass (Zhao et al. 2013). Inorganic species present in the biochar influence the catalytic applications of the biochar, such as tar cracking, bio-oil upgrading and methane decomposition (Dong et al. 2015). The inorganic portion in the biochar endows it with a catalytic activity towards reactions such as methane decomposition and tar cracking.

5.4.1.3 Functional Groups

Usually, biochar has functional groups bound at the surface. These functional groups are important for the characterization and functionalization of the biochar (Lua et al. 2004). To enhance the performance of metal catalysis by biochar, some functional groups are added to the biochar network, which can bind to the metal ions (Liu et al. 2018). Some surface functional groups may boost the biochar-based catalysts for several processes. It has been found that biochar having sulphonic groups as surface functional groups can efficiently catalyse the hydrolysis of cellobiose because the phenolic, -OH and -COOH groups in the biochar act as adsorption *sites* (Cha et al. 2016).

5.4.1.4 The Biochar Framework

In some cases, the microstructure of the biomass is maintained after the pyrolysis as well. The biochar derived from wood possessed vertically aligned microchannels and fibrous ridged surfaces as in raw wood. The biochar obtained from the sisal leaves also retained the natural quality of the starting biomass having associated porous frameworks (Zhao et al. 2018). These examples suggested the localized formation of biochar via biomass pyrolysis. The biochar framework is mainly amorphous with some crystalline conjugated aromatic sheets. These sheets are cross-linked in an unsystematic fashion. The crystalline nature increases with the increase in the temperature of pyrolysis, and the structure attains more order (Li et al. 2015). Heteroatoms such as N, P and S may be introduced into the biochar matrix. The difference in the electronegativity between these atoms and the aromatic C leads to chemical heterogeneity in biochar, which has an imperative role in catalytic applications (Muradov et al. 2012).

AU: Please check and approve the edit made in the sentence 'The biochar obtained from the sisal leaves ... having associated porous frameworks'.

5.4.1.5 Temperature and Its Effect

The properties of biochar may be greatly affected by pyrolysis temperature. The effect of temperature is more significant than that of the heating rate and residence time (Jeffery et al. 2015). A positive correlation has been obtained between the pyrolysis temperature and pH, carbon content, biochar stability and ash content, whereas a negative correlation is obtained with biochar yield, O and H contents and the surface functional groups. The porosity is also affected by the pyrolysis temperature; as the temperature increases, volatile substances evaporate from the biomass surface, which increases the porosity and surface area (Smernik et al. 2002). A rise in temperature has led to smaller average pore sizes, while a previous study (Haefele et al. 2011) quoted that a high pyrolysis temperature facilitated the fusion of pores with expanded pore sizes. The chemical behaviour of biochar is also somewhat related to the pyrolysis temperature.

5.4.2 Physical and Chemical Characterization Methods

The characteristics of biochar depend upon the pyrolytic conditions and the type of feedstock used, such as crop residues, industrial organic by-products or bioenergy crops, thereby causing diversity in its composition. Biochars synthesized by wood having a high lignin content possess a greater carbon content than those obtained from herbaceous feedstocks (Yu et al. 2011), but they lack N. Still, these chars can be useful for soils favouring the growth of microbes. A synthesized biochar is often characterized through the variations in the elemental concentrations of C, H, O, S and N (Lee et al. 2010). A fixed amount of carbon is left behind once the sample is carbonized after the expulsion of volatile matter (Lu et al. 2012). It is used to quantify the carbonaceous substances yielded from a solid sample. H/C and O/C ratios are used to assess the degree of aromaticity and maturation, as often described in van Krevelen diagrams

(Swiatkowski et al. 2004). O/C, O/H and C/H ratios have been found to provide a consistent measure of both the degree of pyrolysis and level of oxidative adjustment of biochar in the soil and solution systems and are fairly easy to be determined.

Biochars can be characterized by Fourier transform infrared (FTIR) spectroscopy technique. The technique helps in the identification of the main functional groups such as carbohydrates, lignin, cellulose, lipids and proteins. Recently, the characterization of biochars by FTIR has become a very common practice. The FTIR spectra usually change with the change in temperature. However, biochars produced by fast pyrolysis at high temperatures cannot be characterized by FTIR due to the carbon formation that results in weak IR signals. Structural changes due to high-temperature pyrolysis mainly occur between 1,800 and 1,200 cm^{-1} . Feedstocks rich in protein, cellulose, lignin and fatty acids mainly show bands due to amide I (1,642–1,638 cm^{-1}) and amide II (1,515–1,536 cm^{-1}) groups, respectively. C=O stretching band due to ketonic group is obtained at 1,642 cm^{-1} , and C=C aromatic skeletal vibrations in lignin structure occur around 1,515 cm^{-1} . In cellulose, CH_2 scissoring vibration occurs at 1,434 cm^{-1} and O–H bending vibrations in saturated fatty acids occur between 1,500 and 1,240 cm^{-1} (Zhang et al. 2013). It has been found that biochars obtained by fast pyrolysis show characteristic bands as in cellulose. Baseline correction of FTIR spectra showed that with rise in temperature, there is a distinct decrease in frequencies associated with O–H (3,600–3,100 cm^{-1}), C=C and C=O stretching (1,740–1,600 cm^{-1}) and aromatic C=C and C–H deformation modes of alkenes (1,500–1,100 cm^{-1}), and the C–O–C symmetric stretching (1,097 cm^{-1}) characteristics of cellulose and hemicelluloses.

Biochar derived from sludge when combined with Pb^{2+} has been shown to have abundant carboxyl and hydroxyl groups (Hale et al. 2011). The band for the complexed carboxyl ($-\text{COOMe}$) showed no shifting in its position even after being replaced by Pb at 1,400–1,500 cm^{-1} . The noticeable shift of the band at 3,404–3,406 cm^{-1} (pH=2.0), 3420 cm^{-1} (pH=3.0), 3,429 cm^{-1} (pH=4) and 3,422 cm^{-1} (pH=5.0) supported the proposed complexation between Pb^{2+} and hydroxyl as well as carboxyl groups. The identification of acidic and basic groups on biochars may be done by Boehm titration (Hammes et al. 2008), where the biochar is equilibrated in the presence of strong bases such as HCO_3^- , CO_3^{2-} or OH^- or strong acids such as H_2SO_4 , HCl and HNO_3 , followed by titration of the extract with a strong acid or base to estimate the reacting fraction. The amount of acid or base determines the quantification of lactonic, phenolic and carboxylic groups (Li et al. 2013). Surface charge on the biochar can be measured by cation exchange capacity (CEC), which increases as the biochar ages and has been described to grow in some oxygenated functional groups on the surface of the biochar (Bagreev et al. 2001).

Scanning electron microscopy is a microscopic technique through which the physical morphology and microporosity of a solid substance are measured (Chen et al. 2014). The pore size of the biochar is dependent upon the inherent structure of the feedstock and is an important factor for water-retaining and adsorption capacities in different phases (Chen et al. 2014). The biochars produced at different pyrolytic temperatures have different structures. The biochars possess a high Brunauer, Emmett and Teller (BET) area, which usually increases with an increase in carbon burn-off, irrespective of the pyrolytic temperature (Yuan et al. 2019), indicating that the carbon burn-off has a most important consequence on the growth of the surface area.

Functional group identification in rice straw and bran biochars at 100°C–800°C using ^{13}C NMR spectroscopy showed dehydroxylation/dehydrogenation and aromatization. It was observed that with the increase in temperature, the formation of O-alkylated groups and anomeric O-C-O carbons occurred before aromatization. At the temperature below 300°C, aliphatic O-alkylated carbons were more prominent, whereas at higher temperatures, aromatic structure predominated. A relatively new correlative technique based on mid-infrared (MIR) spectroscopy has evolved for the quantification of biochars. Earlier, the technique was used for the estimation of carbon content in soil and solutions. Through UV oxidation method, several algorithms have been proposed, which can relate MIR response spectrum to biochar (Al-Wabel et al. 2013) (Figure 5.5).

5.4.3 Properties/Characteristics of Biochar

The physicochemical properties of biochars significantly affect their sorption efficacy. Following are the important parameters.

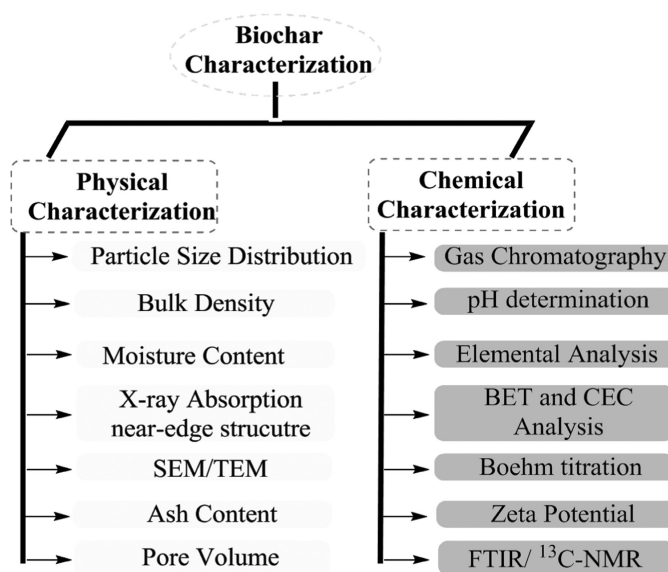


FIGURE 5.5 Characterization methods of biochar.

5.4.3.1 Surface Area and Porosity of the Biochar

The sorption efficiency of biochar is dependent on the surface area and porosity. Porosity is developed because of water or dehydration upon pyrolysis of biomass (Chen et al. 2014). Biochar pore size varies from nano- (<0.9 nm), micro- (<2 nm) and macropores (>50 nm). The biochars having small pores are unable to trap large particles irrespective of their charge or polarity. Pyrolysis conditions lead to variation in pore size. It has been found that a high temperature leads to the formation of large pore size and large surface area. With increasing temperature from 500°C to 900°C, the porosity of biosolids biochar increased from 0.056 to 0.099 cm³/g, while the surface area increased from 25.4 to 67.6 m²/g (Hossain et al. 2011). However, in some cases, at high temperatures the biochar porous structure gets disturbed by the formation of tar, leading to a lower surface area. The biochar composition also depends upon the material or feedstock used for the preparation of biochar. Generally, biomass rich in lignin (e.g. bamboo and coconut shell) develops a macroporous-structured biochar, while biomass rich in cellulose (e.g. husks) yields a predominantly microporous-structured biochar.

5.4.3.2 Biochar pH and Charge Over the Surface

The pH of biochar also varies with pyrolysis temperature and feed material. Usually, biochar is alkaline. Biochars obtained by pyrolysis at low temperature are generally acidic, and the biochar produced from oak wood at 300°C and 600°C was acidic with its pH lying between 4.84 and 4.91 (Subedi et al. 2016). With increasing temperature, the pH usually increases. A positive correlation was observed between the biochar pH and pyrolysis temperature as in wheat, corn and maize residues (Subedi et al. 2016). This may be due to the formation of ash at high temperature. Metal sorption is also influenced by its surface charge. The point of zero charge refers to the pH at which the surface charge becomes zero. When solution pH is >pHPZC, the biochar is negatively charged and binds to metal cations such as Cd²⁺, Pb²⁺ and Hg²⁺, whereas at pH < pHPZC, the biochar is positively charged and binds to metal anions such as HAsO₄²⁻ and HCrO₄⁻. With increasing temperature from 500°C to 900°C, the pHPZC of biosolids biochar increased from 8.58 to 10.2 (Mohan et al. 2014). At elevated temperature, the anionic functional groups on biochars (e.g. -COO⁻, -COH and -OH) have been found to be fewer in number, which leads to high pHPZC and relatively less negative charge on the surface.

5.4.3.3 Presence of Different Functional Groups

For effective metal sorption, the presence of carboxylic, amino and phenolic groups is highly required. The presence of these functional groups can be controlled by the pyrolysis conditions and surface charge. Generally, the availability of functional groups reduces with the rise in temperature owing to high carbonization. At high temperatures, the abundance of hydroxyl, carboxylic and amino groups increases. In the case of biochar derived from lignocellulose, most of the functional groups are lost at elevated temperature.

5.4.3.4 Mineral Composition

Mineral concentration including K, Ca, Mg and P is also accountable for the sorption of metals from aqueous solution. These minerals can be exchanged or precipitated with heavy metals, reducing their availability. Pyrolysis temperature and feedstock both determine the mineral content in the biochar. It has been found that the concentration of K, Ca, Mg and P increases with the increase in pyrolysis temperature in the biochar obtained from biosolids. The water-soluble amount of K, Ca, Mg and P increases when heated up to 200°C, but decreases at higher temperatures. Feedstock is also a significant factor upon which the mineral concentration of biochar is dependent. It has been observed that the P content in oak wood biochar is much lower than `.

5.4.4 Applications of Biochar as an Adsorbent

Biochar is a promising and reasonable adsorbent used for metal removal from water. Metal sorption capacities of biochar are 2.4–147, 19.2–33.4, 0.3–39.1 and 3.0–123 mg/g for Pb, Ni, Cd and Cr, respectively (Wang et al. 2010). Suitable modifications have been suggested in the biochar framework, which improve the metal binding potency usually by infusing the parent biochar with minerals, oxygen-rich functional groups, reducing agents and nanoparticles or by activation of biochar with alkali solution.

5.4.4.1 Sorption of Organic Materials

The sorption of organic pollutants on biochar is dependent upon the pyrolysis conditions as well as the feedstock. It has been observed that biochar has a high adsorptive potential for pesticides and organic pollutants such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), chlorinated compounds and dyes (Yao et al. 2012). The sorption mechanism was assisted by π -electrons in case of wood and manure, and the reaction propagated through the pore-filling action. Biochars obtained from carbonaceous materials such as peat, soya bean stalk and coke remediate organic substances and reduce their bioavailability by repartitioning organic pollutants to carbonaceous adsorbents. Biochars derived from bamboo when mixed in soil amended the leachability and bioavailability of pentachlorophenol. Biochars derived from pepper wood and sugarcane bagasse were found useful in the removal of sulphamethoxazole from water (Dong et al. 2011).

5.4.4.2 Application of Biochar in Water Treatment

Biochars have a high surface area, fine porous structure and several functional groups on their surface, and these properties make them very useful for water purification. According to previous studies, the biochars may be applied with the removal efficiency of nearly 45% for heavy metals, 40% for organic contaminants, 13% for nanoparticles and 2% for other pollutants. Heavy metal contamination in water has become an enormous issue. Thus, their remediation has grown as one of the major research areas using biochar. Adsorption isotherm emphasizes on optimizing adsorbents, which describes the interaction between the adsorbates and adsorbents. Arsenic is a metalloid and is carcinogenic in nature. In natural water, As(V) and As(III) are dominant species with As(III) being more toxic. The arsenic sorption usually occurs through complexation and electrostatic interactions (Cao et al. 2009).

The biochar obtained from pinewood pyrolysis at 600°C sorbed As(V) up to 0.3 mg/g at pH 7. As mainly occurred as HAsO_4^{2-} with an abundance of positively charged functional groups at its surface. Some functional groups were protonated when the solution pH was $< \text{pH}_{\text{PZC}}$. As(V) interacted with positively charged functional groups. Cr is another metal of environmental concern. Cr(VI) species have a high solubility in aqueous medium and of great significance because of the carcinogenic, mutagenic and teratogenic nature of chromium in +6 oxidation state. Cr(III) is comparatively 300 times less toxic than Cr(VI). HCrO_4^- , CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are the dominant species in +6 oxidation state. For Cr(VI) sorption, two mechanisms have been proposed, *viz.* electrostatic attraction between Cr(VI) and biochar and reduction of Cr(VI) to Cr(III) in the presence of oxygenated groups such as carboxyl and hydroxyl groups. The reduction is subsequently followed by Cr(III) complexation. The biochar obtained from sugar beet tailing has been an effective Cr(VI) adsorbent with the highest sorption of 123 mg/g at pH 2.0 (Kong et al. 2011). The mechanism involves reduction of Cr from +6 to +3 oxidation state followed by complexation by hydroxyl and hydroxyl groups. Oak wood and oak bark biochars having a high quantity of lignin, cellulose and hemicellulose have a high capacity for Cr(VI) sorption. The biochar obtained from oak wood has been found to contain considerable percentage of oxygen (8%–12%). Cr(III) sorption mainly occurs through (i) complexation with oxygen-containing functional groups, (ii) ion exchange and (iii) electrostatic attraction between positively charged Cr(III) ions and negatively charged biochar. Biochars obtained from crop straws have been studied for Cr(III) sorption, and it was found that peanut-derived biochar had a sorption capacity of 0.48 mmol/kg. Cr(III) complexation with functional groups is important for its sorption by biochar (Singh et al. 2010). Pb in aquatic environment is present as Pb^{+2} and $\text{Pb}(\text{OH})^+$ at $\text{pH} < 5.5$ and as $\text{Pb}(\text{OH})_2$ at $\text{pH} > 12.5$ (Liu and Zhang 2009).

Biochars derived biosolids, dairy manure, oak wood, oak bark and bagasse have been studied for their role in lead sorption from water. Pb sorption mainly occurs through cation exchange, complexation and precipitation. Ca and Mg are the ions that are exchanged, contributing to 40%–52% of Pb sorption at pH 2–5, while exchange with Na and K contributed to 4.8%–8.5% Pb sorption. Cation exchange is also responsible for Pb sorption by biochar derived from oak wood and bark (Chen et al. 2011). Divalent Hg is a very common species in the environment. It exists as Hg^{2+} at $\text{pH} < 3.0$ and as HgOH^+ and $\text{Hg}(\text{OH})_2$ at pH 3.0–7.0. Complexation of Hg usually occurs with carboxylic and phenolic groups. In Brazilian pepper biochar, the sorption capacity decreased at higher temperatures as it was found that there was a reduction in these functional groups as the temperature rose above 600°C (Regmi et al. 2012). Chemical reduction is another route for Hg sorption as investigated in a soya bean stalk biochar. Hg^{2+} was reduced to Hg_2Cl_2 in the presence of Cl^- , which was precipitated on the biochar surface.

5.4.5 Mechanism of Interaction between Biochar and Heavy Metals

Heavy metals can be removed from the aqueous phase as well as soils using biochar. The removal can be done through various mechanisms including precipitation, complexation, ion exchange, electrostatic interaction and physical sorption. Biochars have a large surface area and porosity; therefore, they have a strong affinity for metal cations which can be physically sorbed on the surface and get trapped in pores (Yuan et al. 2011). Heavy metal adsorption mechanism can be studied by various methods including adsorption isotherms and kinetic models, desorption studies and industrial analyses such as XRD, FTIR and SEM. Sorption may be due to electrostatic attraction and formation of inner sphere complex with the available carboxyl, alcoholic hydroxyl or phenolic hydroxyl groups on biochar surface (Ahmad et al. 2014) as well as co-precipitation. Carboxyl (R-COOH) and alcoholic or phenolic hydroxyl groups (R-OH) present on the sorbent surface are considered as the main groups that coordinate with the heavy metals. The presence of mineral impurities such as ash and basic nitrogen groups present in heterocyclic bases such as pyridine serve as other adsorption sites of the carbon-containing substance. Thermodynamic aspects have shown that metal sorption is an endothermic process (Li et al. 2019), which takes place by the electrostatic interaction between the positively charged metal cations and π -electrons of C=O ligand or C=C of a shared electron cloud on the aromatic part of the biochar.

To improve the sorption capacity, methods such as magnetization, incorporation of nanoparticles, modifications in coating and alkaline treatment have been used. Alkali activation process is an efficient method to enhance the porosity and sorption properties. The metal sorption ability of the biochar varies between

1 and 3 from 1 to 200 mg/g. The pH of the solution also influences the metal sorption and specific charge of the biochar. An alteration in pH influences the complexation behaviour of the functional groups such as carboxyl, hydroxyl and amino groups. The carboxyl group ionization is maximum at pH 3–4. Based on the previous studies in the literature, five different mechanisms have been proposed for metal sorption: (i) electrostatic interactions between metals and biochar, (ii) cation exchange between metals and other metal ions such as alkali and alkaline earths and H^+ ions on the biochar surface, (iii) metal complexation with functional groups and π -electrons present in the aromatic framework of biochar, (iv) precipitation of metal ions and (v) reduction of metal ions and their subsequent sorption. The mechanistic action and the potential of sorption vary for different biochars and heavy metals. Many researchers have studied and devised numerous methods for the synthesis of biochars and for determining their metal binding capacity, which include thermodynamics and kinetic factors from water (Batool et al. 2018).

5.4.5.1 Chemical Sorption

Upon exposure to the environment, oxygenation occurs, resulting in the abundance of oxygenated functional groups on the internal surface area of the biochar (Fraga et al. 2019). These functional groups including hydroxyl and carbonyl groups induce a negative charge on the biochar surface. This happens at low temperature, and as the pyrolysis temperature increases, the abundance of anionic functional groups decreases, which reduces the surface charge on the biochar. Upon surface sorption, H^+ ions are released from the biochar directly (Fraga et al. 2019), but at the same time, many alkali and alkaline earth ions are passed into the solution, which shows metal exchange with other positively charged ions. The preferential sorption of a single metal cation from an aqueous solution is more prominent than the sorption of multiple metals because of the competition for binding sites on the biochar surface (Nartey and Zhao 2014). Ligands which have P and S donor atoms show a greater affinity for metal ions such as Pb and Hg that have strong likeness towards sulphates and phosphates (Verheijen et al. 2010).

5.4.5.2 Precipitation

The mineral fraction in biochar, such as CO_3^{2-} , PO_4^{3-} , SiO_4^{4-} , Cl^- , SO_4^{2-} and OH^- , reacts with heavy metal ions to form water-insoluble compounds such as metal oxides, phosphates and carbonates, leading to adsorption and immobilization of heavy metals. Biochar source material consists of varying fraction of minerals, which result in non-organic ash formation. The mineral fraction found in ash fraction is usually in oxidized form, and its concentration increases with the increase in pyrolysis temperature (Hassan and Carr 2018). Pb minerals have very low solubility, and their formation results in an increase in Pb-absorbing capacity as compared to other bivalent cations. Cu, Cd and Zn can also be precipitated as insoluble carbonates and phosphates at high pH.

5.4.5.3 Physical Sorption

In physical sorption, the biochar adsorbs heavy metals and other contaminants on its surface. The large surface area and porosity are responsible for physical adsorption. The pollutants usually diffuse through the fine pores present in the biochar framework. The adsorption can be either single- or multi-layer, which is usually fitted by Langmuir and Freundlich model (Dong et al. 2017).

Thermodynamic parameters show that sorption is an endothermic process (Kołodynska et al. 2017). Sorption occurs as a result of electrostatic interaction between metal cation and π -electrons associated with $C=O$ and $C=C$ present in biochar. Because of the presence of vacant orbitals on metal, π -electrons associated with the biochar are slightly shifted towards the metal ions, causing a polarity in the bond and creating a weak interaction between them. An increase in pyrolysis temperature enhances the aromatic character and decreases the oxygenated functional groups (Zhao et al. 2017). The low-temperature pyrolysis results in metal immobilization, which is for a small term owing to the synthesis of inner and outer sphere complexes with oxygen-rich functional groups. Pyrolysis at high temperature results in a negative surface charge that lasts for a longer time period, but that makes the biochar a weak adsorbent

for metal ions. Over a certain time period, owing to oxidation on the biochar surface, negatively charged functional groups are created.

5.4.5.4 Ion Exchange

In the process of ion exchange, ions having like charges are mutually exchanged with each other. Carboxyl, carbonyl and hydroxyl groups present on the surface of biochar possess replaceable H^+ ions, which can be exchanged with alkali and alkaline earth metal ions or other organic contaminants possessing positive charge (Sizmur et al. 2017).

5.4.5.5 Electrostatic Interaction

Electrostatic interaction occurs between the negative charge on the surface of biochar and the positively charged metal ions, and that usually occurs when the pH of the solution is more than the charge point of the biochar. The phenomenon is also termed as electrostatic adsorption. The interaction mainly occurs due to the presence of oxygen-containing functional groups such as carboxyl, carbonyl and hydroxyl groups (Dong et al. 2017).

5.5 Modification of Biochar to Improve Sorption

Several modifications have been made in the structure of biochar to improve sorption properties. Physical and chemical methods have been adopted to achieve the modified and enhanced activity. The modifications in biochar can be brought about by varying starting biomass, pyrolysis temperature, reaction time, etc. The alteration in the framework can be brought about prior to pyrolysis by using an appropriate catalyst, usually NaOH or KOH, or by using metal salts that undergo reduction to metal or metal oxide nanoparticles. Modifications can also be made by chemical or physical methods such as enrichment with different functional groups on the surface of biochar by different methods such as oxidation, sulphonation, amidation or reaction of monomers (oligomers) to form composite materials. Some of the methods used for the improvement of sorption capacity of the biochar are discussed below.

5.5.1 Chemical Oxidation

In chemical oxidation, hydrophilicity is enhanced by oxidation on the biochar surface, which yields oxygen-containing functional groups such as $-OH$ and $-COOH$. Oxidation also leads to an increase in the pore size, thereby improving the adsorption capacity for the polar substances. HCl , HNO_3 , H_2O_2 and H_3PO_4 are commonly used oxidants for the purpose (Ho et al. 2014). It has been found that biochar modified by HNO_3 has more acidic oxygen-rich functional groups and a greater sorption potential for NH_3-N . Biochar modified by H_3PO_4 is more productive in the remediation of Pb. The increased specific surface area and pore volume, as well as the role of phosphate precipitation, increase the biochar affinity for Pb (Zhao et al. 2017).

5.5.2 Chemical Reduction

Non-polarity is increased by the reduction of functional groups. Chemical alterations also improve pore formation and surface area of biochar. The common reducing agents used for the purpose are NaOH, KOH, NH_4OH , etc. (Sizmur et al. 2017). Different reducing agents have varying effects. KOH and NaOH activate biochar through different mechanisms. It has been found that potassium atoms which are released during potassium hydroxide activation intercalate between adjacent carbon crystallite layers, although the phenomenon is not observed in case of interaction of sodium with carbon (Figure 5.6).

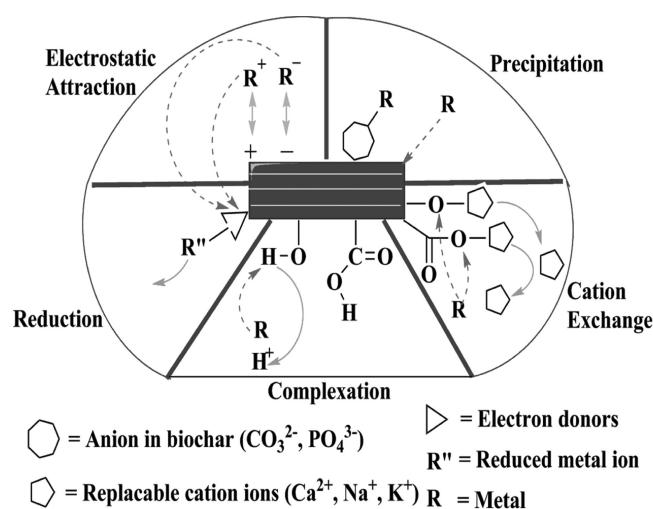


FIGURE 5.6 Mechanistic approaches for the modification of biochar.

5.5.3 Impregnation of Metal

Some of the heteroatoms are adsorbed onto the biochar surface during metal impregnation. Metal ions combine with the adsorbate to improve the adsorption efficiency. Fe, Mg, Ag and Zn (Angin et al. 2013) are some of the ions that improve the biochar sorption upon impregnation. Biochar material (CMC–FeS@biochar) through association with carboxymethyl cellulose (CMC) and iron sulphide (FeS) showed active sorbing capacity of CMC–FeS@biochar composite for Cr(VI).

5.6 Future Prospects of Biochar

Biochar has lesser ability to act as an adsorbent than activated carbon. Studies and researches have been concentrated to enhance the surface area, porosity and functional groups of the biochar. These modifications have been done by adding minerals, organic functional groups and other nanoparticles. Haematite ($\gamma\text{-Fe}_2\text{O}_3$), magnetite, Fe, hydrated MnO and CaO have been used to enrich the biochar during or after pyrolysis (Wang et al., 2015b). The adsorption capacity of a biochar loaded with Fe oxides for As(V) increased because of the electrostatic attraction between the two. Biochar sorption is also modified by the presence of exogenous functional groups such as amino, carboxylic and hydroxyl groups. Amino groups were incorporated into biochars obtained from husk and saw dust via polyethylenimine modification and through nitration and reduction. The sorption capacity of such a modified biochar for Cr(VI) increases ten times from 30 to 120 mg/g (Zhang et al. 2015). The surface area can also be modified and enhanced for sorption by incorporating nanoparticles. Magnetic biochars infused with ZnS nanocrystals induced magnetic behaviour in the biochar. The biochar thus produced showed a better sorption capacity for Pb, which was up to 368 mg/g (Yan et al. 2015). Biochars incorporated with Zn and obtained from sugarcane bagasse showed an increased Cr(VI) absorption. A graphene-coated biochar resulted in π - π interaction, and an increase in surface area was obtained from 4.5 to 17.3 m²/g for acidic functional groups and the sorption capacity for Hg increased from 0.77 to 0.85 mg/g (Tang et al. 2015). Other than nanoparticles, the surface area of biochar has been seen to increase with the solution of bases such as sodium and potassium hydroxide, leading to improved sorption of metals.

Thermodynamic studies of biochar are very scarce, which makes uncertain whether a particular biochar can be used for the sorption of each heavy metal or not. Mathematical models should be implied to explore the exact mechanism of action of biochar and how the interaction occurs. Pre-nourishment of

biochar can be useful for wastewater management. Although studies have been focused on the removal of heavy metals, very less work has been done to understand and modify the interaction with metalloids such as As. Although the biochar has conventionally been prepared by pyrolysis, the properties of biochar are greatly affected by pyrolysis temperature. Hydrothermal carbonization (HTC) is usually performed at preferably low temperatures (180°C–250°C) in the presence of water. The technique has a distinct advantage of producing high-moisture biomass and structure in the presence of inorganics and surface functional groups made up of highly conjugated aromatic sheets. Strategies should be adopted so that the modified biochar can act as a better catalyst. The biochar should also be used in small amounts so that the wastewater treatment is cost-effective.

Studies have reported the quantification of extractable toxic elements in the biochar itself, and recommendations and guidelines have been implemented to minimize the potential risk of toxicity. The International Biochar Initiative (IBI) has established standards (Standardized Product Definition and Product Testing Guidelines for Biochar that Is Used in Soil) to characterize crucial qualities and biochar material characteristics in soils. Similar guidelines are needed for water treatment as well, where biochar is used as a remedial agent. Very few reports in the literature are available that describe the usage of biochar for the treatment of contaminated sediments, which needs to be explored because of the proven remedial properties of biochar in overcoming heavy metal contamination in water.

5.7 Conclusions

The present chapter has summarized the heavy metal contamination in environment with an emphasis to heavy metal pollution in water. Several diseases are associated with consumption of polluted water and to address the issue numerous remedial measures have been explored, of which biochars have emerged as promising adsorbents. The chapter has taken a closer look at different aspects of biochar including its synthesis, characterization, properties applications and mechanistic action. Chemically, biochar mostly contains carbon, hydrogen, oxygen, nitrogen, phosphorus and sulphur. The physico-chemical features of biochar depend upon the feedstock used and temperature of pyrolysis. Potential applications of biochars include their use as an energy source, as an additive in soil amendment and as a sorbent in waste management. Biochar as an adsorbent has received significant attention due to its advantageous physical and chemical characteristics including cation exchange capacity and porous network. However, large-scale studies have been scarce and experiments using biochars derived from different sources have been done on a laboratory scale. Usually, the studies have been focused on the removal of one single metal. In natural water bodies, several metals coexist with other contaminants, creating a competition for the binding site on the biochar surface. Very few reports are available on the remediation of heavy metals from water. Simulated water should be replaced with natural water to ascertain the actual removal ability and functionality of biochar in a particular environment. This can be achieved by using various physicochemical conditions. Studies are also needed to understand the actual mechanism and efficiency of heavy metal removal, which is mostly dependent on the application rate, dosage of the biochar and recovery approaches, and the regeneration and disposal approaches of the adsorbed biochar.

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