Riti Thapar Kapoor
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Biochar and its Application in Bioremediation

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Application of Biochar for Wastewater Treatment

1

A. I. Abd-Elhamid and M. Emran

Abstract

Due to the increased progress in the industrial activities, considerable quantities of inorganic (such heavy metals Pb^{2+}, Cd^{2+}, As^{2+}, Cu^{2+}, Ni^{2+}, As^{3+}, Cr^{7+}, etc.) and organic (such as dyes, antibiotics, phenols, etc.) materials resulted as effluents. The discharge of these pollutants without proper management will cause a serious threat on the surrounding environment. Moreover, the accumulation of these contaminants in the waterway becomes a health threat as they are toxic, recalcitrant, mutagenic, and carcinogenic. Therefore, it is very necessary to exploit new adsorbents for efficient recovery of clean water. Activated biochar is derived from biomass by-products via thermal pyrolysis followed by activation step. The resulted biochar will own superior physical and chemical properties, which include high porosity, large surface area, enhanced surface properties, and excellent adsorptive performance toward the pollutants. These properties make the activated biochar excellent adsorbent that can be applied for water remediation.

Keywords

Biomass · Biochar · Wastewater treatment · Inorganic pollutants · Organic pollutants

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1.1 Introduction

Biochar (BC) is an organic C-rich material, stabilized through pyrolysis of biomass by-product in limited oxygen atmosphere at elevated temperature. Due to availability of biochar precursor, low-cost preparation, high surface area, large porosity, and easy modification, biochar is widely applied in several application fields such as soil amendment, C-sequestration, and the removal of organic and inorganic contaminants from wastewater. The raw BCs provide low adsorption capacity of the pollutants; thus further modification will be required to improve different physicochemical properties: surface area, pore structure, and surface functional groups. In this regard, physical and chemical activation may be investigated to enhance the removal affinity of BC during environmental application. Meanwhile, the prepared modified biochar could be considered as alternative adsorbent to various carbonaceous materials (activated carbon, carbon nanotubes, and graphene) with equalized removal capacity for organic and inorganic pollutants. Another major property of preparing biochar is to get rid of the biomass waste problem which is considered an extra environment challenge.

1.2 Preparation of Activated Biochar

The preparation of biochar passed through three various stages: biomass precursor selection, carbonization/pyrolysis process, and activation of biochar, as illustrated in Fig. 1.1.

1.2.1 Biomass Precursor Selection

The precursor material used for preparation of activated biochar should be low-cost, available, diverse, renewable, and nonhazardous to the environment. These raw materials may be derived from agricultural waste or industrial biomass waste such as various portions of crops shell, stem fibers, seed, husk and stones, woody biomass, herbaceous, etc. The biomass type and the pyrolysis conditions used induce the surface morphology and the physical function of produced biochar. For example, the celluloses, hemicelluloses, and lignin biomasses presented a strict structure similar to the plant because they are firmly interacted and non-covalent chemically bonded. Consequently, the biochar obtained has an excellent surface area including internal network porous structure along with high abundant functional groups which are preferable in the adsorption process. Therefore, it is more important to choose the biomass precursors to produce biochar with acceptable adsorption performance, textural properties, and porosity structure, available for decontamination of waste water.

Batista et al. (2018) observed that the biochar samples prepared from various biomasses showed pores with different sizes, where the charcoal fines (CR) and coconut shells (CS) owned pore size approximately 10 μm, while the oil palm bunch

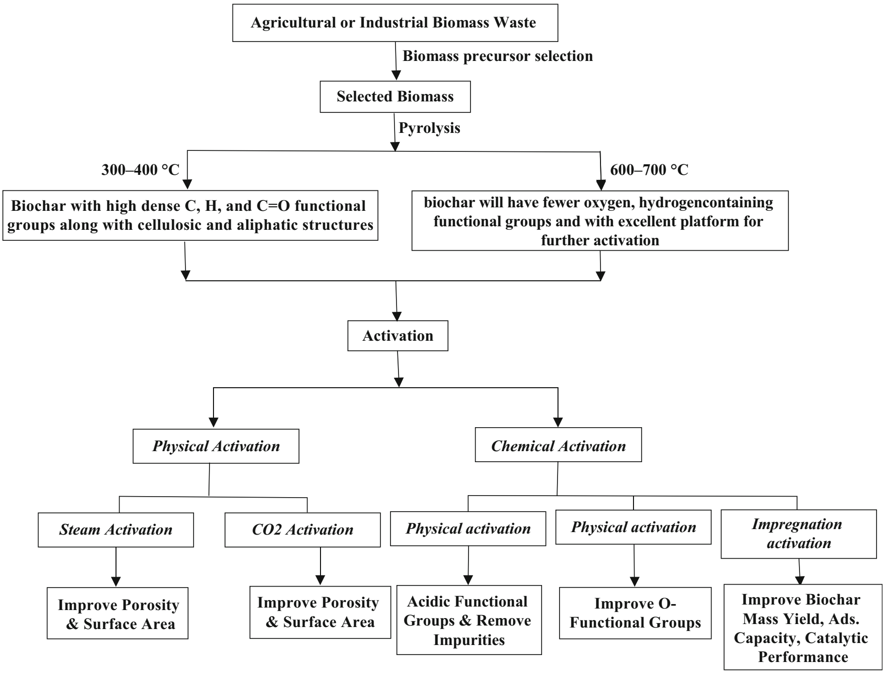

Fig. 1.1 Schematic illustration of various steps for preparation and activation of biochar

(PO) and sugarcane bagasse (SB) samples presented 6 μm pore size. Moreover, the water hyacinth plants (WH) sample exhibited a rough surface, probably due to breakdown of the pores and further filling of the porous system with ash; see Fig. 1.2a.

1.2.2 Carbonization/Pyrolysis Process

The preparation of activated biochar from the selected precursor biomass is investigated through two main steps: initially, **pyrolysis of the biomass** and, secondly, **activation of biochar**. In the pyrolysis stage, thermochemical reactions execute; moisture as well as the volatile matter content is liberated from the biomass under controlled oxygen atmosphere, heating rate, and pyrolysis time. At presence of oxygen during the pyrolysis process, the oxygen will diffuse interior the prepared materials and those with the biomass decomposition rate increasing, and it will be unstoppable. For efficient carbonization operation, the remoting of the pyrolysis temperature plays a vital role in detecting the quality and applicability of the prepared biochar. The pyrolysis of biomass at temperature range of 350–650 °C resulted in breaking and rearrangements of the chemical bonds in the selected biomass, leading to formation of new functional groups (e.g., carboxyl, lactone, lactol, quinine, chromene, anhydride, phenol, ether, pyrone, pyridine, pyridone, and

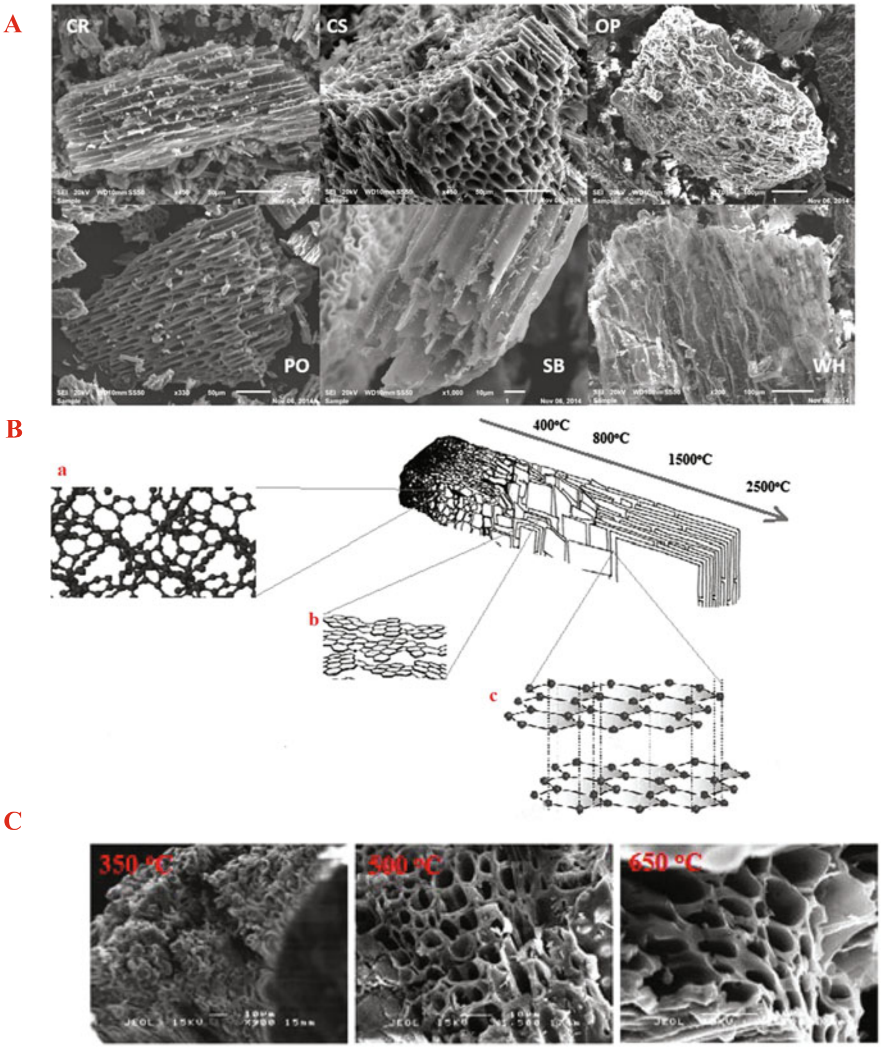

Fig. 1.2 (**a**) Scanning electron micrographs of biochar samples at magnifications of 450× (CR, CS), 170× (OP), 330× (PO), 1000× (SB), and 200× (WH) (*CR* charcoal fines, *CS* coconut shell, *OP* orange peel, *PO* palm oil bunch, *SB* sugarcane bagasse, *WH* water hyacinth) (Batista et al. 2018). (**b**) Pyrolysis temperature effect on biochar: (**a**) amorphous carbon; (**b**) turbostratic carbon; (**c**) graphite carbon (Tomczyk et al. 2020). (**c**) SEM images of rice husk biochar produced at different pyrolysis temperatures (Claoston et al. 2014)

pyrrole) (Mia et al. 2017). This produced biochar will be efficient in removing of organic and inorganic pollutants from contaminated water during its treatment process.

The biochar produced at elevated pyrolysis temperatures exhibits a highly hydrophobic nature with well-organized C layers; see Fig. 1.2b. This behavior attributed to loss of water content and oxygenated groups; thus the obtained biochar will have fewer oxygen- and hydrogen-containing functional groups. Consequently, the surface groups can serve as electron donors or acceptors, which result in generation of appropriated areas whose behavior can range from acidic to basic and from hydrophilic to hydrophobic (Tomczyk et al. 2020).

In addition, during the pyrolysis process, the network porous structure of the biochar will be generated. Where, the high temperature cause thermal decomposition and releasing of the materials that are clogging the pores, leading to creation of pores, network channel structures, or amorphous carbon structures, consequently increasing the specific surface areas (Rafiq et al. 2016). Moreover, Claoston et al. (2014) observed that the further increase in the pyrolysis temperature, the porosity of the biochar enhanced, and the biochar structure become more ordered and the pores become more wider, as illustrated in Fig. 1.2c.

1.2.3 Activation of Biochar

Un-activated biochar suffers from poor active groups, limited pore properties, and reduced surface area. Therefore, the raw biochar exhibits lower adsorption affinity toward various organic and inorganic water contaminants which makes it of limited use in the water treatment applications. For instance, great efforts are carried out to prepare a class of biochar with a well-improved porous structure, high surface area, high density of surface functional groups, and efficient physiochemical stability. Two main activation routes, the physical and chemical activation, were employed for enhancement of the physical and chemical behaviors.

1.2.3.1 Physical Activation

In the physical activation process, the precursor will be carbonized at high elevated temperature (<800 °C), thereafter, it will be activated using steam or CO_2. *The steam modification* of the biochar aimed to enlarge the surface area, volume of pore, and surface morphology through reducing the aromaticity, as well as the polarity. This will be achieved due to at the reaction of the steam with carbonized biochar induce the volatile matter and fixed carbon transformation into CO and CO_2 as well as trapped particles will be eliminated. In case of *CO_2 activation*, carbon dioxide interacts with the carbon of the biochar and yields carbon monoxide (i.e., hot corrosion); consequently, a microporous structure was formed.

1.2.3.2 Chemical Activation

Chemical activation is the most applied method for activation of the biochar. The chemical activation may be carried out during (single activation process) or after (two-step activation process) the carbonization of the selected raw biomass using a chemical agent (acid or alkaline modifier, metal salts, oxidizing agent, etc.). Table 1.1 listed various biomass precursors, preparation and activation methods,

Table 1.1 Various biomass precursors, preparation and activation methods, and adsorption capacities of the prepared biochar and activated biochar toward various inorganic and organic pollutants

Feedstock material	Preparation method	Biochar	Contaminated	Q^o (mg g^{-1}), %R	Ref.
Crayfish shell	– Pyrolysis – $MgCl_2$-modified biochar	– C600 – MgC600	Cd^{2+}	52.40 93.90	Zhang et al. (2021a, b, c)
Oil tea camellia shells	– Pyrolysis in presence of Na_2SiO_3	– Biochar – Biochar high Si	Cd^{2+}	62.18 211.49	Cai et al. (2021)
Coconut shell	– Pyrolysis in presence of $MgCl_2{\cdot}6H_2O$	– BC400 – MgBC400	Cd^{2+} Pb^{2+}	6.80, 205.14 22.10, 532.28	Wu et al. (2021)
A. compressus	– Hydrothermal in presence of conc. H_2SO_4	– SBC	Cd^{2+} Pb^{2+}	85.76 191.07	Yu et al. (2021a, b)
Rice straw	– Pyrolysis – Precipitation of Fe_3O_4 on biochar – *Bacillus* sp. K1 anchored onto Fe_3O_4 biochar	– MB – MBB	Cd^{2+} As^{3+}	10.2, 20.9 6.05, 5.04	Wang et al. (2021a, b, c)
Sewage sludge	– Pyrolysis – $CaHPO_4$	– HAP-SSBC	Cd^{2+} Cu^{2+}	114.68 89.98	Chen et al. (2021)
Peanut shells	– Pyrolysis in presence of $KHCO_3$ – Precipitation of manganese oxide	– MO-L-BC	Cu^{2+} Sb^{2+}	126 248	Wan et al. (2020)
Konjac starch	– Hydrothermal in presence of PVP	– HCSs	Pb^{2+}	22.9516	Li et al. (2020a, b, c)

Corn stalks	– H_2SO_4 (5 wt%), hydrothermal – KOH, pyrolysis – Acid $(NH_4)_2S_2O_8$ oxidation – $FeCl_3$, $NaBH_4$	– nZVI-HPB	Pb^{2+}	589.9	Li et al. (2020c)
Sludge	– Pyrolysis	– SDBC	Pb^{2+}	~2	Sylwan et al. (2020)
Rice husk	– H_2SO_4 – Pyrolysis – β-CD	– BC – BC_{MW}-β-CD	Pb^{2+} BPA	15.76, 240.13 56.61, 209.20	Qu et al. (2020)
Raw jujube seeds	– Sulfuric acid – Ultrasonic	– UAJS	Zn^{2+} Pb^{2+}	221.10 119.8	Gayathri et al. (2021)
Banana stalk	– Pyrolysis	– BB	Zn^{2+} Mn^{2+} Cu^{2+}	108.10 109.10 134.88	Deng et al. (2020)
Palm kernel cake	– Carbonization – Fe_3O_4 precipitation – $KMNO_4$ impregnation	– CP-Fe-Mn	Cd^{2+} Pb^{2+} Hg^{2+} Cr^{3+}	18.60 49.64 13.69 22.38	Maneechakr and Mongkollertlop (2020)
Sugarcane bagasse	– Pyrolysis – KSCN, H_2O_2	– BC_{SB700} – BC_{SCN700}	Cd^{2+} Cr^{3+} Ni^{2+} Pb^{2+}	3.56, 6.14 35.2, 37.5 2.60, 9.67 53.2, 62.9	Macedo et al. (2021)
Banana leaves	– Pyrolysis – $FeSO_4{\cdot}7H_2O$, $KMNO_4$, NaOH	– MFBC	Tl(I)-	170.55	Liu et al. (2021)
Rice husk (RH) Coconut shell (CS)	– Pyrolysis – $KMnO_4$	– RHBC-Mnx – CSBC-Mnx	Li^+	62.85 57.8	Kamran and Park (2020)
Shrimp shells	– $FeCL_3$, pyrolysis – GO, EDA	GO3DH-MSSB	Cr(VI)	350.40	Mahmoud et al. (2021)

(continued)

Table 1.1 (continued)

Feedstock material	Preparation method	Biochar	Contaminated	Q° (mg g^{-1}), %R	Ref.
Corn straw	– Granulated, pyrolysis – $FeCl_3$, pyrolysis	– HGCs	Cr(VI)	19.51	Zhu et al. (2020)
Eleocharis dulcis (ED)	– Pyrolysis – Fe_3O_4 precipitation – Siltstone – Calcination	– SNB	Cr(VI)	35.57	Ud Din et al. (2021)
Corn straw	– Pyrolysis – KOH, pyrolysis	– PBCKOH	Cr(VI) NAP	116.97 450.43	Qu et al. (2021)
Corn straw	– Sulfourea, pyrolysis – $Bi(NO_3)_3.5H_2O$, $Na_2WO_4.2H_2O$, solvothermal	– Bi_2WO_6/NSBC	Cr(VI) CIP	99.7% 90.3%	Mao et al. (2021)
Sesbania bispinosa	– Pyrolysis – $CuSO_4.5H_2O$ OR $MnCl_2$, KOH	– SBC – SBC/MnO – SBC/CuO	As(V)	7.33 7.34 12.47	Imran et al. (2021)
Hickory wood	– Pyrolysis – Vermiculite, ball mill	– BC/VE	As(V)	20.10	Li et al. (2020b)
Yellow ginkgo leaves	– Freeze-drying – Pyrolysis – $FeSO_4{\cdot}7H_2O$, $KMnO_4$, NaOH	– BC-MF	As(V) p-ASA	90 105	Wen et al. (2021)
Rice husk	– Pyrolysis – Manganese(II) acetate tetrahydrate, $KMnO_4$	– MBC	As(III, V)	94.6%	Cuong et al. (2021)
Rice straw	– Pyrolysis – ATMAC, CTS, polymerization	– PATMAC-CTS-BC	SeO_4^{2-}	98.99	Zhang et al. (2021a)

Longan shells	– Pyrolysis – KOH, pyrolysis – Fecl$_3$, NaBH$_4$	– A-BC-NZVI	U(VI)	331.13	Zhang et al. (2021b)
Spent-tea residue	– H$_3$PO$_4$, pyrolysis	– STR400	MB	91.13	Salehi et al. (2020)
Castor seed cake	– Pyrolysis – Conc. H$_2$SO$_4$	– AB1	MB	96%	Silva et al. (2021)
Potato straw	– Pyrolysis – Chitosan – MnCl$_2$·H$_2$O, FeCl$_3$·6H$_2$O	– MnFe$_2$O$_4$@CPB	MO	90.35	Wang et al. (2021b)
Phoenix dactylifera leaves	– Pyrolysis – MnCl$_2$, NaBH$_4$	– PBC – nZVMn/PBC	CR	25.316 117.647	Iqbal et al. (2021)
Shrimp shell	– Pyrolysis – 2 M HCl	– HPB	RHB TC DCP	301.205 392.157 452.489	Yu et al. (2021a)
Food scraps and plant trimmings	– Pyrolysis	– Biochar	TC	15.5208	Hoslett et al. (2021)
Flueggea suffruticosa	– ZnCl$_2$, pyrolysis – HCl	– Zn-BC	CTC TC OTC	200.0 188. 7 129.9	Wang et al. (2021c)
Dewatering sludge	– Pyrolysis – FeSO$_4$·7H$_2$O, CuSO$_4$·5H$_2$O, sodium oxalate, pyrolysis	– BC-FeCu	TC	26.09%, 73.91%	Liu et al. (2020)
Rape straw	– Dil. H$_2$SO$_4$ – FeSO$_4$ FeCl$_3$, pH 10 – Pyrolysis	– MRSB/PS	TC	98.02	Huang et al. (2021)
Corn straw	– Pyrolysis – Fe(NO$_3$)$_3$·9H$_2$O, dried, pyrolysis with or without N$_2$ flow	– Fe^0@BC – Fe$_3$C@BC – Fe3O4@BC	CH	97.63 69.79 59.08	Zhao et al. (2021)

(continued)

Table 1.1 (continued)

Feedstock material	Preparation method	Biochar	Contaminated	Q° (mg g^{-1}), %R	Ref.
Chinese medicinal herb residue (*Astragalus membranaceus*)	– Pyrolysis – FeSO4.7H2O, NaBH$_4$	– nFe(0)/BC	TC	86.97	Shao et al. (2020)
Palm dates	– Pyrolysis – Fe(NH$_4$)$_2$(SO$_4$)$_2$.6H$_2$O, NH$_4$Fe(SO$_4$)$_2$.12H$_2$O, NaOH	– BCDP – MBC-DP	TIGC	77.31% 99.91%	El-Azazy et al. (2021)
Dendro wood biochar (*Gliricidia sepium*), by-product of the gasification (700 °C)	– Crushed, sieve – Grounded, sonication	– CBC – BC – NBC	OTC	136.7 129.34 113.2	Ramanayaka et al. (2020)
Sugarcane bagasse fibers	– 40% NaOH – Hydrothermal	– HTC	SMX	400	Prasannamedh et al. (2021)
Bermudagrass	– FeCl$_3$, dried, pyrolysis	– IA-BC$_{2.0}$	SMX	265.43	Zeng and Choi (2021)
Dry yeast powder (*Saccharomyces cerevisiae*)	– Glucose, lyophilizer – Co(NO$_3$)$_2$, dry, pyrolysis	– Co$_2$P/ biochar	SMX	>99.9%	Peng et al. (2021)
Anthriscus sylvestris	– Pyrolysis 4 M NaOH, dried, pyrolysis	– ACT-B	DF CPX	392.94 724.54	Shirani et al. (2020)
Carica papaya or pine cone seeds	– Clay, 0.1 M NaOH, dry, pyrolysis	– KPA – KPC	Ivermectin	200 200	Olu-Owolabi et al. (2021)
Coconut fiber	– Pyrolysis – *P. putida*	– Cell-loaded biochar	PQ	16.79	Ha et al. (2021)
Cherry stones	– FeCl$_3$, dried, milled, pyrolysis	– BAC/FeOX	BPA	100%	Li et al. (2021)
Sugarcane waste	– Pyrolysis	– SugBC900	BPA	100%	He et al. (2021)

and adsorption capacities of the prepared biochar and activated biochar toward various inorganic and organic pollutants.

Acid activation is supplied for decoration of biochar surface by acid functional groups. Usually it is carried out using acidic agent such as sulfuric acid, hydrochloric acid, nitric acid, oxalic acid, phosphoric acid, and citric acid. An extra function for the acid treatment is to remove the undesired metallic impurities present in the biochar. *The alkaline activation* of biochar is investigated to improve the surface area and oxygen functional groups on the obtained modified biochar. Commonly employed alkali-modifying agents include NaOH or KOH. *Impregnation* of biochar with metal oxides (MO) or metal salts MX_n was expected to increase the mass yield production as well as enhance the adsorption capacity of anionic species.

1.3 Designed Biochar for Treating Polluted Water

Recently, activated biochar has been awarded more attention and extensively studied by scientists in various fields. This is attributed to availability of biochar precursor, low cost, easy preparation, high reactivity, easy modification, and getting rid of an environment-waste challenge. Especially, in water treatment applications, the activated biochar is heavily used because it is an economically feasible and eco-friendly carbonaceous material and has high surface area, large porosity, excellent adsorption capacity, and ion-exchange capacity. All of these features make the biochar an efficient adsorbent in waste water treatment applications.

1.3.1 Biochar for Removal of Inorganic Pollutants

With further progress of industrial activities and the employment of mines, heavy metal contamination is becoming a challenge environmental problem. The discharge of these elements to the raw water will cause a serious threat to the human life. These elements are carcinogenic and it may cause renal, liver, and prostatic diseases. Therefore, it is very necessary to investigate an efficient adsorbent to eliminate these elements from the wastewater. Modified biochar has several properties such as high porosity, enhanced surface area, and high adsorptive performance suitable adsorbent for these pollutants.

Zhang et al. (2021c) studied Cd(II) adsorption onto $MgCl_2$ functionalized biochar (MgC600), and results showed that the adsorption capacity of MgC600 was exceeded more than twice of that of pristine biochar attributed to its preformed ion exchange ability. Oil tea camellia shell biochar was prepared by pyrolysis (500 °C) in the introduction of sodium silicate and applied for adsorption of Cd (Cai et al. 2021). The characterization results revealed that The SEM silicon (Si) is anchored on biochar surfaces as fine particles, in the form of quartz (SiO_2) as indicated from XRD data. Cai et al. found that the addition of silicate highly increases the specific surface area (~45–112%) and slightly improves the porosity (~5–12%) of biochar. Batch results indicated that Si modification highly enhances Cd adsorption (at $pH > 5$).

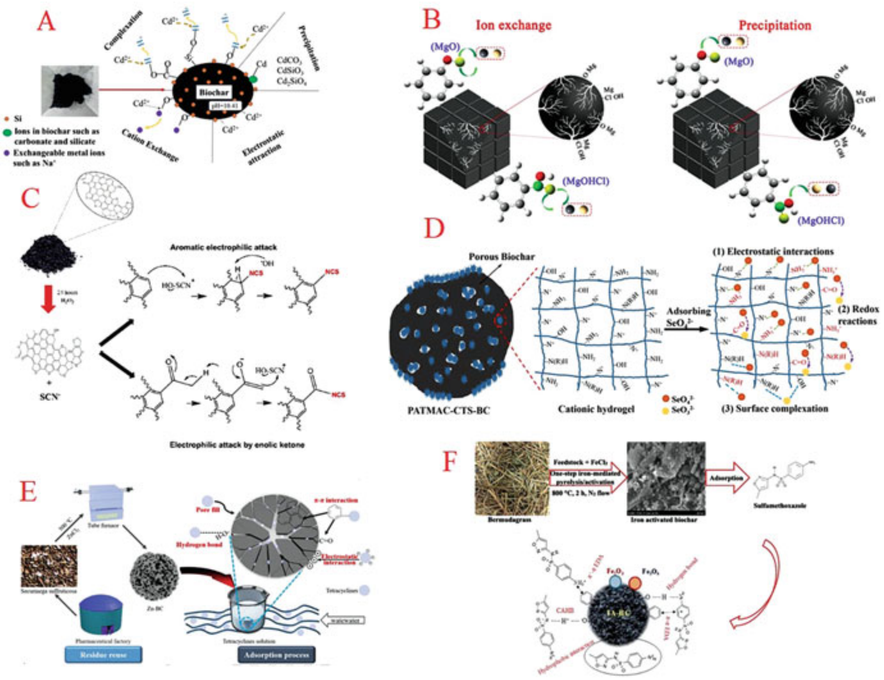

Fig. 1.3 (**a**) Schematic representation of different adsorption mechanism of Cd^{2+} biochar, Si (Cai et al. 2021). (**b**) Schematic diagram of the main adsorption mechanism of MgBC400 to Pb^{2+} and Cd^{2+} (Wu et al. 2021). (**c**) Reaction mechanisms of biochar with thiocyanate ion (Macedo et al. 2021). (**d**) Schematic illustration of removal mechanisms of SeO_4^{2-} by PATMAC-CTS-BC (Zhang et al. 2021a). (**e**) Schematic presentation of the preparation of Zn-BC and its adsorption mechanism (Wang et al. 2021c). (**f**) Schematic diagram of the preparation of IA-BCs and its adsorption mechanism (Zeng and Choi 2021)

Furthermore, silicate functionalization allows the internal diffusion of Cd on biochar. According to FTIR and XPS, ion exchange with Na^+, surface precipitation ($CdCO_3$, $CdSiO_3$, or Cd_2SiO_4), coordination with π electrons (C=C), and complexation with carboxyl and C–Si–O groups are explained sorption mechanisms; see Fig. 1.3a. Magnesium-modified coconut shell biochar (MgBC400) was investigated (Wu et al. 2021) for high adsorption performance of Pb and Cd from wastewater. As a result of modification, the adsorption capacity of Mg-coated biochar (MgBC400) was found 20 (For Pb) and 30 (for Cd) times compared with the pristine biochar (BC400). The removal mechanism (Fig. 1.3b) may be explained on bases of ion exchange (Q_e), mineral precipitation (Q_p), interaction with oxygen functional groups (OFGs) [(Q_f)], and metal-π electron coordination (Q_π). Compared with the BC400, the adsorption capacity of the four routes of MgBC400 especially enhanced the ion exchange and precipitation. The Q_e values of MgBC400 were almost 49 (Pb) and 59 (Cd) times that of BC400, and the Q_p values of MgBC400 increased by 214.4 and 81.7 mg/g, respectively. Sulfonated biochar (SBC) from *Axonopus compressus* was prepared via a simple one-step solvothermal route under a mild-temperature condition (Yu et al. 2021b). The generation of –OH, –COOH, and $-SO_3H$ moieties on the surface of SBC during the sulfonation process was confirmed by FTIR and XPS analysis. Attributed to high electronegativity and strong complexation of these active sites, SBC can adsorb Pb(II) and Cd(II) rapidly (in 5 min) with capacities of 191.07 and 85.76 mg/g, respectively. SBC can be recycled for 5 times with a negligible loss of adsorption capacity. Effective cadmium (Cd) and arsenic (As) removal from aqueous solution was achieved (Wang et al. 2021a) by using of composite synthesized by *Bacillus sp.* K1 anchored onto Fe_3O_4 biochar (MBB). The blending with *Bacillus* sp. K1 exhibited new biosorption active sites such as amine and hydroxyl groups in the composite surface, which highly enhances the removal activity of Cd(II) by 230% compared with the raw magnetic biochar. Moreover, the adsorption of As(III) will act as a new active site for adsorbing Cd(II), which is introduced on the surface of the MBB. The maximum adsorption capacity of Cd (II) is 25.04 mg g^{-1} and As(III) reached 4.58 mg g^{-1} in a binary system.

A biochar derived from sewage sludge functionalized with hydroxyapatite (HAP) was prepared as a novel and efficient adsorbent (HAP-SSBC) for adsorption of Cu^{2+} and Cd^{2+} from aqueous solution (Chen et al. 2021). Adsorption experiments indicated that HAP-SSBC presented higher adsorption performance compared to the raw sludge-based biochar (SSBC). According to Langmuir model, the HAP-SSBC showed maximum adsorption capacity of Cu^{2+} (89.98 mg/g) and Cd^{2+} (114.68 mg/g). Moreover, the characterization analysis of the solid after the adsorption process provided that the main mechanisms involved in the adsorption process were ion exchange with Ca^{2+}, interaction with –OH and –COOH, and forming Cu-π or Cd-π binding with aromatic C=C on HAP-SSBC surface. A hybrid adsorbent (MO-L-BC) was fabricated (Wan et al. 2020) via dispersing manganese oxide (MO) inside a biochar with enlarged pore structure (L-BC). The used carrier (porous L-BC) promoted a high proportion of large pores (>2 nm) (87%) and thus allows the target pollutants to diffuse in pore region of MO-L-BC. Consequently, Sb(III) and Cu(II) could be adsorbed rapidly (within 15 min) onto MO-L-BC. The XPS analysis demonstrated that 53.3% of the sorbed Sb(III) was oxidized to Sb(V) by the mixing MO. Coexisting substances such as HCO_3^-, SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+} and humic acid with concentration up to 20 times higher than target contaminants (Sb(III) or Cu (II)) resulted in <20% drop in sorption amount of MO-L-BC. The fixed-bed column adsorption experiments presented MO-L-BC success in the tertiary treatment of either the singly contaminated (Sb(III) or Cu(II)) or the copolluted wastewater at a high flow rate of 0.27 m h^{-1}; moreover, the saturated MO-L-BC can be effectively regenerated. Konjac starch was dispersed in polyvinylpyrrolidone (PVP) solution to fabricate various sizes of hydrophilic carbon spheres (HCSs) by hydrothermal approach (Li et al. 2020a). Interestingly, with further increase in the temperature, adsorption thermodynamics are more consistent with the Freundlich model. In addition, HCSs possessed excellent selectivity for the adsorption of Pb^{2+} and Cu^{2+}.

Hydrophilic biochar (HPB) is produced by an acid ammonium persulfate oxidation treatment with an adsorption capacity of up to 135.4 mg g^{-1} for Pb^{2+} (Li et al. 2020c). Due to the strong Fe–C–O covalent bond, nano-zerovalent iron (nZVI) forced the binding with the carbon matrix. Moreover, the used composite is featured by high specific surface area, porous structure, and richness with oxygenated functional groups, which makes the obtained composite appropriate for Pb^{2+} diffusion and adsorption. Therefore, nZVI-HPB presented maximum adsorption capacity of 589.9 mg g^{-1}. Several interaction mechanisms for the Pb^{2+} removal could be supposed such as the reduction reaction, complexation, and coprecipitation which proceed simultaneously. Sylwan et al. (2020) studied sorption of heavy metal to sludge-derived biochar (SDBC) via batch experiments and modeling and compared to that of wood-derived biochar (WDBC) and activated carbon (AC). The SDBC presented superior Pb^{2+} sorption capacity (maximum ~2 mg/g) compared to WDBC (<0 mg/g) and AC ($(3.5 \pm 0.4) \times 10^{-3}$ mg/g); however, at the lowest concentration investigated (0.005 mg/L), SDBC released Pb^{2+}. B-Cyclodextrin (β-CD)-modified rice husk-derived biochar (BC) was conveniently and rapidly prepared through microwave (MW)-assisted one-pot strategy (BCMW-β-CD) and applied for simultaneous removal of bisphenol A (BPA) and lead (Pb) (Qu et al. 2020). Profiting by microwave irradiation, the surface functionalization was proceeded in 15 min, and the prepared BCMW-β-CD introduced an excellent adsorption efficiency (209.20 mg/g) for BPA and (240.13 mg/g) for Pb(II). Furthermore, the BCMW-β-CD could simultaneously achieve efficient cleanup of BPA and Pb (II) in binary system without further competition with each other, which was referred to the different adsorption mechanisms for Pb(II) (i.e., electrostatic attraction and complexation) and BPA (i.e., host-guest supramolecular and π-π interactions). Moreover, the BCMW-β-CD could be reused with mild decrease in the adsorption efficiency even after five runs in the Pb(II)-BPA multicomponent system.

Raw jujube seeds (RJS) activated with sulfuric acid followed by ultrasonic treatment to yield ultrasonic-assisted jujube seed (UAJS)-based biochar have been studied (Gayathri et al. 2021) as a viable material for managing Zn(II)- and Pb(II)-contaminated water. UAJS Langmuir capacity was found 221.1 mg/g for Zn(II) ions and 119.8 mg/g for Pb(II) ions which were higher than that obtained by RJS. The mechanism of the separation process is controlled by internal and external diffusion. Moreover, the real electroplating industrial wastewater was also blended with UAJS biochar to eliminate the metal ions such as copper, nickel, chromium, and zinc ions from wastewater. The adsorbent efficiency maintains the maximum over five adsorption/desorption runs. Low-cost banana stalk (Musa nana Lour.) biochar (BB) was synthesized (Deng et al. 2020) using oxygen-limited pyrolysis (at 500 °C) and employed to remove heavy metal ions (including Zn(II), Mn(II), and Cu(II)) from aqueous solution. Adsorption experiments presented that the initial solution pH affected the ability of the biochar to adsorb heavy metal ions in single- and multi-metal systems. Compared to Mn(II) and Zn(II), the biochar possessed highly selective Cu(II) adsorption. The results showed that the heavy metals were chemically adsorbed from single system with maximum adsorption capacities (mg g^{-1}) in order Cu(II) (134.88) > Mn(II) (109.10) > Zn(II) (108.10). The results indicated that the ion exchange was likely involved in Mn(II) and Zn(II) removal, while C–O, O–H, and C=O possibly were responsible for Cu(II) removal by complexing or other reactions.

Maneechakr and Mongkollertlop (2020) studied the adsorption behaviors of heavy metal cations such as Cd^{2+}, Cr^{3+}, Hg^{2+}, and Pb^{2+} using active MnO_2-anchored magnetic biochar coming from palm kernel cake residue. The Fe_3O_4 is synthesized via coprecipitation and simply assembled on surface of carbonized biochar powder (CP). The adsorption efficiency of magnetic biochar (CP-Fe) was highly enhanced by doping with $KMnO_4$ (CP-Fe-Mn). According to Langmuir, all heavy metal ions studied adsorbed over CP-Fe-Mn as a monolayer-physisorption process, with maximum adsorption capacities ($q_{max,}$ mg/g) of Cd^{2+} (18.60), Cr^{3+} (19.92), Pb^{2+} (49.64), and Hg^{2+} (13.69). At the end of the adsorption experiments, the composite simply recovered from the solution by external magnetic field. Sugarcane bagasse BCs (produced at pyrolysis temperatures from 300 to 700 °C) were functionalized in a one-step reaction with isothiocyanate (Macedo et al. 2021). The performance and selectivity of original and modified BCs for elimination of Cd^{2+}, Ni^{2+}, Pb^{2+}, and Cr^{3+} from mono- and multi-element aqueous solutions were studied. The analysis results showed that the modification of organosulfur will lead to increase of S and N quantity on the surface of the BCs, particularly isothiocyanate groups, as shown in Fig. 1.3c. The results displayed that the adsorption of metal ions by treated biochars follows the order $Pb^{2+} > Cr^{3+} > Cd^{2+} \cong Ni^{2+}$ and $Cd^{2+} > Pb^{2+} > Ni^{2+} \cong Cr^{3+}$ in case of mono- and multi-element systems, respectively. The mechanisms explained the adsorption processes were physisorption, chemisorption, complexation, precipitation, and ion exchange. Moreover, the introduction of other metal ions in the multi-element system resulted in a synergistic effect on adsorption of Cr^{3+}, Cd^{2+}, and Ni^{2+} and an antagonistic effect on adsorption of Pb^{2+}.

$MnFe_2O_4$-biochar composite (MFBC) was synthesized (Liu et al. 2021) through coprecipitation route as an efficient adsorbent for treating Tl(I)-contaminated wastewater. Based on Langmuir model, the MFBC has high Tl(I) removal capacity (170.55 mg/g). The removal mechanisms combine physical and chemical adsorption, ion exchange, surface complexation, and oxidation. Rice husk (RH) and coconut shell (CS) biomasses were applied to fabricate honeycomb-networked biochar (BC) precursors through slow pyrolysis (Kamran and Park 2020). Furthermore, the RHBC- and CSBC-based MnO_2 composites were prepared by precipitation of MnO_2 in altered ratios onto RHBC and CSBC by changing the $KMnO_4$ concentration (2%, 3%, and 4%), subsequent by simple ultrasonication and heat-treatment routes. The comparative adsorption analysis indicated that the RHBC-Mnx composites excite stronger Li^+-adsorption ability than the CSBC-Mnx composites. Moreover, further increasing the MnO_2 deposition to 3% in both composites resulted in maximum Li^+ adsorption capacities (62.85 mg g^{-1} and 57.8 mg g^{-1}), respectively. Finally, Li^+ was successfully recovered using HCl (eluting agent).

A novel anchored and combined N-doped graphene oxide hydrogel with shrimp shell magnetic biochar (NGO3DH-MSSB) biosorbent was prepared as a preformed material for Cr(VI) adsorption (Mahmoud et al. 2021). The obtained results showed that the NGO3DH-MSSB composite owns high surface area (398.05 m^2/g) compared with that of MSSB (138.64 m^2/g). Moreover, the hydrogel exhibits maximum swelling ratio (800%) within 300 min. The binding mechanisms among Cr(VI) ions and NGO3DH-MSSB biosorbent were explained by electrostatic adsorption

(ion-pair), pore filling, and reduction coordination reaction. According to Langmuir, the adsorption capacity (350.42 mg/g) was obtained at pH 1.0, using initial Cr (VI) concentration (100 mg/L) and contact time (180 min) at room temperature. Additionally, NGO3DH-MSSB biosorbent could be efficiently reused after eight cycles. Moreover, the removal percentage of Cr(VI) were recorded as 99.79% (tap water), 99.20% (seawater), and 98.00% (wastewater). In hybridization of corn straw, attapulgite, zeolite, starch, and iron oxide, a series of hematite-anchored biochar-clay granular composites (HGCs) were prepared via two-step pyrolysis routes used for efficient Cr(VI) removal from an aqueous solution (Zhu et al. 2020). The characterization data of HGCs described that a mesoporous structure and the hematite were successfully formed on the surface of HGCs. The maximum adsorption capacity of Cr(VI) on the HGCs at pH 5.0 was 19.51 mg/g as related to the Langmuir model. The mechanisms of Cr(VI) removal by HGCs could be explored with electrostatic interaction, hydrogen bond attraction, redox reaction, and coprecipitation reaction. Moreover, the strong electrostatic interaction bounded HGCs and Cr(VI) might describe the decreased adsorption capacities of Cr(VI) along pH range 1.0–10.0. A new and efficient composite of siltstone-nanomagnetite-biochar (SNB) composite based on *Eleocharis dulcis* biochar with magnetite nanoparticles and siltstone (Ud Din et al. 2021) was prepared to remove chromium from water. Batch adsorption mode was used to evaluate the adsorption capacity of composite for the decontamination of chromium. The adsorption capacity obtained in this study was found to be 35.57 mg/g. It was suggested that hexavalent chromium reduced to the trivalent chromium Cr(III) which, thereafter, interacted with functional groups of MBS, which was confirmed by FTIR and XPS analysis. A high-efficient porous biochar (PBCKOH) (Qu et al. 2021) was prepared through two-step pyrolysis of corn straw and chemical activation of KOH and was applied for the removal of Cr (VI) and naphthalene (NAP) from water. The KOH activation promoted the PBCKOH with huge specific surface area of 2183.80 m^2/g and many well-improved micropores with average size of 2.75 nm and the main pore diameters distribution range (1–2 nm). The PBCKOH possessed a suitable adsorption performance with a theoretical monolayer uptake of 116.97 mg/g for Cr(VI) and a heterogeneous adsorption capacity of 450.43 mg/g for NAP. Furthermore, the PBCKOH improved the Cr(VI) adsorption mainly through the electrostatic attraction, complexation, ion exchange, and reduction action, while it exhibits the high NAP elimination by pore filling and π-π stacking interactions. Mao et al. (Mao et al. 2021) prepared a novel Bi_2WO_6-anchored N, S co-doping corn straw biochar (Bi_2WO_6/NSBC) with a simple solvothermal approach for the elimination of ciprofloxacin (CIP) and Cr (VI) under visible light irradiation. The Bi_2WO_6/NSBC was characterized with preformed and fast catalytic removal toward CIP (5 mg/L) (~90.33%) and Cr (VI) (10 mg/L) (~99.86%), within 75 min. More importantly, this composite can be used over a wide pH range (3.0–9.0) and with weak influence by coexisting ions (Cl^-, CO_3^{2-}, SO_4^{2-}, and Ca^{2+}). It was observed that N, S co-doping of the BC owns fibrous structures, high catalytic feature, and appropriated specific surface areas, which aid for avoiding the agglomeration of $Bi_2WO_{6.}$ This synergistic effect of

Bi_2WO_6 and NSBC will optimize the bandgap and improve the response toward the visible light, consequently increasing the photocatalytic activity.

A novel nanocomposite of *Sesbania bispinosa* biochar (SBC) (Imran et al. 2021) is combined with copper oxide (SBC/CuO) and manganese oxide nanoparticles (SBC/MnO) for the efficient and low-cost removal of arsenic (As) from contaminated water at batch scale. The findings indicated that the maximum adsorption of As increases in order SBC/CuO composite (12.47 mg/g) > SBC/MnO (7.34 mg/g) > SBC (7.33 mg/g). Moreover, the SBC/CuO exhibited excellent reusability and stability over four adsorption/desorption times. Li et al. (Li et al. 2020a, b, c) applied the ball milling to prepare a nanocomposite of 20% hickory biochar (600 °C) and 80% expanded vermiculite (20% BC/VE). This novel composite adsorbent had much higher removal of As(V) from aqueous solutions than ball-milled biochar and expanded vermiculite, individually. Characterization of these adsorbents showed that the enhanced As(V) adsorption was attributed to much larger surface area and pore volume (two-to sixfold), notable variations in crystallinity, activation of cations, and increased functional groups density in the nanocomposite compared with the ball-milled products of their pristine counterparts. The As(V) was adsorbed with maximum capacity (20.1 mg g^{-1}) based on Langmuir. The adsorption efficiency was not affected with the presence of NO_3^-, Cl^-, SO_4^{2-}, and humic acid. However, the adsorption capacity for As(V) was highly decreased at addition of PO_4^{3-}. Porous biochar-supported $MnFe_2O_4$ magnetic nanocomposite (BC-MF) was successfully prepared and employed as an efficient adsorbent for simultaneous elimination of *p*-arsanilic acid (*p*-ASA) and As(V) from water environment at pH range 3–7 (Wen et al. 2021). The BC-MF possess adsorption capacities of *p*-ASA (105 mg/g) and As(V) (90 mg/g) at a 10μg/L equilibrium concentration. The suggested adsorption mechanism could be explained on basis of electrostatic interaction and surface complexation which involved the *p*-ASA and As(V) immobilization; moreover, H-bonding and π-π interactions may also be involved on the *p*-ASA removal. An active MnO_2/rice husk biochar (BC) composite (MBC) was fabricated (Cuong et al. 2021) to improve As(III) removal for groundwater remediation. The removal studies revealed that MBC presented a high elimination capacity for As(III), which was tenfold higher than that of BC. This enhancement can be explained based on the redox conversion of As (III) via MnO_2, leading to more effective removal of As(V) species. In addition, under alkaline environments, the As(III, V) removal capacity of MBC was highly lower than those under acidic and neutral conditions; this is attributed to the negative effects of electrostatic repulsion. Importantly, a powerful transformation ability of As(III) via MBC was observed, where only 5.9% As(III) remained in solution under neutral conditions. Both MnO_2 and the BC substrate are involved in the removal of arsenic by MBC. MnO_2 provided Mn-OH functional groups to create surface complexes with As(V) produced by As(III) oxidation, while the reduced Mn (II) and As(V) could precipitate on the MBC surface. Moreover, the BC substrate also exhibited COOH and OH functional groups for As(III, V) removal through a surface complexation mechanism with removal percent reaching up to 94.6%.

A new poly(allyltrimethylammonium) (ATMAC)-modified chitosan (CTS) and biochar composite (PATMAC-CTS-BC) was prepared for the removal of selenate (SeO_4^{2-}) from water (Zhang et al. 2021a). Results suggest that the PATMAC-CTS-BC possess high capacity of SeO_4^{2-} adsorption (98.99 mg g^{-1}) based on Langmuir model. Also, the composite could be used over a wide initial pH range (2–10) with high removal performance of SeO_4^{2-}. This is due to the permanent positive charges related to quaternary ammonium groups ($=N^+–$). The adsorption mechanisms of SeO_4^{2-} were mainly based on electrostatic interactions with $=N^+–$ and protonated $–NH_3^+$ groups as presented in Fig. 1.3d and redox-complexation interactions with $–NH_2$, –NH–, and –OH groups. Besides, the hexavalent chromium ($Cr_2O_7^{2-}$) was supplied as another model to examine the capability of cationic hydrogel-BC composite for anion removal. Activated biochar-anchored nano-zerovalent iron (A-BC-NZVI) (Zhang et al. 2021b) was applied to remove heavy metal uranium (U(VI)) from sewage water. The A-BC-NZVI composite was prepared by aqueous phase reduction using biomass longan shell as carbon source under N_2 at 800 C. The batch sorption experiments indicated that the removal of U(VI) decreases in pH range 7–10 and at pH 6.0, and the maximum U(VI) adsorption quantity referring to Langmuir model was 331.13 mg/g. The XPS analysis indicated that A-BC-NZVI has two effects on U(VI), involving adsorption and reduction.

1.3.2 Biochar for Removal of Organic Pollutants

Organic pollutants are effluents from several industries, such as textile, plastics, pharmaceuticals, food, paper, etc. However, the discharge of contaminants in water resources always caused a negative influence on the surrounding environment and can seriously threaten living organism life. As a result, great efforts have been carried out for the preparation of a preformed material to enhance the removal of these wastes from contaminated water.

Salehi et al. (2020) prepared biochars by treating spent-tea residue (STR) with phosphoric acid and pyrolysis at different temperatures. Results demonstrated that the further increase in the pyrolysis temperature could improve the porous structure and increase the surface area, whereas it might cause loss in the surface functional groups. The produced biochar samples were employed for the adsorption of methylene blue (MB) from water. The batch adsorption process indicated that the STR biochar prepared by pyrolysis at temperature of 400 °C offered the maximum MB removal of 99.26% and the maximum adsorption capacity was 91.13 mg/g. Silva et al. (2021) prepared biochar-derived castor seed cake by the pyrolysis process. Thereafter, the crude biochar (40.6% yield) was treated with concentrated sulfuric acid (H_2SO_4) to produce activated biochar 1 (AB1) with specific area (603.29 m^2 g^{-1}) for removal of methylene blue dye. The adsorption results showed that the removal percent reached to 96% of the dye and the intraparticle diffusion controls the adsorption rate of the dye by AB1. A novel composite of chitosan-modified biochar (CPB)-anchored $MnFe_2O_4$ ($MnFe_2O_4$@CPB) (Wang et al. 2021b) was fabricated via simple chemical coprecipitation process which does well for methyl orange (MO) removal in adsorption and photo-Fenton processes. Under the same adsorption condition, the adsorption capacity of $MnFe_2O_4$@CPB was 1.48, 1.06, and 7.90 times of pure biochar, CPB, and $MnFe_2O_4$, respectively. This is referring to H-bonding and π-π interactions between MO and $MnFe_2O_4$@CPB. Moreover, $MnFe_2O_4$@CPB has ability to degrade 99.50% of MO in visible LED light/H_2O_2 system under the synergetic effect of $MnFe_2O_4$ and CPB. The abundant surface functional groups of CPB (especially amino groups and C–O) presented active sites for H_2O_2; thereafter, the hydroxyl radicals ($^{\bullet}OH$) will be generated. In addition, the redox catalytic cycles of Fe(II)/Fe(III) and Mn(III)/Mn(II) were developed under visible LED light, which qualify $MnFe_2O_4$@CPB to have great removal efficiency over five recycle tests. Mesoporous nano-zerovalent manganese (nZVMn) and *Phoenix dactylifera* leaves biochar (PBC) composite was synthesized for the removal of CR from water (Iqbal et al. 2021). The nZVMn/PBC adsorbed 117.647 mg/g of CR versus 25.316 mg/g by PBC under similar condition, based on Langmuir calculations. The addition of H_2O_2 to the nZVMn/PBC system will enhance the removal of CR; this is attributed to the possible generation of hydroxyl radical ($^{\bullet}OH$) and resulted to 95% removal of CR versus 77% by nZVMn/PBC alone. Finally, the nZVMn/PBC presented a good reusability and efficient removal of CR up to the seventh cycle of treatment. A hierarchical porous biochar (HPB) prepared from shrimp shell presented enhanced adsorption capacity ($Q_m > 300$ mg/g) and rapid adsorptive equilibrium (≤10 min) toward three typical aromatic organics 2,4-dichlorophenol (DCP), rhodamine B (RHB), and tetracycline hydrochloride (TC) (Yu et al. 2021a). Whereafter, the analysis model explored that the adsorptive forms (mono- and multilayers) on HPB relied on whether the contaminant is charged. Compared to the benzene-ring site of organics, the charged site shared 5.13 times to adsorption promotion in monolayer but −0.49 times in inhibition for multilayers forms. Simultaneously, the active sites functional group contributed relatively weak (0.023–0.342 times only). Finally, it was important to note that the hierarchical pore structure of HPB was the key for the rapid adsorption speed, and highly graphitic structure was vital for the high adsorption capacity.

An innovative heat pipe reactor was applied to prepare biochar from food and garden materials residue (Hoslett et al. 2021). The biochar fabricated had an adsorption capacity about 2.98 mg/g and 8.23 mg/g for initial tetracycline concentrations of 20 mg/L and 100 mg/L, respectively. Wang et al. (2021c) employed the residue derived from Chinese herbal medicine, *Flueggea suffruticosa*, to synthesize biochar for antibiotics pollution management. Furthermore, the biochar was anchored by zinc chloride (Zn-BC) and utilized as an adsorbent to eliminate tetracyclines (TCs) from water, as presented in Fig. 1.3e. Referring to the Langmuir model, the maximum removal capacity of Zn-BC to chlortetracycline (CTC) is 200.0 mg/g, tetracycline (TC) 188. 7 mg/g, and oxytetracycline (OTC) 129.9 mg/g. Hydrogen bonding and electrostatic interaction explain the mechanism of the adsorption process. An economical biochar-supported iron-copper bimetallic composite (BC-FeCu) was prepared and utilized to remove tetracycline (TC) from water (Liu et al. 2020). The experimental results showed that BC-FeCu presented higher removal (92.50%) than FeCu (67.30%) under the same condition. Moreover, the TC removal by

BC-FeCu constantly increased within pH range 4.50–9.03. Desorption studies displayed that the adsorption and degradation were calculated for 26.09% and 73.91% of the total TC removal by BC-FeCu, respectively. N_2 sparing tests explored that the degradation proceeded via dissolved oxygen (DO) and the direct degradation by BC-FeCu were calculated for 17.02% and 56.89% of the total TC removal, respectively. The $O_2^{\bullet-}$ was confirmed to be the main active species for TC degradation by BC-FeCu. The degradation mechanism could be explained via the electron transferred from –COOH, –OH, and Cu/Cu^+ in BC-FeCu to O_2 to form $O_2\bullet^-$. A magnetic rape straw biochar (MRSB) catalyst was prepared by a high value-added and energy-saving strategy (Huang et al. 2021). The MRSB catalyst presented high catalytic activity and recyclability for activating persulfate (PS) to degrade tetracycline hydrochloride (TC) in water. Moreover, the presence of Fe_3O_4 in the MRSB greatly enhances the activation of PS. Additionally, the MRSB catalyst presented excellent catalytic activity over a wide pH range (2.99–11.01) for activating PS to degrade TC in water. Moreover, good catalytic activity for TC degradation was maintained over eight recycling runs and was easily recovered by an external magnetic field for reuse. The electron spin resonance (ESR) data explored that the production of the sulfate radicals ($SO_4^{\bullet-}$), hydroxyl radicals ($^{\bullet}OH$), and superoxide radicals ($O_2^{\bullet-}$) was greatly allowed in the MRSB/PS system. Therefore, MRSB showed 13.24-fold higher reaction rate for activating PS than those of pure rape straw biochar (RSB). Both radical and non-radical mechanism presented in the MRSB/PS system, and $SO_4^{\bullet-}$ and singlet oxygen ($^1O_2$) displayed a determinative role. Zhao et al. (2021) successfully fabricated and structurally characterized Fe0-, Fe3C-, and Fe_3O_4-anchored biochars (BCs) for elimination of chlortetracycline hydrochloride (CH). The experimental result presented higher removal rate and affinity revealed to Fe0@BC toward CH than Fe3C@BC and Fe_3O_4@BC. The removal rate was controlled by the O–Fe content and solution pH after the reaction. The CH adsorption takes place on the O-C groups of Fe0@BC and the O=C and O—Fe groups of Fe3C@BC and Fe3O4@BC. Electron paramagnetic resonance analysis and radical quenching experiments demonstrated that $HO^{\bullet}$ and $^1O_2/O_2^{\bullet-}$ were mainly the key for CH degradation by biochar/Fe composites. Biochar-supported nanosized iron (nFe(0)/BC) was prepared and applied as a persulfate (PS) activator for degradation of tetracycline (TC) (Shao et al. 2020). In the nFe(0)/BCePS system, TC could be effectively removed in pH range 3.0–9.0. The degradation performance of TC (100 mg/L) was 97.68% using nFe(0)/BC (0.4 g/L) and persulfate (1 mM) at pH 5.0. Coexisting anions (HCO_3 and NO_3) retard the degradation TC. Electron spin resonance (ESR) analysis and scavenging experiments supposed that sulfate radicals ($SO_4^{\bullet}$) and hydroxyl radicals ($HO^{\bullet}$) were responsible for TC degradation. Even after five reused cycles, nFe(0)/BC could still maintain 86.38% of its original removal capacity. Two biochars derived from date pits (DP) non-magnetic (BCDP) and magnetic (MBC-DP) were prepared and used to remove tigecycline (TIGC) from TIGC artificially polluted water samples (El-Azazy et al. 2021). The experimental results presented that the MBC-DP possessed higher removal (%R) (99.91%), compared to 77.31% for BCDP. Moreover, according to Freundlich isotherms, the maximum adsorption capacity of TIGC is 57.14 mg/g using MBC-DP. Ramanayaka et al. (Ramanayaka et al. 2020) applied macro- (BC), colloidal (CBC), and nanobiochar (NBC) for studying the particle size to induce the adsorptive removal of oxytetracycline (OTC) and co-occurring nutrients, which are present in simulated hydrolyzed human urine. The highest maximum adsorption capacity for CBC is 136.7 mg/g, BC 129.34 mg/g, and NBC 113.2 mg/g. Colloidal biochar related the highest adsorption for NH_4^+, PO_4^{3+}, and SO_4^{2+} nutrients. All three types of chars presented strong recovery with a poor desorption (6% in average) of OTC in synthetic hydrolyzed urine medium.

The production of biochar from sugarcane bagasse using HTC followed by NaOH treatment at inert atmosphere for removing sulfamethoxazole (SMX) from water (Prasannamedh et al. 2021). The XRD and FTIR analysis indicated that presence of aromatized graphitic structure combined with oxygenated functional groups is responsible for the adsorbing of SMX. The SEM images showed the sphere-shaped structure of biochar with hydrophobic groups interior and hydrophilic groups exterior. BET provided the active surface area equal to 1099 m^2/g with high coverage of mesopores structure. Pzpc of adsorbent is evaluated to 6.5 confirming that effective uptake of SMX based on ionization effects was induced due to reaction medium. The adsorption of SMX on ABC surface is referred to charge-assisted hydrogen bonding and π-π interaction with graphitized carbon, showing maximum sorption capacity of 400 mg/g through spontaneous reaction. Zeng and Choi (2021) study the influence of $FeCl_3$ impregnation ratio on the functions of $FeCl_3$-activated bermudagrass (BG)-derived biochars (IA-BCs) for adsorption of sulfamethoxazole (SMX). Compared with the pure BC (85.82 m^2/g), IA-BCs produced by pyrolysis with $FeCl_3$-to-BG mass ratio between 1 and 3 (1–3 g $FeCl_3$/g BG) caused enhancement in the surface area (1014–1035 m^2/g), hydrophobicity, Fe amount in IA-BCs (3.87–7.27%), and graphitized carbon. The results indicated that IA-BCs exhibited magnetic separation and higher adsorption (32–265 mg SMX/g BC) than the control BC (6–14 mg SMX/g BC) at various pH. The adsorption mechanisms of SMX over IA-BCs could be supposed by π-π EDA, hydrophobic interactions, and hydrogen bond with intraparticle diffusion limitation, as illustrated in Fig. 1.3f. The IA-BC prepared at $FeCl_3$-to-BG mass ratio of 2 (IA-BC2.0) presented the maximum adsorption capacity for SMX (253 mg SMX/g BC) based on Langmuir isotherm calculations. Furthermore, the IA-BC2.0 could be regenerated by both NaOH desorption and thermal oxidation. After three cycles of adsorption-regeneration, 64% (thermal treatment at 300 °C) and 62% (desorption with 0.1 M NaOH solution). Peng et al. (2021) investigated a simple route to fabricate cobalt phosphide/carbon composite for PMS activation. Combining impregnation route with pyrolysis treatment allows the formation of Co_2P/biochar composites using baker's yeast and Co_2P as precursors. The as-prepared products presented high catalytic activity for sulfamethoxazole (SMX) degradation over the pH range 3.0–9.0 by activating PMS. For example, 100% of SMX (20 mg L^{-1}) removal was reached in 20 min with catalyst dosage of 0.4 g L^{-1} and PMS amount of 0.4 g L^{-1}. Near-zero Co_2P leaching was obtained during catalytic reaction, which significantly lowered the toxic risk of transition metal ion in water. Meanwhile, the reusability of catalyst could be attained by thermal treatment.

Anthriscus sylvestris-derived activated biochar was investigated (Shirani et al. 2020) to yield raw biochar (R-BC) and activated biochar (ACT-B) for adsorption of diclofenac (DF) and cephalexin (CPX). Batch studies showed that the maximum adsorption capacity of ACT-B was 392.94 mg g^{-1} for DF and 724.54 mg g^{-1} for CPX and the removal of DF and CPX was affected by temperature and the coexisting ions. The kinetic data fitted well with the pseudo-second-order kinetic model, whereas the isotherm data showed the best correlation with Langmuir isotherm model. Electrostatic adsorption, hydrophobic interaction, and π-π bonding were the responsible for adsorption of both adsorbates by ACT-B. Additionally, column studies conducted using ACT-B were investigated for the practical applicability of ACT-B in removal of the target contaminants. Cost-effect kaolinite (KAC) clay was synergistically mixed with blended *Carica papaya* or pine cone seeds and calcined to yield composites of KAC-*Carica papaya* seeds (KPA) and KAC-pine cone seeds (KPC) for removal of ivermectin in aqueous media (Olu-Owolabi et al. 2021). The composites presented significant property differences involving over 250% increases in cation exchange capacity and ≥50% decreases in the surface area, but KAC still unchanged. The adsorption data showed that the adsorption rate on KAC decreased over time, while rates for KPA and KPC increased until equilibrium at 180 min; the introduction of biomaterials in the composites explained better ivermectin adsorption and retention under continuous agitation. Freundlich adsorption isotherm model was better fitted (≥0.9887) the experimental data; this indicates complex interactions among ivermectin and the adsorption sites of both composites. Furthermore, the KPA possessed better reusability with 83.5 and 67.5% initial adsorption strengths remaining in the second and third adsorption cycles, respectively, compared to the 73.8 and 58.8% for the KPC. Cell-immobilized biochar was investigated to remove paraquat (PQ) from polluted water through immobilizing *Pseudomonas putida* onto coconut fiber-derived biochar (BC) (Ha et al. 2021). The FTIR spectrum analysis demonstrated that the adsorption mechanism of bacteria and BC belongs to the interaction between cell surface proteins and the functional group on biochar. The cell-loaded biochar using the covalent bonding and adsorption approach presented superior PQ removal capacity (16.79 mg/g) with 30–35% increases in efficiency compared with original biochar. More interestingly, after 48 h of using cell-immobilized biochar, the PQ was converted to 4,4-bipyridyl and malic acid as assessed by GC/MS.

An innovated FeOX nanoparticle-immobilized biomass-activated carbon (BAC/FeOX) composite was fabricated via one-pot calcination strategy using $FeCl_3$ and cherry stone powder as precursors (Li et al. 2021). The carbonization of biomass, reduction of Fe^{3+}, and FeOX supported on carbon substrate could be done at the same time. Bisphenol A (BPA) was used to study the degradation efficiency of BAC/FeOX activating peroxydisulfate (PDS). The results showed that the free radical determination and quenching experiments explored that both $SO_4^{\bullet -}$ and $^{\bullet}OH$ were contributed in BPA degradation. Low-cost and eco-friendly biochar catalyst (SugBC900) with high catalytic activity toward peroxymonosulfate (PMS) was fabricated by facile pyrolysis of sugarcane waste and employed for preformed degradation of organic pollutants (He et al. 2021). Combining high sp^2 hybrid carbon density, large surface area, and good electron transfer ability, the SugBC900 coupled with PMS possessed far enhanced catalytic degradation ability toward bisphenol A (BPA). The oxidative species of $^1O_2$ and $O_2^{\bullet-}$ were indicated to be responsible for catalytic degradation, and the route of $SO_4^{\bullet-}$ and $^\bullet OH$ was minor. Even at the extremely acidic (pH of 1.0) or low-temperature (10 °C) environment, the degradation efficiencies maintain more than 90%. In addition, the SugBC900 was successfully applied efficiently to degrade BPA and other organic pollutants in different real environmental water.

1.4 Conclusion

Recently, water resources are contaminated by an increasing number of various pollutants, such as inorganic and organic compounds. These contaminations have a negative impact on all the living organisms. Therefore, great efforts have been done to put forward effective remediation agent. The biochar is a carbon-rich material derived from organic biomass through thermal carbonization process. The physicochemical properties of the biochar highly depend on the type of biomass used, thermal pyrolysis conditions, and the activation method. By optimizing the previous parameters, a low-cost, highly porous, enhanced surface area, and efficient biochar adsorbent was obtained. The activation methods, especially chemical activation, can make a highly difference in the surface properties and, consequently, enhanced the adsorption performance of modified biochar.

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Utility of Surface-Modified Biochar for Sequestration of Heavy Metals in Water

2

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Abstract

Increased industrial growth in the world serves a significant role in the water contamination with heavy metals. Heavy metals such as arsenic, copper, lead, chromium, mercury, nickel, and cadmium impart several health hazards to humans, plants, and animals. Moreover their accumulation potential disturbs the food chain. Freshwater demand is higher in the world which may lead to a severe water crisis in the upcoming years. Hence feasible water treatment technologies must be identified and its efficiency must be concentrated. Heavy metals bear the risk of biodegradation and transformation. Hence adsorption is found to be an attractive method nowadays for sequestration of such metals. It is an economically feasible and eco-friendly method. Biochar is advantageous over other adsorbents such as activated carbon, graphene, silica, etc. It is the product of a thermochemical process which possesses better adsorption capacity. It reduces the production time and in addition provides fuel. Different pyrolysis conditions influence the quantity and yield of char. The degree of biochar adsorption is mainly focused on the type of biomass used, metal species concentrated, functional groups, and surface area of the biochar. Regeneration of biomass is also an important phenomenon to be considered as the adsorbed biochar may cause secondary pollution if not disposed in a proper manner. In order to improve the surface properties, physical structure, and regeneration capacity of biochar, various modification technologies have been adopted. It will also pave way for

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the effective utilization of waste biomaterials in wastewater treatment. The modification may be carried out before pyrolysis or after pyrolysis. It is categorized under physical, chemical, magnetic, and mineral impregnation methods. This review focuses on the mechanism and improvements of the treated biochar in comparison to the pristine biochar for heavy metal sequestration.

Keywords

Biochar · Surface modification · Biosorbent · Heavy metals

2.1 Introduction

Water is an essential commodity for which our entire life relies on. Save water to save the earth and to secure future generation are what the human aims and needs. With the improvement in scientific works, our earth is attaining newfangled spheres, but the amount that the people are giving and will give in upcoming years will be surely too high putting the people in appalling situation. One of the upshots is environmental pollution which hits our country both economically and ecologically. The demand for water has increased tremendously with the production of huge quantities of wastewater with manifold pollutants. Among the innumerable pollutants known so far, the heavy metals have drawn a special concern considering its carcinogenicity, and it causes serious threat to the aquatic ecosystem. Among the variety of industries in operation, tanneries drain effluent rich in chromium which in turn reaches the human through the biomagnification processes. Therefore, a suitable cleanup technology is needed for making our environment pollution-free. To overcome the aforesaid lacuna and to justify a suitable technology, the literature pertinent to the sources of contamination, environmental impact, available conventional methods, suitable technology, and its impact on crop growth are reviewed and presented below.

2.2 Water Contamination

“When the well’s dry, we know the worth of water.” Water is an asset to be carried over for the future generation benefits. But nowadays water has been polluted anthropogenically in many ways. The industries play a prime role comprising metals like cadmium, zinc, nickel, chromium, arsenic, lead, iron, etc. (Debnath et al. 2020). These heavy metals enter into food chain and bioaccumulate in the body of humans and animals (Salam et al. 2011). Among various inorganics, chromium is an egregious contaminant released by the industries comprising leather tanning, pigment manufacturing, metal finishing, and wood preservation.

A recent study estimated that wastewater generated from municipal and urban centers is about 61,754 million of liters per day (MLD) out of which 62% is left untreated due to insufficient facilities and dispersed into the water and groundwater sources (Kamble et al. 2019). Because the treatments vary with financial status of the nation where 70%, 38%, and 8% of the wastewater are treated by high-income, middle-income, and low-income countries, respectively. As a result, water availability is much reduced, for example, per capita availability of water in India had decreased from 5177 m^3/year in 1951 to 1545 m^3/year in 2011 given by the Ministry of Water Resources (2011). Although the industries came after various pavements for the metal contamination eradication, huge volume of discharge is carried out annually into the environment which is the gateway for diverse impairment to the life forms on the earth.

2.2.1 Leather Industries and Its Production

Among the different industries, the highest activity is recorded by the leather industries where the discharge contains about 4–5% of Cr in 15% of mineral components. Here, 70–80% of the input in the industry acts upon hides and the remaining expelled as waste. They consume water of about 15–20 m^3/ton of raw skin. Wastewater expelled by the tanneries lies within 1500–3000 mg L^{-1}. World-wide production of leather is around 2108.94 Mmt^2. It exceeds 551,000 tons/year affecting 1.8 million people (Rafique et al. 2019; Tamersit and Bouhidel 2020).

India is one of the major exporters of leather-related products which ranks fifth in the world. It contributes about 15% of the world leather production capacity (Alam et al. 2007). In Tamil Nadu, Dindigul and Vellore are the preponderant districts in tannery industries which release enormous volume of wastewater that affects major parts and causes several diseases (Princy et al. 2020).

2.2.2 Chromium and Its Toxicity

Chromium (III) and Cr (VI) are the two major forms present in nature. Chromium (III) persists in two forms as $Cr(OH)_3$ and Cr_2O_3. They are less soluble, immobile, and less toxic. In contradiction, hexavalent chromium leads to serious damages to human beings due to its carcinogenic and mutagenic properties as it is highly mobile, toxic, and rapidly soluble. They prevail in terms of anions such as $HCrO_4^-$, $Cr_2O_7^{2-}$, and CrO_4^{2-}. Hexavalent ions show comparatively 10–100 times more toxicity than the trivalent ions (Sarkar et al. 2019; Qin et al. 2020).

According to the World Health Organization, the admissible limit of total chromium in drinking water is $50 \mu g L^{-1}$ although chromium (III) was found to be an essential nutrient. But potable water has been reported to have as high as $120 \mu g L^{-1}$ (WHO 2011). The maximum contaminant level (MCL) for chromium is 5×10^{-2} $mg L^{-1}$ reported by USEPA (Bej et al. 2020). In human, chromium exposure is contributed more by the oral uptake, whereas 1.9–7% by means of water and role of air is trivial. Once ingested, the hexavalent chromium is reduced to trivalent and binds to the macromolecules. Hilar lymph nodes and lungs registered higher concentrations. Those Cr (III) ions result in producing more reactive oxygen species and reactive chromium intermediates causing apoptosis. In addition, they cause lung cancer, nephrotoxicity, DNA damage, and intravascular hemolysis. Ongon’g et al. (2020) found that children who consume vegetables cultivated in Cr (VI) soils are more prone to health risks than the adults. The major route for crops is by means of growing in the chromium-contaminated soil. The vegetable crops uptake, translocate, and accumulate Cr (VI) in the edible parts and roots which results in the decline of carbohydrates, sugars, amino acids, and proteins. Stambulska et al. (2018) had specified that these hexavalent Cr ions will disturb the pigment and cellular function. It also has impact on nodular formation affecting their symbiosis and gets accumulated there. Other effects on plants were inhibition of seed germination, protein modification, and damage to DNA.

2.2.3 Treatment Methods

There are various physicochemical and biological methods for the treatment of wastewater such as precipitation, filtration, flocculation, adsorption, membrane separation, and ion exchange. The suitable treatment method is chosen based on the factors such as treatment energy, cost, environmental effects, and influent and effluent quality. The physical methods have certain complications including high cost of equipment, toxic sludge generation, and high space requirements and time. Chemical methods also beneficial in terms of higher pollutant removal efficiency but have some disadvantages like secondary waste production, higher operational cost etc. Other drawbacks are incomplete removal, continuous checking, and higher energy requirement (Crini 2005; Siyal et al. 2020). Among them adsorption was found to be an effective one compared to others as the amount of secondary waste generated is comparatively less (Renu et al. 2017). Adsorption mostly relies on the surface characteristics of adsorbents particularly their surface area and porous structure (Wu et al. 2017).

The frequently used adsorbents for metal removal are silica gel, activated carbon, biochar, and alumina (Ahmed et al. 2016). Activated carbon is found to have higher cost in commercial purpose and poor regeneration capacity, and hence its usage is foreshortened. Hence biochar prepared by exploiting agricultural and industrial wastes have been widely utilized.

2.2.4 Adsorption

Adsorption has been in practical use for longer time. It is used for the purpose of separation or purification. Adsorption and absorption differ with the fact that adsorption takes place on a two-dimensional matrix, whereas absorption occurs on a three-dimensional matrix. Adsorption takes place at the interface of two phases. Usually, it happens on a pore-filled solid matter in which the other phase liquid or gas is attracted. There are two types of sorption based on the interaction of adsorbate and adsorbent: physisorption and chemisorption. The physisorption is due to the forces such as dipole-dipole forces, London forces, and van der Waals interaction. On the other hand, covalent bond forms between the adsorbent and adsorbate by transferring of electrons in case of chemisorption. Physisorption has low enthalpy and it is reversible, while the chemisorption is irreversible and has high enthalpy (Sims et al. 2019; Ghouti and Da'ana 2020).

The main advantage of adsorption process is regeneration potential of the adsorbent. Isosteric heat is also considered as an important factor in this study. It is calculated by dividing the infinitesimal change of the adsorbate enthalpy by change in the infinitesimal of the adsorbed amount. The most important thing for gaining knowledge on adsorption process is adsorption equilibria. This helps in understanding how much components can fit on the biosorbent (Ayawei et al. 2017). Isotherms of adsorption give the equilibrium of the adsorbents. It depends on various properties like pH, temperature, initial ion concentration, adsorbent, dosage, and adsorbate.

2.2.5 Biochar Production

Biochar is a finely grained porous, stable, and carbon-rich material produced by thermal decomposition (pyrolysis, gasification, and torrefaction) of biomass at a temperature of about 300–700 °C with limited or no supply of oxygen (Ahmed et al. 2015). Thines et al. (2017) reported that their production dates back to the past history as native Indians produced char by burning the wood stocks piled up in the pits which resulted in fertile soil known as terra preta. It has an excellent application in pollutant removal as it is simple to produce, eco-friendly, economic, and efficient compared to other methods of heavy metal remediation. In addition, they possess unique properties such as high microporosity, higher ion exchange, larger surface area, and high adsorption capacity (Mohanty et al. 2013). Apart from adsorption they possess multiple applications comprising soil remediation, carbon sequestration, and bioenergy production.

Biochar production is influenced by temperature. For instance, at elevated temperature it possesses high aromatic nature but due to deoxygenation possesses fewer functional groups and lesser ion exchange capability. In case of lower temperature of about 300–400 °C, the biochar shows more functional groups (C–H and C=C) and contains numerous organic characters.

Such biochar are prepared nowadays from various feedstocks including rice husk, pomelo peel, water hyacinth, *Lantana camara*, pinewood, sugar beet tailings, pineapple peel, sugarcane bagasse, sewage sludge, peanut straw, wood bark, and dairy manure at different temperature for adsorption of the specific inorganics from effluent (Nithya et al. 2020). Those nonliving biomass by producing biochar remove the inorganic contaminants by means of passive binding over their surface. Amid different sources, water hyacinth is a poisonous and dreadful weed found ubiquitously in the water bodies globally. The weed was brought as ornamental plant in India from Brazil. IUCN (International Union for Conservation of Nature and Natural Resources) has classified it as one of the most aggressive invasive species. Its growth is vigorous as it could increase its size twofold within 5 days. It is an urgent need to get rid of this serious issue. It creates the way for evapotranspiration rate increase and greenhouse gas emissions. It has high cellulosic carbon and high biomass yield. The conversion into biochar happens by the transformation of cellulose carbon into aromatic carbon, which is more stable.

2.2.6 Water Hyacinth as a Biosorbent

Water hyacinth (*Eichhornia crassipes*), belonging to Pontederiaceae family, is a rooted aquatic macrophyte. The leaves of the weeds accumulate higher concentration of heavy metals followed by stem and roots. This pickerel weed leads to several adverse effects because of their vigorous growing ability. They affect the biodiversity of water body by reducing the dissolved oxygen concentration as they block the pavement for sunlight penetrance. Moreover, they interfere in the activities of fishing, irrigation, and power generation and lead to navigation jam. Besides these disadvantages, they also possess some of the properties such as improved pores, mineral components, functional groups, and larger surface area. Hence, they are utilized as "low-cost" adsorbents of heavy metals. Absence of natural enemies in the newly introduced places paves way for them to grow exponentially. In a hectare of water, 270–400 tons of *Eicchornia* are noticed present. Utilization of this widespread species for wastewater treatment is very suitable as it is an eco-friendly, economic, and efficient technology. This abundant weed gives good biomass yield, and it is a rich source of cellulose (64.51%), lignin (7.69%), and ash (12%). In addition, they acquire both the cationic and anionic binding sites. Though raw biochar is a good adsorbent, they are less efficient compared to the modified char. It involves functional modification and surface oxidation that enhances the adsorption potential. For instance, acid or alkali treatment will increase the metal uptake. In case of chromium, Cr^{6+} uptake was improved, whereas Cr^{3+} uptake is lowered in acidic enhancement.

2.2.7 Mechanism of Adsorption

There are mainly five different mechanisms (Fig. 2.1) for removal of heavy metals from industrial washouts which are as follows (Inyang et al. 2016):

1. Physical sorption
2. Ion exchange
3. Complexation
4. Electrostatic interactions
5. Precipitation

Hexavalent chromium follows the mechanism of electrostatic attraction and reduction where they are converted into trivalent which forms complex with the functional groups. Heavy metals form complex with the biochar due to the occurrence of special O-containing functional groups including carboxylic, hydroxyl,

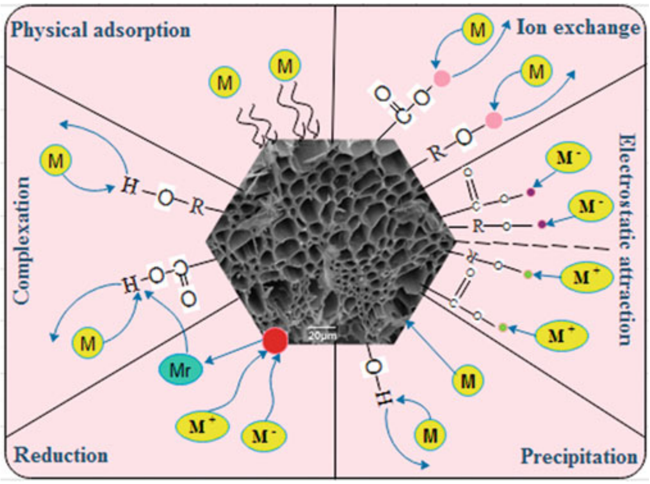


Fig. 2.1 Various mechanisms for sorption of metal ions on biochar (Shaheen et al. 2018)

amine, alcohol, etc. The O-containing functional groups such as catechol, diols, and unsaturated anhydro sugars on the adsorbent surface reduce Cr (VI) into Cr (III)). Xu et al. (2018) found out that besides reducing the ions, they also aid in adsorbing the reduced metal ion. The authors also quoted that at lower pH the biochar acts as electron donors, whereas at higher pH acts as electron shuttle (O-centered radicals).

2.2.8 Impact of Surface Properties

Surface properties highly affect the adsorption process of biochar. It is based on the type of biomass used, pyrolysis temperature, and pretreatment/posttreatment handling. Biochar is an amorphous and honeycombed structure. They have heterogeneous adsorption sites. If pore size is too narrow for the ions to bind and diffuse into the surface, steric hindrance occurs. The criteria for hindrance lie in the fact that the ratio of pore size to the minimum critical diameter is less than 10^{50}. The pore aperture of the surface varies. The different sizes include nanostructures, micropores (<2 nm), and mesopores (2–50 nm). The micropores are produced on the surface of biochar due to dehydration during the pyrolysis process. Composition of biochar predicts the pore aperture. Plant biochar shows higher porosity than biochar from biosolids. Cellulose-rich biochar produces micropores, whereas macropores are developed from lignin-rich material.

Another surface factor influencing sorption is surface charge. As the biochar added for wastewater treatment, surface charge is controlled by the pH of the solution. Point of zero charge is the pH where net charge of the surface is zero. When $pH > pH_{pzc}$, negative charges dominate the surface so it attracts cations and vice versa. At higher pyrolysis temperature, pH_{zpc} is increased where positively charged functional groups increased resulting in less negative charges.

Organic content is an important surface property. It is determined by aromaticity and polarity. Aromaticity is represented by ratio of aromatic to total carbon content in the biochar. Polarity is subjected to the aliphatic portion of the biochar. The overall polarity is increased by the oxygen-containing functional groups. The organic content can be carbonized and non-carbonized due to improper carbonization which influences isotherm. Carbonized and non-carbonized fractions represent isotherm with curvature and linear isotherm, respectively.

Another surface property of biochar is elemental composition. When the feedstock is pyrolyzed, chemical composition of the biomass gets changed. When the temperature increases, the detachment of oxygen- and hydrogen-containing functional groups occurs and leads to increase in carbon groups. Hence, the carbon can increase for about 90% and greater reduction in oxygen and hydrogen. Modified biochar assists in amelioration of the surface properties. Chemical oxidation of the biochar increases the hydrophilicity as the functional groups (Table 2.1) such as –OH and –COOH are increased. It also enhances pore size and structure of biochar. On the other hand, chemical reduction decreases the oxygen-containing groups and improves the nonpolarity of biochar. In addition, it expands the surface area and strengthens the pore volume (Yang et al. 2019).

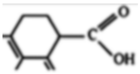
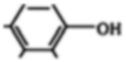
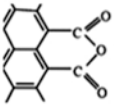
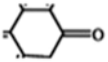
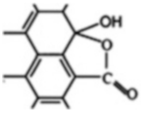
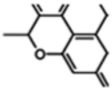
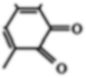
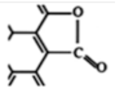
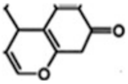
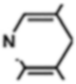
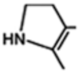
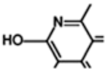
2.2.9 Factors Affecting Adsorption Process

2.2.9.1 Effect of pH

The pH is a significant factor influencing adsorption. The pH differs not only for the different metals but also for different kinds of biomass. As aforesaid, anion adsorption is facilitated more at $pH_{pzc} > pH$. On the other hand, $pH_{pzc} < pH$ favors cationic sorption. Chromium prevails in $HCrO^{4-}$ form at pH 1.0 and as $Cr_2O_7^{2-}$, $HCrO_4^-$, and $Cr_3O_{10}^{2-}$ at pH 2–6, while the dominant species is $HCrO_4^-$. At pH greater than 6–11, CrO_4^{2-} dominates. Hexavalent chromium adsorption is higher at lower pH and decreases as the pH increases. Because at lower pH, the biosorbent surface is dominated by H ions and hence the surface becomes positively charged which improves the Cr (VI) adsorption onto surface, while at higher pH, OH ions influences the surface which causes electrostatic repulsion between the adsorbent surface and the negatively charged Cr (VI) species. The Cr (VI) adsorption at pH below 2 is administered by reduction to Cr (III). The pH is also varied due to changes in acidic groups on adsorbent surface.

Modified biochar surface also shows variations in different pH range due to changes in the chemical nature of the adsorbent functional group. Those modified char adsorb Cr (VI) more efficiently because they have low surface net negative charge compared to the unmodified biochar. In addition to higher acidic conditions, modified biochar could remove the ions at high rates even in the wide range of pH up to 7.0. Adsorbate solution pH influences the solution chemistry of ions such as redox reactions, hydrolysis, and precipitation which in turn influences biosorption

Table 2.1 Functional groups on the surface of biochar (Tomczyk et al. 2020)

Functional groups	Structural formula
Acidic groups	
Carboxyl	
Phenol	
Ether	
Anhydride	
Carbonyl	
Lactol	
Chromene	
Quinone	
Lactone	
Pyrone	
Basic groups	
Pyridine	
Pyrrole	
Pyridone	

availability and speciation of ions. Finally, increase in pH resulted in negative charges on the surface and therefore decreased the sorption. In addition, more number of protons is required for hexavalent reduction.

2.2.9.2 Effect of Dosage

Amount of biochar added is a vital parameter affecting the biosorption. It is studied by fixing other factors constant. Usually, the adsorption increases with increase in dosage. This fact is due to increase in surface area of the adsorption resulting in large number of active sites. But in many cases, lower amount of adsorbent shows higher uptake of heavy metals. This is due to overlapping of Cr (VI) ions on surface of the biosorbent decreased the unit adsorption. It also increased the diffusion path length. Thus, increase in dosage of biochar increased the removal efficiency but decreased the biosorption per unit weight of biochar. There may be interference in binding sites due to deficiency of solute for all the exchangeable sites present on the biochar. The removal efficiency stays constant after reaching the optimum level. Adsorbent functional group and their concentration influence the adsorption of different adsorbents (Singha and Das 2011).

2.2.9.3 Effect of Reaction Time

Chromium (VI) adsorption increases with increase in time. Equilibrium time is determined by the adsorbent nature and its sorption sites (Singha and Das 2011). The adsorption is higher at the initial stage and then it decreases near the equilibrium. Presence of more number of binding sites increases the surface area which is later occupied by the Cr (VI) and gets saturated. The initial metal ion concentration facilitates the monolayer formation on the surface. Hexavalent chromium ions are adsorbed within short period to reach equilibrium in physical adsorption. When the contact time increases, the chemical binding of species with the surface of biochar also increased.

2.2.9.4 Effect of Temperature

Temperature also plays a crucial role in adsorption process. The adsorption potential increases with increase in temperature indicating that the process is endothermic. This is because the rise in temperature results in higher diffusion rate of the metal ions on the adsorbent internal pores and outer surface. Equilibrium capacity is varied by the temperature for various absorbents. Hence, the adsorption is favored by lower temperature for some cases. For example, biochar made from peanut hull have higher potential for Cr (VI) removal at lower temperature as the functional groups containing “O” are more at this condition which favor metal ion interaction. But when this biochar is treated with magnetic property (γ-Fe_2O_3), it is favored by higher temperature.

2.2.10 Isotherm Study for Adsorption

In order to enhance the adsorption process, isotherms must be studied well. These equilibrium relationships are essential for the assessment of effective adsorption system and how the adsorbate interacts with the surface of adsorbents. As a result, isotherm explains the mobility of heavy metal ion from aqueous solution into the porous solid adsorbent. It also describes the degree of affinity, surface properties, and capacity of adsorbent used. The isotherms are classified as one-, two-, three-, four-, and five-parameter isotherms. One-parameter isotherm is the simplest isotherm model where the adsorbate is directly proportional to the partial pressure of the gas. The most commonly used isotherm models are Langmuir and Freundlich isotherms.

Langmuir isotherm is used to quantify the adsorption potential of various adsorbents though it was initiated for gas-solid phase. It is a monolayer adsorption that occurs at a fixed number of sites. It follows a dynamic equilibrium which balances the rate of adsorption and desorption. This theory has arrived that rise of distance results in rapid decrease of the intermolecular forces. In contrast, Freundlich isotherm is based on the multilayer adsorption between the liquid and solid phase. It occurs on a heterogeneous surface. In this model stronger binding sites are filled first and then the energy of adsorption decreases exponentially. Temkin isotherm takes into account the indirect interactions of the adsorbate and adsorbent. Increase in surface coverage leads to decrease in the heat of adsorption of molecules. Though nonlinear regression analysis is used by the researchers, linear analysis is frequently used for analyzing adsorption performance. Therefore, the successful adsorption isotherm modeling influences the accuracy of sorption process (Ayawei et al. 2017).

2.2.11 Kinetic Models for Adsorption of Heavy Metals

Kinetic study is used to express the rate of chemical processes that governs the residence time in adsorption process. It is used to determine the performance and mechanism of adsorption. The rate of kinetics depends on the species concentration, and the law is expressed as follows (Gupta and Bhattacharyya 2011):

$$R = K\,[\mathrm{A}]^{\mathrm{a}}[\mathrm{B}]^{\mathrm{b}} \ldots\ldots\ldots.$$

where K is the kinetics coefficient and A, B, etc. are the species involved in adsorption which have the order a, b, etc.

The rate-limiting step and kinetics have been portrayed by different kinetic models. They are pseudo-first-order, pseudo-second-order, Adam-Bohart-Thomas model, Elovich model, Ritchie's equation, intraparticle diffusion, and external mass transfer model. Pseudo-first-order rate equation was first presented by Lagergren in 1898. He explained the oxalic and malonic acid adsorption by the charcoal, i.e., liquid-solid phase adsorption. Though it is the earliest model, it was found that it is not suitable for whole contact time, whereas appreciable only for about initial

20–30 min. Pseudo-second-order kinetic model was introduced by Ho which involves the divalent metal ion adsorption on peat. This model is interpreted as special kind of Langmuir kinetics that gives two assumptions. They are (1) amount of ion species determines the total number of sorption sites at equilibrium and (2) ion concentration is constant with time. Intraparticle diffusion model is found to be a suitable model in case of diffusion of ions into the pores for porous substance. It is a rate-limiting factor but not for the whole process where other models control the rate simultaneously. Homogeneous solid diffusion model (HSDM) is the typical intraparticle diffusion model. Elovich rate equation was initially introduced by Zledowitsch for chemisorption of gases onto solids, whereas it has expanded to the aqueous phase adsorption. Elovich model states that adsorption takes place on particular sites and the energy is directly proportional to surface coverage in adsorption.

2.2.12 Response Surface Methodology

Biosorption is a multifactor-dependent process which impacts the sorption performance. Hence, optimization is a best method to find the specific condition that results in best efficiency. The response surface methodology (RSM) is one of the excellent methods for optimization of parameters. It will help in reducing the number and cost of experiments. The RSM is a set of mathematical and statistical tools developed by Box and Wilson. It defines the interaction and relation between the dependent and independent variables. The results will be in the form of 2-D contours and 3-D plots (Nair et al. 2014).

Optimization in RSM is carried out by the following six steps. They are (1) independent variable selection, (2) suitable design selection, (3) carrying out the experiment and data generation, (4) the results were fitted with model equation, (5) verification of the obtained response graphs, and (6) graphical representation and determination of optimal conditions. The popular experiment designs involved are Box-Behnken design, central composite design, full three-level factorial design, and Doehlert matrix. The full factorial design includes three levels such as maximum, mean, and minimum which are represented by +1, 0, and −1, respectively. It includes all possible combinations. The disadvantage is second-order and higher-order polynomials. Hence to overcome this, Box and Wilson (1951) have introduced the central composite design (CCD). This CCD is highly efficient up to six factors and then decreases. The CCD is applied for parallel experiments instead of sequential experiments. In order to produce an alternative to the full factorial design, Box and Behnken developed the incomplete block design. It includes only two-level factorial (+1, −1) which is less labor extensive and more economical in industrial research. Apart from these advantages, RSM find difficulty over wide range. Hence the selection of domain must be concentrated by the experimenter (Nair et al. 2014).

2.2.13 Significance of Column Experiment

The contact between adsorbate and adsorbent is brought out by various techniques such as batch, column, continuous fluidized bed, and pulsed bed experiment. For adsorption of heavy metals, batch experiment is widely used in the laboratory scale, while column setup will facilitate treatment of large quantities of wastewater in commercial scale (Parameswari et al. 2020). The adsorption performance of the column study is explained by the breakthrough curve analysis. The determining factors for operation of column are time to attain breakthrough point and shape of the breakthrough curve. The effect of variables on the adsorption efficiency is described by various models. Among them, Adam-Bohart, Yoon-Nelson, and Thomas models are widely utilized. Thomas model predicts the breakthrough curves and it follows second-order reversible kinetics. It describes the column performance and predicts the monolayer adsorption. It is applied in adsorption process where internal and external diffusion limitations are absent. Yoon-Nelson model is a simple assumption which states that decreasing rate of probability of adsorption is directly proportional to breakthrough and adsorbate adsorption. Adam and Bohart model is based on the assumption that adsorption rate depends upon the residual capacity and sorbate concentration. Column experiment is better, fast, and feasible for industrial scale. Further studies are required to overcome the challenges of column study (Patel 2019).

2.2.14 Activation of Biochar

Tailoring the properties of biochar to improve the surface properties is an emerging technology for efficient removal of both organic and inorganic pollutants. Surface enhancement of biochar can be achieved by different methods (Fig. 2.2). They are as follows:

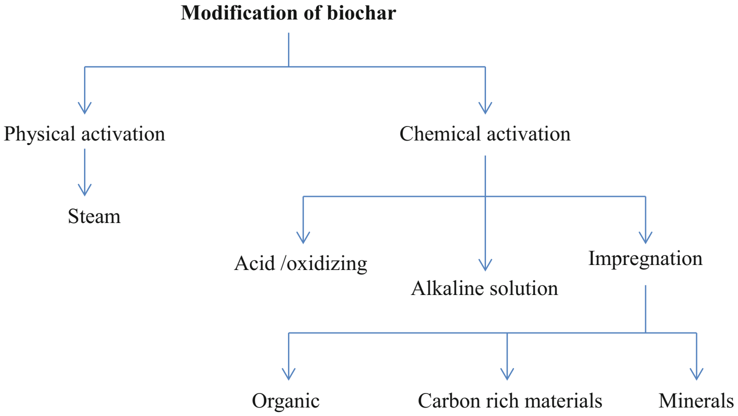


Fig. 2.2 Different methods of biochar modification (Shakoor et al. 2020)

1. Steam activation
2. Heat treatment
3. Acid modification
4. Alkali modification
5. Impregnation methods

Steam activation is the widely used method where improvement is obtained by exposure of biochar to steam for partial gasification which enhances the surface pores and surface area. Bardestani and Kaliaguine (2018) found an increase in BET surface area by steam activation from 50 to 1025 m^2/g.

The disadvantage of this process was found out that it does not have significant impact on the functional groups. Heat treatment increases the surface hydrophobicity and functional groups of biochar by exposing to heat at temperature of about 800–900 °C.

Acidic modification by introducing the oxidants improves the surface area due to increase in porosity. The expansion of micropores leads to increase in the oxygen-containing functional groups such as carboxylic, ketonic, and hydroxyl groups. Due to the presence of these groups, there is an increase in O/C and H/C molar ratios which leads to decrease in hydrophobicity. Sulfuric acid, oxalic acid, phosphoric acid, and nitric acid are the common oxidizing agents used for the biochar amelioration. Sarkar et al. (2019) in his study reported that acid modification enhanced the active sites 10 times and 25.29% increase in carbon content. It has also improved BET surface area of about $142.78 \pm 2.57\ m^2g^{-1}$.

The phosphoric acid treatment increases the micropores enhancing the specific surface area. The micropores were formed by two mechanisms: (1) H^+ catalysis process generates the micropores, utilizing H^+ ions from H_3PO_4, and (2) the organic PO_4^{3-} bridge ensured the carbon skeleton from collapse of micropores by means of phosphate radical cross-linking.

Enhancement of biochar with alkali like potassium hydroxide and sodium hydroxide offers additional positively charged sites which assist in absorbing negatively charged species. Alkali treatment increases the surface area as it increases the surface basicity. For example, potassium hydroxide-tailored biochar has improved surface area from 14.4 to 49.1 m^2g^{-1}. Sun et al. (2015) reported that effect of alkali modification depends on the preparation methods and feedstock nature. In addition to surface area, there is an increase in the surface aromaticity (H/C). When compared to acid treatment, alkali modification showed lesser O/C and higher N/C ratio. Mahdi et al. (2019) suggested that alkali pretreatment can consume long time and is performed at low temperature and high concentration. In case of acid pretreatment, it can be at lower temperature and long retention time, otherwise at higher temperature in a short retention time. Hence, time is one of the important factors to be considered during surface modification of the biosorbent.

Impregnation is accompanied by different materials such as metal oxides, minerals, organic compounds, nano-materials, clay, and carbonaceous materials. This method is quite different from the physical method as it introduces new functional groups which are absent on the surface earlier. It involves two methods of impregnation pre-pyrolysis and post-pyrolysis. The mineral impregnation is mostly carried out using $FeCl_3$, FeO, and $MgCl_2$ which introduces positive charge favorable for the removal of inorganics like chromium. The γ-Fe_2O_3 nanoparticles on surface enhance the sorption sites through electrostatic interactions. The major mechanisms for sorption on the biochar impregnated with magnetic material are electrostatic attraction, surface complexation, ion exchange, and O-containing groups. Coating with carbon-rich material is mostly assisted by the introduction of graphene oxide for effective sorption of heavy metals.

Treatment with polyethylenimine solution increases the sorption sites by introduction of primary and secondary amine groups (Table 2.2). In nanocomposite, establishment of particles such as MnO_x and ZnO reduces the overall O/C ratios which shoot up the metal uptake capacity. The nZVI has been utilized for reduction and adsorption of Cr (VI). The removal efficiency of 98.35% was recovered wherein the virgin biochar tends to remove only 64.04%. Wang et al. (2019) had modified the bamboo biochar with polyethylenimine for adsorbing U(VI) and compared with the unmodified biochar. As a result, PEI (polyethylenimine)-alkali/acid biochar showed 9–10 times higher adsorption capacity.

2.2.15 Regeneration of Adsorbents

As the biochar can undergo several adsorption-desorption cycles, it is a good option to go for effective desorption and regenerating the adsorbent from the adsorbate. The desorption process helps in reducing the biochar cost in treatment and also the environmental risk of secondary pollutant. The eluted metal can also be used for various purposes. It should be noted that the desorbents used are cheap and nonpolluting. The adsorbate must be easily readsorbed and the desorbing agent should not damage the structure of adsorbent. The elutant used may be of varying concentration from 0.01 to 5 M (Table 2.3). The efficiency increases with increase in molarity. For instance, Pb (II) ions adsorbed on the surface have been regenerated with 0.01 M at 77.7% efficiency and 0.5 M HCl at 98.3% efficiency. However, in some cases biochar structure may be degraded at higher concentration.

The best desorbent is chosen from the first desorption cycle. Double-distilled water is found to express worst behavior in detachment of bounded metal ions. Hence, adsorbed heavy metals are desorbed by undergoing multiple washes with various desorbents such as strong acids (HNO_3, HCl, H_2SO_4), strong alkali (NaOH), salts ($NaNO_3$, KNO_3), and chelating agents. These elutants provide cations which could replace the adsorbed metal ions on the surface of adsorbent. However, the metal ions regeneration cannot be 100% as they may be tightly bonded in the porous space and hence cannot be removed easily.

Acid favors regeneration process as acidic condition prevents the metal ion sorption. Desorption with alkali has less efficiency compared to the acids. The acid condition provides a space for the surface to be protonated by H_3O^+ ions desorbing the ions of positive charge. The sorbents were washed with distilled water after desorption followed by treating with 1 M $CaCl_2$. The use of calcium

Table 2.2 Adsorption capacity of various surface-modified biochar

Sl. no	Modifications	Feedstock	Adsorption capacity (mg/g)	Significance/effect	Reference
1.	Polyethylenimine	Rice husk	435.7	Introduced more amino groups, good stability in the adsorption-desorption cycles. Adsorption is very effective than pristine biochar, i.e., 18%	Ma et al. (2014)
2.	H_2SO_4	Sugarcane harvest residue	62.89	Promising adsorbent, releases less amount of trivalent Cr and less secondary sludge	Xiao et al. (2018)
3.	H_3PO_4	Pomelo peel	57.64	Electrostatic interaction followed by ion exchange enhanced the adsorption	Wu et al. (2017)
4.	$FeCl_3$	Sugarcane bagasse	13.37	At lower pH and higher temperature, the removal percentage is found to be higher at 99.89%	Zhu et al. (2012)
5.	Ca and Fe modification	Rice husk		Removal rate is 95%. The adsorption increased due to the mechanism of metal precipitation and electrostatic interactions	Agrafioti et al. (2014)
6.	Chitosan + Fe modifications	Water hyacinth	120	The adsorption is influenced by pH and found to be maximum at pH 2	Zhang et al. (2013)
7.	HCl	Willow residue	217.39	Removal efficacy is 97.40%, whereas in the pristine biochar found to be 64.04%	Zhu et al. (2018)
8.	H_2SO_4	Plum	14.024	High efficiency is attributed to the occurrence of surface complexation of sulfur-containing functional groups with the heavy metal ions	Pap et al. (2018)
9.	H_3PO_4	Jute fibers		Removal efficiency of Cr (VI) is about 98%, and also reduction percentage of Cr (VI) to Cr (III) is in the range of 86–97%. It could remediate the pollutant at the inherent pH	Chen et al. (2015)

(continued)

Table 2.2 (continued)

Sl. no	Modifications	Feedstock	Adsorption capacity (mg/g)	Significance/effect	Reference
10.	$FeCl_3$	Corncob	25.94	Fe^{2+} ions on the surface oxidized to Fe^{3+} and hence enhanced the hexavalent Cr reduction	Wang et al. (2019)
11.	Polydopamine-polyethylenimine	Rice husk	42.8	It has more stability and recyclability. However it loses the stability slightly only after eight cycles	
12.	Zn nanocomposite	Bagasse	102.66	The adsorption is twofold increased than the pristine biochar, and the ability withstands even after six desorption cycles	

chloride removes the excess protons and repairs the damage caused by the acid creating the new sites for binding. It also reduces the loss of sorbent mass and hence decreased by 18%. It has been recorded that even after three sorption cycles, the change in sorption and desorption efficiency is negligible. Hence the acid elutants have been used for better regeneration. But it fails in one or two cases. In case of recovery of Pb (II), sulfuric acid should not be used because of the lower solubility of lead sulfate resulting in lower pore volume (Abdolali et al. 2015).

Alkaline salts such as NaOH, $NaHCO_3$, and Na_2CO_3 were utilized as elutants. Alkaline desorbents can elute the metal ions based on the pH. The pH responsible for elution is alkaline condition (pH 8–10) because the adsorption forces weaken and the bounded Cr ions get eluted into the aqueous solution. Desorption of fixed bed column is carried out by purging with inert fluid, change in pH, and heat treatment.

Chelating agents desorb the heavy metals from the surface of adsorbents and produce the water-soluble compounds. Chatterjee and Abraham (2019) had reported that commonly used chelation agents are ethylenediaminetetraacetic acid (EDTA) and [*S*,*S*]-ethylenediamine disuccinic acid (EDDS). Without altering the nature of the adsorbent, 0.1 M EDTA showed good removal of chromium and copper. The EDDS also effectively desorbed the contaminants mainly Cu (II), Zn, and PB. In addition, it is also economic because it can be reused in several cycles.

2.2.16 Chrome Tanning from Recovered Chromium

As aforesaid chromium discharged from the tannery would cause serious damage to the environment. Hence chromium in the discharge must be treated and disposed. The used chrome liquor must be filtered and precipitated as chromium hydroxide

Table 2.3 Desorption of adsorbents using various desorbents

Adsorbent	Elutant	Adsorbate	Removal efficiency	Reference
Wheat straw biochar	HNO_3	Cr (VI)	79%	Tytłak et al. (2015)
Bagasse	0.1 M HNO_3	Pb^{2+}	90%	Kumari (2017)
Seaweed	4 N H_2SO_4	Cr	47%	Aravindhan et al. (2004)
Aminated chitosan bead	EDTA	Hg	95%	Jeon and Park (2005)
Titanium dioxide nanoparticles	0.1 M NaOH	Se (IV)	95%	Zhang et al. (2009)
Nano-zerovalent iron	0.1 M NaOH	As	100%	Zhu et al. (2009)
Alkali-treated apricot shells	0.1 M HCl	Fe, Pb, Cu, Cr, Ni, Zn	95%	Šoštarić et al. (2018)
Sulfonated expanded graphite	0.1 M HCl	Pb (II)	90.8%	Jiao et al. (2017)
Spirulina sp.	0.1 M EDTA	Cr	60%	Chojnacka et al. (2005)
Cellulose acetate membrane	1 M H_2SO_4	Cu (II)	32.1%	Kamaruzaman et al. (2017)
Cladosporium cladosporioides	0.1 M H_2SO_4	Cu	43%	do Carmo et al. (2013)
Titanium dioxide nanoparticles	0.01 M $NaNO_3$	Zn (II)	88%	Hu and Shipley (2012)
Mesoporous γ-Fe_2O_3	0.1 M NaOH	Cr	90%	Wang and Lo (2009)

using alkali. When required quantity of sulfuric acid was added to the precipitate, basic chromium sulfate is regenerated. Thus recovered chromium can be utilized in tanning process.

2.3 Conclusion

The prevailing purification technologies used to remove contaminants are too costly and not eco-friendly. As the research is oriented toward economically sound and environmentally safe technology for contaminant removal, it has paved the way for the present investigation for the use of water hyacinth biochar as a suitable adsorbent to bind the metallic ions. The biosorbent is renewable in nature and have more binding sites towards heavy metals which adds strength to the development of a viable biological system for adsorption of heavy metals from industrial effluent. Besides this, the possibility of metal recovery and reuse of desorbed chromium in tanning process will reduce approximately 10–20% of production cost incurred through the process of chrome tanning. Hence, this proposed study can be a viable green technology which is highly useful for the industry to treat their wastewater effectively and economically ensuring the socioeconomic status of the people besides protecting the environment.

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Biochar and Microbes: Collaborative Approach for Bioremediation of Industrial Effluents

3

Sonia Sethi

Abstract

Contamination of environment with highly toxic chemicals is increasing and warning us to find the technologies which are sustainable to protect the environment and human health. Presently, a variety of technologies are being applied to decontaminate the environment and human health. However, these technologies are costly and are not environmental-friendly. As an alternative approach, bioremediation technologies using microbes, plants, and their enzymes are eco-friendly and sustainable. Biochar is a charcoal produced by pyrolysis of biomass and a stable solid rich in carbon and is recognized as effective and promising method to remediate various contaminations in soil and water. The biochar application to groundwater systems with organic and inorganic pollutants can be used as an additive/support media during anaerobic digestion and as filter media for the removal of suspended matter and pathogens. The current chapter discusses on the different methods for biochar production, its application, and its use with microbes in wastewater treatment.

Keywords

Biochar · Thermal conversion · Modification · Adsorption · Wastewater treatment · Nutrient removal

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3.1 Introduction

An important and continuous problem related to environment is water pollution which accompanies with worldwide human population increase and economic development. The eutrophication of water bodies occurs through release of organic pollutants, including phosphorus (P) and nitrogen (N) through runoff, which causes harmful effects on human health and to ecological environment (Wang Beaver et al. 2014).

Various processes like mineral processing, mining, and energy generation result in production of large quantities of contaminated effluent. The contaminated effluent contains elements at different concentrations which are of potential environmental concern, including Al, As, B, Cd, Mo, Se, Sr, V, and Zn, and therefore extensive treatment is needed before discharge (Jankowski et al. 2006).

Deterioration of the world's water resources is due to the continuous discharge of variety of organic and inorganic contaminants from municipalities and industries including pesticides, dyes, pharmaceuticals, heavy metals, surfactants, and personal care products. The discharge of uncontrolled pollutants is of major concern because of their negative effects on ecosystems because they are highly persistent and cannot be converted into degradable form (Zulfiqar et al. 2019).

Therefore, it is desirable to establish cost-effective and environmental-friendly measures to keep such pollutions under control. Worldwide, various conventional technologies are used for the removal of these pollutants from wastewater including adsorption, flotation, coagulation-flocculation, reverse osmosis, electrochemical treatment, solvent extraction, photocatalytic oxidation, and biodegradation (Vunain et al. 2020).

However, these technologies offer disadvantages stretching from inefficiency to remove pollutants to completely convert pollutants into less toxic by-products, consumption of high-energy chemicals, complex process, and high maintenance and operation costs (He et al. 2017). Each and every approach has its own plus and minus points, and none has the merits in all aspects. Therefore, a cost-effective and sustainable technique for remediation of complex industrial effluents and even scientists are looking for practices that can improve water treatment. Therefore, an efficient and viable treatment process should be included with both economic and environmental requirements to be marketed and applied in large scale to increase the process efficiency.

Some water discharges need a specific treatment. Methods of conventional wastewater treatment typically include primary and secondary treatment. Precipitation, oxidation, and separation are methods of primary treatment. Other methods of removal or recovery from industrial effluent include advanced treatment such as membrane separation, advanced oxidation processes, and ion exchange. Secondary treatment is usually accomplished by activated sludge systems, which is possible after a proper pretreatment. However, conventional systems, based on activated sludge, result in the generation of a considerable amount of sludge, which requires treatment before final disposal.

Microorganisms are generally used in biological wastewater treatment which has been proven as an effective and environmental-friendly strategy. Metabolic activity of microbes uses different substrates, for example, *Pseudomonas aeruginosa* (Shukla et al. 2014), *Aspergillus niger* (Vassilev et al. 1997), and *Rhodopseudomonas sphaeroides* (Liu et al. 2015a, b).

Microorganisms are able to degrade toxic pollutants in aqueous media during their metabolic process. Among them photosynthetic bacteria (PSB) have been found to be an effective and eco-friendly species that can degrade carbon, nitrogen, and phosphorus in the wastewater simultaneously (Idi et al. 2015). This process is called as bioremediation which is considered as a standard practice for the restoration of heavy-metal-contaminated soils and water. This process is eco-friendly and cost-effective compared to other conventional methods, which are often very expensive, in addition to producing significant amounts of toxic sludge. Degradation of pollutants by the microorganisms depends on the environmental conditions suitable for their growth and metabolism including temperature, pH, and moisture (Ayangbenro and Babalola 2017).

Of all those methods, promising technology that can be used to remediate various contaminations, bioremediation, especially biochar-amended phytoremediation, is increasingly being recognized. Biochars through immobilization influence the bioavailability and bioaccessibility of metals for bioremediation. Biochar is a carbon-rich product, which plays significant roles on the bioaccessibility and bioavailability, in turn biotransformation and bioremediation of heavy-metal-contaminated ecosystems. Biochar is a low-cost eco-friendly product produced from organic wastes including municipal, forest, and agricultural wastes (feedstocks) under different pyrolysis systems, and thus, the surface properties could be varying significantly.

Conversion of organic wastes into biochar can be achieved by different techniques including pyrolysis, gasification, hydrothermal carbonization (HTC), and torrefaction. Of all, pyrolysis is the conventional carbonization method for producing biochar, while other methods do not meet the definition of biochar which has been specified in the guidelines for the European Biochar Certificate (EBC). Feedstock comprises of lignin, cellulose, hemicellulose, fat, and starch which gets thermally broken down during pyrolysis forming three products: biochar (solid), bio-oil (partly condensed volatile matter), and non-condensable gases (CO_2, CO, CH_4, and H_2) (Suliman et al. 2016). The bio-oil and gases can be captured to produce energy and depending on the feed valuable coproducts like wood preservatives, food flavoring, adhesive, or biochemical compounds, and the yield of biochar depends on the pyrolysis condition.

High yield of biochar can be obtained by slow pyrolysis at moderate temperature (350–500 °C) and slow heating rate than around 10% or less yield with fast pyrolysis (600–700 °C and fast heating rate) or gasification (temperature 700 °C or above). Biochar production also depends upon the type of feedstock used, which also changes the physiochemical properties of biochar such as surface area, polarity, pH, etc. and determines the effectiveness of biochar in wastewater treatment. Biochar and its derivatives can be used efficiently for the removal of various contaminants because of its properties such as rich carbon content, enhanced surface area, high cation/anion exchange capacity, and stable structure. Biochar can be used for pathogenic organisms (Kaetzl et al. 2020), inorganic such as heavy metals, and organic contaminants such as dyes.

Biochars remove organic and inorganic pollutants from wastewater due to its adsorption capacity, which depends on their physicochemical characteristics (Brassard et al. 2016). The properties of biochar can be modified for better removal efficiency of recalcitrant molecules, which are present at low concentrations. Biochar can be modified by different ways which are regrouped into two classes. The methods include chemical modification methods such as acid modification, alkalinity modification, and oxidizing agent modification and physical modification methods.

Biochar contains both positively and negatively charged surfaces (zwitterionic) of which negatively charged functional groups contribute to cation exchange capacity (CEC) such as oxygen (O)-containing alcohol, carbonyl, and carboxylate functional groups and positively charged surfaces to anion exchange capacity (AEC) such as oxonium groups (Kong et al. 2011).

3.2 Substrate Used for Biochar Preparation

Biomass feedstock and its properties play a significant role in the yield of biochar. The properties of biochar can be increased by pyrolysis catalytic effects (Kan et al. 2016). Biomass feedstock is divided into lignocellulosic and non-lignocellulosic biomass which provides biochars different properties.

Biomass Containing Lignocellulose: Biomass obtained from agriculture, forest, and wood as raw material is lignocellulosic biomass. It consists of cellulose (25–50 wt%), hemicellulose (15–40 wt%), and lignin (10–40 wt%), with a small fraction of extractives (0–15 wt%) and minerals. Each composition manifests characteristic retaliation during the pyrolysis process, resulting in divergence of products. For example, increased amount of biochar results from lignin and bio-oil yield from cellulose and hemicelluloses (Akhtar and Amin 2012).

Agricultural waste, forest residues, softwood from gymnosperms, and hardwood from angiosperms cover a wide variety of suitable feedstock having 47–50% carbon content and high cellulose-to-lignin ratio. Examples include evergreen plants and deciduous plants; herbaceous biomaterials have been used as a potential source of carbonaceous material and in biochar production offering various benefits due to their cost-effective and renewable nature (Wang et al. 2017).

Biomass Containing Non-lignocellulose: Biomass obtained from sewage sludge, algae, insects shell, and animal and poultry manure is non-lignocellulosic biomass. It contains a distinct proportion of protein and lipid, which gives the biochar a high mineral content and distinct functionality of surface. Another most abundant biopolymer rich in nitrogen is chitin and provides functional biochar. Non-lignocellulosic biomass comprises of organic and inorganic matters like carbohydrates, proteins, minerals, and lipids (Li and Jiang 2017).

3.3 Approaches for Biochar Preparation

There are several approaches for biochar production from different feedstocks. Among them are pyrolysis, torrefaction, flash carbonization, gasification, and hydrothermal carbonization (HTC) the most important technologies which include thermochemical conversion.

Pyrolysis: Decomposition of biomass at 300–1200 °C in the absence of oxygen is called pyrolysis. It produces carbons which are pyrogenic in nature named as biochar. Pyrolysis process is divided into slow, intermediate, and fast depending upon the modes, flash, and vacuum (Keiluweit et al. 2010).

Slow Pyrolysis: Also called conventional pyrolysis. It occurs at low process temperatures (400–600 °C), slow heating rate (~10 °C min^{-1}), long vapor residence times (5–30 min), and long holding times (hours to days) (Inyang and Dickenson 2015). Slow pyrolysis results in 20–40% of biochar and it decreases with increasing temperature and heating rate. Different size of pores and high thermal stability of biochars can be obtained from broad range of mineral composition at around 500 °C like bagasse and wood stem as compared to cocopeat, paddy straw, and palm kernel shell. Optimum temperature was found to be 450 °C for high yield with low carbon content, cation exchange capacity, high pH, ash, inorganic nutrients, and nitrogen (Bird et al. 2011).

Fast Pyrolysis: It is defined as a high-temperature treatment of biomass in the absence of oxygen. For this, the feedstock needs drying and grinding for rapid heat transfer and conversion which gives high yields of bio-oil instead of char. For example, pyrolysis of wheat straw results in production of biochar containing labile unpyrolyzed carbohydrate fraction. These two methods result in production of biochars with different characteristics including pH, particle sizes, and SBET (Qian et al. 2015).

Intermediate Pyrolysis: The process of intermediate pyrolysis operates at conditions between slow and fast pyrolysis, i.e., at moderate temperatures up to 500 °C, vapor residence times of 2–4 s, and solid residence times of 0.5–25 min yielding 15–35 wt% of dry biochar. For example, wood and barley straw pellets at intermediate pyrolysis result in production of 30 wt% char with 75 wt% carbon (Yang et al. 2014).

Other Methods: Other popular processes of pyrolysis include flash and vacuum pyrolysis. Flash pyrolysis occurs at very high temperature (around 1000 °C) and heating rate (1000 °C s^{-1}) for less than 1 s, leading to high yield of liquid and low char production. Vacuum pyrolysis is somewhat similar to slow pyrolysis except the low pressure at tens to hundreds kPa.

Another method of producing biochar is torrefaction which is a mild pretreatment of raw material (200–300 °C), heating at very slow rate for short period of time prior to pyrolysis. The solid product obtained is rich in carbon, often porous, with low O/C ratio and moisture content, thus easy to store and deliver. The carbon yield during torrefaction depends on the raw material used, temperature at which it is heated, its retention time, and the atmosphere of the furnace (Chen et al. 2015). Torrefaction, a kind of mild pyrolysis which is operated at a temperature range of 200–300 °C, for producing biochar increases drastically. Torrefaction is dependent on biochar yield, densification factor, and heating value and energy yield. The higher the weight loss or the lower the solid yield, the higher the torrefaction severity. Three different torrefaction extents based on pretreatment temperature, including light torrefaction (200–235 °C), mild torrefaction (235–275 °C), and serve torrefaction (275–300 °C), have been classified to identify the impact of the pretreatment on hemicellulose, cellulose, and lignin (Chen et al. 2015).

Another technology that involves heat and steam as controlled process is gasification of biomass to convert it into hydrogen and other products. Various types of biomasses like rice straw, palm kernel, switchgrass, coffee, grape waste, sawdust, sludge, algae, etc. have been used and evaluated for biochar production. Major problem related to gasification is the formation of tar which on the catalytic decomposition leads to enhanced hydrogen production. So, two-stage gasification can be one of the alternatives for tar reduction. Also, different steps of gasification (drying, pyrolysis, and gasification) in conventional one-stage gasification can be controlled in the two-stage (Xin et al. 2017).

Another type of conversion is hydrothermal carbonization (HTC), type of thermochemical conversion, also referred to as wet torrefaction that converts raw biomass into a coal-like product, called hydrochar. It is an induced coalification process which is characterized by high carbon content and high calorific value and can be applied to a variety of nontraditional sources including sewage, algae municipal solid waste, etc. This process involves the treatment of substrates at high pressure (10–50 bar) and high temperature (180–250 °C) for a few hours (0.5–8 h) with elevated moisture content, up to 75–90%, without requiring a drying pretreatment step. During process, the biomass undergoes various reactions involving dehydration, decarboxylation, and decarbonylation and converts into a carbon-densified product, hydrochar, which has many applications (Libra et al. 2011).

3.4 Preparation of Biochar Catalysts

For physicochemical properties of biochar, various approaches of activation and functionalization have been used to enhance reactivity in various processes and device architectures (Liu et al. 2015a, b). The most common methods of preparation of biochar catalysts are impregnation and physical and chemical activation.

Impregnation method is a method in which biochar structures are incorporated with active metallic species via mixing biomass feedstock with metal precursors, forming active interfaces and binding sites. This method develops composite with higher SBET, macroporosity facilitating both the adsorptive and degradative removal. For example, biochar with zerovalent iron has been synthesized from a lignin-magnetite pellet at 900 °C. A biochar-Co_3O_4 composite was prepared from rice straw by impregnating the biochar with $Co(NO_3)_2$, followed by calcinations and hydrothermal treatment. The resulting catalyst was found to be effective in the oxidative degradation of ofloxacin mediated by peroxymonosulfate (PMS) (Lawrinenko et al. 2017).

Chemical Activation: Chemicals such as nitric acid, phosphoric acid, ammonium nitrate, and urea change surface properties of biochar, introduce surficial acidic or basic groups, decrease pore volume, and introduce oxygen, carbonyl groups, and nitrogen leading to improved hydrophilicity of biochar and adsorption capacity (Chu et al. 2018).

Activation by Physical Methods: Methods like stream of steam, mild air oxidation, and air activation help in modifying the structure of biochar with increased SBET, introducing groups with enhanced catalytic activity (Rajapaksha et al. 2016).

3.5 Aquatic Biomass as Biochar

Aquatic biomass includes algae, giant kelp, other seaweeds, and marine microflora with phytoplankton and zooplankton. Aquatic wastes are generated after fishing and other activities and are found in rivers, lakes, and ponds. Algae are the most prominent among aquatic wastes which is a fast-growing unicellular and microscopic biomass which can grow in freshwater, seawater, or damped oils. Algal biochar is more nutritionally rich than lignocellulosic biochar containing N, P, K, Ca, and Mg. Algal biochar cultivation has established markets as food, alginate, agar, and carrageenan, giving more commercial value. Algal biomass is used to sequester atmospheric carbon dioxide to minimize greenhouse effect. Algal biomass converted into biochar through thermochemical processes such as pyrolysis, hydrothermal carbonization, or torrefaction has an application as adsorbent for environmental pollutant uptake or biomaterials for medical applications.

Algal biochar has lower surface area, carbon content, higher cation exchange capacity, high pH, high nutrient content of nitrogen, ash, and inorganic elements compared to lignocellulosic biochar. These properties of algal biochar make it suitable for soil amendment in agriculture (Kołtowski et al. 2017) and as a bio-adsorbent in water treatment for remediation (Awad et al. 2017).

3.6 Modification of Biochar

Biochars adsorb heavy metal ions with an excellent capability which is relatively lower in comparison with other known biosorbents such as activated carbon. Application of biochar has been focused primarily on the modification with improved surface properties and novel structures to enhance its environmental benefits and remediation efficacy. Several approaches are there to modify the biochar, i.e., chemical modifications, physical modifications, magnetic modifications, and impregnation with mineral oxides.

Chemical Modifications Biochar can be modified by chemical means by carbonization and activation in presence of activating chemical agent. Acidic or alkaline modification of biochar changes the functional groups resulting in increase of O/C and H/C molar ratios which signifies the occurrence of decrease in hydrophobicity

(Vithanage et al. 2015). Some causes increase in polarity of biochar which leads to chemisorptions of pollutants from wastewater, while some increase aromaticity with higher N/C ratio enhancing sorption of organic pollutants from wastewater.

Functional Group Modification Biochar functional group modification by use of hydrogen peroxide, $KMnO_4$, etc. can be done by oxidation. These modifications have significant effect on remediation of pollutant due to complexation for heavy metals in wastewater (Rajapaksha et al. 2016). Introduction of functional groups gives the biochar basic properties with strong affinities toward metal ions in contaminated water. Coating of biochar with chitosan can be used as adsorbent for uptake of heavy metal ions; peanut shell modification with hydrogen peroxide improves lead ion adsorption capacity; biochar modifications with amino group improve adsorption capacity for copper ions in wastewater.

Engineered Biochars Previous studies have demonstrated that engineered biochars loaded with various metal oxyhydroxides can effectively remove P from aqueous solutions under various conditions. Engineering nanoparticles with biochar results in new composite with improved physical and chemical properties. Recently, different substrate-based nanocomposite materials have been developed for decontamination of wastewater even the nuclear wastewater (Awual et al. 2016).

Magnetic Biochars Coprecipitation of iron ion and iron oxides onto biochar results in synthesis of nano-sized magnetic iron oxide including Fe_3O_4, c-Fe_2O_3, and $CoFe_2O_4$ particles. These can be coated on the surface of biochar, which results in the introduction of magnetism and active sites of iron oxide onto the biochar for the removal of contaminants. These magnetic biochars can be easily separated from solution by application of external magnetic field (Chen et al. 2011).

3.7 Chemically Modified Biochars

Biochars obtained from feedstock of biomass with nanocomposites containing MgO were prepared by pyrolysis at 600 °C with N_2 and $MgCl_2$ results in dispersal of particles of MgO all over the surface of biochar. Therefore, nanocomposites then can be used for removing phosphate and nitrate from water. Sugar beet achieved adsorption capacity of 835 mg/g (in the presence of phosphate). Peanut shell with MgO biochar adsorption was 12% nitrate from water, which is the highest value among these chars, having an adsorption capacity of 94 mg/g. High amounts of phosphate and nitrate capacities could be due to either surface area or porosity enhancement by the introduction of MgO (Zhang et al. 2012).

3.8 Application of Biochar for Wastewater Treatment

3.8.1 Color/Dye Removal

The effluent from dye industry poses majority of problems because it contains acids, toxic compounds, dissolved solids, and color. Various conventional wastewater treatments are there to wipe out textile dyes due to their stability in oxidizing agents and light. But later on biochar was developed for dye removal from wastewater which can be obtained from straw (Xue et al. 2012) and bamboo (Yang and Jiang 2014).

3.8.2 Removal of Metal Ions

Anthropogenic activities such as manufacturing units, mining activities, smelting process, etc. are responsible for contamination of heavy metals in water. Use of biochar for heavy metals removal from contaminated water depends on the valence state of metal. There are four mechanisms in which biochar can be applied for the removal of heavy metals and they are as follows: (1) electrostatic attraction, (2) ion exchange, (3) complexation with π electron-rich domain or surface functional groups, and (4) coprecipitation to form insoluble compounds (Li et al. 2017).

Biochar can be applied at different stages of wastewater treatment to improve efficiency and recovery of value-added by-products and can be governed by the mechanism of adsorption and immobilization of microbial cells. Modified biochar efficiently adsorbs nutrients from environment and can be used later as nutrient-rich material for remediation purposes. Biochar can be applied in activated sludge treatment, and settling ability by adsorption of inhibitors and toxic compounds can be improved (Mumme et al. 2014). It can also be used for the removal of organic and inorganic pollutants including agrochemicals, volatile compounds, antibiotics/drugs, cationic dyes, etc. (Adeel et al. 2017).

Adsorption occurs due to high surface area, microporosity, and functional groups having high affinity to polar organic compounds. For example, rice husk, soybean-derived biochar, red-gum woodchips, and broiler litter-derived biochar facilitate removal of nonpolar carbofuran (pesticide) and trichloromethylene (VOC), pyrimethanil and diesopropylatrazine (fungicide/pesticide), 1-naphthol, norflurazon, and fluridone from contaminated water. Biochar in wastewater removes heavy metals and compounds like nitrate, nitrite, ammonium, phosphorus, etc.

Biochar with high organic carbon content, specific porous structure, and numerous functional groups interacts with heavy metals through ion exchange, complexation, precipitation, and coordination of metal ions with π electrons (C=C) due to increased pH and surface area with biochar addition. Hardwood and crop-derived biochars, *Sida hermaphrodita*, guayule shrub, soybean straw, wheat straw-derived biochars, alkaline biochars derived from various agricultural residues, manure, and animal manure-derived and cocoa husk biochar showed high affinity toward Cu^{2+}, Cd^{2+}, Ni^{2+}, Zn^{2+}, and Hg^{2+} removal.

Biochar due to high surface charge density allows retaining cations by cation exchange, and the high surface area, internal porosity, and presence of both polar and nonpolar surface sites enable it to adsorb nutrients like NH_4, NO_3^-, and PO_4^{3-}. Sugar beet tailing biochar, orange peel biochars, rice husk and a mixture of tree trunks and branches, and bamboo charcoal biochar can be used (Pokharel et al. 2020).

Suspended aerobic microbe growth decomposes organic matter in wastewater in activated sludge treatment, where numerous micro-pollutants from pharmaceuticals, personal care products (PCPs), pesticides, disinfectants, and antiseptics are of great importance. Therefore, biochar can be added to the aeration basin of activated sludge system. Biochar results in increased process stability by (a) adsorption of inhibitors (heavy metals, polycyclic aromatic hydrocarbon), (b) increasing the buffering capacity of the system, and (c) immobilization of microbial cells.

Among different approaches anaerobic digestion is one of the most promising treatment technologies for wastes management. It is an eco-friendly process because of its ability to combine bioremediation and energy recovery. The anaerobic digestion process removes efficient pollutants under stable conditions with high energy recovery, and their metabolic intermediate products could inhibit microorganisms by acclimation of bacterial cells and hinder their activity. In order to counteract the inhibition in anaerobic reactors, the adoption of packing materials has been proved as an advantageous alternative allowing for the development of a large bacterial biomass within the digester.

For anaerobic digestion, the addition of biochar increases the rate and amount of biogas production and also yield of CH_4 attributed to the buffering properties of biochar, promoting methanogenesis for higher biogas yield. Biochar increases microbial metabolism and growth because of the support provided. Biomass immobilization onto a packing material with large surface areas for growth of microbes has been proved as an advantageous alternative, which allows formation of bacterial film within the reactors, facilitating electron transfer between interspecies and reducing the distance between syntrophic bacteria and methanogens (Gehring et al. 2016). The biochar could reduce the mobility or availability of the inhibitors like heavy metals, pesticides, antibiotics, and other organic compounds by binding them in its porous structure and maintain proper microbial activity for the digestion process.

As a Filtration Support Medium: Biochar can be used as a layer/column into a slow sand filter or bio-sand filter systems for the treatment of wastewater. In a study *Miscanthus* biochar filter was used, and higher removal efficiency of COD was observed (Kaetzl et al. 2020) as compared to a sand filter. Also, higher removal of *E. coli* with a mean reduction of 1.35 ± 0.27 log-units compared to that of sand filters with a mean reduction of 1.18 ± 0.31 log-units was observed.

Biochar as filter media has an ability to remove total suspended solids, nutrients, *E.coli*, and heavy metals from wastewater (Reddy et al. 2014). The removal of suspended solids and organic matter in an anaerobic biochar filter could be performed by series of steps including coagulation sedimentation and the filtration. Removals of smaller particles are carried out by straining and adsorption, while organic matter is hydrolyzed under anaerobic conditions.

Biochar filter efficiency increases with increase in surface area and the attachment sites on the biochar surface. It also supports the biofilm establishment and the bacterial deposition within the filter column. Filtration and adsorption of viral and bacterial cells reduces the load of pathogens (e.g., protozoa, amoeba). Also, electrostatic attraction of bacteria to the biological film developed on the surface of the biochar filter and the attachment of *E. coli* to the biochar filter coupled with the increase in the water-holding capacity.

The biochar after filtration becomes enriched with nutrients and therefore can be reused for remediation and as fertilizer. In the study performed by Werner et al. (2018), the biochar filter showed removal of pathogens, and concentrations of P, Mg, and K were reduced during filtration, while N content remained unchanged. The agronomic effects of the biochar filter on spring wheat biomass production on an acidic sandy soil were evaluated. The results showed higher wheat biomass production for biochar filter (37%) treatment (20 t/ha), compared to the unamended control.

As a Catalyst During Heterogenous Oxidation: For the remediation and degradation of biorecalcitrant compounds, biochar-based catalysts can be used in different systems, including catalytic ozonation processes, Fenton-like reactions, and photocatalytic systems. Biochar prepared from pistachio hull biomass with macroporous structure and hydroxyl and phenolic functional groups can be used for the ozonation of a water recalcitrant contaminant (reactive red 198 dye) (Moussavi and Khosravi 2012). Biochars originating from pine needles, wheat, and maize straw having free radicals transfer electrons to oxygen to form superoxide radical anion and hydrogen peroxide which can induce OH generation. Biochar obtained from HTC results in degradation of alachlor and methylene blue by transferring electrons from biochar to Fe (III) (Izghri et al. 2019).

3.8.3 Biotransformation

Another important and promising application of biochar is biodegradation treatments. It can be brought about by the immobilized-microorganism technique (IMT) which combines the degradation and adsorption technologies by immobilizing microorganisms on the surface of carriers. This creates a favorable degradation environment for the microorganisms through the effective adsorption of pollutants on the carrier to achieve the efficient removal of pollutants. Microorganisms immobilized on biochar could directly or indirectly ameliorate environmental contamination of organic and inorganic pollutants. IMT results in high microbial density and activity, a fast reaction speed, strong stability, better resistance to environmental impact, etc. and, therefore, can be used in water pollution remediation (Chuaphasuk and Prapagdee 2019).

Using adsorption method, a surfactant-enhanced biochar immobilized with bacteria was prepared for the removal of PAHs in wastewater (Lü et al. 2014). Another way of immobilizing microorganisms on biochar is gel embedding method which immobilizes microbial cells in the limited space of microcells or microcapsules of gelatin. Adding biochar and surfactant on the basis of a general sodium alginate embedding agent may give rise to immobilized materials with higher microbial immobilization efficiency and degradation activity and can also be applied to more types of reactors.

Immobilized *Pseudomonas aeruginosa* beads with biochar and alginate as the composite carriers and the nonionic surfactant TX100 as a promoter were prepared by the gel embedding method and applied in both batch and continuous reaction systems for efficient removal of organic pollutants in wastewater.

Biochar immobilized with phosphate-solubilizing bacteria forms stable pyromorphite by precipitation and has an ability to immobilize Pb (Chen et al. 2019). Moreover, biochar immobilized with PAH-degrading bacteria and chromium-reducing bacteria was effective in remediation of pyrene and chromium (Wang et al. 2019) and also atrazine, nonylphenol, and petroleum hydrocarbon (Lou et al. 2019). Apart from heavy metals and organic compounds, biochar immobilized with microorganisms helps in the removal of nitrogen, phosphorus, and bioavailable carbon as quantified by chemical oxygen demand (COD). Efficient removal of ammonium, phosphate, and COD from wastewater can be achieved by modified biochar with immobilized heterotrophic nitrifying bacteria or photosynthetic bacteria (Yu et al. 2019).

Paracoccus sp. strain YF1 (Liu et al. 2012), *Pseudomonas stutzeri* strain T1 (Yao et al. 2013), *Acinetobacter* sp. SZ28, and *Enterobacter* sp. FL (Wang et al. 2018) can be applied in the field of wastewater bioremediation. Woodchip biofilters as biochar with mixed bacterial inoculum can increase the nitrate removal capacity. An aerobic denitrifier, isolated from surface flow constructed wetland and identified as *Pseudomonas mendocina* immobilized on biochar, exhibited excellent aerobic denitrification ability (Zhang et al. 2019).

EC removal in existing treating systems is one of the key focus areas to mitigate; therefore, immobilized biomass (biochar and microorganism) can be applied for improving the performance of treatment systems. Immobilized systems can also be easily retrofitted with the existing biological systems for wastewater treatment. Biofilters, rotating biological contactors (RBCs), moving bed biofilm reactors (MBBRs), and fixed bed reactors (FBRs) employ immobilized systems and have been reported to show better EC removals than conventional activated sludge processes. In addition, membrane bioreactor systems (MBRs), which show high potential for EC removal, also involve cell immobilization onto the biochar. Studies have also been conducted with conventional biological systems augmented with carrier materials to encourage biomass attachment and adsorption removal of contaminants. Bioreactors have also been developed for biomass attached on carrier supports for the wastewater treatment (Naz et al. 2015).

Cell-immobilized-biochar bead is another form which can be used to treat various water pollutants. For example, cell-biochar beads can be used to treat BTEX and Cr6+ from wastewater, and polyvinyl alcohol (PVA)-alginate beads placed in solution of storage tank reduced the inhibitory effects of high-load isopropyl alcohol (IPA) vapor on microbial growth. Bamboo biochar and microorganisms are combined with PVA to make the novel cell-immobilized bamboo-biochar beads (cell-biochar bead) as a packing material in a BTF for treating toluene-contaminated waste gas, and the biodegradation kinetics and changes in the microbial community in the BTF under various operating conditions were elucidated.

Softwood bark charcoal biomass with immobilized bacteria was able to remove naphthenic acids. In one study, bamboo charcoal (BC) and wood charcoal (WC) were used as carriers for removal of nonylphenol (NP), an environmental pollutant with estrogenic activity, which persisted in the sewage sludge in wastewater treatment plants. Furthermore, *Pseudomonas*, *Achromobacter*, *Ochrobactrum*, and *Stenotrophomonas* were the dominant bacteria for NP degradation. The addition of biochar (especially bamboo charcoal) could promote the growth of microorganisms and slow down the change of the dominant microflora for NP degradation (Lou et al. 2019).

One of the developing industries is the pharmaceutical industry which generates a lot of wastewater during manufacturing process from complex raw materials like solvents. Wastewater contains high amounts of refractory organic compounds and inorganic salts which continuously accumulate into natural environments and human bodies through food chains, resulting in toxic hazards to health.

Due to high chemical oxygen demand in wastewater of pharmaceutical industry, various strategies have been used for treatment including anaerobic technology, advanced oxidation processes (AOPs), adsorption, biodegradation, and multi-technology combination. Another promising technology for treatment is anaerobic membrane bioreactor (AnMBR) (Ng et al. 2014) along with the combination of modern membrane separation technology for high organic removal, low energy consumption, and biogas recovery.

The most popular adsorbent material used for membrane bioreactor is powdered activated carbon (PAC) for wastewater treatment as biofilm. It can retard membrane fouling and increase membrane flux and improve sludge flocculation. Compared with PAC, biochar is a low-cost product of biomass with various functional groups besides large specific surface area and porosity. AnMBR system with biochar and without biochar was set to achieve AOX and COD removal and mitigating membrane fouling (Chen et al. 2020).

Another industry generating major pollutants in water is leather processing industry with azo dyes and hexavalent chromium (CrVI) as common pollutants in wastewater. A treatment strategy to remove azo dyes, their by-products, and CrVI using a biochar packed bioreactor was introduced. Various feedstock materials were evaluated, after which biochar produced from pyrolysis of corn cobs at 400 °C was selected as a packing material for the reactor, based on its large surface area (1275 m^2 g^{-1}), microporosity (2–5 μm), and ability to support microbial biofilm formation.

In an experiment tannery wastewater containing reactive black-5 azo dye and aniline was treated using bacteria *Pseudomonas putida* strain K1 with pyrolyzed carbon (biochar) as a support matrix. The results showed complete biodegradation of reactive black-5 within 5 h. Strain KI could also reduce dye and CrVI simultaneously in 24 h in a continuous packed bed bioreactor. Complete biodegradation of aniline (by-product of reactive black-5) in the bioreactor was obtained within 24 h in the absence of CrVI, whereas degradation was decreased to 84% in the presence of CrVI.

Another industry is battery manufacturing industry releasing mainly Pb2+ pollution. Pb2+ is removed from water using a variety of procedures, including lime precipitation, reverse osmosis, ion exchange, electrochemical process, coagulation, and ion flotation, although these treatments are costly and produce secondary waste. Battery industries effluent has high pH, electrical conductivity, COD, BOD, DO, TDS, TSS, and TS which are due to different inorganic and organic pollutants such as nitrate, phosphate, and sulfate affecting quality of water. Bagasse biochar with immobilized microbes is a cost-effective adsorbent for the successful removal of pollutants and heavy metals from different wastewater-generating industries (Poonam et al. 2018).

Another commonly immobilized biomasses are of algal origin. Using microalgal cells with biochar for the bioremediation of industrial effluent involves biotransformation and biodegradation processes of metabolism. Microalgal biochar as an adsorbent can be applied for the removal of recalcitrant pollutants (PNP) which can be used as nutrients by algal cells. Therefore, biochars derived from three microalgae species *Chlorella* sp. *Cha-01*, *Chlamydomonas* sp. *Tai-03*, and *Coelastrum* sp. Pte-15 can be used for PNP removal, released by dyes production, petroleum refining, and plastics manufacturing. Biochar prepared from microalgae exhibited superior adsorption capacity for pollutants because they contain high N/C and O/C ratios with polarizable functional groups. This biochar could be applied as an adsorbent for the removal of organic pollutants in wastewater treatment.

Microalgal biomass, e.g., kelp; *Undaria pinnatifida*; *Saccharina japonica* and *Sargassum fusiforme*; *Sargassum* sp.; *Cladophora coelothrix*, *Cladophora patentiramea*, *Chaetomorpha indica*, *Chaetomorpha linum*, *Cladophoropsis* sp., *Ulva flexuosa*, as well as freshwater *Spirogyra* and *Cladophora*; *Cladophora vagabunda*; and *Oedogonium intermedium*, can be used as biochar. It is characterized by a comparatively low carbon content, surface area, and cation exchange capacity when compared with lignocellulosic biomass, but has a high pH plus nitrogen and inorganic nutrients such as Ca, K, Mg, and P, which is why it is proposed to be used in agriculture as a soil fertilizer/soil additive. Its other applications include its use as an adsorbent for the removal of organic or inorganic pollutants or energy sources. Algal biochar is suitable for wastewater treatment like the removal of ammonium-N ($NH^{4+}N^{-}$) and various organic and inorganic pollutants from wastewaters (Michalak et al. 2019).

Also, algal biochar as a biosorbent can be used for the removal of toxic metals from wastewater even when their concentrations are low and range from 1 to 100 mg L^{-1}. The possibility of the production of “bio-ore” from the metal-loaded sorbent at the end of the process is very advantageous. Combustion of biochar after sorption enables the recovery of metals and energy accumulated in biomass. The sale of recovered elements is known as “phyto-mining.” Algal biochar has already been tested as a sorbent of some heavy metals such as Cu, Cd, and Zn ions from aqueous solutions. Kidgell et al. (2014) used the biochar produced from freshwater macroalga *Oedogonium* to remove metal ions from the industrial effluent coming from a coal-fired power station. Johansson et al. (2016) showed that biochars produced from *Gracilaria* and *Oedogonium*, which were treated with Fe before pyrolysis, have a high affinity also for oxyanions such as As, Mo, and Se, which are difficult to remove through conventional techniques.

Wastewaters are severely polluted that will consequently lead to environmental problems due to the high chemical oxygen demand (COD) and biological oxygen demand (BOD) and rich in organic and inorganic nutrients. Microalgae can be used as absorbent during cultivation stage and after converting into biochar. Cultivation of microalgae adsorbs the nutrients and metals contained in wastewater to improve wastewater quality and sustainability. Microalgae reduce large amount of carbon dioxide because microalgal biomass required carbon dioxide to cultivate. Microalgae consist of high carbon fixing or photosynthetic efficiency compared to plants at lands to allow low-cost efficiency carbon mitigation. Conversion of microalgal biomass to biochar stores the carbon dioxide in the form of solid to mitigate carbon to atmosphere. Production of microalgal biochar efficiently mitigates the carbon and adsorbs contaminant from cultivation stage to biochar production process.

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Application of Biochar for Wastewater Treatment

4

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Abstract

Biochar has been widely applied in wastewater pollution control due to its high stability, excellent surface properties, high-developed pore structure, and rich surface functional groups. In this chapter, the research progress of biochar application in recent years was reviewed. The application of biochar technology in the removal of heavy metals, organic pollutants, and nitrogen and phosphorus nutrients was mainly summarized. In fact, although biochar is made of agricultural and industrial wastes such as crop straw, litter, dewatered sludge, and sediment by pyrolysis, it plays a substantially important role in environmental treatment, reflecting the concept of "treating wastes with wastes." Therefore, biochar is a new, economic, and environmental material which can be used in the wastewater treatment technology.

Keywords

Biochar · Heavy metals · Organic pollutants · Adsorption · Treating wastes with wastes

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4.1 Application of Biochar as Absorbents

Biochar is used for wastewater treatment as a low-cost and environmentally friendly adsorbent with high efficiency. It has been commonly used to adsorb pollutants in wastewater (Sanjrani et al. 2019).

4.1.1 Adsorption of Heavy Metals in Wastewater

Heavy metals (e.g., Cr, Cu, Ni, Zn, Pb, Cd, and Hg) are elements of great concern due to their toxic and persistent nature in the environment. They find their way in the aquatic stream through various industrial operations, like mining, smelting, electroplating, etc.

The adsorption capacity of biochar is closely related to physical and chemical properties (Inyang et al. 2016). High specific surface area and developed pore structure can provide more adsorption sites. Oxygen-containing groups and mineral components can be chemically adsorbed with heavy metals to improve the adsorption effect. High specific surface area and developed pore structure can provide more adsorption sites. The choice of adsorbent to be used for a specific application depends on various factors, such as its cost, its selectivity for different metals, its adsorption efficiency, reusability and regeneration, the adsorption and desorption rates, its ease of synthesis, and mechanical strength (Gupta et al. 2020). For instance, elevated pyrolysis temperature is helpful to increase capacities of rice husk biochar for Pb (Shi et al. 2019).

Since biochar is a porous material whose ability for sorption is greatly affected by its surface area, increasing its surface area by adding nanoparticles increases its potential for metal sorption. For example, Yan et al. (Yan et al. 2015) synthesized magnetic biochar/ZnS composites by depositing ZnS nanocrystals onto magnetic biochar-based sorbents. The biochar-based sorbents showed a maximum sorption capacity of Pb up to 368 mg/g, which was tenfold of the unmodified biochar. To modulate the properties of biochar-based sorbents for heavy metal removal, a range of modification methods have been adopted. Popular approaches are chemical alteration and physical alteration. Chemical alteration is the most common form of alteration used. This primarily involves acid alteration, alkalinity alteration, oxidizing agent modification, metal salts or oxidizing agent modification, and carbonaceous material modification. Physical alteration primarily includes the purging of steam and gas (Wang and Wang 2019). Metal nanoparticles, in particular iron, are the most cost-effective and advantageous modification materials due to their ferromagnetic properties for the preparation of magnetic biosorbents (Gupta et al. 2020). Magnetic biosorbents boost surface areas, functional groups, and active sites and, consequently, improve removal performance. While nanoparticles have high adsorption capacities, they are typically not used directly in practical applications due to their expensive regeneration. As a result, the regeneration of the adsorbent is an extremely difficult process. Therefore, to solve this problem and simplify the process of regeneration, nanoparticles with magnetic properties have been synthesized (Liu et al. 2010).

Biochar with specific porous structure, higher organic carbon content at noncarbonized fraction, and a number of functional groups interacts with heavy metal contaminants in several ways. Among divalents, Cu showed greater affinity toward biochar due to the formation of surface complexes with carboxylic and phenolic hydroxyl groups on hardwood- and crop straw-derived biochars (Tong et al. 2011). It was found that Cu bind with phosphate and silicate groups on biochar surface, which was the adsorption mechanism for copper ion removal from water (Meng et al. 2014; Tareq et al. 2019).

In the recent years, modified biosorbents are being widely for improved metal removal efficiency even at low concentrations and easy recovery and reuse due to several limitations of pristine biochar and other biosorbents. Metal-induced sorbents or magnetic biosorbents/biochar are being developed by incorporating metal nanoparticles (Fe, Ni, Cr, Ti, Zr, Zn, Cu, etc.) (Nisticò et al. 2018). It was found that they have improved surface area, pore size, thermal stability, crystalline nature, and surface functionality leading to higher adsorption capacity and easy recovery (Yin et al. 2017). The properties of magnetic biosorbents were found to be dependent on the nature of biomass itself, metal nanoparticles, and modification methods, besides process parameters like pyrolysis temperature and duration and particle size (Alizadeh et al. 2018; Dinari and Tabatabaeian 2018). Ultrafine nanoparticles like metal oxides could be used as successful modifiers to enhance the structural and thermal stability of the adsorbents. Different types of modifications (e.g., pretreatment/single step, posttreatment modification/double step, microwave-assisted modification, hydrothermal modification, etc.) are employed in the synthesis of magnetic biosorbents. In the pretreatment method, metal nanoparticles are incorporated into biomass before pyrolysis leading to a larger surface area, porosity, and superparamagnetic behavior. In the second method of posttreatment, biosorbents and nanoparticles are prepared separately before mixing. However, this is less efficient and more expensive than the pretreatment method. Microwave-assisted synthesis of magnetic biosorbents is commonly used (Thines et al. 2017) but with some difficulty in customization. This method is replacing conventional pyrolysis in the synthesis of magnetic biochar.

Recently, engineering biochars and magnetic biosorbents are being explored as innovative alternatives due to improved physical-chemical attributes and adsorption capacity (Gao et al. 2015). However, they are still in experimental phase and need further exploration. Magnetic biochar can be produced using coprecipitation method. In this process, a carbon material is heated in the absence of fusion in a pressurized autoclave to remove water and drive off gases and other volatile constituents. Magnetic biochar synthesized using this method with $FeCl_3.6H_2O$ resulted in larger surface area, diverse morphology from macro-mesoporous structure, and high crystallinity besides simple recovery and reusability (Gao et al. 2015). Moreover, a scavenger of Mg-Al layered double hydroxide (Mg-Al LDH) with ethylenediaminetetraacetic acid (EDTA) intercalated between the layers was found to be extremely successful in the removal of heavy metals. For example, Cu, Cd, and

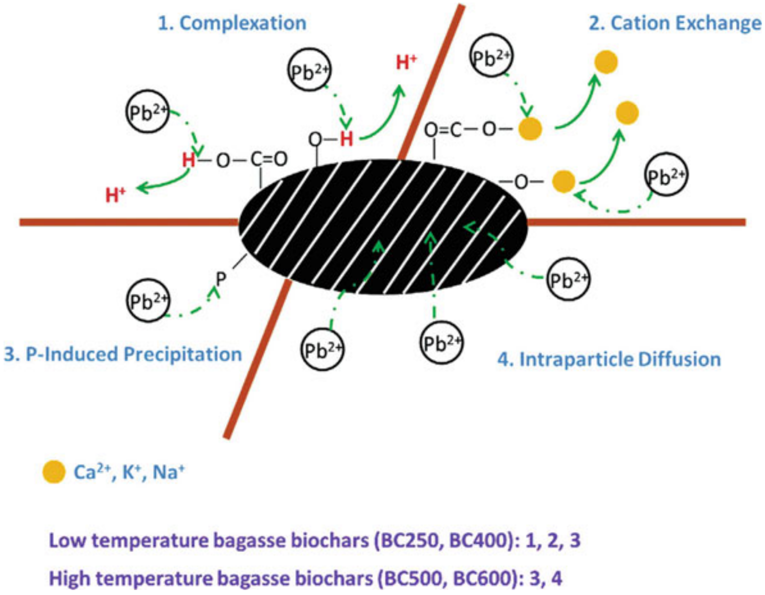

Fig. 4.1 Mechanisms of Pb sorption by bagasse biochars (Ding et al. 2014)

Cr(VI) could be removed from wastewater rapidly by them (Huang et al. 2019). Since biochar without appropriate modification and functionalization was not very competent in the metal removal, it is an urgent to develop these novel and effective techniques to enhance the utility of biochar (Gupta et al. 2020).

On the other hand, the decrease in oxygen-containing functional groups can affect the metal sorption capacity of biochars. It was found that higher Pb adsorption capacity was achieved at lower temperature (Ding et al. 2014). Figure 4.1 explains the mechanisms of Pb sorption by bagasse biochars. The possible reason was that oxygen-containing functional groups were responsible for Pb sorption at low temperature, while Pb sorption was affected by the abundant pores at high temperature (Sizmur et al. 2017).

Pretreatment is frequently advised to maintain adsorption efficiency. In most cases, it increases removal efficiency and selectivity in comparison to unmodified biosorbents. This pretreatment can enhance ion-exchange ability, improve the formation of functional groups, and provide a greater number of binding sites, which, in turn, favors metal uptake. It has been found that pretreatment modifications led to improved attributes in biochar-based sorbents, thereby enhancing its performance (Gupta et al. 2020).

4.1.2 Adsorption of Organic Pollutants in Wastewater

Rapid industrialization and agrochemical-based cultivation produce considerable amounts of organic pollutants (e.g., pesticides, herbicides, fungicides, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBS), dyes, antibiotics) and thus affect the environment greatly. The removal of these pollutants from soil, drinking water sources, and wastewater still remains a challenge. Organic contaminants are of special concern (Beesley et al. 2010; Tareq et al. 2019; Xu et al. 2012). They can persist in the environment for long periods of time and badly affect aquatic environments as well as human health via the food chain. For example, phenols affect the taste and odor of fish and drinking water even at very low concentration; tetracycline is one of the most abundant antibiotics in livestock farm wastewater (Zhang et al. 2020b).

Conventional techniques such as chemical precipitation, ion-exchange, adsorption, and membrane separation processes are often costly and yield considerable amounts of chemical waste. In recent years, applications of biochar in organic remediation have attracted significant research interest as a sustainable, environment-friendly, and low-cost alternative (Thompson et al. 2016; Tareq et al. 2019), i.e., dyes challenge conventional waste treatment methods due to their resistance to light, oxidation, and aerobic digestion and hence amenability to adsorption technology (Zhang et al. 2020b).

Solution pH has a predominant influence on the charge characteristics of biochars through the protonation and deprotonation of oxygen-containing groups on the composite surface which, in turn, affects pollutant adsorption. When the solution pH is lower than the point of zero charge (pzc) of biochars, that is, $pH < pH_{pzc}$, the composite surface is positively charged, and anion adsorption is favored. On the contrary, when $pH > pH_{pzc}$, the surface charge is negative and hence conducive to cation adsorption (Wang et al. 2020a). When the pH increases beyond a certain value (amino groups are deprotonated), the contribution of the π^+-π electron donor-acceptor interaction is suppressed, and sulfathiazole adsorption by biochar is decreased. For example, the ZrO_2-biochar composite had a pzc of 7.35 and showed maximum adsorption of reactive yellow 39 at pH 6.0 when its surface was positively charged (Khataee et al. 2017). Positively charged ZrO_2-biochar composite was also a good adsorbent of anionic dyes which may be degraded by hydroxyl produced during the reaction. The adsorption of organic dyes by biochars decreases as solution pH increases. Moreover, solution pH also has a significant effect on the adsorption of phosphorus by biochars, reaching a maximum at about pH 3.0 (Peng et al. 2020; Zhao et al. 2021).

4.1.3 Adsorption of Inorganic Pollutants in Wastewater

The adsorption of phosphate and nitrate are widely studied over biochars. Small amount of phosphate (>25μg/L) in surface water can promote algal blooms and eutrophication, leading to a decline in water quality, aquatic ecosystems, waterway transport, and human health (Zhang et al. 2020b). Generally, adsorption of oxyanions from aqueous solution takes place on positively charged biochar surface through electrostatic attraction. Therefore, the solution pH is an important factor in nitrate adsorption as biochar surface demonstrates an amphoteric nature in response to solution pH (Tareq et al. 2019).

Another major hazardous inorganic pollutant is fluoride. According to the World Health Organization (WHO), the concentration of fluoride in drinking water should not exceed 1.5 mg/L because ingestion above this level can lead to dental and skeletal fluorosis. It was found that acidic condition is more favorable for fluoride uptake due to higher positive charges on biochar surface (Oh et al. 2012). Oxidized aluminum and iron species on the surface of sludge-based biochar were positively charged at low pH and thus induced greater electrostatic attraction with fluoride ions. Greater adsorption of fluoride ions at acidic pH has also been reported for the defluoridation of drinking water (Mohan et al. 2012; Tareq et al. 2019).

Competitive adsorption by other anions suppressed phosphate adsorption with the impact decreasing in the order of $F^- > SO_4^{2-} > NO_3^- > Cl^-$. Phosphate adsorption was also pH sensitive, reflecting the acid-base properties of the LDH component and corresponding electrostatic attraction and surface complexation. Mg-Al mixed metal oxides (Zhang et al. 2020b).

4.1.4 Adsorption Mechanism

4.1.4.1 Heavy Metal Adsorption

The five mechanisms believed to govern metal adsorption by biochars are complexation, cation exchange, precipitation, electrostatic interactions, and chemical reduction. However, the contribution of a certain mechanism to a particular metal adsorption depends primarily on the nature and valence states of the target metals (Tareq et al. 2019).

Adsorption mechanisms governing remediation of lead from water are surface complexation, cation exchange, and precipitation. Lu et al. performed analysis of the relative distribution of mechanisms for Pb^{2+} adsorption on sludge biochars in a pilot plant-scale study for wastewater treatment (Lu et al. 2012). In this case study, exchange with K^+ and Na^+ contributed up to 4.8 and 8.5% adsorption, whereas surface complexation contributed 42% of the adsorption. The adsorption was also governed by precipitation as lead phosphate, surface complexation with active carboxyl and hydroxyl functional groups, as well as coprecipitation of lead with organic matter and mineral phases of biochars (Cao et al. 2009). However, Xu et al. (Xu et al. 2014) separated biochars into organic and inorganic fraction and showed that lead adsorption was higher onto inorganic fraction. This observation indicates that cation exchange and precipitation are the dominant mechanisms, while complexation with functional groups has a small contribution (Baig et al. 2014; Tareq et al. 2019).

Batch adsorption of cobalt showed that cobalt uptake was rapid and was governed by ion exchange through calcium release (Pan et al. 2009). However, cobalt adsorption had a competitive disadvantage due to the presence of co-ions like zinc and copper. These co-ions showed higher affinity toward biochars (Tareq et al. 2019). Therefore, cation exchange was found to be predominant at eliminating cadmium for high cation-exchange biochars (Harvey et al. 2011). When mineral content of biochar is higher, the main mechanism for the adsorption of cadmium is precipitation (Xu et al. 2013).

Cation exchange, surface complexation with functional groups or π electrons, and precipitation have been cited as the remediation mechanisms controlling adsorption of mercury from water. Surface complexation with carboxylic, phenolic hydroxyl, and thiol groups is the most dominating mechanism. For biochars derived at higher temperature or where functional groups are less or absent, binding with the π electron system becomes the major contributor (Dong et al. 2013; Xu et al. 2016). The presence of sulfur and chlorine species on alkaline biochar obtained from soya bean stalk and dairy manure effectively removed above 90% of toxic Hg^{2+} in the form of $HgCl_2$ or $Hg(OH)_2$ through precipitation (Kong et al. 2011). However, Hg precipitates with Cl_2 species during adsorption in the form of Hg_2Cl_2 (Lloyd-Jones et al. 2004). Therefore, more research concerning the precipitation mechanism for the remediation of mercury from water has been recommended (Li et al. 2017a; Tareq et al. 2019).

The three major mechanisms in Cr(III) removal are complexation with oxygenated functional groups, cation exchange, and electrostatic interaction between negatively charged biochar and positively charged Cr(III) ions. Pan et al. prepared biochar from peanut, soybean, canola, and rice husk and showed that adsorption capacity increases as functional groups on biochar increase, suggesting complexation with functional groups as the controlling remediation mechanism for trivalent chromium (Pan et al. 2013). Chen et al. observed release of Ca^{2+} and Mg^{2+} cations into solution during adsorption. These released cations correlated well with adsorbed Cr(III) indicating cation exchange as the main removal mechanism (Chen et al. 2015). At lower pH of solution, cation exchange between Cr(III) and minerals of biochar was hindered due to higher concentration. When solution pH is 2.5, surface biochar becomes negatively charged, and trivalent chromium species remains positively charged leading to electrostatic interaction and the removal of the chromium. Electrostatic attraction between positively charged biochar and negatively charged Cr(VI) species, reduction of Cr(VI) to Cr(III) by oxygenated functional groups, and subsequent Cr(III) complexation with functional groups of biochar are the dominating mechanisms for remediation of Cr(VI) species (Mohan et al. 2011). Due to reactive surface functional groups such as unsaturated anhydrosugars, diols, catechol, and substituted catechol structures originating from pyrolysis of lignin, cellulose, and hemicellulose, Cr(VI) is easily reduced to Cr(III) at lower pH (<2.5). Although the surface area of these biochars was very small compared to those of commercial-activated carbons, adsorption of Cr(VI) per unit surface area for the biochars was higher than that of activated carbons due to the swelling effect. Biochars showed interesting swelling properties that led to additional adsorption sites by increasing internal char/water contact with maximum chromium removal at pH 2 (Tareq et al. 2019).

Arsenic also retains a pentavalent state in the form of arsenate under aerobic condition and is less mobile and toxic than arsenite (Sizmur et al. 2017). Complexation and electrostatic interaction are the major mechanisms governing remediation of arsenic from aqueous solution. In the remediation of both As(III) and As(V) from water, the adsorption capacity of biochars to the presence of oxygenated functional groups counterbalanced the impact of lower surface area (Samsuri et al. 2013).

Although the surface porosity and micropore structure may be destroyed due to the growth or assembly of nano-metals, more abundant surface functional groups could be generated from the catalysis of metal ions (Ma et al. 2015). The formed functional groups showed great affinity toward HM ions to develop the metal-ligand complexes. In addition, taking iron oxide as the example, surface oxides or hydroxides could provide coordinative bonds (i.e., Fe–O) in the liquid phase and then transferred HM ions into H–Fe–O–Mn^+ species. In this case, the specific surface functional groups (e.g., Fe–O and –OH) are considered as the main mechanism to remove some HM ions (e.g., Zn^{2+}, Cu^{2+}, and Pb^{2+}) (Wang et al. 2019). During the removal process of As^{5+}, the inner sphere complexation is produced between surface –OH groups and As^{5+} at pH = 4.1, where –OH groups are derived from the nZVI NPs on the surface of BC (Wang et al. 2017; Ho et al. 2017).

Different adsorption mechanisms are also postulated for metals in different oxidation states. For example, Cr(VI) and Cr(III) exhibit different adsorption maxima (7 and 20 mg/g, respectively) over biochars. The higher affinity for Cr(III) was attributed to synergistic precipitation and ion-exchange processes as follows (Zhang et al. 2020b):

1. Ca and Mg dissolve in the aqueous Cr(III) solution:

$$\mathrm{CaO} + \mathrm{H_2O} = \mathrm{Ca(OH)_2}; \mathrm{MgO} + \mathrm{H_2O} = \mathrm{Mg(OH)_2}$$

$$\mathrm{Ca(OH)_2} = \mathrm{Ca^{2+}} + 2\mathrm{OH^-}; \mathrm{Mg(OH)_2} = \mathrm{Mg^{2+}} + 2\mathrm{OH^-};$$

2. The resulting pH increase promotes precipitation of $Cr(OH)_3$:

$$\mathrm{Cr^{3+}} + 3\mathrm{OH^-} = \mathrm{Cr(OH)_3(solid)};$$

3. Ca(II) and Cr(III) undergo simultaneous cation exchange:

$$\mathrm{Biochar} - 3\mathrm{Ca^{2+}} + 2\mathrm{Cr^{3+}} = \mathrm{Biochar} - 2\mathrm{Cr^{3+}} + 3\mathrm{Ca^{2+}}$$

$$\mathrm{Biochar} - 3\mathrm{Mg^{2+}} + 2\mathrm{Cr^{3+}} = \mathrm{Biochar} - 2\mathrm{Cr^{3+}} + 3\mathrm{Mg^{2+}}$$

Mechanisms of heavy metal removal are vital as they control the efficacy of the process, to have deeper insight into the micro-aspects of the process and to develop novel sorbents through effective synthesis and modification protocols as they are strongly correlated. Heavy metal removal by biochar-based sorbents follows different mechanisms like physical adsorption, electrostatic interaction, complexation, ion exchange, and precipitation. Metal removal is found to occur through individual or combination of mechanisms stated above. Biochar-based adsorbents have high surface area with diverse pore network ranging from micro-, meso-, and macropores (Mukherjee et al. 2011). Pore volumes with high affinity toward metals can follow adsorption, negatively charged surface of the sorbent can attract positive metals through electrostatic attraction, and ligands and various modifiers can form complexes or precipitates with metals to be removed (Gupta et al. 2020).

In physical adsorption, metal removal occurs through diffusional movement of metal ions through pores without chemical bond formation. Higher carbonization temperatures favor this mechanism due to enhanced surface area and pore volume, and the mechanism could be better explained by film pore diffusion model. In ion-exchange mechanism, the ionizable cations on the sorbent are exchanged with heavy metals in solution whose efficiency depends on the contaminant size and surface functionality. It has been found that nonwoody and grassy biochars with high O content and acidic sites exhibit higher cation-exchange capacity (Harvey et al. 2011). In electrostatic interaction, surface-charged sorbent and metal ions lead to their immobilization. The pH, point of zero charge (pzc), and carbonization temperatures are found to play a critical role in this mechanism (Dong et al. 2011; Mukherjee et al. 2011).

In the mechanism of complexation, the ligands and metals are found to form multiatom complexes. This is mostly prevalent in the presence of transition metals and oxygen-containing functional groups and employing plant-derived biochars. In the last mechanism of precipitation which is very common in the removal of metals and rare-earth elements, immobilization occurs by the formation of solids either in solution or on the sorbent surface during the sorption process.

Precipitation mechanism is widely observed at high pH and mineral content, in both plant- and animal-derived biochars (Inyang et al. 2011). As discussed in the preceding sections, biochar by itself is inferior in metal removal. Hence, to enhance biochar performance, various kinds of modification methods, such as mineral impregnation, nanoscale metal additions, surface oxidation, and surface reduction have been applied. These modifications are found to enhance biochar performance in terms of metal removal capacity, thermal and structural stability, desired morphology, and easy recovery and reuse (Gupta et al. 2020). It has been found that modifications and mechanisms of metal removal are strongly correlated. It was revealed that carboxyl and hydroxyl functional groups introduced through modification underwent complexation with heavy metals before and after adsorption. Also, oxygen-containing functional groups are found to release H^+ after ion-exchange, thereby reducing solution pH (Mohan et al. 2014).

The charge characteristics on the sorbent surface are found to affect the strength of materials through electrostatic adsorption with pH playing a vital role in achieving the desired metal removal capacity. It is found that when pH is more than pH_{zpc} (point of zero discharge), the negatively charged surface due to deprotonation led to

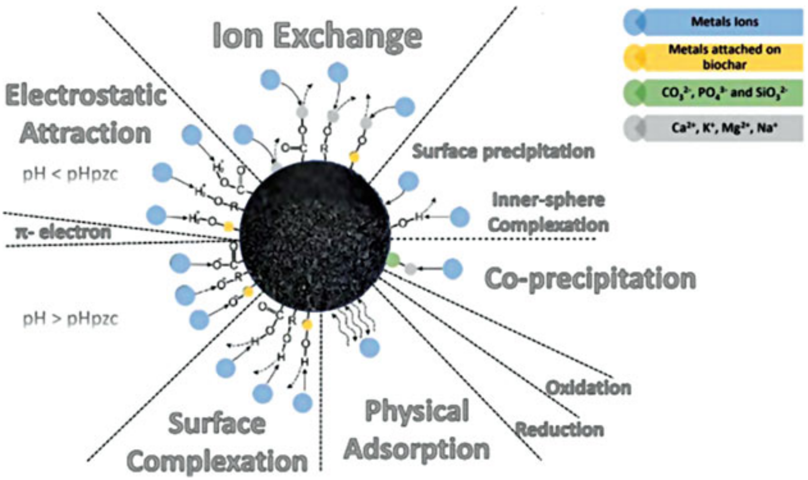

Fig. 4.2 Principles of metal removal mechanisms (Gupta et al. 2020)

strong electrostatic attraction toward the metals leading to enhanced removal. Conversely, with pH higher than pH_{zpc}, the positively charged surface due to protonation led to lower affinity toward the metal besides lower availability of sites due to competition between protons and metal, thereby leading to lower metal removal (Jin et al. 2014; Mohan and Skews 2013).

Besides abovesaid mechanisms, the modified biochars are also found to follow precipitation and reduction mechanisms to further enhance affinity toward metals. Oxygen-containing functional groups were found to follow electrostatic attraction, ion exchange, and complexation mechanisms (Ding et al. 2016). The presence of metals through modification was found to enhance metal removal through the formation of precipitates like carbonates, phosphates, and silicates with metals (Xu et al. 2013). Nanoscale modifications in the biochar-based adsorbents led to metal removal through the mechanisms of electrostatic attraction and ion exchange (Erdinç et al. 2010). Variable valence metals (e.g., Cr and Pb) were found to follow reduction mechanism primarily in metal removal besides others (Gupta et al. 2020; Li et al. 2015a, b). The principle of metal removal mechanisms is shown in Fig. 4.2.

4.1.4.2 Organic Pollutant Adsorption

Basic mechanisms involved for the adsorption of organics are π-π interaction, hydrophobic sorption, hydrogen bonding, electrostatic interaction, pore diffusion, surface complexation, and partitioning through functional groups (Tareq et al. 2019).

Surface functional groups are responsible for the surface effect on the sorption of biochars. The dissociation/association of biochar surface functional groups and the ionizable organic pollutants control the H-bond interactions. Many researchers reported a pH-dependent sorption behavior of ionizable organic pollutants (Xiao et al. 2018). For the sorption of sulfamethazine onto biochars, the sorption mechanism was proposed to be a $\pi^+-\pi$ donor-acceptor interaction at low pH and a negative charge-assisted H-bond at high pH. A quantitative study on the H-bond interactions is still needed to evaluate the contribution of H-bonding with pKa considerations from both biochar functional groups and ionizable pollutants (Xiao et al. 2018).

The polar π interaction along with the π stacking between the antibiotics and the benzene bundles on the biochar are responsible for the greater adsorption onto biochars. The slightly higher adsorption affinity of naproxen is attributed to its hydrophobicity as well as its polarizability. The more polar sites of naproxen induce greater interaction with the quadrupole moment of benzene bundles on the biochars compared to acetaminophen. Moreover, greater adsorption is eminent for naproxen since it has a naphthalene aromatic ring, whereas acetaminophen has a single benzene ring only (Tareq et al. 2019).

Electrostatic interaction between pollutant species and biochar surface is the prime mechanism responsible for the removal of aromatic cationic dyes (Qiu et al. 2009; Tareq et al. 2019; Xu et al. 2011). For example, the mechanism underlying the removal of sulfonamides and tetracyclines is probably due to the electron donor-acceptor interactions and associated with the attracting groups on surface area rings (Peiris et al. 2017); SMX adsorption onto biochars was mainly controlled by p-p interaction and effected by the solution pH value; iron- and zinc-doped biochars showed high simultaneous removal of tetracycline from aqueous solution. The predominant adsorption mechanisms include site recognition, bridge enhancement, and site competition (Zhou et al. 2017).

4.1.4.3 Inorganic Pollutant Adsorption

Sorption of inorganic pollutants by biochars is due to stoichiometric ionic exchange, electrostatic attraction, or surface precipitation (Sizmur et al. 2017):

1. Chemical sorption occurs due to ion exchange with the abundant functional groups on the carbonaceous surface of biochar, such as carboxylic, hydroxylic, or phenolic groups. These groups confer cation-exchange capacity (CEC) to biochar depending on feedstock and pyrolysis temperature, probably due to the loss of oxygenated functional groups above this temperature. Chemical sorption of cations relies on releases of protons and base cations (Na, K, Ca, or Mg) from the biochars. Since chemical sorption is stoichiometric, sorption efficiency is pH dependent and thus dictated by the pH of the medium (Sizmur et al. 2017).
2. Physical (electrostatic) sorption occurs between positively charged ions in water and the delocalized cloud of electrons associated with aromatic groups on the surface of carbonaceous biochars, creating cation-π interactions with the C=C aromatic bonds. Unlike chemical sorption, physical adsorption does not require stoichiometric release of cations or protons from the biochars (Sizmur et al. 2017).
3. Precipitation (or coprecipitation) of inorganic pollutants (particularly metal cations) with insoluble salts occurs on the surface of biochars with a high mineral ash content. For example, precipitation of Pb has been demonstrated on the surface of phosphate-rich biochars derived from manures. Biochars may also

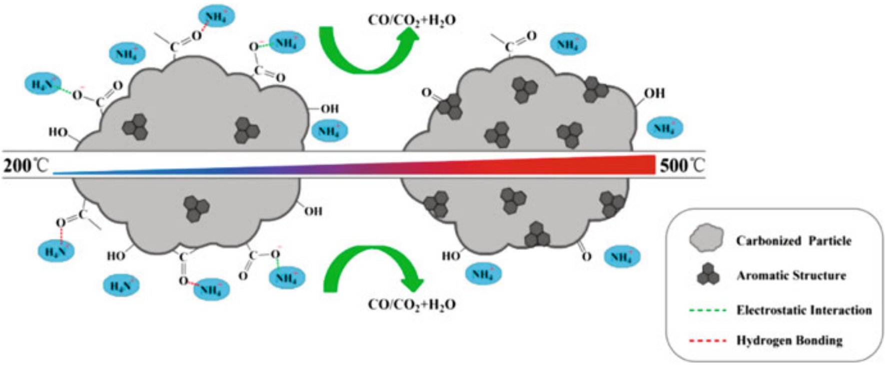

Fig. 4.3 Sorption schematic diagram between NH_4^+ and biochar (Cai et al. 2016)

raise the pH of the solution, leading to the precipitation of metal oxides, which are generally sparingly soluble (Sizmur et al. 2017).

Ammonium has a low charge-to-radius ratio similar to alkali metal ions and hence does not form a stable bond with biochar surface like divalent metal ions do. The most influential factor for the adsorption of ammonium ions is the amount of acid functional groups present on the biochar surface and not the pore structure and micromorphology. Biochars prepared from different agricultural wastes at varying temperatures were found to be capable of retaining over 90% of ammonium (Cai et al. 2016). In this case, adsorption of ammonium was governed by electrostatic interaction and hydrogen bonding with biochar surface containing carboxylic acid and ketone groups (Fig. 4.3). Ion exchange was reported as another mechanism involved in the remediation of ammonium ion by biochar derived from pig manure and straw (Tareq et al. 2019).

The nitrate removal was primarily due to outer-sphere complexation arising from the electrostatic interaction, but cationic exchange also contributed to some extent (Chintala et al. 2013). However, the majority of investigations concerning nitrate remediation from water have focused on the application of acid-activated biochars and metal oxide-biochars. The possible reason is that it is easy to create positive surface charge on biochar surfaces after modification (Tareq et al. 2019).

4.2 Application of Biochar as Catalysts

4.2.1 Biochar-Based Photocatalysts

Photocatalysis has emerged into an efficient and viable technique for purification of wastewater. Various nanoparticles such as TiO_2, RuO_2, SiO_2, ZrO_2, ZnO, CdS, and ZnS have been used as semiconductor photocatalysts (Mian and Liu 2018). Despite the excellent functionality, high photostability, and nontoxicity properties, the quick recombination of hole-electron pairs and poor visible-light response limit the photocatalytic performance of semiconductors (Cui et al. 2020; Shaban et al. 2016).

To date, considerable attempts have been made to improve the photocatalytic ability using TiO_2 modification. In the beginning, metal or metal oxides were used to dope TiO_2 to lower the bandgap energy and motivate the visible-light response. However, metal-based doping photocatalysts increase the carrier recombination rate, induce the photo-corrosion and secondary pollution, and are subject to poor thermal stability (Choi et al. 2010; Zhang et al. 2015). The high price also hinders its wide application under visible light. In 2001, Asahi (Asahi et al. 2001) first synthesized a nonmetal-semiconductor composite by doping nitrogen. Nitrogen can extend the optical absorption spectra of TiO_2 to 500 nm without reducing ultraviolet light. Subsequently, researchers began to study various nonmetal-based photocatalysts (Devi and Kavitha 2013, 2014). Doping of semiconductors (e.g., TiO_2, ZnO, ZrO_2) with nonmetals such as C, S, N, B, F, and P helped to improve the photocatalytic efficiency. Moreover, nonmetals could extend the visible region absorption close to the edge of the valence band, which is more advantageous than metal in improving the visible-light response (Cui et al. 2020; Lai et al. 2010; Mian and Liu 2018).

Among them, combining semiconductors with carbonaceous nanomaterials has been increasingly investigated due to their tunable structural, electrical properties, a wide range of visible-light absorption, and enhanced electronic conductivity (Zhang et al. 2015). Khan et al. (2002) first achieved the doping of carbon in the natural gas flame by heating the Ti metal. It significantly changed the absorption characteristics of the catalyst to visible light. Its photoelectric conversion efficiency can reach 8.35%, compared with that of pure TiO_2 (1.08%). Sakthivel et al. (Sakthivel and Kisch 2003) found that the photocatalytic effect of carbon doping was five times higher than that of nitrogen-doped samples. Chen et al. (2007) compared the photocatalytic activities of carbon- and nitrogen-doped TiO_2 samples under visible-light irradiation. They suggested the higher photocatalytic activity was due to the synergistic effect of carbon and nitrogen atoms. Wang and Lewis (2005) theoretical calculation results demonstrated the forbidden bandgap of C-TiO_2 was narrowed down to 2.35 eV. They proposed that the introduction of carbon can narrow the bandgap, thus enhancing the photocatalytic performance. However, the widespread application of carbon-based photocatalysts was most limited because of the high price and complicated fabrication methods of these materials. Thus, the development of cheap, sustainable, and efficient photocatalysts will be of great interest (Cui et al. 2020).

In comparison with most conventional activated carbon, biochar possesses a well-developed mesoporous structure and abundant surface functional groups. Furthermore, it can be served as a versatile catalyst or catalyst support (Colmenares et al. 2016). In recent years, biochar-based photocatalysts (BCPs) have received great attention in various environmental fields. Some of those recently reported BCPs were TiO_2-coconut shell, TiO_2-*Salvinia molesta*, TiO_2-reed straw, TiO_2-ramie char, TiO_2-corn cob, TiO_2-paper sludge and wheat husks, TiO_2-bamboo, ZnO-waste biomass, g-C_3N_4/$FeVO_4^-$ *Pinus roxburghii*, Bi_2O_3-corn cobs, TiO_2-walnut shells,

TiO_2-olive pits and TiO_2-wood shaving, TiO_2-wood pellets, TiO_2-plum stones, etc. (Cui et al. 2020).

4.2.2 Fe/Biochar (Fe-BC) Catalysts

Fe-based biochar composites (Fe-BC) are promising catalysts for generating reactive oxygen species (ROS) for environmental remediation considering their low costs and excellent physicochemical surface characteristics. Various methods have been used to prepare Fe-BC composites, and the synthetic methods and conditions used affect the properties of the Fe-BC material, thereby influencing its pollutant removal performance. The mechanisms of pollutant removal by Fe-BC are intricate and include adsorption, degradation, and reduction. Fe loading on BC could improve the performance of BC by affecting its surface area, surface functional groups, and electron-transfer rate (Li et al. 2021). To date, several methods have been employed to prepare Fe-BC from different feedstocks. Among them, impregnation-pyrolysis, coprecipitation, hydrothermal carbonization, and ball milling are the four most commonly used technologies among the methods reported (Li et al. 2021).

Since they are efficient, economical, and environmentally friendly catalysts, Fe-BC composites have been extensively used for removing organic pollutants, including decabromodiphenyl ether, 2,4,6-trichlorophenol, trichlorobenzene, and 4-nonylphenol from wastewater (Li et al. 2021). Fe-BC catalysts can also be applied for the reduction of inorganic pollutants, reducing their toxicity. To enhance the feasibility of Fe-BC composites, it is extremely important to clarify the mechanism of the removal process. Loading iron species would change the properties of BC, such as their specific surface area, porous structure, surface functional groups, and defect degrees. On the other hand, Fe species could offer high reduction reactivity, make them effective coprecipitation precursors, and provide high electron-transfer capability. Moreover, the mechanisms might also be correlated with the properties of the contaminants. Thus, the mechanisms of pollutant removal by Fe-BC composites are usually complicated.

4.2.2.1 Adsorption

Due to its large specific surface area, Fe-BC could remove contaminants by adsorption. The adsorption mechanisms involved different interactions, including electrostatic interactions, hydrophobic effects, π-π interactions, hydrogen bonds, and pore filling (Wu et al. 2017). It was found that the removal efficiency of pollutants by the Ag/Fe/MB system was higher than those of other systems (OB, Ag/Fe, Ag/Fe/OB, and MB) (Wu et al. 2017). This phenomenon has been explained by the fact that the adsorption capacity of MB enhanced the contact between the pollutants and Ag/Fe nanoparticles, and the simultaneous reduction released surface sites previously occupied by pollutants to promote further adsorption. Ahmed et al. produced nZVI-BC composites and used them to remove chloramphenicol. The results verified that chloramphenicol was simultaneously reduced and adsorbed by nZVI-BC and that sorption was the predominant mechanism (Ahmed et al. 2017). The removal of BPA by BC was investigated and found that no depletion of BPA was observed (Diao et al. 2020; Li et al. 2021).

4.2.2.2 Reduction

Reduction is another mechanism of pollutant removal by Fe-BC. Owing to the presence of Fe^0, Fe(II), and S(II), Fe-BC has redox properties. S-nZVI/BC composites were used for tetrabromobisphenol A (TBBPA) removal. A portion of the TBBPA was removed through reduction debromination by S-Fe^0, and bisphenol A and monobromobisphenol A, which were the reduction products of TBBPA, were detected. The reduction was significantly enhanced by the loading Fe and S. 2,4-Dinitrotoluene (DNT) and 2,4-dichlorophenol (DCP) were removed from water by Fe^0-containing BC, which could reduce the pollutants. The presence of BC promoted the reductive transformations of DNT and DCP in the Fe^0-included BC system. The reduction of nitrobenzene (NB) was carried out by modified BC-supported sulfidated nano-zerovalent iron (S-nZVI@HCl-BC), and the results showed that S-nZVI@HCl-BC had excellent performance in reducing NB to aniline (AN), a less toxic reduction product (Zhang et al. 2019a). In addition, surface functional groups such as C–O, C–O–C, and O–C–O bonds were important redox-active moieties for pollutants reduction. Fe-BC has been proven to reduce Cr (VI) and TCE due to its abundant carboxyl groups and aliphatic carbon (Liu et al. 2019; Zhang et al. 2020c).

Moreover, PFRs in biochar were another redox-active moiety to stimulate the reduction of pollutants through electron donation. Researchers found that Fe species promoted the electron transfer to pollutants via the formation of PFRs. PFRs reduced Fe(III) into Fe(II) and consequently facilitated the reduction of pollutants (Li et al. 2021; Wang et al. 2020c; Zhang and Lu 2018).

Fe-BC catalysts have been widely applied in redox systems. The removal efficiencies of the contaminants were significantly higher with BC-coated Fe(0). BC-coated Fe(0) acted as an electron-transfer mediator in the reductive transformation, and the surface functional groups of BC could enhance the catalytic electron transfer. It was found that the removal efficiency of Cr(VI) by the ZVI/PC system was more than four times greater than that of Cr(IV) by the pristine PC and ZVI systems, and ZVI was an important reductive active site for Cr(IV) removal (Zhao et al. 2020). Ni/Fe nanoparticles supported by BC were successfully synthesized, and the removal efficiency of 1,1,1-trichloroethane (1,1,1-TCA) was 99.3% under the optimal conditions. The main mechanism of 1,1,1-TCA degradation is the reduction of hydrogen atoms produced by ZVI corrosion. Therefore, Fe-BC composites can be used as efficient and cost-effective catalysts for the removal of redox-sensitive pollutants (Li et al. 2017b, 2021).

4.2.2.3 Degradation

ROS (e.g., ·OH, $O^{2-}\cdot$, $SO^{4-}\cdot$, $^1O_2$) could be generated in Fe-BC catalysis processes, which, along with electron transfer, are responsible for the degradation of organic pollutants. Fe species (ZVI, iron oxides, and iron sulfides) can not only activate PDS, PMS, H_2O_2, and O_2 to produce ROS but could also be used as electron donors to

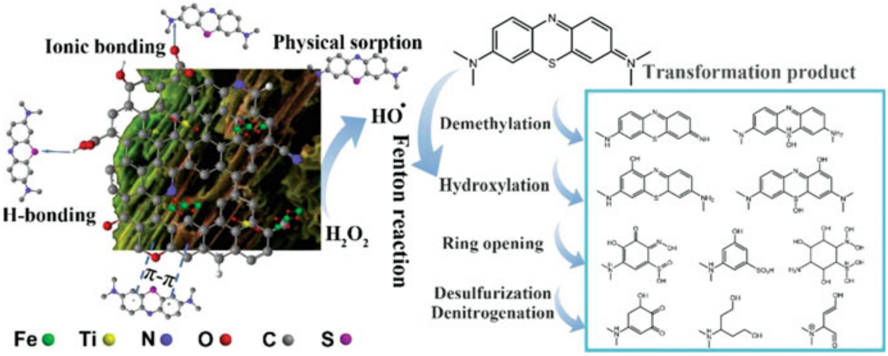

Fig. 4.4 Schematic diagram of possible mechanism of Fenton process of Fe_2O_3/TiO_2-BC (Chen et al. 2020)

degrade pollutants. Fe-BC materials activate oxidants in the following ways: (1) through the OFGs and PFRs on the surface of Fe-BC, (2) through defects in the Fe-BC, and (3) as an electron-transfer mediator between oxidants and targeted pollutants. The degradation mechanisms of pollutants by Fe-BC mainly involved Fenton-like and photocatalytic process (Li et al. 2020a; Tao et al. 2019).

Numerous researchers found that Fe-BC can be used as catalyst for H_2O_2 activation. For example, Yi et al. (Yi et al. 2020) developed an approach to produce magnetic BC composites (SMBC300, SMBC400, and SMBC500) at various temperatures (300 °C, 400 °C, and 500 °C), which were used to activate H_2O_2. SMBC400 had good H_2O_2 activation and metronidazole (MNZ) degradation properties. The results of EPR and free radical quenching showed that all three materials could activate H_2O_2 to produce ·OH and $O_2^{-}\cdot$ and that surface-bound ·OH played a pivotal role in MNZ degradation. Zhang et al. (2020a) synthesized Fe-impregnated BC (FBC) by impregnation-pyrolysis. FBC was used to activate H_2O_2 for SMX degradation, and the mechanism suggested that C–OH would activate H_2O_2 to generate ·OH, which cooperated with nonradical sites to attack SMX. Rubeena et al. prepared iron-loaded rice husk BC (Fe-RHB) and coir pith BC (Fe-CPB) to activate H_2O_2 for acid red 1 (AR1) removal (Rubeena et al. 2018). It was found that FeOOH, Fe_2O_3, and Fe_3O_4 were formed on the surface of BC. The removal efficiencies of AR1 and TOC were 97.6% and 84.2% in the Fe-RHB/H_2O_2 system and 99.1% and 86.7% in the Fe-CPB/H_2O_2 system, respectively. Both Fe-BC composites also displayed favorable stability and reusability with very little iron leaching. Zhang et al. prepared magnetite BC (SMBC) to activate H_2O_2 for aniline degradation (Zhang et al. 2019b). They verified that ·OH and $O_2^{-}\cdot$ both contributed to aniline degradation, indicating that BC in SBMC could mediate ROS generation by Fe_3O_4. Moreover, a conventional one-step pyrolysis method to prepare functionalized biochar (Fe_2O_3/TiO_2-BC) was investigated, and results indicate that it provides great potential for removing dye pollutants from water in a Fenton-like system (Chen et al. 2020). Figure 4.4 describes the possible mechanism of Fenton process of Fe_2O_3/TiO_2-BC. Fe_2O_3/TiO_2-BC exhibits outstanding performance for

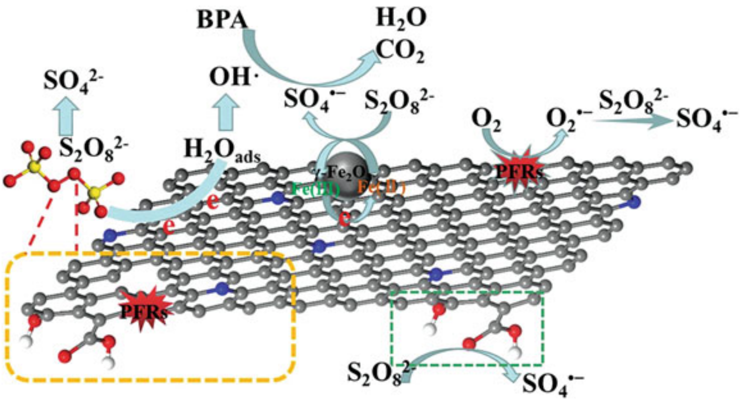

Fig. 4.5 Possible mechanism of persulfate activation by γ-Fe_2O_3@BC for BPA degradation (Rong et al. 2019)

the degradation of dye pollutants, and the TOC removal efficiencies reached above 65%. The combination of Fe_2O_3/TiO_2 and BC could accelerate the activation of H_2O_2 to generate ·OH. The mechanisms of dye pollutant removal were sorption and catalytic processes; adsorption is attributed to the material's abundant channels and pores, and the catalytic process is due to the presence of π-π interactions, ionic bonding, and H-bonding between the pollutants and Fe_2O_3/TiO_2-BC (Li et al. 2021).

Compared to ·OH, $SO_4^{-}\cdot$ possesses higher oxidative potential, a wider operative pH range, and a longer lifetime, and it was applied for the oxidation of organic contaminants. An increasing number of researchers have focused on the activation of PDS or PMS via Fe-BC composites. Rong et al. applied magnetic B (γ-Fe_2O_3@BC) derived from banana peel to active PDS (Rong et al. 2019). Figure 4.5 explains the possible mechanism of persulfate activation by γ-Fe_2O_3@BC for BPA degradation. There are more active sites, including OFGs, on iron oxides and doped nitrogen in γ-Fe_2O_3@BC, which contributed to bisphenol A (BPA) degradation. In addition, they found that the signal intensity of the DMPO spin-trapping ESR spectra in the γ-Fe_2O_3@BC system was stronger than those in the PS, γ-Fe_2O_3@BC, and BC/PDS systems. Noticeably, within 20 min, BPA (20 mg/L) was completely removed, and the mineralization efficiency was approximately 90% in the γ-Fe_2O_3@BC/PS system without pH adjustment. The Fe@HC-800 catalyst also exhibited stable performance after three cycles of regeneration.

Radical scavengers were used to determine which reactive species were responsible for contaminant degradation. Li et al. reported the degradation of TCE by the nZVI-BC/PMS system. The degradation efficiency of TCE (0.1 mM) was 100% in 20 min (5 mM PMS, Fe-CB600 1 g/L, bicarbonate buffer solution at pH 8.2) under groundwater conditions (Li et al. 2020b). They proved that ·OH, $SO_4^{-}\cdot$, $O_2^{-}\cdot$, and $^1O_2$ were responsible for TCE degradation. $O_2^{-}\cdot$ and $^1O_2$ mediated by Fe0 and OFGs played major roles in TEC degradation. Wang et al. studied the removal of phenolic contaminants via PMS activation with magnetic Fe,N-codoped carbon catalysts

(UBC-x), and the results showed that the UBC-x/PMS system could almost completely remove phenolic contaminants under a wide pH range (2–11) (Wang et al. 2020b). $^1O_2$ was the dominant ROS for the degradation of phenolic contaminants, and the catalytic activity of UBC-x could be enhanced by loading Fe and N active sites. Jiang et al. quantified the contributions of $SO_4^{2-}\cdot$, the nonradical pathway, and absorption for BPA degradation in the Fe-BC/PMS process (Jiang et al. 2019). Under the optimal conditions, degradation reached 53%, and of that, $SO_4^{2-}\cdot$ degradation accounted for 23%, the nonradical pathway accounted for 30%, and the other 47% was attributed to adsorption.

4.3 Conclusion and Future Outlook

As a green, environmentally friendly, cheap, and easy-to-obtain new functional material, biochar has unique structural advantages such as large specific surface area, dense pore structure, wide sources, environmental friendliness, rich oxygen-containing functional groups, and good adsorption characteristics and is used for sewage treatment. Future research on the application of biochar in wastewater treatment should focus on the following issues.

1. The current research on biochar in related fields is mainly concentrated in the laboratory test stage, which lacks a systematic theoretical basis. In the actual operation and application process, there are harsh production conditions, the production process is not easy to realize, and the cost is high, and the production process is difficult to promote on a large scale, thereby restricting the large-scale preparation and use of biochar. Therefore, it is necessary to carry out further experiments to promote its practical application and pay attention to its long-term stability in the environment.
2. Strengthen research on the potential hazards of biochar materials; while paying attention to and studying the advantages of biochar/modified biochar, it is necessary to pay attention to its negative effects. Both biochar and its modified products are derived from biomass residues (including primary agricultural and forestry production residues, agricultural and forestry secondary residues, bio-utilization and transformation wastes, etc.). In the process of biomass processing, substances harmful to the environment (organic, inorganic, and heavy metals) may be released. At the same time, biological carbon and its modified products are a kind of nanoparticles, and their release may also cause potential harm to the environment and ecology. In addition, biochar and its modified materials still have the risk of secondary pollution after the pollutants are treated. The recycling of waste should avoid the diffusion and release of pollutants. Therefore, the harmlessness of biochar materials should be strengthened in subsequent research. Especially during chemical treatment of biochar, its environmental hazard monitoring, and analysis etc.
3. Activated carbon has become an indispensable and important means in water treatment technology. The treatment technology has changed from single

activated carbon adsorption to the combined application of multiple treatment methods such as adsorption reduction, catalytic oxidation, electrolysis, and biodegradation. According to the water quality of the treated water source, selecting appropriate activated carbon or modified activated carbon combined with other water treatment technologies can often achieve better treatment effects than the combined effects of various single methods. However, the current various activated carbon treatment technologies are not very complete. Although some have improved the removal rate of pollutants, the process is complicated, and the economic benefits are poor, making it difficult to promote and apply. Therefore, in the future, the research direction of activated carbon should be comprehensively considered from reducing costs, improving efficiency, and simplifying operations to achieve the unity of environmental and economic benefits.

4. The research on biochar has not formed a complete system and standard, and the adsorption and fixation capacity of biochar is affected by many factors. Therefore, it is difficult for many studies to conduct systematic comparative analysis, so in the future, we need to pay attention to the formulation of biochar-related standards.

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Synergistic Approaches (Use of Biochar and Microbes) in the Bioremediation of Industrial Effluents

5

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Abstract

The generation of effluents in industrial processes is a constant problem that accompanies economic development and population growth. Most of these effluents have in their composition high concentrations of organic compounds and heavy metals, among other substances that are harmful to the environment. The treatment and final disposal of these wastes become a problem for many industries due to these processes' complexity and costs. Seeking to solve this problem effectively and economically, different techniques have been developed. The synergistic approach involving microbial action and biochar is one of these techniques and stands out for being potentially efficient, of low cost, and environmentally friendly. The metabolic diversity of microorganisms, combined with the biochar's adsorption capacity, ensures effectiveness in different effluent bioremediation types. Thus, this chapter will address information on microorganisms used in conjunction with the biochar in the bioremediation of effluents generated in industrial processes.

Keywords

Biochar · Microorganisms · Effluent · Bioremediation · Industry

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5.1 Introduction

Intense economic development in recent centuries has caused many environmental problems. The generation of effluents from the most diverse industrial processes stands out due to the significant deterioration that has been caused to water resources. According to the United Nations reports World Water Development, it is estimated that approximately 80% of industrial and domestic effluents generated in several countries are released into the untreated environment (Water UN 2018). Therefore, research that seeks efficient and cheap technologies to treat industrial and urban wastewater is necessary.

Bioremediation is a promising treatment method in which microorganisms are used to reduce contaminants. This process has been intensively researched and recommended by the scientific community as an ecologically suitable, sufficient, and inexpensive alternative for treating organic and inorganic pollutants present in soil and water (Huang et al. 2019).

However, the application of microorganisms in bioremediation is often limited by substrate inhibition and concentration of constituents (Zhuang et al. 2015; Lou et al. 2019). When exposed to highly heterogeneous environments with large loads of contaminants, microorganisms perform poorly since these compounds inhibit their activity (Biswas et al. 2015; Enaime et al. 2020). Thus, different approaches are being tested, seeking to stabilize these processes, such as biochar's combined use with microorganisms.

Biochar has been standing out as an adsorbent and immobilizer due to its characteristics such as porosity, stability, and bioavailability, which help metabolism and microbial growth. Another way to apply biochar in bioremediation processes is to add it to reactors as a buffer since alkaline/neutral characteristics prevent the acidification of the medium (Enaime et al. 2020; Pokharel et al. 2020).

However, the possible adverse effects of using biochar-microorganisms must be taken into account. The biochar's strong affinity for contaminants can decrease its bioavailability for microorganisms. Also, few studies in the literature portray how the biochar's complex characteristics impact the biodegradation of pollutants. Therefore, there is much to be investigated about its use in wastewater treatment (Zhao et al. 2020).

Considering the search for efficient and economical treatment processes, this chapter will present information on the main methods used in applying biochar-microorganisms. Studies reported in the literature on effluents in which these techniques have already been applied will be discussed, gathering relevant information to apply these approaches in the new research.

5.2 Mechanisms of Biochar-Microorganism Interaction During Contaminants Degradation

The application of biochar in a synergistic way with microorganisms in the treatment of effluents can occur through mechanisms of adsorption, buffering, and immobilization of microbial cells. The application of these mechanisms can increase the efficiency of treatments and provide, in some instances, the recovery of value-added by-products present in the effluent (Pokharel et al. 2020). The following sections will discuss how to apply these mechanisms and how processes are affected by this approach.

5.2.1 Immobilization of Microbial Cells

Immobilization consists of the physical retention of cells in a defined region, in which biological activities are maintained, allowing for a higher rate of cell multiplication (Karel et al. 1985). The higher concentration of microbial cells in the support allows an increase in the efficiency of removing pollutants. Also, it facilitates the reuse of inoculated supports and provides more resistance to microorganisms in the face of toxic components present in the effluent (Mollaei et al. 2010; Lou et al. 2019).

The support used in cell immobilization must have unique characteristics to be considered adequate. Among these characteristics are low toxicity to cells, chemical stability, and high mechanical resistance, in addition to good mass transfer performance (Chen et al. 2012).

Biochar has stood out as efficient support due to its good physical and chemical properties and its cost-benefit, since it can be produced from several sources, such as agro-industrial waste (Lou et al. 2019). Table 5.1 gathers some studies in which this technique was applied to remediate pollutants, showing its removal efficiency.

One of the techniques used to immobilize cells in the biochar is through absorption. In the studies by Lou et al. (2019) and Zhang et al. (2020), a cell suspension was added over the biochar, and then the mixture of cell suspension and biochar was stirred on a rotary shaker until the cells were adsorbed on the surface and pores of the biochar, thus forming an immobilized biofilm. The time in which the mixture remained stirred in the two studies was 24 h, with a temperature of 30 °C. Lou et al. (2019) applied a 150 rpm agitation in his experiment and Zhang et al. (2020) 160 rpm.

5.2.2 Adsorption of Inhibitors

The adsorption capacity of the biochar enables a higher rate of microbial growth in bioremediation processes. The transformation of pollutants from the soluble state to the state adsorbed on the biochar's surface can decrease its toxic inhibition to microorganisms (Wang et al. 2020a, b, c).

Table 5.1 Performance of microorganisms immobilized in different biochars used in the bioremediation of pollutants from industrial effluents

Biochar feedstock	Microorganism	Industrial effluent	Contaminant	Removal efficiency	References
Bamboo (I-BC)	*Pseudomonas* *Achromobacter* *Ochrobactrum* *Stenotrophomonas*	Oil and textile industry	Nonylphenol (NP)	93.95%	Lou et al. (2019)
Bamboo	*Streptomyces* sp. *N01*	Chemical industry	Quinoline	85.3%	Zhuang et al. (2015)
Bamboo	*Pseudomonas mendocina GL6*	Food industry	Nitrate	99.6%	Zhang et al. (2020)
Softwood bark charcoal	Microbial community isolate from OSPW	OSPW	Naphthenic acids	87%	Frankel et al. (2016)
Rice straw (RSB) Chicken manure (CMB) Sewage sludge (SSB)	*Bacillus cereus RC-1*	Mining, refining, plastic manufacturing	Cadmium	43.62% (RSB) 56.28% (CMB) 57.22% (SSB)	Huang et al. (2020)
Crude biomass gasification	*Rhodococcus opacus*	Gasification wastewater	MAHs and PAHs	96.2%	Goswami et al. (2020)

OSPW process water generated by oil sands mining operations

Lou et al. (2015) investigated how the application of biochar affects the adsorption-biodegradation of nonylphenol. The biochar used in this study is derived from rice straw and was applied as an adsorbent. The results showed that approximately 47.6% of the nonylphenol was biodegraded in 2 days, representing a 125% increase in degradation compared to the experiment in which the biochar was not added.

In the study by Zhao et al. (2020), the biochar produced pyrolytically from peanut shells was applied together with the bacterium *Pseudomonas citronellolis* in the biodegradation of wastewater that has high concentrations of phenol. According to the authors, phenol's initial adsorption by biochar alleviated the toxicity of phenol to the bacterium. Then, the slow release of phenol in the aqueous medium controlled its bioavailability. This mechanism resulted in a high efficiency of removing the compound, which increased from less than 46% when the biochar was not added to up to 99% in the highest concentrations evaluated.

However, this mechanism can promote adverse effects, as shown in the study Xin et al. (2014), where there was a reduction of approximately 90% in the efficiency of removing ether when adding the biochar in the process. The authors raised the hypothesis that the slow desorption of this substance by biochar may be one of the factors responsible for decreasing the rate of degradation.

Xu et al. (2020) evaluated the influence of biochar adsorption on pentachlorophenol's degradation (PCP) in an anaerobic environment. The biochar inhibited PCP biodegradation due to a strong sorption affinity with PCP, reducing the compound's bioavailability for microbes.

These studies show that biochar can cause positive and negative effects on its adsorption mechanism applied to the degradation of pollutants, requiring further investigation to be done regarding the relationship between the adsorbed pollutants and microbes.

5.2.3 Increasing Buffering Capacity

The biochar can be alkaline depending on the biomass source. The alkaline characteristic is mainly related to inorganic minerals and ash formed during pyrolysis and carbonization, present in its composition (Yuan et al. 2011). Due to this characteristic, the biochar is added to biological waste and effluent treatment processes to promote a buffering effect, avoiding acidification of the medium. Also, the cost of using biochar as a buffer in these processes is more economical when compared to other buffering agents used, such as CaCO3 and NaHCO3 (Wang et al. 2020a, b, c).

The use of biochar to increase buffering capacity is not well known; however, some studies such as that of Luo et al. (2015) show that the application of biochar in anaerobic digestion reactors causes a reduction in the acidification of the medium, providing an increase in the production of bioproducts such as methane (86.6%).

Shen et al. (2015) report that the addition of biochar increased the medium's alkalinity and attenuated the inhibition of ammonia, providing stability in the anaerobic digestion process of wastewater sludge.

5.3 Biochar and Microorganisms in the Treatment of Industrial Effluents

Industries such as textiles, leather tanning, and thermoelectric and oil refineries, of extreme importance for the economic sector, are sources of effluents with high loads of paints, heavy metals, and other chemical substances, such as hydrocarbons, which cause significant damage to the environment if the effluent is not treated correctly.

Alternatives that aim to reduce chemical substances in the treatment of these effluents are very desirable. Among them is the use of biochar and microorganisms. Biochar, best known for its application in soil correction, has shown, through studies, several other forms of use, mainly in the environmental area, such as in the treatment of effluents, due to the improvement of its properties over the years (Sanroman et al. 2017; Wang et al. 2020a, b, c).

Because it is a product resulting from vegetable biomass residues, such as corn cobs, coconut husks, and characteristic properties that define it, it may vary depending on the biomass used, being neutral/alkaline pH, aromatic carbon chains, porosity, cation exchange capacity, and its high nutritional value (Karim et al. 2019), in addition to the low cost concerning the use of chemical substances in the treatment of effluents.

In addition to biochar, as previously mentioned, many studies have used microorganisms to treat effluents since, when discarded without treatment, they can cause damage to health and the environment (Bhattacharjee et al. 2020).

This topic addresses the application of biochar and microorganisms in treating industrial effluents, such as those of the textile, tannery, thermoelectric, and oil refineries industries, which are described below.

5.3.1 Textile Industry Effluents

The textile industries are considered enterprises that are highly impactful for the environment due to their transformation processes using large amounts of water, reaching 200 L/kg of fabric (Ghaly et al. 2014). These processes range from degumming with enzymes to bleaching and neutralizing the fabric for dyeing it (Ntuli et al. 2009). At the end of these processes, the water used has many chemicals such as dyes, phenols, and other highly toxic substances to the environment (Ghaly et al. 2014; Bhattacharjee et al. 2020).

According to Ghaly et al. (2014), some dyes have organic substances that are difficult to break down, requiring microorganisms that are following the composition of the effluent, which can be isolated from areas contaminated by these pollutants found in the effluents (Bhattacharjee et al. 2020).

Bharti et al. (2019) used the biosorption technique, using biochar as a packaging medium for immobilizing bacteria, in the biodegradation of methylene blue dye, widely used in textile industries. In this study, the authors isolated *Alcaligenes faecalis* from a river near a textile industry in India and used it in consortium with the biochar from the seed from *Casuarina equisetifolia*.

The use of biochar as a means of packaging for the immobilization of *Alcaligenes faecalis* in a packed bed bioreactor resulted in a removal of 81.5% and 89.1% for free and immobilized cells of *Alcaligenes faecalis*, respectively (Bharti et al. 2019).

Talha et al. (2018) applied biochar from coconut shell and the bacterium *Brevibacillus parabrevis*, isolated from a river near a textile industry in India, in the bioremediation of Congo red dye using a packaged bed bioreactor. In that study, the authors used the biochar to immobilize *Brevibacillus parabrevis*. When carrying out the research, they obtained a 65.95% dye removal at 100 mg/L for free cells and 63.23% at 300 mg/L for the cells immobilized with biochar, in batch tests ranging from 50 to 500 mg/L (Talha et al. 2018).

When performing the continuous test, increasing the concentration and varying from 100 to 500 ppm, *B. parabrevis* cells immobilized with biochar were also more effective, reaching a degradation of 88.92% of the dye. In contrast, free cells degraded only 77.82% (Talha et al. 2018).

Other studies that used a continuous process packed bed bioreactor to remove dyes also demonstrated effectiveness in this procedure, such as the study by Giri et al. (2020), which also used *Brevibacillus parabrevis*, isolated from effluent, and biochar from ears of corn for the removal of bright green dye from effluent. As a result, Giri et al. (2020) removed approximately 90% of the dye for concentrations of 50, 100, 400, and 500 mg/L in 5 days.

Raj et al. (2021), on the other hand, carried out a study using a strain of the bacterium *Escherichia fergusonii* and activated carbon from rice husk, with the bacterium being evaluated for color removal (reaching 98%) and reduction of total dissolved solids (reaching 75%) (Raj et al. 2021). When using activated carbon, after treating the effluent with *E. fergusonii*, there was a reduction in chemical and biochemical oxygen demand (reaching 92.5% and 85%, respectively) (Raj et al. 2021).

As can be seen in the studies mentioned above, the use of biochar and microorganisms in the treatment of effluents and dyes used in textile industries showed the efficiency of these processes, resulting in removals of approximately 92%. This is since biochar and microorganisms have the sorption mechanism. Hence, the combination of both enhances this mechanism since adsorption is an effective method for removing these contaminants and is environmentally friendly and of low cost (Giri et al. 2017; Weng et al. 2009).

5.3.2 Petroleum Refinery Wastewater

Oil refineries are major environmental polluters and generate high volumes of wastewater in their production process. These effluents are composed of complex elements such as hydrocarbons and naphthenic acid, which often have high toxicity and low biodegradability (Wang et al. 2020a, b, c).

Some technologies currently used in treating wastewater from oil refineries consist of biological treatments such as activated sludge and aerobic granular sludge (Wang et al. 2016). The use of biochar to stabilize these biological processes is a promising technique. Wang et al. (2020a, b, c) added biochar produced from waste oil-activated sludge in the refinery wastewater treatment process. According to the authors, the addition of biochar increased the removal efficiency of organic compounds (3%), oil (4%), and total nitrogen (10%). Wang et al. (2020a, b, c) explain that the porous structure and the high degree of hydrophilicity of the biochar facilitated colonization and microbial adhesion, providing the formation of more substantial and stable aerobic granules.

Ming et al. (2020) investigated the effect of adding different biochars on the aerobic granulation process of refinery effluent. The biochar was produced from rice bran (biochar-rb), rice husk (biochar-rh), and nutshell (biochar-ws). According to the authors, the addition of biochar reduced aerobic granulation time in 15 days compared to the control. It increased the efficiency of removing chemical oxygen demand (COD) by 3.2–5.1% and nitrogen total (10–13%).

This study also shows how the physicochemical properties of different biochars influence aerobic systems of granular sludge. According to the authors, the reactor containing biochar-rb was the most stable and removed most of the nutrients, and the reactor containing biochar-rb had the largest granule size (Ming et al. 2020).

The results of these studies indicate that the use of biochar in aerobic granulation processes in the treatment of wastewater from an oil refinery is an efficient and viable option; however, research in this area is still scarce, so further research is needed.

5.3.3 Tannery Wastewater

The tannery industry has a vast movement of products and goods worldwide, producing tons of leather per year (Saxena et al. 2020). To obtain the final product, leather undergoes treatment. It receives approximately 170 types of chemicals, such as acids, chromium salt, solvents, and dyes, thus generating many effluents with high concentrations of toxic compounds (Hansen et al. 2020; Cassano et al. 2001).

The pretreatment of the tannery effluent consists of two processes. The first treatment is done with oxidation, separation of solids, and precipitation of chromium (Di Iaconi 2012), and the second treatment is given by activated sludge systems, generating a large amount of sludge that will need to undergo a new treatment (Dotro et al. 2011; Cassano et al. 2001). Microalgae in the bioremediation of this activated sludge is a promising technique that is gaining more and more attention because it can reduce concentrations of inorganic nutrients (nitrogen and phosphorus) and reduce the concentrations of dissolved heavy metals. However, tannery effluents can inhibit the growth of microorganisms due to the presence of toxic compounds, especially chromium (Sforza et al. 2020).

Seeking improvements in this process, Sforza et al. (2020) evaluated the combination of the application of biochar and the cultivation of microalgae to treat tannery effluents. The authors tested two different biochar types: pine biochar (PB) and commercial one (CB). The biochar was applied as a pretreatment step before the cultivation of *Chlorella protothecoides*, resulting in a significant increase in the growth rates of microalgae (61% and 126% for PB and CB, respectively).

Chromium is a significant pollutant in wastewater from the leather processing industry. Mahmood et al. (2015) combined the use of biochar produced from corn cobs' pyrolysis with a strain of *Pseudomonas putida* KI in a bioreactor to treat simulated tannery wastewater, containing azo dye Black-5 and hexavalent chromium (CrVI). The results of this study showed that Reactive Black-5 completely biodegraded in 5 h. The KI strain also reduced the CrVI concentration from 100 to 10 mg/L in 24 h.

Another toxic component present in tannery wastewater is dye. Ortiz-Monsalve et al. (2020) investigated in their study the combined treatment of adsorption in woodchip biochar and biodegradation under solid-state fermentation by *Trametes villosa* in the removal of the acid blue leather 161 dye from wastewater.

The authors tested biochar as an adsorbent and as a basis for immobilization and growth of *Trametes villosa*. After 15 days, this fungus showed a growth rate of 86.8 ± 0.8%, in addition to biodegrading 91.4 ± 1.3% of the adsorbed dye.

These studies clearly illustrate the feasibility of using microbiological strains combined with biochar for the biological treatment of tannery wastewater as a support matrix for microbial cells.

5.3.4 Effluents from Thermal Power Plants

The increase in the world population and the need for mass production of energy have led to a search for alternative sources due to the scarcity of fossil fuels. The generation through thermal plants appears with great potential for large-scale production and means to reuse some organic waste. In addition to organic energy production, nuclear plants have a high potential for energy production through uranium, showing efficiency for generating large amounts of energy through nuclear reactions. In contrast, the waste generated by this activity causes severe environmental problems due to its radioactivity and toxicity (Ying et al. 2020).

Uranium is one of the main toxic components found in this industry's wastewater. Several methods are studied to remove uranium ions, such as surface precipitation, sorption, solidification, ion exchange, photocatalysis, filtration, and membrane filtration (Li et al. 2018).

Studies like the one by Ding et al. (2018) show that microorganisms are also gaining space in the uranium remediation in aerobic media when combined with biochar to synthesize compounds to increase the stability of the adsorption process. After evaluating eight species, the strains of *Leifsonia* sp. showed the best removal with 68%. When pH adjustment ranges from 2.5 to 7.5, the adsorption in aqueous phase with pH 3.5 was carried out, and it was possible to obtain 99.59% U (VI) adsorption.

Biosorption using macroalgae is a promising technology for the bioremediation of industrial effluents, as shown by the study by Kidgell et al. (2014), where the efficiency in removing pollutants from industrial effluent from a coal-fired power station was investigated, using macroalgae biomass in the production of biochar. The biosorbents were produced from the macroalgae *Oedogonium* sp. (Chlorophyta) and showed excellent removal of metals such as Al, Cd, Ni, and Zn, at pH-dependent rates.

Studies regarding the remediation of residues from thermal plants such as uranium are still scarce. Still, they are economically and environmentally viable in using biochar combined with microorganisms, mainly in adsorption processes.

5.4 Biochar-Microorganisms in the Treatment of Industrial Effluents and Energy Recovery

The wastewater generated in industrial processes is composed of several biopolymers, such as starch, lignocellulose, glucose, protein, lactose, lipids, fats, and minerals, which can be converted into sustainable biofuels and biocomposite through their bioremediation followed by fermentation and anaerobic digestion (Bhatia et al. 2020).

Anaerobic digestion is a technique that has stood out because it provides the treatment of this material while it generates products with high-added value, such as biomethane. However, this process is impaired due to the heterogeneous environmental conditions that microorganisms face when coming into contact with these effluents. The use of biochar as a stabilizer of these processes has been investigated. Torri and Fabbri (2014) applied biochar produced from corn stalk in the anaerobic digestion of the effluent generated in the biochar pyrolysis process (aqueous pyrolysis liquid, APL). The addition of biochar increased the methane yield by 65 ± 5% compared to the process where pure APL was used (34 ± 6%) and improved the reaction rate.

Shen et al. (2015) obtained a 27.6% increase in the maximum rate of methane production by adding biochar wastewater sludge produced by corn straw to the anaerobic digestion process. The addition of biochar also increased the medium's alkalinity and attenuated the inhibition of ammonia, providing stability in the process.

Huggins et al. (2016) used the biochar-microorganism combination in a different approach. The authors evaluated the biochar derived from residual wood as an electrode in a microbial fuel cell (MFC). MFCs are bioreactors that convert chemical energy stored in biodegradable materials into electrical current through microorganisms' metabolic activity (Logan et al. 2006).

Huggins et al. (2016) applied biochar electrodes to wastewater containing large amounts of nutrients such as ammonia and phosphorus. The reductions in these nutrients were 73% and 88%, respectively. The authors observed a stable energy peak with a power density of 6 W/m^3, showing the potential use of biochar as an electrode in MFCs to treat wastewater and simultaneous energy production.

Other bioproducts can be generated from the anaerobic digestion of effluents. The influence of biochar on the production of volatile fatty acids (AGVs) from anaerobic digestion of the tannery sludge supernatant was investigated by Zhai et al. (2020). The biochar produced from the sludge decreased the concentration of ammoniacal nitrogen, which caused a reduction in the inhibition of bacteria during anaerobic digestion. The experimental results showed that the AGV yields improved in the biochar presence, with a maximum yield of 1037.5 mg/g. According to the authors, the recovered volatile fatty acids can be reused in water treatments.

The potential of the biochar-microorganism mechanism in the treatment and energy recovery of industrial wastewater is high but still little explored. This mechanism can be applied to obtain different bioproducts using different raw materials, making these processes cheaper and more sustainable.

5.5 Challenges and Perspectives in the Use of Biochar Associated with Microorganisms in the Treatment of Industrial Effluents

One of the differential characteristics of biochar is that it is a promising material derived from waste, which makes it a unique renewable resource, with the potential for several environmental issues currently addressed, among them remediation of pollutants in soil, water, and gaseous medium (Oliveira et al. 2017).

However, studies investigating the contribution of biochar to the bioremediation of wastewater generated in industrial processes are still scarce. The influence of different sources of raw material used in the production of biochar and physical-chemical factors that affect the efficiency of removing contaminants are still in the initial evaluation phase (Ambaye et al. 2020). Also, there is little knowledge about what is degraded by bacteria and what is adsorbed by biochar (Wang et al. 2020a, b, c).

Investigations involving adsorption with biochar mostly focus on individual pollutants or single groups of environmental contaminants. Studies that include expanding knowledge about biochar's adsorption capacity with multi-pollutants (heavy metals present in effluents) still need to be more widespread and applied (Lyu et al. 2016).

The recovery and regeneration of biochar after pollutant adsorption is also an area that needs more attention. Few studies are related to this critical topic since adsorbed toxic and harmful substances can be effectively converted or solidified into potential sources of pollution that not be released (Dai et al. 2019). According to Li et al. (2019), the disposal of biomass polluted by toxic components such as heavy metals obtained in bioremediation processes is a significant challenge.

Also, the application of biochar in bioremediation was limited to the laboratory scale. Studies that aim to use it on a large scale should be carried out and analyzed in technical and economic aspects (Lyu et al. 2016). However, Dai et al. (2019) highlight that the cost of production of biochar is still the main limiting factor for its application in the field and the selection of cheap raw materials for its production and reuse methods.

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Role of Biochar in the Removal of Organic and Inorganic Contaminants from Wastewater

6

A. M. Joe Cyril Harrish and Hitesh S. Pawar

Abstract

Biochar is a carbonaceous (C-65-90%) solid product which can be produced from biomass as a result of thermal decomposition such as pyrolysis, hydrothermal carbonization, gasification, torrefaction, and rectification where there is little or no oxygen at all. The source of biomass is from a wide range of diverse organic materials such as plant residue, sewage solids, poultry manure, human manure, goat manure, agro-industrial biomass, etc. The characteristic physiochemical properties provide a wide range of applications such as climatic change mitigation, carbon sink to reduce emission of greenhouse CO_2, soil remediation, carbon sequestration, wastewater treatment, etc. In the recent years, there are several advance developments in the field of water and wastewater treatment using biochar as an adsorbent. Ideally, activated carbon is considered as a universal adsorbent to remove dissolved contaminants from wastewater but the downside is the high cost. Thus, researchers are directed toward replacement through biochar to drop down the process cost and avail the specific characteristic properties of biochar. Biochars have been reported to remove toxic metals, organic pollutants, and nutrients by substituting them in wastewater as an adsorbent. Adsorption capacities of the biochar in the removal of contaminants mainly depend on the source of biomass and type of thermal decomposition employed for biochar conversion as it directly affects its yield and its chemistry. However, biochar can be a new remunerative and nature-friendly solution for the treatment of wastewater. Thus, the present book chapter is mainly focused on the significance of biochar for treatment of wastewater. Various methodologies for biochar

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production, feedstocks, characteristic properties, and specific applications in wastewater treatment etc. were covered.

Keywords

Biochar · Adsorbent · Wastewater · Biomass

6.1 Introduction

The quality of our life has been increasing day by day with the rapid growth of industrial sectors and their economics. But along with that growth, there is subsequent increase in environmental concerns. One such alarming concern can be water pollution. Of the total water resource available, only a mere 0.14% is the total water available for consumption. For the ever-growing population, the water scarcity is increasing day by day and the demand for water increases by 1% every year. The major cause of water pollution is due to the discharge of effluents from various industries into them without any prior treatment. In accordance to the reports of the United Nations World Water Development, about 80% of municipal and industrial wastewater were discharged into natural water bodies. The effluents from these industries contain a diverse range of inorganic and organic contaminants such as organic molecules, toxic metal ions, dyes, and some cancer-causing carcinogens. These contaminants are persistent in nature, are nonbiodegradable, and may easily pass into food chain through bioaccumulation. To overcome water pollution and its shortage, drastic measures were taken by the development of many effective water treatment technologies such as membrane separation, adsorption, precipitation, advanced oxidation process, ozonation, and biological treatment methods such as aerobic and anaerobic digestion. Although these treatment methods may seem effective, they are quite costly, and there arises a need to develop more remunerative technologies. Activated carbon was often considered as the universal adsorbent for the treatment of water. But employment of activated carbon in wastewater treatment is very costly. So, the cost problem can be rectified by the employment of biochar as it requires only less investment and on the other hand it reduces the cost of disposal of the wastes from wide variety of sources, as biochar is derived from it (Huang et al. 2019).

Biochar is a charred organic matter also known as pyrogenic black carbon generated by thermal carbonization of carbon-rich biomass in an environment where the oxygen content is sparse [66]. Thermal carbonization at different temperatures yields diverse range of biochar. In the recent decade, biochar has attained remarkable attention owing to their multifunctional application in bioenergy production, soil fertility, environmental remediation, climate change mitigation, and carbon sequestration. The biomass feedstock can be of any organic materials such as algal biomass, agri-residue, manure, activated sludge, and forest residues. The interest in biochar is peaked due to two distinct benefits. The first one is that the production of biochar decreases the greenhouse gas emission into the atmosphere by preserving the carbon in their stable form (Yang et al. 2018b; Creamer and Gao 2016). Secondly, biochar is a highly efficient, remunerative, environmentally viable adsorbent (Inyang et al. 2016; Cha et al. 2016), which has large surface area and abundant surface functional groups. The biochar produced after-water treatment can be applied to soils to remediate soil fertility, thus increasing the crop productivity.

The biochar's physical and chemical properties are affected by the feedstock characteristics, thermal carbonization method, operation temperature, and duration of the carbonization. Naturally, after the thermal carbonization of the biomass, three fractions are obtained. They are bio-oil, biochar, and syngas. The distribution of the fraction depends on the thermal carbonization temperature. The biochar is graded into three categories by the International Biochar Initiative based on their carbon composition. They are Class I biochar which has carbon content above 60%, Class II biochar containing carbon content between 30 and 60%, and Class III containing carbon content below 30%.

6.2 Types of Thermal Carbonization Technologies

The biomass conversion to biochar by thermal process includes pyrolysis, hydrothermal carbonization, gasification, torrefaction, and rectification. The abovementioned process of biomass feedstock yields biochar, syngas, and bio-oil in different fractions based on the type of thermal carbonization.

Usually, there are pretreatment and posttreatment technologies that are employed to further enhance the properties of the biochar. Some of them are pore volume, specific surface area, surface chemistry, etc. Crushing, sieving, washing, and drying come under physical pretreatment technologies. In chemical pretreatment technology, the chemical precursors or functional agents are loaded into the biomass by immersing them in chemical solution or colloidal suspension, for example, immersing them in metal ions solutions such as $AlCl_3$ and $FeCl_3$, to convert them into biochar-based nanocomposites. After immersing them in these, they are dried prior to biochar production. Biological means include bacterial treatment, anaerobic digestion, biofuel process, etc.

Post-treatment technologies physical and chemical modifications which include ball milling and corrosive and magnetic treatment. Biochar is converted into magnetic particles in magnetization. For example, magnetic iron oxides are loaded into biochar by immersing in aqueous solution. In ball milling, the kinetic energy breaks the chemical bonds, changes the shape of particle, and finally produces them in the range of nanoscale. Corrosive treatment includes acid, alkali, and oxidation treatment and this treatment alters the surface chemistry of the biochar. Posttreatment of biochar increases the specific surface area, negative zeta potential, pore volume, surface functional groups, and adsorption capacity.

6.2.1 Pyrolysis

In this method, a thermal decomposition of biomass was condcuted for conversion into biochar in hypoxic or anoxic environment without combustion. The yield of biochar, composition, and physicochemical properties depend on the operating parameters such as temperature, residence time, and heating rates. The increase in biochar pyrolysis temperature decreases the biochar yield. Of all these parameters mentioned above, the heating rate and the residence time distinguish this process into conventional/slow pyrolysis and fast pyrolysis. The residence time is low, while the heating rate is high for fast pyrolysis on comparison to slow pyrolysis.

In fast pyrolysis, biochar usually has volatiles, but degree of carbonization is low indicating the presence of low fixed carbon mass. Hence, the yield of the biochar is low in fast pyrolysis which will be in the range of 10–20%, while the yield of biochar is 30–60% in slow pyrolysis. In slow pyrolysis, the yield has equal composition of biochar, bio-oil, and biogas which contradicts the fast pyrolysis process as the bio-oil yield is quite high. The reduction in bio-oil yield in slow pyrolysis is due to the cracking reaction. Biochar from fast pyrolysis usually consists of conjugated aromatic structures. The pyrolysis temperature is the main factor in affecting the aromaticity and aromatic condensation of the biochar. At high temperature, the hydrophobicity of the char is increased by the destruction of surface functional groups. The biochar surface area along with the micropore structure increases with increase in pyrolysis temperature. This is due to the devolatilization of the biomass. But too high temperature can cause blockage of the pores and collapse of the microstructure reducing the surface area. So, the recommended pyrolysis temperature is around 400–700 °C.

The heating rate greatly affects the biochar yield. The low heating rate increases the aromatic character and preserves the structural complexity. The high heating rate yields a large number of liquid fractions reducing the biochar yield due to the depolymerization of lignin, cellulose, and hemicellulose from the biomass, phase transition, localized melting, and swelling of the cells.

A long residence time and low temperature are ideal for high biochar yield. This long residence time increases the fixed carbon content by increasing the degree of carbonization (Mohan et al. 2006; Czernik and Bridgwater 2004).

6.2.2 Gasification

In gasification, the thermal decomposition of biomass will be at very high temperature which yields less than 10% of biochar and the majority being syngas or biogas. Partial combustion happens in gasification. Usually, the biochars from pyrolysis are fused rings. But the char from gasification is highly condensed aromatic rings. The chars obtained from gasification are fine powders. Aromaticity is less in comparison to char from pyrolysis. The chars from gasification contain alkaline earth minerals and alkali salts in high amounts (Brewer et al. 2009).

6.2.3 Hydrothermal Carbonization (HTC)

All the carbonization techniques discussed above are dry carbonization techniques, so the biomass feed is usually dried before the carbonization techniques. The main advantage of HTC is energy needed for drying is eliminated. In this method, wet biomass is heated under pressure in a confined space. The activation energy for HTC is also quite low on comparison to the above-discussed techniques. Char obtained from HTC is called hydrochar, which is a solid-water slurry and from this solid char is separated. Hydrochar usually contains alkyl moieties and abundant acidic functional groups, while the char from dry carbonization techniques consists of aromatics. In HTC, the reaction temperature is the governing parameter (Libra et al. 2011; Wiedner et al. 2013).

6.2.4 Torrefaction and Rectification

From the above processes, adsorbent chars can be generated. But this technique was used just to increase the energy density by lessening the water content. This reduces the transportation costs as it lessens the weight of the biomass and mainly prevents the rot of the biomass. So adsorbent-based char cannot be generated in this technique as only partial decomposition of the biomass occurs. The difference between torrefaction and rectification is the reaction temperature ranges (Antal and Grønli 2003).

Apart from the techniques discussed above, there are some sustainable techniques such as flash carbonization and microwave-assisted pyrolysis. The main advantages are short processing time, lesser energy requirement, and effectual heat transfer. In MAP, better volumetric heating is obtained. But the main disadvantage is degradation of microstructure when treated for a long time, and yield of biochar is also less as it can be attributed to inflated heating rates at high microwave power levels. In flash carbonization, the biochar yield is quite high on comparison to conventional processes.

In the development of biochar, apart from feeds different types of reactors are employed for different types of carbonization processes. Some of the reactors include agitated drum sand rotating kilns, screw pyrolizers, vacuum reactor, fluidized-bed reactor, transported-bed reactor, rotating-cone reactor, vortex-centrifuge reactor, ablative reactor, augur reactor, gasifiers, etc. (Table 6.1).

6.3 Classification of Biochar

6.3.1 Types of Feedstock

The biochar production can be from a wide range of feedstocks. The source of these feedstocks classifies them into three categories such as (1) forest and agricultural residues, (2) industrial by-products and municipal wastes, and (3) nonconventional

Table 6.1 Thermal carbonization methods for production of biochar (Brewer 2012)

S. no	Thermal carbonization method	Temperature (°C)	Heating rate	Pressure	Residence time	Product distribution
1	Slow pyrolysis	350–800	Slow (<10 °C/min)	Under atmospheric pressure	Hours–seconds	Biochar
2	Torrefaction	200–300	Slow (<10 °C/min)	Under atmospheric pressure	Minutes–hours	Stabilized friable biomass
3	Fast pyrolysis	400–600	Very fast (1000 °C/s)	Under vacuum to atmospheric pressure	Seconds	Bio-oil
4	Gasification	700–1500	Moderate-very fast	Under atmospheric to elevated pressure	Seconds–minutes	Syngas/producer gas
5	HTC	175–250	Slow	–	Hours	Hydrochar

materials. The value addition of these waste biomasses into biochar will drastically reduce the operation cost for the disposal of these wastes, and the aftereffects caused by them to the environment can be kept in check to some level.

6.3.1.1 Forest and Agricultural Residues

Global production of these forest and forest residues is increasing day by day over the years. It amounts to more than 500 million tonnes based on the record of the year 2011. This may be doubled or tripled over the coming years (Duku et al. 2011). Most of the agricultural residues includes wastes or by-products generated as a result of harvesting and processing of crops such as sugarcane, sorghum, etc. Forest residues include sawdust, wood chips, and wood mills etc. The operating cost associated with disposal of these residues is costly and is scarcely utilized. The ease of collection, reduction of operational cost for disposal, and abundancy of these residues make them a better feedstock for biochar production.

The biochar produced from these residues has good sorption ability for a diverse group of organic and inorganic contaminants which is due to the surface properties of the feedstock materials (Mohan et al. 2007). This sorption ability can be explained by few examples such as the following: The oak bark has high contents of suberin, flavonoids, and polyphenolic tannins. The beet tailings have complex heteropolysaccharides such as galacturonic acid, galactose, arabinose, and some variation of pectin substances. Thermal carbonization of these residues yields abundant oxygen-containing groups. Some of these groups are C–O, C–OH, C=O, C–O–R, and –OH (Aksu and Isoglu 2005). In addition to this, oak and pinewood chars consist cationic micronutrients such as Na, Mg, and K (Mohan et al. 2007).

6.3.1.2 Industrial By-Products and Municipal Wastes

The generation of biochar from industrial by-products and municipal wastes has been noted, and interest in them has been growing day by day (Yao et al. 2011a, b; Phuengprasop et al. 2011). In industries, biodegradation is an important step in waste treatment. Anaerobic digestion is the most common biodegradation step which degrades waste by employing a variety of microorganisms. The biochar produced from this feedstocks has a high ion exchange capacity as it has anaerobically digested wastes and has high concentrations of cationic or metallic elements (Hanay et al. 2008; Gu and Wong 2004).

In contrary to this, municipal wastes are another possible source for potential biomass feedstock for biochar production. Fauna wastes such as poultry litter which comprises of bedding material, spilled feed, and feather and manure from cattle rearing have excess amounts of ash and inorganic micronutrients which can bind heavy metals in aqueous phase (Uchimiya et al. 2010; Duku et al. 2011; Cao et al. 2011).

6.3.1.3 Nonconventional Materials

Some examples of nonconventional materials include waste tires (Karakoyun et al. 2011), scraps of newspaper (Li and Zhang 2004), bones (Dimovic et al. 2011;

Cheung et al. 2000), plastic wastes (Gil et al. 2010), and food wastes (Rhee and Park 2010; Ahmed and Gupta 2010). Owing to the abundancy of waste tires, using them as biochar feedstock has made them attractive, and their operating cost for disposal will be greatly reduced. The ignition of crushed and distilled animal bones yields a heterogenous sorbent called bone biochar. This biochar has high concentration of hydroxyapatite and calcium carbonate which has high ion exchange capacity (Cheung et al. 2000).

6.3.2 Hybrid Biochar Through Modification

The biochar potential in wastewater treatment can be ascribed to their relative inexpensiveness, feedstock abundancy, and surface characteristics. Although biochar exhibited great potential, sure it has its won limitations such as restricted limitations to its ability to adsorb contaminants from wastewater containing high concentrations, because the small particle size of biochar makes it difficult to remove from aqueous systems. These shortcomings can be dealt by modifying or engineering them to have novel structures and surface properties. These modified biochars are called biochar-based nanocomposites. These nanocomposites were classified into three categories such as (1) nano-metal hydroxide/oxide-biochar composites, (2) magnetic biochar-based composites, and (3) functional nanoparticles-coated biochar.

6.3.2.1 Nano-metal Oxide/Hydroxide-Biochar Composite

In this, there are three pursuits to engineer the abovementioned composite. In the first two methods, the target metals were impregnated before thermal carbonization, and in the third technique, the target metal is directly introduced into the biochar. In the first method, bioaccumulation of the target metal element by the biomass and on thermal treatment yields the nano-metal oxide/hydroxide biochar. For example, Mg-enriched biochar derived from tomato tissues obtained by slow pyrolysis had a substantial adsorption propensity to phosphate in aqueous solution (Yao et al. 2013).

Pretreatment of biomass using metal salt by immersing the biomass in metal salt solution. The ions will get attached to the surface or may flow into the inside of the biomass. The metal ions will be modified into metal oxides/hydroxides after pyrolysis. Thus, the biochar saturated with metal ions will transmute into biochar-based nanocomposites. The development of Al_2O_3, AlOOH, CaO, MgO, MnO_x, and ZnO nanoparticles onto the biochar surface can be obtained by pretreating the biomass with metal salts such as $AlCl_3$, $CaCl_2$, $MgCl_2$, $KMnO_4$, $MnCl_2$, and $ZnCl_2$ (Yao et al. 2013).

In the last method, the metal oxides/hydroxides were impregnated after the thermal carbonization of biomass. Some of the techniques for impregnation involves evaporative, heat treatment, and wet impregnation method. For example, the biochar modified by evaporative method using $Fe(NO_3)_3.9H_2O$ has increased surface area by a factor of approximately 2.5.

6.3.2.2 Magnetic Biochar-Based Composites

To overcome the difficulty of separating from aqueous solution after contaminant removal, the biochar can be converted into magnetic materials. So, the magnetic biochar can be easily segregated under the presence of a magnetic field. In addition to this, the adsorption capability of the magnetic biochar was also increased (Zhang et al. 2013; Chen et al. 2011). For conversion, two techniques are followed. They are as follows: (1) pretreatment of biomass in the presence of iron ions and (2) iron oxide precipitation onto biochar.

In the first technique, the biomass was impregnated with Fe^{3+}/Fe^{2+}, and subsequent thermal carbonization of the impregnated biomass yields the magnetic biochar, for example, thermal carbonization of the $FeCl_3$ along with Fe ions, and other ions can also be impregnated along with them (Zhang et al. 2014), for example, magnetic biochar synthesized by pretreating the biomass with $Fe(NO_3)_3.9H_2O$ and $Co(NO_3)_2.6H_2O$ followed by slow pyrolysis (Reddy and Lee 2014).

The second technique is chemical coprecipitation of Fe^{3+}/Fe^{2+} directly onto the biochar. The synthesis involves the mixing of aqueous biochar solution with aqueous ferrous/ferrous solution, followed by treatment using aqueous NaOH solution (Han et al. 2015).

6.3.2.3 Functional Nanoparticles-Coated Biochar

To make the biochar-based nanocomposites affordable to some extent, functional nanoparticles are integrated into them. Some of the functional nanoparticles include chitosan, carbon nanotube, graphene, ZnS nanocrystals, graphene oxides, layered double hydroxides, etc. The main advantage of the functional nanoparticles along with adsorption is degradation of the contaminants. Synthesis of these involves two methods which are precoating of the biomass before thermal carbonization with functional nanoparticles and saturation of functional nanoparticles onto biochar after pyrolysis treatment.

In precoating technique, the biomass is immersed in homogenized functional nanoparticles suspension which is called dip-coating procedure. Some illustrations are as follows: Graphene-coated biochar is produced from the congelation of graphene/pyrene derivative-treated biomass, and dip coating of biomass in carboxyl-functionalized carbon nanotube solution followed by pyrolysis yielded multiwalled carbon nanotube-coated biochar (Inyang et al. 2014). Both biochars show increased thermal stability, surface area, and porosity.

Saturation of functional nanoparticles onto the biochar after thermal carbonization holds advantage over the previous technique as there may be blockage of pores in the latter technique. Hydrogel, Mg/Al LDH, chitosan, zerovalent iron (ZVI), and ZnS nanocrystals were commonly used in this synthesis of these biochars.

6.4 Role of Biochar in Wastewater Treatment

Biochar is an emerging substitute for treatment of organic pollutants such as volatiles, antibiotics, aromatic dyes, polychlorinated biphenyl (PCB), and polyaromatic hydrocarbons (PAHs) from aqueous systems, and it application was extended to inorganic pollutants, for instance, heavy metals, ammonia, nitrate, phosphate, etc. Mechanisms such as ion exchange, pore filling, precipitation, and surface sorption are involved in removal of contaminants from aqueous systems (Fig. 6.1).

6.4.1 Inorganic Contaminant Removal

The potential adsorption mechanism involved in removal of inorganic pollutants includes synergistic effects of various interactions such as ion exchange, electrostatic

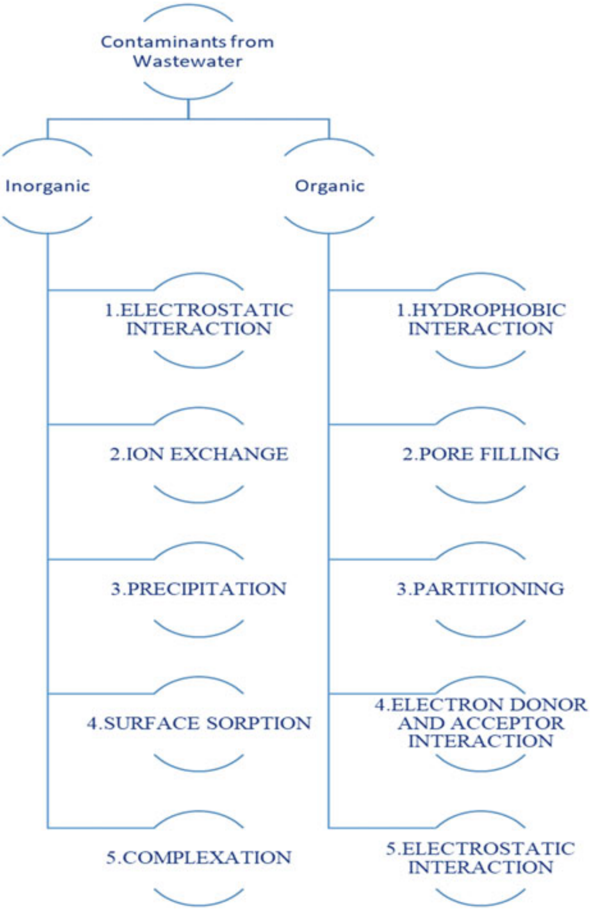

Fig. 6.1 Various mechanisms involved in removal of contaminants from wastewater

interaction, precipitation, surface sorption, and complexation. Some illustrations for the adsorption of inorganic contaminants were given in Table 6.2.

6.4.1.1 Heavy Metal Removal

The high concentration of heavy metals present in aqueous system gives rise to a serious threat to the environmental remediation which can adversely affect human beings, plants, and animals. In the event of long exposure, it can cause severe health concerns to the living beings. Thus, there are studies that confirm biochar can be a suitable adsorbent for the treating of heavy metals in wastewater. The adsorption of uranium and copper ions by pinewood char and grass char occurs through surface sorption (Kumar et al. 2011; Liu et al. 2010a, b). Sort of a physical sorption involves the formation of chemical bonds between ions and sorbent when diffusing between the pores of the sorbent (Patra et al. 2017). The thermal carbonization temperature of the biomass influences the adsorption capacity. The higher the temperature, the higher the number of pores and surface area which in turn increases the diffusion. Surface adsorption is the governing mechanism in the adsorption of Co(II), Zn(II), Cu(II), Pb(II), and Cd(II) to dairy manure biochar (Wang et al. 2015). Similar to this surface precipitation mechanism is a governing mechanism for adsorption of Zn, Cr, Mn, and Cu by municipal sewage sludge-derived biochar (Zhou et al. 2017a, b).

Next, electrostatic interaction of ions to biochar depends on the pH of the aqueous system along with point of zero charge pH of the biochar. The interaction between the metal ions and charged biochar surface causes the immobilization of the ions (Mukherjee et al. 2011; Dong et al. 2011). In the adsorption of anionic metal ions, electrostatic interaction is the dominant mechanism. The rate of production of graphene in biochar directly influences electrostatic interaction between the contaminants and surface. This is why thermal carbonization temperature exceeds 400 °C to favor electrostatic interaction (Keiluweit and Kleber 2009). In the adsorption of Cd and aluminum, electrostatic interaction is the main mechanism.

Ion exchange mechanism is the exchange of protons and ionized cations between the surface of biochar and metals in aqueous system. This sorption behavior depends on the size of the metal ion in the aqueous system and surface functional groups on the biochar. In ion exchange process, based on the ionic radii, bond characteristics and charge difference occur with the substitution of metal ion from aqueous system in the biochar system by removal of positively charged ions (Krauskopf 1967). Cation exchange capacity (CEC) depends on the presence of surface functional groups, and the higher the CEC, the higher the capability or potential for elimination of metal contaminants from aqueous system (Ali et al. 2017; Rizwan et al. 2016). In the adsorption of Pb and Cd by biochar derived from feedstocks such as wheat straw, grape stalk, nut shield, and stone husk, cation exchange is the governing mechanism (Trakal et al. 2016).

During precipitation a sorption mechanism involves the development of solids in the aqueous system or on the biochar surface. Biochar rich in alkaline minerals is usually involved in the precipitation of metal ions from aqueous system. This suitable biochar that supports this mechanism was derived by degradation of feedstock rich in cellulose and hemicellulose by thermal carbonization (Cao and Harris

Table 6.2 Adsorption of inorganic contaminants by biochar and removal mechanism

S. no	Biochar	Contaminant	Removal percentage/ sorption capacity	Mechanism of adsorption	Reference
1	Corn straw char	Hg	136.7 mg/g	Ion exchange	Wang et al. (2018a), Wang et al. (2018b)
2	Marine algae char	Cu	63.52–69.37 mg/g	Ion exchange	Srivatsav et al. (2020)
3	Corn straw char	As (V)	6.80 mg/g	Precipitation, electrostatic interaction	He et al. (2018)
4	Banana peel char, cauliflower leaves char	Cu Cd Pb	77.1–59.6 mg/g 128.0–262.1 mg/g 74.1–186.0 mg/g	Electrostatic attraction	Ahmad and Gao (2018)
5	Corn straw char	Cr(VI)	116.28 mg/g	Complexation	Zhao et al. (2017b)
6	Sewage sludge char	Zn Cr Mn Cu	5.905 mg/g 5.724 mg/g 5.681 mg/g 5.342 mg/g	Surface precipitation, complexation	Zhou et al. (2017a), Zhou et al. (2017b)
7	Buckwheat husk char, corn cobs char, mulberry wood char, poultry manure char, and peanut shell char	Pb Cd As	(97.5–99.8%) (<90%) (42%)	Electrostatic interaction, precipitation	Zama et al. (2017)
8	Eggshell char	Pb	103–261 mg/g	Electrostatic attraction	Wang et al. (2017a), Wang et al. (2017b), Wang et al. (2017c), Wang et al. (2017d)
9	Peanut shell char	Cd(II)	80%	Electrostatic interaction	Xu et al. (2017)
10	Pine cone char	Ni	106.4–117.7 mg/g	Surface sorption, precipitation	Sara et al. (2017)
11	Wood shaving char, chicken litter char	Cd	48.5–60.9 mg/g	Electrostatic attraction, complexation	Qi et al. (2017)
12	Rice straw char	Cr(VI)	40.0 mg/g	Electrostatic attraction	Qian et al. (2017)

(continued)

Table 6.2 (continued)

S. no	Biochar	Contaminant	Removal percentage/ sorption capacity	Mechanism of adsorption	Reference
13	Celery char	Pb	288–304 mg/g	Ion exchange, complexation, precipitation	Zhang et al. (2017a), Zhang et al. (2017b)
14	Swine manure char	Cd (II) Pb (II)	45.8 mg/g 268.0 mg/g	Ion exchange	Liang et al. (2017)
15	Corn stem char	As	8.25 mg/g	Surface sorption	Lin et al. (2017)
16	*Miscanthus giganteus* grass char	Cu Zn	15.7 mg/g 10.4 mg/g	Electrostatic interactions	Cibati et al. (2017)
17	Aromatic spent char	Cd, Pb, Cu, Cr	>60 mg/g	Ion exchange	Khare et al. (2017)
18	Pineapple peel char	Cr (VI)	7.44 mg/g	Ion exchange	Wang et al. (2016)
19	Herb residue char	Cr (VI)	23.85 mg/g	Precipitation	Shang et al. (2016)
20	Sesame straw char	Pb Cd Cr Cu Zn	102 mg/g 86 mg/g 65 mg/g 55 mg/g 34 mg/g	Precipitation	Park et al. (2016)
21	Sugarcane char, orange peel char	Pb(II)	27.86–86.96 mg/g	Ion exchange, surface sorption	Abdelhafez and Li (2016)
22	Water hyacinth char	Cd	70.3 mg/g	Ion exchange, surface sorption	Zhang et al. (2015c)
23	Hickory wood char	Pb(II) Cu(II) Cd(II)	153.1 mg/g 34.2 mg/g 28.1 mg/g	Surface sorption	Wang et al. (2015)
24	Peat moss char	Pb Cd Cu	81.3 mg/g 18.2 mg/g 18.2 mg/g	Surface sorption	Lee et al. (2015)
25	Brewers draff char	Cu	8.77–10.3 mg/g	Precipitation, electrostatic interaction	Trakal et al. (2014a), Trakal et al. (2014b)
26	Municipal sludge char	Cr	7–20 mg/g	Surface sorption, ion exchange	Chen et al. (2015a)
27	Broadleaf hardwood char	Pb	30.04–47.66 mg/g	Electrostatic attraction	Shen et al. (2015)
28	$MgCl_2$ solution immersed sugar beet tailings char	PO_4^{3-}	835 mg/g	Surface sorption	Zhang et al. (2012)

(continued)

Table 6.2 (continued)

S. no	Biochar	Contaminant	Removal percentage/ sorption capacity	Mechanism of adsorption	Reference
29	Mg-enriched tomato leaves biochar	PO_4^{3-}	100 mg/g	Surface sorption, precipitation	Yao et al. (2013)
30	$AlCl_3$ solution immersed cottonwood biochar	PO_4^{3-}	135 mg/g	Sorption by their distinctive nanostructure	Zhang and Gao (2013)
31	Anaerobically digested sugar beet tailings biochar	PO_4^{3-}	25 mg/g	Surface sorption	Yao et al. (2011b)
32	Mg-Al layered double hydroxide-modified bamboo biochar	PO_4^{3-}	13.11 mg/g	Ion exchange and surface sorption	Wan et al. (2017)
33	MgO-modified wood waste char	PO_4^{3-}	116.4 mg/g	Struvite precipitation, surface sorption	Xu et al. (2018)
34	Acid wash and water wash-willow wood char	Phosphorus	1.93 mg/g	Sorption and surface precipitation	Dugdug et al. (2018)
35	Acid and water wash-hardwood char	Phosphorus	1.2 mg/g	Sorption and surface precipitation	Dugdug et al. (2018)
36	Acid and water wash-wheat straw char	Phosphorus	1.06 mg/g	Sorption and surface precipitation	Dugdug et al. (2018)
37	Aluminum salt-treated hickory wood chips char	Phosphorus	8.346 mg/g	Electrostatic attraction	Zheng et al. (2019)
38	MgCl2 solution immersed peanut shell biochar	NO_3^-	94 mg/g	Surface adsorption	Zhang et al. (2012)
39	Mg-Fe layered double hydroxide-modified wheat straw char	NO_3^-	24.8 mg/g	Surface sorption and interlayer anion exchange	Xue et al. (2016)
40	MgO particle-impregnated sugarcane char	NH_4^+	22 mg/g	Struvite crystallization, electrostatic attraction, and π-π interactions	Li et al. (2017)

(continued)

Table 6.2 (continued)

S. no	Biochar	Contaminant	Removal percentage/ sorption capacity	Mechanism of adsorption	Reference
41	MgO-modified wood waste biochar	NH_4^+	47.5 mg/g	Struvite precipitation	Xu et al. (2018)
42	Cottonwood biochar	PO_4^{3-}	386 mg/g	Surface sorption	Zhang et al. (2014)

2010). For example, bagasse biochar forms hydrocerussite precipitate with Pb on the biochar surface (Inyang et al. 2011). For precipitation mechanism, the thermal carbonization temperature for the biochar feedstock should be less than 200 °C as these minerals in the biochar should be soluble to interact with metal ions in the aqueous system to form non-soluble precipitation, thereby enhancing the sorption behavior of the biochar (Cao and Harris 2010). The biochar is produced with thermal carbonization temperature between 300 °C and 650 °C, and the alkaline minerals are slightly soluble form, thus slowing down the sorption behavior of the biochar (Inyang et al. 2011). In the sorption of Cr(III) and Cr(VI) to municipal waste sludge-derived biochar, precipitation is the dominant mechanism (Chen et al. 2015a).

Complexation of metal ions involves the formation of complexes with specific metal ligands. This is a multiatom arrangement formation. Biochar produced at low thermal carbonization temperature has an abundant oxygen functional groups like lactonic, phenolic, and carboxylic groups which showed greater efficiency of metal ion binding in the aqueous systems (Liu and Zhang 2009; Mohan et al. 2007). Surface oxidation of biochar surface increases the oxygen content which in turn increases the sorption capacity (Harvey et al. 2011). Plant-based biochar has more complexation capacity than animal-based biochar. Ni, Cd, and Pb form complexes with carboxylic and phenolic groups in plant-based biochar. Biochar derived from dairy manure and poultry litter binds the phosphate ligand to Pb to form pyromorphite (Guo et al. 2010; Cao et al. 2009).

6.4.1.2 Nitrogen and Phosphorus Removal

Biochar was able to adsorb phosphorus and nitrates in the aqueous systems. They usually exist in the water bodies in the form of nitrate (NO_3^-), ammonium (NH_4^+), and phosphate (PO_4^{3-}). These inorganic nitrogen and phosphorus lead to eutrophication. This water eutrophication in water bodies is one of the biggest concerns in the world today. Although carbon (C), magnesium (Mg), and potassium (K) also play a role in the eutrophication, the major proportion is caused by nitrogen and phosphorus. The large surface area and pore structure enables for sorption of high concentration of N/P from aqueous systems. In comparison of wood biochar with rice husk biochar, the former has more surface area than the latter one which in turn shows more efficiency for adsorption of ammonium ions by the wood biochar (Kizito et al. 2015). And biochar modified by magnesium oxide shows high adsorption capacity to nitrate owing to the high surface area provided by the MgO nanoflakes (Zhang et al. 2012). Phosphate adsorption capability is affected by surface area and active sites distribution in the biochar. The surface area increases with increase in operation temperature in pyrolysis but only in the range between 200 and 400 °C. Although adsorption capacity of phosphate is increased in these temperature ranges, it decreases for temperature above 400 °C. Thus, the adsorption of N/P not only depends on the surface area of the biochar.

Surface functional groups are important for the removal of NH_4^+/NO_3^- from aqueous systems. There is a positive interrelationship between the removal rate of NH_4^+, NO_3^-, and the acidic, basic functional groups on the surface of biochar (Wang et al. 2015). The aromatic C=C, C=O, $-CH_2-$, and aliphatic C–O–C functional group on the surface of biochar is mostly involved in the adsorption of NH_4^+ (Zeng et al. 2013). Naturally, acidic functional groups are mostly present in the biochar. But for adsorption of NO_3^-, basic functional groups are required. Thus, by modification of the surface of the biochar with ammonia, basic functional groups are introduced on it. This increases the sorption capacity of NO_3^- (Iida et al. 2013).

The adsorption of phosphate occurs in the biochar due to the presence of metallic oxides such as CaO, MgO, AlOOH, Fe_2O_3, etc. These metal oxides either form hydrogen bonds or react with phosphate to form precipitation in the aqueous system which is the reason for the sorption behavior. Phosphate removal is in direct correlation to the presence of Ca and Mg fraction in biochar (Takaya et al. 2016). Peanut shell biochar has the highest content of Ca and Mg, thus showing high efficiency for phosphate removal (Jung et al. 2015). The reason for affinity toward phosphate is due to the presence of nanoflakes of MgO widely distributed over the surface of the biochar. The surface of MgO is always positively charged as the point of zero charge of pH is 12 and most aqueous system naturally has pH below than this (Yao et al. 2011a).

Some other factors which influence the sorption behavior are pH and coexisting ions. The pH of the aqueous system greatly influences the sorption by altering the surface charge of the biochar. In alkaline conditions, the ammonium ions get converted to NH_3 greatly lowering the sorption capacity (Huang et al. 2010). The surface charge of the biochar surface is influenced by pyrolysis temperature. Biochar produced at thermal carbonization temperature more than 400 °C shows higher value of point of zero charge pH than the pH of the aqueous system. But biochar generated at temperature less than 200 °C has point of zero charge pH at 7. So, on this case the phosphate sorption capacity of biochar is low (Jung and Ahn 2016).

Wastewater contains not only the target ions but also other coexisting ions. These coexisting ions affect the adsorption capacity of the biochar. When the biochar is selective or site specific for a particular target ion, then the coexisting ions' influence will be minimal or none at all. For example, Cl^-, NO_3^-, and SO_4^{2-} show no effect on the adsorption of ammonium ions, but chloride, sulfate, and phosphate inhibit the extent of adsorption of nitrate to some level which is due to the competitiveness between the coexisting ions and nitrate (Liu et al. 2010a, b). The phosphate sorption capacity of the biochar greatly decreases with increase in bicarbonate concentration; this may be due to the competitiveness or the increase in the pH of the aqueous system (Yao et al. 2011a, 2013).

6.4.2 Organic Contaminant Removal

The removal mechanism of organic contaminants by biochar is a combination of many mechanisms such as electrostatic and hydrophobic interaction, pore filling, partitioning, and electron donor and acceptor interaction. Some illustrations for adsorption of organic contaminants were given in Table 6.3.

6.4.2.1 Dye Removal from Textile Effluent

The effluent discharged from textile industry has vast amounts of acids, bases, toxic compounds, dissolved solids, and mainly dyes which are responsible for the color of the effluent. This effluent poses major threat to the environment. The textile dyes do not degrade easily as they are resistant to light, aerobic digestion, and oxidizing agents. Some of the mechanisms involved in the sorption of dyes in biochar include electrostatic interaction, pore filling, cationic π interaction, π-π interaction, ion exchange, etc. Electrostatic interaction is the governing mechanism for sorption of ionizable and ionic organic contaminants, and most of the textile dyes comes under this category. Ionic sorbates naturally show affinity to oppositely charged sorbent surface. Ionic strength and pH are the determining factor in sorption capacity of the biochar based on the electrostatic interaction mechanism. During repulsive electrostatic interaction, sorption between the sorbent and sorbate increases with increase in ionic strength, whereas during attractive electrostatic interaction, sorption between the sorbate and sorbent decreases with increase in ionic strength. Sorption of methylene blue and methyl blue onto the biochar was electrostatic interaction mechanism. Alternate sorption mechanism for methylene blue dye is ion exchange, because at low pH the H^+ ions bind with the binding sites that are involved in electrostatic interaction and metal ions such as Ca^{2+}, Na^+, etc. are released into the aqueous system with sorption of methylene blue dye to the biochar.

Pore filling is the governing mechanism in the sorption of malachite green dye to biochar derived from *Opuntia ficus-indica*. This biochar possesses mesoporous structure. Some other mechanisms involved in the malachite green dye sorption to biochar are π-π electron donor-acceptor (EDA) interactions and cation-π interactions. This occurs due to the presence of electron-deficient groups in malachite green dye and electron-rich groups such as amine and hydroxyl groups present on the biochar surface (Srivatsav et al. 2020; Abbas et al. 2018).

6.4.2.2 Phenol Removal

Phenolic concentrations are present in diverse concentration in various wastewater streams. Usually, phenolics are mass produced for production of drugs, dyes, pesticides, antioxidants, etc. They give rise to serious threat to the environment

Table 6.3 Adsorption of organic contaminants by biochar and removal mechanism

S. no	Biochar	Contaminant	Sorption capacity/ removal percentage	Adsorption mechanism	Reference
1	Corn straw char	Atrazine	67.55 mg/g	Pore filling	Zhang et al. (2018a), Zhang et al. (2018b)
2	*Macadamia* nut shell char	Phenanthrene	53.8%	π-π interaction	Yang et al. (2018a)
3	Sugarcane bagasse biochar	Malachite green	3000 mg/L	Diffusion	Vyavahare et al. (2018)
4	Pine sawdust biochar	Sulfamethoxazole (SMX)	86.82%	Hydrophobic interaction	Reguyal and Sarmah (2018)
5	Apricot stone char	Naproxen Chlorophenols	10 mg/g 500 mg/g	Partitioning Pore filling	Sekulić et al. (2018)
6	Bamboo hydrochar	Congo red 2-Naphthol	90.51 mg/g 72.93 mg/g	Π-π interaction Physical sorption	Li et al. (2018)
7	Rice straw, softwood, hardwood, and nut shell char	Fomesafen	0.69–20.67 mg/g	Pore filling	Khorram et al. (2017)
8	Dissolved black carbon biochar	Naphthalene Pyrene Phenanthrene Anthracene	<81.7%	Hydrophobic partition	Fu et al. (2018)
9	Macroalgae-derived biochar	Malachite green	5306.2 mg/g	Electrostatic interactions	Chen et al. (2018)
10	Ramie biomass biochar	Safranin T	226.7 mg/g	Hydrogen bonding, electrostatic interaction	Cai et al. (2018)
11	Corn straw char	Biphenol A	476.19 mg/g	π-π interaction	Zhao et al. (2017a), Zhao et al. (2017b)
12	Sawdust	Tetracycline	10–25 mg/L	Hydrogen bonding, π-π EDA	Zhou et al. (2017a), Zhou et al. (2017b)
13	Corn straw char, poplar leaf char	Dodecylbenzene sulfonic acid (DBSA)	155.9 mg/g	Partition, anion exchange	Zhao et al. (2017a), Zhao et al. (2017b)
14	Corn straw	Bisphenol A	476.19 mg/g	π-π interaction	Zhao et al. (2017a), Zhao et al. (2017b)

15	Sawdust char	Tetraethyltin	91.6%	π-π interaction, complexation	Zhou et al. (2017a), Zhou et al. (2017b)
16	Digested bagasse biochar	Sulfamethoxazole (SMX)	54.38 mg/g	π-π interaction	Yao et al. (2018)
17	Poplar and conifer wood chips char	Phenanthrene Pentachlorophenol	11.9 mg/kg 132 mg/kg	π-π interactions	Rao et al. (2017)
18	Corn straw char	Perfluorooctane sulfonate (PFOS)	169.30 mg/g	Hydrophobic and electrostatic interaction	Guo et al. (2017)
19	Bamboo char	Carbamazepine	104.85–861.70 mg/L	π-π interaction	Chen et al. (2017a), Chen et al. (2017b)
20	Bamboo and *Eucalyptus* wood char	Chloramphenicol	233 mg/g	π-π interaction	Ahmed et al. (2017), Ahmed et al. (2018)
21	Wastewater sludge char	Sulfamethoxazole (SMX)	45 mg/L	π-π interaction	Shimabuku et al. (2016)
22	Palm kernel shell char	4-Nitrotoluene	23.76–59.92 mg/g	Electrostatic interaction	Saleh et al. (2016)
23	Pine chips	Benzophenone Benzotriazole Bisphenol A 17-β-Estradiol	6.79 mg/L 9.22 mg/L 28.4 mg/L 30.2 mg/L	Hydrophobic interaction	Kim et al. (2016)
24	Potato peels	Bisphenol A	454.62 mg/g	π-π interaction	Arampatzidou and Deliyanni (2016)
25	Pinewood	Salicylic acid, ibuprofen	22.70 mg/g 10.74 mg/g	Hydrogen bonding π-π interaction	Essandoh et al. (2015)
26	Bamboo biochar	*N*-Nitrosodimethylamine	61.68%	Hydrophobic interaction	Chen et al. (2015b)

even at low concentration. The phenolics are considered as human carcinogens, show poor biodegradability, and can cause serious ecological damage. Hydrophobic interaction is the dominant mechanism for the phenol removal in biochar derived from pistachio shells, pecan shells, and sawdust which can be reasoned by the presence of increased carbon content (graphene structure) obtained at high thermal carbonization temperature. Hydrophobic interaction is a combined mechanism which involves both partitioning and hydrophobic mechanism generally driven by entropy (Komnitsas and Zaharaki 2016; Abbas et al. 2018).

Acid-base interactions and hydrogen binding are the sorption mechanism in the phenol removal on the biochar derived from corn cob and rice husk biochar. In catechol sorption onto the biochar derived from loblolly pine, oak, and gamma grass, pore filling is the dominant mechanism. This mechanism depends on the presence of micropore and mesopore on the surface of the biochar. Sorption behavior involving pore filling mechanism is favored at low concentration of solute and small number of volatiles in biochar (Abbas et al. 2018).

6.4.2.3 Pharmaceutically Active Compounds Removal

Pharmaceutically active compounds that come under micropollutants are of great concern to the environment due to their nonbiodegradability along with their toxicity. This effect can rise to permanent long-time side effects to marine organisms. The adsorption mechanism involved in sorption of pharmaceuticals involves hydrogen bonding, electrostatic attraction, π-π interaction, hydrophobic interaction, dipole-dipole interaction, and van der Waals force (Chen et al. 2020).

Hydrogen bonding mechanism involves the intermolecular attraction between the hydrogen donor and acceptor. The sorption of atrazine to the biochar derived from sludge is due to the hydrogen bonding between the amino groups in the contaminant and the hydroxyl groups on the biochar. Rather than normal hydrogen bonds, charge-assisted hydrogen bonds such as negatively charged, positively charged, and doubly charged hydrogen bonds have more strength. Ionizable pharmaceuticals (e.g., sulfamethoxazole) usually form negatively charged hydrogen bonds with the biochar. The charge-assisted bond formation occurs due to indistinguishable pKa values of adsorbent and adsorbate. Charge-assisted hydrogen bond is the sorption mechanism between the pharmaceuticals and oxygen-rich biochar (Chen et al. 2020).

π-π interaction is a type of dipole interaction and is weaker than hydrogen bond. Increase in pyrolysis temperature increases the rate of aromaticity of biochar. This interaction between sorbent and sorbate is polar. π-π interaction is the most usual type of interaction between aromatic groups. So, this interaction is the dominant mechanism between the pharmaceuticals norfloxacin, diclofenac sodium, and chitosan magnetic composite biochar. The sorption of tetracycline onto the bagasse-derived biochar is due to π-π interaction. Due to the high electronegativity of π system, cation attraction is also favorable (Chen et al. 2020).

Some other interactions for sorption behavior of pharmaceuticals include hydrophobic interaction. Phenanthrene removal from aqueous system onto the biochar may be due to the hydrophobic interaction, but it is not the dominant mechanism.

Pore filling mechanism was also seen in case of pharmaceuticals like dimetridazole and metronidazole (Chen et al. 2020).

6.4.2.4 Pesticide and Herbicide Removal

These are compounds which have wide array of applications in parks, industrial sites, educational facilities, farming, and forestry to control rodents and insects which naturally act as vectors for diseases. Usually, based on the chemical structure of pesticides, they are classified into five major categories which are as follows: organochlorines, organophosphorus, chlorophenols, carbamates, and synthetic pyrethroids (George and Shukla 2011; Hamza et al. 2016). Sorption behavior of pesticide onto biochar can be explained by a culmination of mechanism such as partitioning and hydrogen bonding and as usual depends on the biochar surface area.

The composition of biochar usually contains carbonized and non-carbonized fraction. Graphene and crystalline-like fractions come under carbonized fractions and organic carbon, noncrystalline, amorphous fractions under non-carbonized fractions. When the sorption mechanism is partitioning, it occurs by propagation of sorbates into the pores of the biochar, and later it gets solubilized into the matrix of the amorphous carbon which contains polyaromatic and aliphatic compounds. The dominant sorption mechanism that occurs between the biochar enriched with volatile matter and aqueous system containing high concentration of contaminant is partitioning (Abbas et al. 2018). Sorption of 1-naphthol and naphthalene onto biochar derived from orange peel under different thermal carbonization temperature is by partitioning mechanism. The other interaction involved in sorption of 1-naphthol onto the biochar is hydrogen bonding which is due to the presence of hydroxyl group in the contaminant (Chen and Chen 2009).

Dibromochloropropane is a soil fumigant used to prevent nematodes which were treated by using almond shell-activated biochar with 100% removal rate. Pore filling mechanism can also be seen in the sorption of 1,4-dichlorobenzene onto the biochar derived from pinewood (Klasson et al. 2013).

6.4.2.5 Solvents Removal

Some of the solvents used in the industry include benzene, nitrobenzene, 1,2,4-trichlorobenzene, and trichloroethylene. The sorption of benzene and nitrobenzene onto the biochar derived from wheat residues produced under different thermal carbonization temperature. The solvents get adsorbed on the carbonized surface, while low-temperature char follows partitioning mechanism for sorption. More than that, nitrobenzene shows affinities to functional groups on the surface of the biochar owing to the presence of nitro group (Chun et al. 2004).

Pore filling was seen in the sorption of 1,2,4-dichlorobenzene onto the biochar derived from pinewood char (Nguyen et al. 2007). Trichloroethylene adsorption onto the biochar derived from soybean stover and peanut shells is in positive correlation with the carbon contents of the biochar but in negative correlation with oxygen content of the biochar (Ahmad et al. 2013).

6.5 Conclusion and Future Perspectives

Biochar is a remunerative adsorbent generated from a wide range of biomass and is modified as nanocomposites for easiness of operation. The sorption of contaminants from wastewater onto biochar follows a combination of numerous mechanisms. Use of biochar for wastewater treatment for adsorption of both organic and inorganic contaminants has high removal percentage. And the cost of operation is also minimal.

Although there is bright future for their application in wastewater treatment, the work on biochar done was mostly in laboratory level. Future perspective should be to develop technology to modify the biochar to have greater efficiency, practical application of biochar in wastewater treatment, and further improvement of the adsorption capacity of biochar.

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Recent Advances in Biochar-Based Dye Remediation

7

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7.1 Introduction

In recent years, the explication of water resource management has developed significantly because the exponentially growing problem of water pollution has become a major current issue. As an aspect of such initiatives, global pollution agencies and organizations, including the United States Environmental Protection Agency, have identified the control and removal of highly toxic and dangerous substances, such as dyes, as crucial functions (US EPA). Enormous studies are being conducted to establish both the immediate and long impacts of dye on people's well-being and the natural ecosystem (Long et al. 2017). Dyes are the most widely used chemicals in a variety of industries, such as the textile industry; the threat of dye contamination has attained an all-time high degree in recent times. About 10,000 forms of synthetic dyes are reported to be industrial purposes utilized with a yearly output of more than 7×10^5 tons. As such, the utilization of dyes for a variety of

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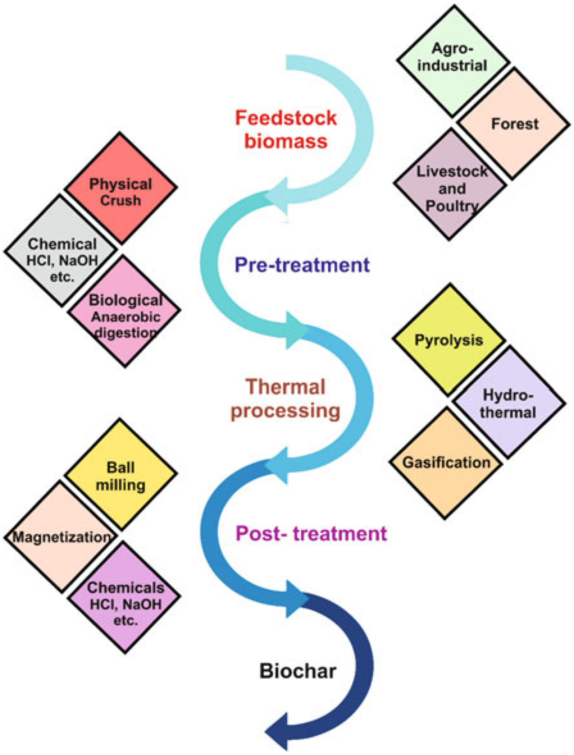
uses, such as textiles, leathers, detergents, medicines, and cosmetics, has seen an upsurge (Ooi et al. 2017).

Adsorption is a method of mass transfer of dyes from the liquid-state to a solid-state adsorbent. Adsorption is one of the most prevalently deployed methods in wastewater treatment processes; it has several strengths, such as clean design, relatively inexpensive, simple operation, and high performance. Biochar (BC) has steadily penetrated the perception of humanity in recent times. BC is a carbon-rich material generated in an oxygen-depleted system by heating biomass, like wood and manure with less or no oxygen, and BC can survive in the soil for hundreds of years (Tan et al. 2015). BC is characterized by high surface area, high porosity, active surface functional groups, and trace minerals, making it possible to extract dyes from aqueous systems as a sensible adsorbent (Zhang et al. 2018). As a sorbent, BC, with a porous nature identical to activated charcoal, is currently the most widely used and efficient adsorbent to remove water contaminants such as dyes. BC, however, is a new form of adsorbent with low cost and high performance, distinct from activated carbon. Higher temperatures and the activation time are needed for the development of activated carbon. By comparative analysis, BC is easier to manufacture and requires less electricity. BC is a renewable resource, and owing to its environmental and economic benefits, it is an excellent product for green technology to process water pollutants like dyes (Tan et al. 2015).

However, significant attention has been paid to improving the pyrolysis parameters to boost the production and properties of the resulting BC. Various variables, including biomass source and operational parameters of the pyrolysis process (time, temperature, heating rate, pressure), increase the efficacy and performance of the BC. For example, materials with heavy lignin and low moisture levels are pertinent for the production of high-yield BCs; the heating rate has an impact on production, pore volume, and surface area. Among them, the pyrolytic temperature is the most important factor in the development of high-quality BCs. In additament, significant advancements in BC design incorporating nanoparticles (NPs) and chemical and biological alteration have culminated in a specific subset of hybrid chars with expanded capabilities for the treatment of a wide range of dyes. BC activities can also be significantly impacted by pretreatment of raw material and posttreatment of BC. As seen in Fig. 7.1, pretreatment probably depends on the feed material and the intent for BC usage, covering physical (dry, crush, sieve, wash, etc.), chemical (chemical treatment, precursor and functional agents processing, etc.), and biological (bacterial treatment, etc.) methods. Posttreatment is primarily based on physical (magnetization, ball milling, etc.) and chemical (corrosive treatment, etc.) approaches (Tan et al. 2016; Tang and Zaini 2017). To date, numerous publications have illustrated pretreatment in connection to raw material decomposition methods and the resulting BC properties and also posttreatment techniques for BC characterization and their implications on dye-contaminated wastewater management.

Preceding researches have been published on the existence and implementation of BC, and several researchers have assessed the development and operation of BC on dye-contaminated wastewater. Interestingly, some research has been conducted on the engineering application to remove industrial contaminants and the recovery of

Fig. 7.1 BC production methods



BCs in recent times. This chapter describes a vast volume of existing research on BC adsorption of synthetic dyes in recent times to include a summary of the updated technology on adsorption of dyes and their implementation in engineering and regeneration. This chapter presents the relevant information of BC (basic physical and chemical properties, sources, forms, mode of production) and incorporates the process of interaction of dyes and BC.

7.2 Sources and Production

Biomass waste products, comprising agro-industrial wastes (Fathi et al. 2015), forestry waste (Boumehdi Toumi et al. 2015), and livestock and poultry manure (Yu et al. 2018), are suitable for the development of BC. BC's raw resources are primarily harvested from agricultural organic matter, including crop residues, wood organic matter, animal waste, and solid waste. The content of the BC (carbon, nitrogen, potassium, calcium) relies on the materials employed, the pyrolysis time, and temperature. The nature and surface characteristics of BC primarily depend on the type of raw resources and the pyrolysis temperature. Distinct raw materials and various temperatures of pyrolysis have differential consequences on BC's total carbon and gray content.

7.2.1 Pretreatment

Pretreatment is the first stage in the development of BC from various raw materials. These approaches can usually be categorized as physical, chemical, and biological pretreatment techniques (Fig. 7.1). In particular, physical pretreatment technology requires drying, crushing, sieving, and biomass feedstock washing. The raw material rich in lignocellulose is normally processed at 110 °C or other temperature to constant mass, crushed using a hammer mill into finer molecules, and then slashed into various parts (Essandoh et al. 2017). As a raw material, papers and cardboard are typically crushed and mixed into pulp (Randolph et al. 2017). Paper manufacturing waste is acid-washed and further washed with deionized water to acquire mineral-free sediment (Cho et al. 2017). Alga is alkaline and is probably washed with freshwater prior to pyrolysis and then processed, granulated, or flaked (Roberts and de Nys 2016).

To alter the attributes of raw material products, chemical pretreatment technology also focuses on chemical reactions. The processing of biomass raw material with chemicals to incorporate chemical precursors or functional agents into the raw material is one of the most widely used chemical pretreatment techniques. The biomass is soaked in a chemical solution throughout processing and then dried before BC production. Biomass can be managed to transform into BC-based nanocomposites with metal oxyhydroxide nanoparticles reinforced on the BC surface by the pores of formulated BC after pretreatment with metal ion solutions, for instance, MgO, AlOOH, and $SnFe_2O_4$ (Zhang et al. 2012; Zhang and Gao 2013; Rai et al. 2015). On the other side, graphene, carbon nanorods, and clay could be mixed with engineered nanoparticles and natural colloids, which also contribute significantly to the efficient development of BC-based nanocomposites (Du et al. 2020a, b; Dil et al. 2016; Liang et al. 2019). Researchers pretreat biomass to develop modified BC with expanded surface area, unique adsorption capacity, highly porous nature, etc.; corrosive chemicals like acid, alkali, and oxidant were also utilized.

A reasonably novel approach is the biological pretreatment technique that enables bioprocesses to enhance biomass feedstock for engineered BC production. Several biomass products have been exposed to the anaerobic digestion process, namely, sugar beet tailings, bagasse, industrial sludge, and animal waste, and then the products were processed by slow pyrolysis into BC (Inyang et al. 2010; Yao et al. 2014). The pretreatment of anaerobic digestion would render the procured BC to possess a larger specific surface area (SSA) and boosted adsorption potential (Inyang et al. 2010).

7.2.2 Thermal Carbonization

Thermal processes primarily include pyrolysis, hydrothermal carbonization, and gasification for raw material conversion into BC. In an anaerobic climate, pyrolysis is a thermochemical mechanism for biomass decomposition. The processing temperature, heating period, and residential time are employed to impact the pyrolysis mechanisms, which can influence the chemistry and morphological attributes of products. With increased pyrolysis temperature, BC quantities decrease, while ash and carbon products increase. Gasification is the mechanism by which the biomass is converted by gasification agents into gas fuel. Generally, the gasification temperature is greater than 800 °C. Elevated concentrations of alkali salts and alkaline earth minerals are generally present in the BC formed during gasification.

Hydrothermal carbonization (HTC) is the processing without pre-drying of wet raw material at a temperature scale of 120–260 °C into BC. Predominantly, the BC formed by HTC is called hydrochar. During the HTC, the reaction temperature is defined as the regulatory variable. Hydrochar develops ample acidic functional groups on its exterior with the rising temperature, which can enhance the capacity of dye adsorption. The porosity of the hydrochar can be improved by rising retention temperature and residence time which enhances the implementation of hydrochar being applied as an adsorbent. Gasification is the mechanism used by gasifying agents to turn biomass into BC. The temperature of gasification is usually above 800 °C. During gasification, the BC formed typically contains high concentrations of alkaline salts and soil minerals.

7.2.3 Posttreatment

Magnetic, ball milling, and corrosive (i.e., acid, alkali, or oxidation) processings are the three foremost widely employed methods for posttreatment of BC. Magnetization is the process of transforming BC into a magnetic product where magnetic iron oxides are placed into BC, like $SnFe_2O_4$, $CoFe2O_4$, and NiZnFe particles (Rai et al. 2015; Liang et al. 2019; Amin et al. 2020). Therefore, from the aqueous solution, magnetic altered BC can effectively be retrieved. Ball milling is an easy, convenient, and straightforward technique that uses kinetic energy by rotating balls to disrupt chemical bonding, modify the structure of molecules, and produce nanoscale particles. BC features, namely, specific surface area, pore size, oxygen-bearing functional groups, and adsorption capability, were strengthened after ball milling. In order to manufacture novel engineered BC, ball-milling technology, therefore, becomes an efficient engineering process. Corrosive therapies such as acid, alkali, and oxidation approaches are widely applied methods of chemical alteration that modify the BC's surface chemistry. For various reasons, corrosive chemicals, e.g., HCl, HNO_3, KOH, NaOH, $KMnO_4$, and H_2O_2, have been used to alter the BC. There are a higher surface area, more mesoporous nature, more functional groups, and improved sorption ability of the chemically modified BC.

7.3 Native-State BC

In agricultural production, agricultural waste is an umbrella term for organic products disposed of by living creatures. As shown in Table 7.1, it consists mainly of forest waste, animal and poultry waste, and processing materials from

Table 7.1 BC adsorption of dyes in aqueous solutions

BC or its composite	Dye	Kinetic model	q_e (mg g^{-1})	Isotherm model	Adsorption capacity (q_m/k_f) mg g^{-1}	Thermodynamic parameters			References
						ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K)	ΔG (kJ mol^{-1})	
1. **Native-state BC**									
Agro-industrial wastes									
Durian seed	Remazol Brilliant Blue Reactive (RBBR) dye	Pseudo-second order	147.80	Freundlich	0.18	11.98	17.16	13.08–14.16	Ahmad et al. (2015)
Corn stalks	Direct Red 23	Pseudo-second order and intraparticle diffusion	10.50	Freundlich	1.55	22.77	97.48	−4.79–(−8.12)	Fathi et al. (2015)
Peanut shell (citric acid-modified)	Methylene blue	Pseudo-second order	52.63	Freundlich	7.48	−24.33	−60.28	−18.26–(−20.07)	Wang et al. (2016)
Palm petiole	Crystal violet	Pseudo-first order, pseudo-second order, Elovich, Avrami	23.9, 24.1, 2.95E + 43, 24.0	Langmuir	226	14.80	12.90	−22.80–(−25.4)	Chahinez et al. (2020)
Coconut coir dust	Methylene blue	Pseudo-second order	11.84	Langmuir, Freundlich, and Temkin	29.50 (L), 13.62 (F).	14.97	73.0	−6.83–(−9.16)	Etim et al. (2016)
Forest wastes									
Lemongrass	Crystal violet	Pseudo-second order	37.45	Langmuir	36.10	–	–	–	Putri et al. (2020)

Stipa tenacissima fibers	Methylene blue	Pseudo-second order	110.13	Sips	178.75	56.36	250.40	−20–(−25.27)	Bouguettoucha et al. (2016)
Alfa grass	Methylene blue	Pseudo-second order	115.00	Langmuir	200	55.03	199.44	−1.14–(−11.38)	Boumehdi Toumi et al. (2015)
Centaurea stem	Crystal violet	Pseudo-second order	–	Langmuir	476.19	−14.38	–	–	Naderi et al. (2018)
Terminalia arjuna sawdust	Crystal violet	Pseudo-first order	7.79	Freundlich	3.39	10.32	57.86	−6.66–(−8.44)	Shakoor and Nasar (2018)
Livestock and poultry manure									
Earthworm manure EMC 400	Rhodamine B	Pseudo-second order	8.49	Langmuir	14.49	18.78	112.60	−10.77–(−13.50)	Wang et al. (2016)
EMC 500			12.21		17.39	16.64	102.69	−12.73–(−14.94)	
EMC 600			14.53		21.60	16.97	108.22	−14.13–(−16.50)	
Cattle manure	Methylene blue	Pseudo-second order	193.79	Langmuir	192.31	−16.16	82.49	−6.43–(−8.88)	Zhu et al. (2018)
Chicken feather	Crystal violet	Pseudo-first order and intraparticle diffusion	220.5	Langmuir	555.6	–	–	–	Pradhan and Bajpai (2020)
Vermicompost manure	Congo red	Pseudo-second order	14.32	Langmuir	31.28	–	–	–	Yang et al. (2016)
Chicken manure	Methyl orange	Pseudo-second order	43.85	Langmuir	41.49	7.55	32.94	−2.24–(−2.89)	Yu et al. (2018)

(continued)

Table 7.1 (continued)

BC or its composite	Dye	Kinetic model	q_e (mg g^{-1})	Isotherm model	Adsorption capacity (q_m/k_f) mg g^{-1}	Thermodynamic parameters			References
						ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K)	ΔG (kJ mol^{-1})	
2. **Composites**									
Nanomaterials									
Carbonaceous materials									
Fe_3O_4-graphene-BC composite	Crystal violet	Pseudo-first order	199.40	Langmuir	436.68	45.85	161.77	−1.49–(−4.72)	Du et al. (2020b)
LDH of NiZnFe and its composites with carbon nanotubes and data-palm BC	Reactive Black 5 (RB5)	Pseudo-second order	61.73	Langmuir	59.5	2.33	0.017	−2.85–(−3.36)	Amin et al. (2020)
Graphene oxide-BC	Methylene blue	Pseudo-second order	102.04	Langmuir	147.0	–	–	–	Abd-Elhamid et al. (2019)
	Crystal violet		70.20	Langmuir	70.0	73.0	260.81	−5.77–(−16.44)	
Zinc oxide nanorods with BC	Crystal violet	Pseudo-second order and intraparticle diffusion	79.18	Langmuir	113.6	53.55	216.63	−7.67–(−18.42)	Dil et al. (2016)
Metal oxides and MOF									
$SnFe_2O_4$@BC magnetic nanocomposite	Crystal violet	Pseudo-second order and intraparticle diffusion	46.74	Langmuir and Freundlich	105.26 and 104.71, respectively	41.02	147	−3.52–(−6.46)	Rai et al. (2015)
$CoFe_2O_4$/BC magnetic composite	Gentian violet	Pseudo-second order	193.4	Langmuir	203.3	24.60	127. 87	−13.51–(−15.42)	Liang et al. (2019)

Magnetized orange peel waste	Crystal violet	Pseudo-second order and intraparticle diffusion	92.590	Langmuir	555.55	–	–	–	Ahmed et al. (2020)
Macroalgae BC nanomaterials [Bi_2MoO_6/AKB composite (BKBC)]	Methylene blue	Pseudo-first and pseudo-second order	42.11and183.49, respectively	–	–	–	–	–	Zhou et al. (2018)
Cucumber peel BC and chromium-based metal-organic framework [MIL-101 (Cr)]	Acid Green 25 (AG25)	Pseudo-second order	439.64	Langmuir	294	–	–	–	Mahmoodi et al. (2019)
	Reactive Yellow 186 (RY186)	Pseudo-second order	232.70	Langmuir	345				
MIL-53-Fe MOF/magnetic magnetite/BC composites	Rhodamine B (Rh B)	Pseudo-second order	–	Langmuir	73	5.62	0.10	−25.05	Navarathna et al. (2020)
Natural materials									
Bagasse-based BC-montmorillonite (BG-MMT)	Methylene blue (MB)	Ritchie nth-order and Elovich	9.298	Freundlich and Redlich-Peterson	3.211 (Lg^{-1})	–	–	–	Yao et al. (2014)
Bagasse BC-natural attapulgite (ATP)	Reactive Brilliant Red X-3B (RBR)	Pseudo-second order	49.33	Langmuir	72.20	–	–	–	Chen et al. (2018)
Silica-composited swine manure (SMB) and rice straw (RSB) BCs with alkali-fused fly ash (AFFA)	Methylene blue (MB)	Pseudo-second-order model	81.97 and 70.92, respectively	Langmuir	142.86 and 131.58, respectively	–	–	–	Wang et al. (2020a, b)

(continued)

Table 7.1 (continued)

BC or its composite	Dye	Kinetic model	q_e (mg g^{-1})	Isotherm model	Adsorption capacity (q_m/k_f) mg g^{-1}	Thermodynamic parameters			References
						ΔH (kJ mol^{-1})	ΔS (kJ mol^{-1} K)	ΔG (kJ mol^{-1})	
Ball-milled BC encapsulated in calcium alginate beads (CA-BMB)	Methylene blue (MB)	Ritchie's	184.3	Langmuir	1210.7	–	–	–	Wang et al. (2019)
Sugarcane bagasse BC entrapped in calcium alginate (CASB)	Methylene blue (MB)	Pseudo-second order	86.21	Langmuir	71. 21	6.06	24.93	−1.485–(−2.33)	Biswas et al. (2020)

agro-industries (Bouguettoucha et al. 2016; Yu et al. 2018; Etim et al. 2016). Numerous agricultural products and their associated waste have been manufactured worldwide each year in the present history. The key structural constituents of agricultural waste are lignin, cellulose, and hemicellulose. Lignin is an aromatic polymer mainly formed on the surface by carbonyl, hydroxyl, methyl, and other groups. The functional oxygen species, such as carbonyl and hydroxyl, comprise both hemicellulose and cellulose. In BC technology, researchers are now making a major contribution to extending the adsorption capacity of generated waste by strengthening it, using different approaches. BC study has also increasingly begun in several areas of the globe. From 2005 to date, BC technology has gained higher and higher recognition. Depending on raw materials, necessary BC applications, production methods, overall economy, and the formulation and construction of BC systems worldwide differ substantially (Tan et al. 2015).

7.3.1 Agro-industrial Wastes

Durian seeds were chemically synthesized using KOH to produce the durian seed BC by Ahmad et al. (2015) (DSAC). Based on experimental data, the percentage of dye adsorption was augmented with increasing dye concentration, temperature, and contact time. The rise in temperature led to an escalated proportion of adsorbed dye, signifying an endothermic mechanism. The pseudo-second-order model best demonstrated the adsorption kinetics, and both film and intraparticle diffusions governed the process. Confirmation of Freundlich isotherm model to obtained measurements intimated heterogeneity of the surface and unequally distributed energies. Spontaneous and endothermic nature has been observed to interpret the thermodynamic findings (Ahmad et al. 2015). Fathi et al. (2015) emphasized on evaluating the potential and effectiveness of maize stalk (CS) in the removal from aqueous solutions of diazo dye Direct Red 23 (DR23). The sorption processes have adopted the pseudo-second order in conjunction to the intraparticle diffusion kinetics with a good R^2 value. Freundlich isothermal experiments have verified DR23 to be well adsorbed, showing the multiple layer distribution of DR23 dye molecules on the adsorbent surface. Evaluation based on thermodynamic findings showed that the mechanism of adsorption is endothermic (Fathi et al. 2015). For sequestration of methylene blue (MB) from aqueous solutions, a peanut shell was used as a sorbent by mixing it with citric acid. The results of the kinetic assessment revealed that the adsorption process of the system aligned satisfactorily with the pseudo-second-order kinetics. Provided the adsorption results, the Freundlich model is a good fit, affirming surface heterogeneity with the dispersed spectrum of adsorption energies. The thermodynamic constants of adsorption were also assessed and observed to be a spontaneous and exothermic process (Wang et al. 2016).

The purpose of Chalinez' paper was to build the BC (DPP-BC) by pyrolysis of date palm petioles (DPP) and to use the potency of harvesting purified solutions from crystal violet (CV). The adsorption process is especially pH-dependent. The dataset was well assimilated to the pseudo-first-order, pseudo-second-order, and kinetic model of Avrami. The isothermal model of Langmuir adsorption was best suited to the equilibrium results. The homogeneity of the surface with evenly assigned energies and affinities is asserted by the Langmuir isotherm. The adsorption process occurred spontaneously at different modulation temperatures and was endothermic (Chahinez et al. 2020). The adsorption of methylene blue from solution to coconut coir dust (CCD) BC using comparatively cheap agricultural waste material was investigated by Etim et al. (2016). Three isothermal adsorption models, namely, Langmuir, Freundlich, and Temkin, have been tested, and adsorption has been fully tested impeccably well with these models. The kinetic data were well represented by the pseudo-second order of kinetics. The adsorption procedure was endothermic and spontaneous (Etim et al. 2016).

7.3.2 Forest Wastes

A unique cellulose acetate-integrated lemongrass leaf fiber adsorbent (TLGL-CA) was produced, and its attributes and adsorption capability for crystal violet (CV) were explored. The impacts of adsorption at different contact times and specific CV concentrations were well equated with the model of pseudo-second order. With the Langmuir isotherm model illustrating monolayer adsorption, the measured results at an equilibrium state were well-governed. The inclusion of hydroxyl and carbonyl groups on the outside of TLGL-CA and a high potential for adsorption endorse the affinity of CV to the TLGL-CA BC (Putri et al. 2020). BC has been generated using a physiochemical activation process from agricultural waste (*Stipa tenacissima* fiber). In order to extract methylene blue from an aqueous phase, the obtained BC was assessed as a methylene blue (MB) adsorbent. An upsurge in the surface area was detected when activation was accomplished with zinc chloride solution. Compared to conventional processes, the evaluation showed that a combination of water, steam, CO_2, and acetic acid was a stronger inciting agent. In order to assess the fundamentals of adsorption, pseudo-first-order, pseudo-second-order, and intraparticle diffusion rate constants were investigated; it was found that adsorption kinetics followed a pseudo-second-order and an intraparticle diffusion model, inferring that intraparticle diffusion is not just an adsorption-limiting mechanism. In comprehending MB adsorption, Sips isotherm was quite vital. A spontaneous adsorption process and the endothermic nature were evinced by the negative values of ΔG (Bouguettoucha et al. 2016). Adsorption properties of raw Alfa grass were inspected for the removal of methylene blue (MB) dye in the aqueous phase. The experimental database method indicated that the models of Langmuir and pseudo-second order accurately explained the adsorption process. The thermodynamic parameters unveiled that Alfa grass-MB adsorption was a favored endothermic and spontaneous process that bolsters Alfa grass BC interaction to MB. The comprehensive analysis of their work indicated that chemisorption was required for adsorption in contrast to physisorption (Boumehdi Toumi et al. 2015).

The capability to eliminate crystal violet from aqueous solution by the novel bio-adsorbent, *Centaurea* stem, has been deemed. The isothermal results found that both Langmuir and Freundlich models obey the process, and the maximum adsorption capacity of 476.19 mg g^{-1} was amassed for the bio-adsorbent, reflecting *Centaurea* stem's conspicuous and high potential to efficiently extract crystal violet from the aqueous phase. The thermodynamic and kinetic processes of adsorption have been investigated. The positive values of ΔH and ΔS have defined the endothermic nature of adsorption. The kinetic results demonstrate that the pseudo-second-order kinetic model was obeyed by the adsorption of crystal violet (Naderi et al. 2018). *Terminalia arjuna* sawdust (TASd) has been developed to be an effective adsorbent comprising crystal violet (CV) dye to decontaminate wastewater. With the rise in initial dye concentration, the adsorption potential was found to increase, and the equilibrium was reached within 2 h. The medium's pH should be higher than 5 for the effective decontamination of water holding CV dye by the adsorbent TASd. The isotherm studies illustrated that the experimental data complies with the Freundlich isotherm model, suggesting the adsorption of crystal violet by multilayer cooperative form. Thermodynamic experiments have reported that the process of adsorption is spontaneous, endothermic, and followed by an upsurge in entropy at the interface of the CV solution. It has been documented that as temperature rises, the efficiency of adsorptive removal of CV by TASd increases. The best one for representing kinetic data was the pseudo-first-order kinetic model (Shakoor and Nasar 2018).

7.3.3 Livestock and Poultry Manure

Earthworm manure chars (EMCs) are produced from the processing of earthworm waste. There were a high surface area of the EMCs, high porosity, and abundant chemical functional groups. The adsorption process has been heavily impacted by adsorption factors, for example, initial RB (Rhodamine B) concentration, contact time, temperature, and the pH of the reaction solution. The Langmuir isotherm model demonstrated that the mechanism of adsorption inferred monolayer adsorption well. Kinetic and thermodynamic experiments revealed that the adsorption kinetics operated well with the pseudo-second-order and the RB adsorption process was a spontaneous reaction and endothermic state. Oxygen-containing operational, functional groups on the surface of the EMCs might actually communicate with RB molecules via electron transfer, hydrogen bonding, and electrostatic attraction, resulting in a huge effect on RB adsorption (Shen et al. 2017). To adsorb methylene blue (MB) from the aqueous solution, the low-temperature BC (CMB) produced from cattle manure was analyzed. The study revealed that the developed data were well-tailored to the Langmuir isothermal model and the operation of equilibrium adsorption was a system of monolayer adsorption with equal energy distribution. Pseudo-second-order kinetics was the most appropriate model to show the biosorption of MB on BC. The thermodynamic figures demonstrated that the adsorption process was spontaneous and endothermic. CMB behaves as a sorbent by monolayer adsorption, and increasing the temperature and boosting the initial MB concentration are beneficial to the process of adsorption. In MB's adsorption mechanism on CMB200, cation exchange, electrostatic interaction, H-bonding, physical interactions, and others were entangled (Zhu et al. 2018).

For preparing adsorbent films, chicken feathers were utilized as a model adsorbent to extract crystal violet. Interestingly, the chemical composition of the reaction affects the mechanism of adsorption. Adsorption is more reliant on operation conditions, such as solution pH. Exothermic adsorption has, however, been speculated for adsorption mechanism. Freundlich isotherm implies multilayer adsorption on a heterogeneous surface, widely spread adsorption sites, and their energies (Pradhan and Bajpai 2020). The accelerating temperature of the pyrolysis was beneficial for (Congo red) CR adsorption and had a significant effect on BC dynamics. The best description of CR adsorption is the Langmuir isotherm. The kinetics is well demonstrated by the pseudo-second-order model. The experimental findings propose that the BC concentration has a major influence on the CR monolayer adsorption. Electrostatic interaction is ascertained as the decisive CR mechanism in which CR adsorption is dominated by the interaction of π-π dispersion (Yang et al. 2016). For the aqueous extraction of methyl orange (MO), BC adsorbent (CMC) was developed from chicken manure pyrolysis at 600 °C. The pseudo-second-order model correctly represented the kinetic adsorption of varying concentrations, and extrinsic mass transfer and intraparticle diffusion probably influenced the rate of adsorption. The isothermal model of Langmuir showed a better fit with the parameters determined, i.e., $R^2 \geq 99$. The mechanism for the adsorption of MO on the CMC seems to be pore filling, and electrostatic forces have been involved. Furthermore, the thermodynamic parameters of a spontaneous and endothermic system are proclaimed (Yu et al. 2018).

7.4 BC Composites with

7.4.1 Nanomaterials

7.4.1.1 Carbonaceous Materials

To improve the adsorption capability and regeneration efficiency of graphene-BC composites, a new Fe_3O_4-graphene-BC composite (GBC-Fe_3O_4) was developed. Adsorption properties were evaluated for the removal of crystal violet (CV), an industrial wastewater product. After Fe_3O_4 nanoparticles immersed the GBC surface, morphological and structural examination showed an increased surface area, higher temperature stability, and establishment of plentiful functional groups. A maximum q_m value of 436.68 mg g^{-1} at 40 °C was reported. The dynamics of functional groups, let's say aromatic C=C and C=O, –OH, C–C, and π-π, played a crucial role in the adsorption of CV. The thermodynamic investigation of isotherms from Langmuir and Freundlich showed a spontaneous endothermic process. The CV adsorbability of GBC-Fe_3O_4 recollected was 157.31 mg g^{-1}, which was marginally lower than GBC-Fe_3O_4 (199 mg g^{-1}) freshly produced. These studies have shown that GBC-Fe_3O_4 is an effective and recyclable multifunctional BC composite (Du et al. 2020b). This study scrutinized the adsorption efficiency of LDH (NiZnFe) and its composites (LDH-cnt and LDH-DPb) for the removal of RB5 dye from the solution. In all instances, the pseudo-second-order kinetic model fitted almost closely to adsorption data. A strong correlation was noted with the adsorption experiment data utilizing the Elovich kinetic model, thereby indicating a heterogeneous exterior of this adsorbent via chemisorption. Compared favorably to several other adsorbents, the impact of solution temperature was significantly higher for LDH-cnt, whereas a marginal improvement of ~2% in sorption capability and percentage removal was reported for LDH-DPb as the temperature of the solution escalated from 30 to 60 °C. Furthermore, the positive values of ΔH and ΔS were the maximum for plain LDH (NiZnFe), and, despite the negative values of ΔG, a non-spontaneous reaction of the adsorption of RB5 dye on plain LDH and hybrid adsorbents is stated. In addition, they reported an almost proper fit of the Langmuir model to the equilibrium data, indicating the monolayer coverage of RB5 dye on LDH (NiZnFe) or composite adsorbents (Amin et al. 2020).

Using TEOS (tetraethyl orthosilicate) as a linker between composite compositions, a single-mixing route for the production of GO-AC structural absorbent has been successfully executed. The GO-AC composite absorbent has been used to eliminate cationic dyes as an effective adsorbent, e.g., MB and CV, from water bodies that have been polluted. Results indicated that m-AC was integrated into GO and enhanced the thermal resilience of the resulting GO-AC composite (over ~600 °C). Analogously, AC integration has made the GO-AC structural framework appear to be a strong surface structure that improves the composite's adsorption effectiveness. Expanding the contact time and composite concentration have increased the rate of dye adsorption of MB and CV, whereas elevated dye concentration and NaCl concentration have noticed unpredictable adsorption activity. The isotherms of adsorption are suited by the equation of the Langmuir model. The pseudo-second-order kinetics for the composite GO-AC correctly represented the kinetics of adsorption. These findings, therefore, indicate that GO-AC composite is a possible low-cost adsorbent for the abatement of dye from textile wastes and polluted bodies of wastewater. In the scenario of MB dye, the GO-AC composite's desorption/reusability is more effective than in the context of CV dye (Abd-Elhamid et al. 2019). Dil et al. (2016) analysis addresses the extraction by ultrasound-aided adsorption of crystal violet dye solution employing zinc oxide nanorods armed as an adsorbent on synthesized BC. Zinc oxide nanorods were primed and filled with BC in this analysis. The use of zinc oxide nanorods has been found to be an effective, rapid, and inexpensive method of adsorption for CV extraction. Experimental system design has examined the impacts of process parameters on the percentage of CV elimination. The equilibrium data suited Langmuir pretty well. The adsorption rate was proven to obey the kinetic model of the pseudo-second order (Dil et al. 2016).

7.4.1.2 Metal Oxides and MOFs

A carbon magnetic nanocomposite ($SnFe_2O_4$@BC) was effectively produced employing a coprecipitation process and was used to adsorb CV from aqueous. The existence of stannous ferrite does not contribute to major decreases in the surface area, and thus the porosity of the BC has retained its high adsorption properties. The adsorbent has demonstrated substantial CV extraction and a high 95% elimination at a low concentration of 25 mg L^{-1}. The adsorption was done corresponding to the pH, and a higher extraction was reported to be pH 8.0. The extraction mechanism was dominated by the kinetic model of the pseudo-second order. The adsorption isothermic data shows that the Langmuir isothermic model is used to adsorb the CV. The magnetic nanocomposite adsorption potential increased from 105.26 to 158.73 mg g^{-1} with a rise in temperature of 303–323 K. The thermodynamic research findings illustrated that adsorption is an endothermic and spontaneous process. The findings reported that a strong, efficient adsorbent could be employed to extract CV from an aqueous solution using the SnFe2O4@magnetic BC nanocomposite (Rai et al. 2015).

In this piece, the composite $CoFe_2O_4$/BC has been synthesized and employed as an adsorbent for extracting GV (gentian violet) from the liquid solution. The adsorption capacity of GV was determined by the initial concentration, time of interaction, BC concentration, and solution pH. Results of equilibrium adsorption suit the Langmuir model suggesting a monolayer adsorption mechanism. GV's notable adsorption potential on $CoFe_2O_4$/BC was due to a significant bonding, namely, π-π and low electrostatic interaction between GV and $CoFe_2O_4$/BC. The mechanism of adsorption was well represented by the kinetic pseudo-second-order model. The entire process of adsorption was regulated collectively by exogenous mass transfer and intraparticle diffusion. The negative ΔG and positive ΔH suggested that $CoFe_2O_4$/BC adsorption of GV was spontaneous and endothermic in existence. The $CoFe_2O_4$/BC with low cost and high adsorption potential can be an efficient adsorbent product for wastewater extraction of GV (Liang et al. 2019).

The current research study shows the increase in OP (orange peel) adsorption efficiency for segregation of CV from aqueous solutions upon magnetization. Adsorption of CV showed to rely on reaction operation factors such as adsorbent/adsorbate concentration, contact time, solution pH, and the process temperature. Isothermal and kinetic experiments for both have shown that the experimental adsorption results were confirmed for Langmuir isotherm and pseudo-second-order kinetic models. The peak monolayer MOP adsorption (555.6 mg g^{-1}) potential was marginally higher than OP adsorption capacity (138.9 mg g^{-1}). CV decoloration was primarily observed by the chemisorption process with the concurrent involvement of the physical force of attraction. The thermodynamic analysis showed that the adsorption was spontaneous, and the MOP had heat adsorption and entropy upsurge. The CV adsorption analysis from MOP has been found to be optimum with hydrochloric acid, and up to five adsorption/desorption cycles have superior regenerative potential. The current survey asserts that MOP is unique, cost-effective, and efficient to extract dyes from wastewater (Ahmed et al. 2020).

For the efficient adsorption of methylene blue in an aqueous mixture, carbonized kelp BC (AKB) was amended by KOH, and photocatalytic Bi_2MoO_6/AKB composite (BKBC) nanomaterials have been formulated. The excellent dye adsorption efficiency of this composite may certainly be due to its large specific surface area (507.177 m^2 g^{-1}) and its pervasive prevalence of different functional groups, for instance, –OH and =C-H. In the interim, experimental evidence showed that adsorption kinetics aligned perfectly with the pseudo-second-order model. Its successful adsorption and photodegradation operation revealed its immense promise in wastewater treatment (Zhou et al. 2018). In this novel report, composite materials with various AC ratios (2.5 and 10% wt) activated carbon (AC)/metal-organic frame (MIL-101(Cr)) have been produced and employed to extract dyes from wastewater, leveraging historic RSM data models. The related dynamics of the adsorption mechanism are the weak π-π bonding and strong electrostatic attachment between the positive surface charge of AC/MIL-101(Cr) 5% and the negative charge of dye as a powerful dipole force. The amplitude of active surface sites improved as the adsorptive specific area expanded by raising the quantity of adsorbent dose. As the initial concentration of dye is minimal, the pores of adsorbents adsorb the dye efficiently on the adsorbent's surface, and equilibrium contact time becomes very short. Enhancement in dye decolorization was rendered by the volume of dye extraction at the acidic pH attributable to the more positive charge density of the adsorbent. The equilibrium data is well suited to the isothermal model of Langmuir. The findings collected confirmed that the best fit model for this adsorption was the pseudo-second order (Mahmoodi et al. 2019). Using the terephthalic acid linker and $FeCl_3$, the MIL-53-Fe metal-organic framework (MOF) was developed into an already processed, magnetic, adsorbent Douglas fir BC/Fe_3O_4 (MBC). To extract and stimulate the photodegradation of Rhodamine B (Rh B) both with and without Cr^{6+} introduction, this resultant triphase hybrid, multifunctional, magnetically retrievable, adsorptive, photocatalytic, and degradative, adsorbent (MOF-MBC) was employed. This adsorption pursued pseudo-second-order kinetics and Langmuir isotherm model for equilibrium data intimating monolayer adsorption. In Rh B sorption, electrostatic and π-π stacking interactions are assumed to perform a crucial role (Navarathna et al. 2020).

7.4.2 Natural Materials

Over the last 10 years, adsorbents derived from natural sources have piqued the scientific community's interest in utilizing these materials in adsorption techniques. There are numerous natural materials that have adsorbent properties and are found in significant amounts, but among them, siliceous materials, zeolites, clays, and their composites have been efficiently engaged to extract dyes from wastewater (Singh et al. 2018). The minerals in natural clay comprise bentonite, montmorillonite (MMT), kaolinite (KLN), sepiolite, saponite, vermiculite (VMT), zeolite, chlorite, etc. that predominantly occur as hydrous aluminum phyllosilicates together with magnesium, iron, alkali metals, and many other cations (Han et al. 2019). Some of the vital physicochemical characteristics of clay minerals encompass their surface chemistry, high surface area, particle type and size, lamellar structure, and high ion exchange capacity, making them substantial in removing a number of organic pollutants embracing dyes (Yao et al. 2014). Silica has been fetching noteworthy attraction as a modern BC modifier. Silica particles possess a hydrophilic surface because of the presence of silanol groups. The groups are weakly acidic and reactive, enabling the silica surface to be modified chemically and form composites. Silica was identified to mend the BC's carbon stability and decrease the bioaccumulation of contaminants. Nonetheless, natural adsorbents still need comprehensive treatment in order to achieve their most effective adsorbent form.

Hydrogels are three-dimensional cross-linked networks that can be polymerized using water-soluble polymers or monomers to form the gel solution by physical or chemical cross-linking. This synthesis of the hydrogel is known as "inotropic gelation." The specific features of hydrogels, for instance, desired functionality, reversibility, and biocompatibility, fulfill both material and biological needs. Hydrogel adsorbents display super high and rapid adsorption efficiency, pH independence, water affinity, ease of use, relatively high porosity, diverse morphology, and flexible magnitudes and can therefore be preferred as a substitute for dye removal (Du et al. 2020a). The fact that hydrogels are facilely manufactured from natural and synthetic polymers is another significant benefit. Besides, the entrapment of various fillers on the hydrogel matrix creates composite materials with excellent and improved thermal stability, chemical resistance, mechanical characteristics, and adsorption capability. In recent years, hydrogel-composite preparation has fetched substantial interest in environmental remediation applications comprising wastewater treatment. Hydrogels have been commonly used in dye remediation in recent decades; nevertheless, the low mechanical strength restricts their usage in removing dye contaminants due to the hostile environment through the wastewater treatment procedure. Hence, adequate reinforcing agents or fillers must be developed into hydrogel grids to escalate their mechanical strength (Du et al. 2020a).

BC has been demonstrated to be a very powerful dye removal adsorbent. Despite the fact that the chemical compositions and structures of BCs are very diverse, they have many disadvantages to being applied as a sole adsorbent, for instance, limited functionality and low anti-interference capacity. All these mentioned disadvantages led to restricted applications of BC in dye remediation. In view of this, researchers have proposed a range of modification methodologies to boost the adsorption capacity of BC. The methodologies comprise the acid-modified process, alkali-modified method, and several other modifications approach to minimize the cost of BC adsorbents and mend their sorption capability for pollutants and further extend the applications in the environmental pollution control (Chen et al. 2018), but considering adsorption capability we need some modifications. BC is a cheaper material that needs to be combined to fabricate novel adsorbents without losing their adsorbent ability (Laysandra et al. 2018). So far, a variety of BC-based composites, including nanomaterials, metal oxides, carbonated materials, MOF, natural sources, etc., have been developed as described in the earlier section. Here, we will discuss the dye adsorption strategies based on BC composites impregnated with natural materials, like clays, silica, and hydrogels. The adsorption ability of clay, silica, hydrogels, and BC can be amended by synthesizing a composite of these materials. The BC has a decent porous structure and functional groups; therefore, adding clay and silica to the BC upsurges the surface area and exchangeability, thereby boosting the adsorption capacity. Moreover, BC-based materials can also be trapped in the hydrogel and applied to the adsorption process. As an elucidation for the twofold water absorption, the physical and covalent linkage within the BC/hydrogel composite may be anticipated to coexist. Here hydrogel plays a role as scaffold support for BC, maintaining its original functional characteristics.

Earlier attempts were made by Yao et al. (2014) who developed a low-cost adsorbent by engineering a new BC for the adsorption of methylene blue (MB) dye with clay particles scattered on carbon surfaces inside the BC matrix. The BC composite has been developed using the use of MMT and/or kaolin clay, modified by the use of three biomass feedstocks: bagasse (BG), bamboo (BB), and hickory chips (HC). Physicochemical characterizations, comprising microscopy and X-ray investigations, established that clay particles were present on the BC surface and all the BC samples had large surface areas. Adsorption experiments have revealed that the existence of clay particles on carbon surfaces has significantly augmented (almost five times) the BC's MB adsorption capability. The experimental results have demonstrated that MB sorption on the clay-BC composite was regulated primarily by ion exchange mechanisms (with clay) and electrostatic attraction (with BC). The kinetic study has revealed that the sorption mechanism could be regulated by multiple mechanisms and strongly influenced by the intraparticle diffusion mechanism, and Ritchie nth-order and Elovich model kinetics were accompanied. The isotherm results showed that the MMT modification significantly augmented the BG-MMT MB sorption capacity, and the isotherm models Freundlich and Redlich-Peterson fitted better. MB sorption is therefore on a heterogeneous surface, and the process is regulated by several mechanisms consistent with the findings of the kinetic analysis. Later on, Reactive Brilliant Red X-3B (RBR) adsorption by bagasse clay-BC composites and naturally occurring at pulgite (ATP) was subsequently analyzed (Chen et al. 2018). The adsorption data exhibited a strong correlation with the isotherm Langmuir model, and the kinetic data were fitted into the pseudo-second-order model. The adsorption mechanism was due to the surface coverage and monolayer formation. The pseudo-second-order model denotes that the adsorption mechanism was the rate-limiting step encompassing valence forces via sharing or exchanging electrons between BC and RBR. These findings suggested that RBR adsorption on clay-BC involved electrostatic interactions, hydrogen bonding, π-π interactions, and surface involvement. ATP and bagasse employed a synergistic effect on the adsorption of RBR.

MB adsorption in an aqueous solution was scrutinized using state-of-the-art composite ball-milled BC (BMB) encapsulated in beads (CA-BMB) of calcium alginate (Wang et al. 2019). Sorption efficiency was compared with batch adsorption experiments between CA, BMB, and CA-BMB composites. The kinetic adsorption was well elucidated by Ritchie's kinetic model, which showed adsorption on energetically homogeneous solid surfaces by physical sorption. BMB, CA, and CA-BMB adsorption isotherms were well fitted with the Langmuir models displaying substantial changes in BMB's MB adsorption after being cross-linked with CA. The best fit with the Langmuir equation might signify that the MB adsorption phenomenon was monolayer adsorption, probable to be accomplished by Donnan's membrane equilibrium between CA and BMB. CA-BMB

(1210.7 mg g^{-1}) adsorption was in close proximity with CA (1282.2 mg g^{-1}) and much more significant than BMB alone (184.1 mg g^{-1}). Further, the impact of macroalgae (*Saccharina japonica*) (kelp) bentonite mineral co-pyrolysis on physicochemical characteristics and bentonite/BC composite's ability for cationic (CV) and anionic (Congo red) dye removal has been examined (Sewu et al. 2019b). CR and CV dye adsorption was investigated using mathematical expressions by comparing bentonite/BC composites with stand-alone pyrolysis of kelp and bentonite. The key adsorption was chemisorption up to the micropores and mesopores with a boundary layer value which indicated that the CV adsorption was subjected to mechanisms other than intraparticle diffusion. The mechanism of adsorption involved hydrogen bonding, electrostatic interactions, ion exchanges, and the interaction between the π-π and n-π.

Recently, the preparation of silica-composited BCs from alkali-fused fly ash (AFFA) and agricultural wastes (swine manure and rice straw) for boosted adsorption of MB has been performed (Wang et al. 2020a). After pyrolysis, the two different silica-composited BCs were synthesized (AFFA/SWB and AFFA/RSB) with alkaline-fused fly ash (AFFA). The MB adsorption potential of the modified BCs proportionally augmented considerably after the solution's pH escalated from 3 to 13. The adsorption data were well represented with pseudo-second-order model kinetics and Langmuir isotherm. The kinetic analysis indicated that the adsorption of MB on the two AFFA-modified BCs comprised multiple adsorption mechanisms (surface adsorption and intraparticle diffusion). The isotherm analysis revealed that both modified BCs had equally distributed surface adsorption sites. The maximum MB adsorption capacities were 143.76 mg g^{-1} and 131.58 mg g^{-1} for AFFA/SWB and AFFA/RSB, respectively. Finally, Biswas et al. (2020) designed and developed a unique strategy based on a semi-fluidized batch and continuous circuit bed for removing MB dye using bagasse BC (SB) entrapped in calcium alginate (CASB). The kinetics of MB adsorption demonstrated that 70% removal of MB could be achieved within 30 min. The sorption kinetic modeling displayed strong agreement with the pseudo-second-order kinetic model. Chemisorption was involved in the dye adsorption mechanism between the SB adsorbent. Concurrently the external mass transfer is accompanied by liquid film and intraparticle diffusion. The isotherm model Langmuir indicated a superior fit over Freundlich. Thermodynamics studies eventually indicated that the mechanism was irreversible and endothermic. Table 7.1 illustrates all the composite materials based on BC.

7.5 External Factors Affecting Adsorption Reaction

BC works in immensely precise conditions as an adsorbent. pH and temperature of the solution, and initial concentrations of adsorbate, adsorbent concentration, etc., determine the rate of adsorption and play a vital role in defining the efficacy of BC.

7.5.1 pH

One key parameter which has been established to persistently impact the manner BC is utilized as an adsorbent is pH. In the majority of studies, pH changes lead to significant effects on adsorption procedures (Srivatsav et al. 2020). The pH of the aqueous solution has been reported to affect the sorption of contaminants into BC. This is associated with the pH-dependent functional groups that contain oxygen. The surface charge and ionization of the surface of BC are therefore pH-dependent, thus distinguishing the adsorption capability to remove dye contaminants. When the pH of the aqueous solution upsurges, the functional groups are deprotonated. This causes an escalation in BC's sorption capability to cationic metals. Though the pH drops, the electrostatic repulsion forces between the dye and metal ions in the aqueous solution have surged. Subsequently, competition can arise between cations for BC adsorption sites, ensuing in reducing metal ion adsorbent material capability (Ambaye et al. 2020). The pH at zero-point change (pHzpc), a point where net charges on the surface of any adsorbent in solution turn out to be neutral, is also affecting the absorption efficiency of the active BC surface by supplying active functional groups to chemicals in water (Gautam et al. 2021).

In a study conducted by Adekola et al. (2019), it has been observed that the adsorption percentage augmented with elevated pH and reached maximum at pH 7, but then reduced moderately. Protonation of the adsorbent surface was reported to occur at low pH, and as a result, a repulsion was observed between the cationic dye Rhodamine B (RhB) and adsorbent surface with a positive charge. With the augmented solution pH, the adsorbent surface was constantly deprotonated. The adsorption was escalated owing to the attraction between the negatively charged adsorbent surface and cationic dye. An equivalent trend was observed in the research by other researchers, Yek et al. (2020), which scrutinized an impact of various operational factors on the adsorption of CR dye utilizing BC made from organic peel waste. It was detected that acid conditions persisted when pH was between 2 and 3 and the presence of H^+ ions facilitated to adsorb CR dye onto active sites of BC. Simultaneously, alkaline conditions prevailed over a pH of greater than 7, and the occurrence of OH^- ions impeded dye adsorption onto the BC by competing for the BC active sites. On the other hand, an opposite trend has been observed in the experiment on methyl violet (MV) dye adsorption with chitin-derived BC performed by Zazycki et al. (2019). For pH levels >6, the adsorption of dye was preferred, and the trend was perceived attributable to the fact that the concentration of the H^+ ions is substantial at a very low pH, and they compete for the active adsorption sites on the BC with the MV dye, consequently alleviating the dye removal percentage.

From the abovementioned results, it has been recognized that the nature of the dye acts as a catalyst in establishing the optimal pH of adsorption. The acidic pH (<2) is favored when a dye is anionic since the surface of the adsorbent is positive on account of augmented H^+ ions and electrostatically favors anionic dye attraction, and when the dye is cationic, the rising pH (>2) is triggered by the presence of OH^- ions, which alternatingly results in negative BC surface by stimulating the electrostatic attraction between the positively charged dye and the negatively charged BC surface (Sewu et al. 2019a).

7.5.2 Temperature

Adsorption reactions are either exothermic or endothermic reactions; thus, temperature plays a fundamental role in the dye adsorption mechanism. An experiment examined the effects of factors like the adsorbent concentration, pH, and temperature on the adsorption characteristics of MB dye from the aqueous solution into sludge-derived BC (Fan et al. 2017). It was observed that a rise in the temperature boosted the maximum adsorption capacity, signifying that an escalation in operating temperature improved the adsorption behavior, which can be elucidated by the endothermic reaction of the MB adsorption on BC. In addition, Wang et al. (2020b) also found the same results. They observed an escalation in the adsorption capacity for acridine orange (AO) by NiAl-layered double oxide-modified magnetic corncob BC (MC1/NiAl-LDO) with an increase in the temperature. In another study conducted by Yang et al. (2014), where the estimation of adsorption capability of bamboo BC for metal-complex dye was performed, the same trend was observed. The adsorption capacity augmented with temperatures from 20 to 40 °C for the tested dye concentrations. It was suggested that the temperature effects could be ascribed to the reduction in the viscosity of the solution with the temperature rise. The temperature with a relative importance of 28.67% seemed to be the most impactful adsorption parameter by the artificial neural network. In contrast, Chen et al. (2019a, b) conducted adsorption studies of four dyes, viz., Direct Red (DR), Acid Orange II (AO), React Blue 19 (RB), and methylene blue (MB), using sludge-rice husk BC (SRHB) and noticed that the adsorption capabilities augmented with the escalating temperature in the case of RB and MB, whereas the adsorption of DR and AO onto SRHB was exothermic, the adsorption capacities reduced accompanied by the rising temperature. It can be concluded that the dye molecules have enough energy at higher temperatures to interact with the surface of BC. Into the bargain, increasing temperatures also attenuate the viscosity and diffusion of dye molecules via the external surface and inner pores of the material.

7.5.3 Adsorbent Concentration

The amount of BC also affects the adsorption capacity and is the chief factor to be taken into account. In a dye adsorption study with wet-torrefied microalgal BC, the percentage of removal and adsorption capacity was strongly affected by the adsorbent dose. Even with a slight upsurge in adsorbent dosage, the removal rate was substantially augmented (approx. 80% higher) and remained constant after a specific highest dosage was achieved. The authors (Yu et al. 2021) claimed that this phenomenon was owing to the fact that at maximum doses of adsorbent, the number of active sites and the adsorption surface area were dramatically escalated, which successively enhanced the percentages of the dye removal from water. The magnification in the dye removal rate was attributable to the upsurge in adsorbent doses, which amplified active sites for both the adsorption and the adsorbent surface area. Nonetheless, after a certain dosage of the BC, the dye adsorption rate remained constant as a consequence of the reduction in dye molecules adsorbed per unit mass of adsorbent (Nautiyal et al. 2016). Thus, the general removal efficiency of dye by BC will not be altered once a point of equilibrium is attained. High BC concentrations have a positive effect on dye removal. The optimal dose is therefore useful, as it is a fundamental parameter in reducing the cost of BC industrial production.

7.5.4 Initial Dye Concentration

The initial dye concentration could be associated with an adsorbent's adsorption capacity. Overall, with the rise in initial dye concentrations, the removal percentage drops as long as the active site on the adsorbent surface is saturated, while with the upsurge in initial dye concentration, the removal percentage augments in case if the active site is unsaturated where the maximum concentration of dye will act as a catalyst for mass transfer toward adsorption. It was reported that when the initial dye concentration rose from 5 to 360 mg L^{-1}, the removal percentage of MB reduced from 89.78 to 26.32%. An analogous trend has been detected in CR adsorption where the removal rate was dropped from 97.10% to 54.72% when the initial concentration of the dye augmented from 10 to 550 mg L^{-1} (Yu et al. 2021); there are examples in which the rise in dye levels ultimately increased the BC adsorption potential until an equilibrium is attained, beyond which no further adsorption was detected as dye molecules have occupied all the active sites entirely in the BC surface leaving no more space for adsorption (Wang et al. 2020a).

7.6 Adsorption Mechanism

7.6.1 Physisorption

Four forms of physical interactions (van der Waals forces, π-π interactions, hydrophobic interaction, and hydrogen bonding) accelerate the adsorption process. Van der Waals forces occur between each form of adsorbent and dye molecule. The wide surface area and porosity of BC favor the adsorption of dyes by van der Waals forces. As one of the most frequently used adsorbents, BC has a significant volume of sp^2-hybridated carbon and a two-dimensional framework in its structural composition. Various functional groups have been triggered to the carbon surface to enhance adsorption efficiency. For instance, conjugation systems such as amide, ester, aldehyde, and acetyl in BC may involve dipole-dipole associations with dyes. The separation of van der Waals forces is difficult to accomplish. Traditional methods for the recycling of BC comprise, in particular, thermal, biological, and solvent treatment. Whereas several innovative products have also been documented for the removal of BC regeneration, like wet oxidative regeneration, microwave radiation exposure, and electrochemical regeneration, these methods are costly, lead to significant alterations in physical structures, or cause significant carbon deterioration. Aromatic rings in dyes and adsorbents could generate enticing non-covalent associations, i.e., stacking. Off-centered parallel and T-shaped arrangements are two major notions of this kind of stacking. Electrostatic interaction is identified as the key CR mechanism in which the interaction of π-π dispersion is controlled by CR adsorption (Yang et al. 2016). The associated dynamics of the adsorption mechanism were the weak binding of π-π and the intense electrostatic binding between the positive surface charge of AC/MIL-101(Cr) 5% and the negative dye charge as an effective dipole force (Mahmoodi et al. 2019). It isn't easy to distinguish such interactions since they are very strong interactions. Hydrophobic contact occurs commonly between BC and respective dyes despite the hydrophilicity or hydrophobicity of BC. This kind of interaction is generally dependent on shifts in the entropy. The sorption of dyes into BC reduces the interaction between the dyes and the underlying solution and produces free water from the hydration shell of the dyes. Adsorption is thermodynamically worthwhile due to hydrophobic cooperation. While the hydrophobic association is necessary for the adsorption of dyes to BC adsorbent, it is often used to describe the process of adsorption. On the premise of such a process, the inclusion or elimination of free water from the dye hydration shell may enable to regulate its adsorption and desorption mechanism. The key association between dyes and adsorbents is unlikely in most cases due to the hydrogen bonding between anionic dyes and water. Dyes are more dispersible in the water when there is no other force for adsorption. Popular contenders to establish hydrogen bonding with dyes are functional groups such as nonaromatic hydroxyl or those containing heteroatoms with lone pair electrons in BC adsorbent. It was advantageous to build up hydrogen bonds with RB molecules when the solution pH was in the frame of pKa, –OH, and –COOH on the exterior of EMC. When the value of solution pH elevated to be higher than 7 (basic condition), –OH and –COOH were ionized as $–O^-$ and $–COO^-$. As a result, these ionized groups not only repulsed $–COO^-$ but also enticed N^+ in RB molecules based on electrostatic forces. Oxygen-containing functional domains on the exterior of EMCs, therefore, portrayed a key role in the adsorption of RB, relying on ion exchange, hydrogen bonding, and electrostatic attraction interactions (Shen et al. 2017). An overall depiction of adsorption mechanism is represented in Fig. 7.2.

AC and NAC have dynamic charges arising from the solution's adsorption of ions, such as H^+ or OH^-. For pH levels below the zero-load point, Sur-OH + H_3O^+ gives Sur-OH_2^+ + H_2O, and for pH levels above the zero-load point, Sur-OH + OH^- gives Sur-O^- + H_2O. The peak transition in the NAC spectrum suggested that a significant factor in MB adsorption on NAC was exerted by bonded –OH groups in particular. As per the FTIR spectra and the pH adsorption reliance of methylene blue (MB), electrostatic (columbic) repulsion was observed between MB and the positive charge on the AC and NAC exterior at pH below 3 (i.e., $pH \leq 3$) (Sur-OH_2^+ + MB), while for pH levels above 3 ($pH \geq 3$), electrostatic (columbic) attraction was

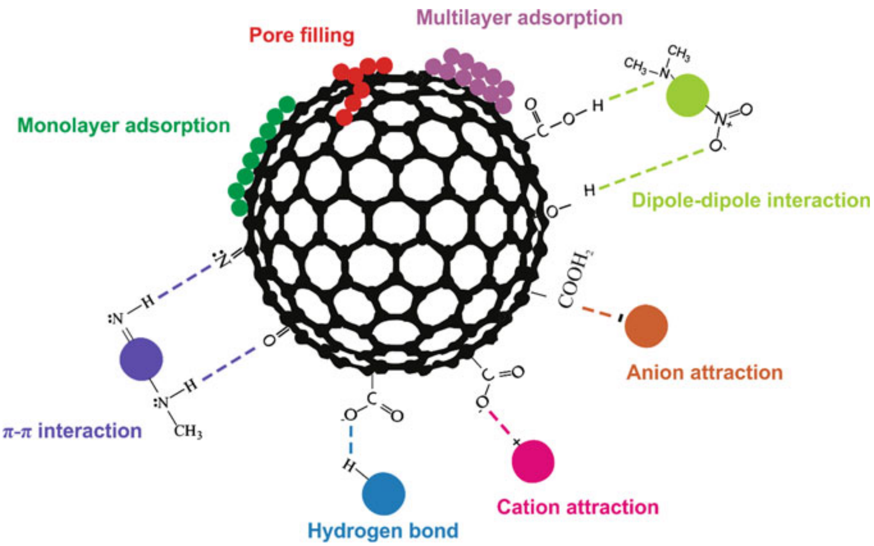


Fig. 7.2 The adsorption mechanism of dye on BC

ascertained between MB and the negative charge on the AC and MB surface (Bouguettoucha et al. 2016).

7.6.2 Chemisorption

The chemical bonding established in adsorption is covalent. This force of adsorption is often supplied by BC; dyes may create complexes with inorganic compounds such as metal oxides or metal hydroxides. Within aqueous environments, the main operational groups which bind to the exterior of metal oxides or metal hydroxides are hydroxyl groups (Rai et al. 2015). Through concurrent acidic or basic dissociation at the solid-liquid interface, metal-hydroxide complexes assemble in such a manner, giving positive or negative charges to the exterior of the complexes (Liang et al. 2019). Between the positively charged exterior of metal complexes and the negatively charged sulfonic groups of anionic dyes, strong electrostatic attraction occurs at low pH values and forms dye-metal complexes by covalent bonding (Nassar 2010). Dissociation of the dye-metal complexes may also be challenging, contributing to lesser efficiency of desorption and thus low adsorbent recyclability.

7.7 BC Regeneration

Adsorbent regeneration is one of the fundamental parameters for the practical application of BC and is very crucial for the enhancement of the adsorption process and economic viability. Regeneration of BC is a reverse adsorption operation, and it has two basic principles, viz., adsorbate desorption and adsorbate decomposition. A competitive adsorbent must exhibit a top-notch recyclable potential for industrial applications and be able to greatly decrease the BC adsorbent cost as a repetitive sorption-desorption cycle. Not only does recycling the adsorbent save money, but it also eliminates secondary environmental pollutants. Several regeneration techniques, including thermal, solvent, electrochemical, ultrasonic, microwave irradiation, supercritical fluid regeneration, etc., have been reported, but the most commonly utilized cost-efficient approach in industrial and wastewater treatment plants is thermal regeneration.

BC produced from brown seaweed *Turbinaria conoides* was used to adsorb Remazol Brilliant Blue R (RBB), and the regeneration experiments have been conducted to investigate the feasibility for three RBB sorting-elution cycles to recycle the same sorbent. BC displayed the ability in all successive cycles to maintain its first-cycle RBB-sorption potential. At the end of the third cycle, the loss of BC weight was 9.5%. In contrast to the first cycle, the reduction in RBB elimination at the end of the third cycle was just 13.5% (Vijayaraghavan and Ashokkumar 2019). In the calcium-rich BC (CRB)-mediated CR and MG adsorption study, the regeneration experiment was repeated for five cycles to assess the regeneration capacity of the used BC using ethanol washing (Dai et al. 2018). With augmented adsorption cycles, CRB's adsorption efficiency progressively declined, which could be either due to a fractional recovery of dye-adsorbed CRB after centrifugation or fractional recovery of active sites available following ethanol washing after recycling. It was imperative to notice that the adsorption potential for MG and CR was as high as >3500 and >6000 mg g^{-1}, correspondingly, after five adsorption cycles. Hence, despite the much lower adsorption potential than that of the original CRB, the regenerated CRB was still superlative over the rest of the adsorbents in dye adsorption. Lian et al. (2016) employed two different techniques, specifically direct combustion and desorption, to recycle the dye-adsorbed N-doped microporous BC (NBC800-3) with 60% ethanol. After five adsorption/combustion cycles, NBC800-3 was observed to retain up to 65% of its original adsorption potential. Concurrently, only a minor mass loss of NBC800-3 occurred owing to its high thermal stability for each cycle.

Guo et al. (2020) performed MB adsorption from an aqueous solution using *Michelia figo* (MFL)-BC and studied recycling of used adsorbents with an eco-friendly thermal process. It was noted that, even after three successive thermal treatments, the recycled MFL had an adsorption potential of about 139.4 mg g^{-1}. The regeneration study concluded that MFL and MFL-BC presented stable and effective recycling efficiency throughout the thermal regeneration method. The liberation of volatile components through carbonization facilitated the expansion of a specific area of the regenerated MFL-BC, which stimulated the adsorption potential of the regenerated MFL-BC. The regeneration efficacy could also have been boosted by π-π interactions as the recycled MFL-BC contained distinct BC graphene layers that might interact with dye molecules. Cassava slag BC (HCS) demonstrated exceptional adsorption recycling potential performed with sodium hydroxide (NaOH). It was revealed that the removal rate of Rhodamine B (RBB) by HCS was 93% after five cycles of NaOH regeneration, signifying remarkable regeneration efficiency (Wu et al. 2020). In a recent study on *Cocos nucifera* shell, the BC (CSB)-mediated removal of the basic dyes Blue 41 (BB41) and Basic Red 09 (BR09) was examined for their ability to adsorb BB41 and BR09 by different elutants such as 0.01 M of NaOH, hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and deionized water. The method of sorption-elution was repeated to establish the regeneration efficiency of the sorbent. Of the three acidic elutants, 0.01 M HCl performed better for cationic dyes with an efficiency of 99.4%. After following several cycles, CSB displayed its capability to retain the first-cycle dye sorption. Successful recycling of used adsorbents possibly will aid in reducing the usage of chemicals by confirming environmental sustainability and to upsurge adsorption potential and economic viability (Saravanan et al. 2020).

7.8 Benefits and Drawbacks of Using BC at an Industrial Scale

The most enticing aspect of BC is that it embodies a low-cost, sustainable, and easily manufactured procedure with large-scale applications relatively cheaper than the products from other chemical approaches. As an adsorbent, BC embraces numerous benefits, for instance, being environmentally friendly, inexpensive, easy to use, high surface area and microporosity, electrical conductivity, recalcitrance, and tensile strength. Plenty of precursors are available for transformation into BC and possess recyclability and high adsorption potential than other traditional adsorbents. BC also has environmental advantages and fewer environmental impacts than other adsorbents, such as activated carbon, predominantly as a consequence of carbon sequestration and energy generation throughout pyrolysis (Thompson et al. 2016). BC encompasses a significant number of residual functional groups, for example, carbonyl, carboxyl, and hydroxyl groups, on its graphitic backbone. Many of these functional groups are oxygen-containing or alkaline and offer BC a strong adsorption potential, hydrophobicity or hydrophilicity, buffering, and ion exchange capability, typically referred to as “cation exchange potential” (Chen et al. 2019a). All these abovementioned unique characteristics make them an ideal candidate for industrial applications compared to several other adsorbents.

It is reported that BC has a great potential for industrial application, but the usage of BC has some disadvantages. In most studies, BC is utilized under extremely precise dosage conditions, pH, temperature, etc. that decide how the process is performed. Consequently, successive stages are essential to eliminate the BC from wastewater prior to reuse in other applications that can raise treatment costs. Some reports have revealed that the efficacy of BC reduced after its repeated use of an adsorbent in the removal of dyes (Tran 2020). Hence, it is observed that BC, as an adsorbent, might entail auxiliary desorption practices and could possibly result in economic disadvantages. The most widely used BCs comprise large amounts of heavy metals; thus, immoderate desorption of these heavy metals raises the possibility of environmental pollution. It was identified that potentially toxic compounds, particularly polycyclic aromatic hydrocarbons (PAHs), heavy metals, and metalloids, inexorably form an association with BC (Tan et al. 2015). Odinga et al. (2020) further scrutinized the effects of environmentally persistent free radicals in BCs on soil and wastewater. It was observed that free radicals could cause a greater threat to the environment unless scrutinized and regulated. On a concluding note, prior to extending the use of BC in practice, possible detrimental effects linked with the use of BC in aqueous substances must be addressed.

7.9 Conclusion and Future Perspectives

BC is an effective and low-cost adsorbent that can be made from a range of biomass resources comprising residues of agricultural crops, forestry products, sewage sludge, and manure and has been employed for the processing of wastewater. This chapter discusses existing BC processing technologies with a focus on pretreatment of raw materials, thermal transformation, and posttreatment techniques and also explores the use of engineered BC for aquatic system dye processing and extraction. Alteration changes BC's surface characteristics (surface area, pore volume, pore size, surface charge, and surface functional groups). Combined with BC, a variety of modifiers have been used, such as clays, metals, metal oxides, and carbonaceous substances (graphene, graphene oxide, and nanorods). Proportionally, the altering factors show positive growth in adsorption ability but often negatively affect the adsorption efficiency of the intended dyes. Therefore, further examinations include the identification of suitable modifiers for precise dye targeting. It can be achieved by modifying the structure, especially the physical and chemical characteristics of adsorbents. Climate effects may also be amended to increase the performance of adsorption, particularly temperature maintenance.

The function of clay-BC composite materials as adsorbents in wastewater abatement has not been thoroughly researched. Although the surface area is so often decreased by blocking pores, the cumulative impact of BC and clay minerals dramatically boosts the ability of clay-BC composites to adsorb dyes, particularly when layered clays are coupled with BC. Further research would therefore be required to improve the understanding of surface chemistry, adsorption mechanisms, and variables affecting the adsorption potential of clay-BC composite materials produced by clay minerals. In addition, a favorable end use may be the use of waste clay materials such as red mud, steel slag, etc., with BC operation. In addition to many pollutants, alteration of BC with metals or metal oxides has been documented. The adsorption of an assigned contaminant was negatively affected by certain triggers, prompting further scrutiny. For different implementations, functionalized BC has currently been successfully introduced. BC's functionalization method facilitates the modification of its surface properties and functionality and can therefore be implemented in different industrial processes. Further to boost the functionality of various applications, the development of functionalized BC-based composites is advised. Most experiments on adsorption have been performed under laboratory settings. The natural atmosphere, moreover, frequently varies drastically from the laboratory setting, especially with regard to continuous pH and temperature variations, each of which has a major impact on the adsorption of most of the adsorbents investigated. To evaluate the strength and efficiency of BCs and their composites in wastewater management, pilot-scale experimentation will therefore be critical. In addition, to determine the stability of BC composites and assure their environmental sustainability, long-term inspections are necessary. In conjunction, there is limited knowledge on the large-scale development of engineered BCs, and it should be published. Another main endeavor that will allow the assessment of the feasibility of BC-based remediation relative to other methods accessible is the cost of production investigation.

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Application of Biochar for the Treatment of Textile Dyes and Wastewater

8

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Abstract

Textile industries use several types of synthetic toxic dyes having complex aromatic structures that lead to detrimental effects on ecosystems. Discharge of effluent directly into the natural environment (soil and water) adversely affects the biota. In recent years, different dye removal strategies have been adopted to control textile pollution including physical, chemical, and biological methods. Recently, exploring agro-industrial waste biomasses into biochar is being studied as an economically sustainable approach for remediation of textile wastewater and other environmental pollutants. Biochar is a black carbon produced after the pyrolysis of biomass under oxygen-limited conditions. It is proving the best adsorbent which offers advantages like high surface area, porosity, and active functional groups important for the effective removal of organic and inorganic contaminants. Biochar reduces the bioavailability of contaminants with additional environmental benefits including soil fertilizer and mitigation of climate change. The present book chapter provides a brief outline of dye types and toxicity and biochar preparation and characteristics with a detailed account of mechanism of biochar-assisted remediation of hazardous textile dyes and wastewater.

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Keywords

Biochar · Pollution · Pyrolysis · Sorption · Textile dye

8.1 Introduction

The developmental anthropogenic activities like manufacturing, transportation, and construction produce a huge quantity of organic and inorganic pollutants which rigorously affect the natural environment leading to air, soil, and water pollution. Few examples demonstrated how human activities are liable to pollute the environment; excessive use of fertilizers, pesticides runoff from the agricultural field, and release of effluents with additional harmful chemicals from various industries emit offensive smell and pollute water bodies. This contaminated water is unsafe for people and the environment (Dil et al. 2017). Environmental pollutants can be classified as chemical, biological, and physical substances that are unwittingly discharged into the natural ecosystem which are consequently injurious to the living organism. Waterborne diseases and other health-related problems are mainly associated with water pollution. The water-carrying pollutants were taken up by aquatic organisms and could reach into the food chain. Thus consumption of such foods adversely affects the body in terms of dry, rough skin and consequently induces cancer-like diseases. However, owing to the valuable coloring properties, an enormous amount of synthetic colors are utilized in diverse industries like paper, food, leather, cosmetics, petrochemicals, and textile. The textile industry in India is booming due to its economic influence on the manufacture and export of goods, thereby leading to a large amount of contaminated water as a highly radioactive, mutagenic, and carcinogenic effluent (Ahmed et al. 2015). Throughout the world, dye production is approximately 800,000 tons per annum. Among these 10–15% dye is released as an effluent which is mainly allied with incomplete exhaustion during the dyeing process. Dyes are broadly classified into natural (indigoid dyes, flavones, anthraquinone, anthocyanidins, carotenoids, etc.) and synthetic dye (basic dye, acidic dye, direct dye, azoic dye, dispersive dye, reactive dye, vat dye, mordant dye, sulfur dye, etc.) depending on the source. Despite its widespread use in the textile industry, it has also been used to monitor protozoa and fungal contamination as a pH predictor, microbiological stain, and additives in medicine and aquaculture (Schnick 1988; Moturi and Charya 2009). However, it is highly toxic to species, which eventually decreases their growth, fertility rates, and food intake with holding carcinogenic features (Culp et al. 1999). Nevertheless, for the survival of organisms, water is an imperative element on earth. Water covers 71% of the earth's surface, and among those 97% are found in the ocean that can't be used for irrigation and drinking purpose. The remaining available freshwater is 3%; out of this 2.997% water is fastened in glaciers. Thus, the access of water for irrigation and other domestic usage is only 0.003%. This denotes water as an extremely valuable resource. Hence, water pollution raising the scarcity of freshwater resources will be a key factor affecting the financial growth of various countries throughout the world. These dye materials alter the water properties; therefore, scientists are given the prime importance for exclusion of pollutants from the aqueous solution. Hence, treating the effluent containing toxic residual dyes was a crucial parameter to reduce the risk of contaminants to the ecosystem. Several researchers have previously used various methods of decolorization of colorants, such as biodegradation, phytoremediation, adsorption, chemical precipitation, photolysis, electrochemical treatment, chemical oxidation, and reduction (Jadhav et al. 2010). These decolorization strategies, however, have a number of disadvantages, such as increased costs, enormous sludge generation, high dissolved O_2 requirements, and the development of highly toxic intermediates such as leucomalachite (Bayramoglu et al. 2009). However, adsorption is one of the more cost-effective approaches used for the treatment of textile waste. Therefore, an exploration of the secret potential of biochar extracted from agro-industrial waste biomass for higher dye sorption capability reveals a sustainable cost-effective strategy for the treatment of polluted dye in the wastewater. Biochar (BC) is nothing but the carbon-rich solid by-product formed by heating to temperatures between 300 and 1000 °C under oxygen-limiting conditions after the carbonization of biomass (Lehmann and Joseph 2009). There are four main areas including agricultural field, waste management, climate change mitigation, and energy production where biochar could be effectively adopted (Lehmann and Joseph 2009). Biochar has ideal physicochemical properties for the secure and long-term retention of carbon in the atmosphere and, possibly, amendment of the soil. Mainly, biochar consists of nutrient components and also has alkaline pH which offers certain advantages not only in remediation but also in agronomical fields for yield improvement via changing the physicochemical properties of soil (Blackwell et al. 2009). BC is a low-cost carbonate sorbent with a better ability to extract organic and inorganic contaminants from the polluted site (Enaime et al. 2020). It is proving the best adsorbent which offers advantages like high surface area, porosity, and active functional groups important for the effective removal of organic and inorganic contaminants. The upcoming phase toward a sustainable future will be the treatment of wastewater for multiple treatments and resource recovery purposes, such as water, nutrients, and electricity. However, biochar is the most widely used technique to remove the pollutants and thus would be a better option to remove the wastewater pollutants. Recently, several industrial toxic pollutants discharged as wastewater have been efficiently sorbed by using biochar (Enaime et al. 2020). Thus, the present book chapter provides a brief outline of dye types and toxicity and biochar preparation and characteristics with a detailed account of the mechanism of biochar-assisted remediation of hazardous textile dyes and wastewater.

8.2 Pollution

Pollution is an unnatural shift in the climate that adversely affects the ecosystem, including livestock, plants, and human beings. The population of India has increased by approximately 1.3 billion people. Overexploitation of resources such as industrialization and certain anthropogenic activities has also been carried out to the

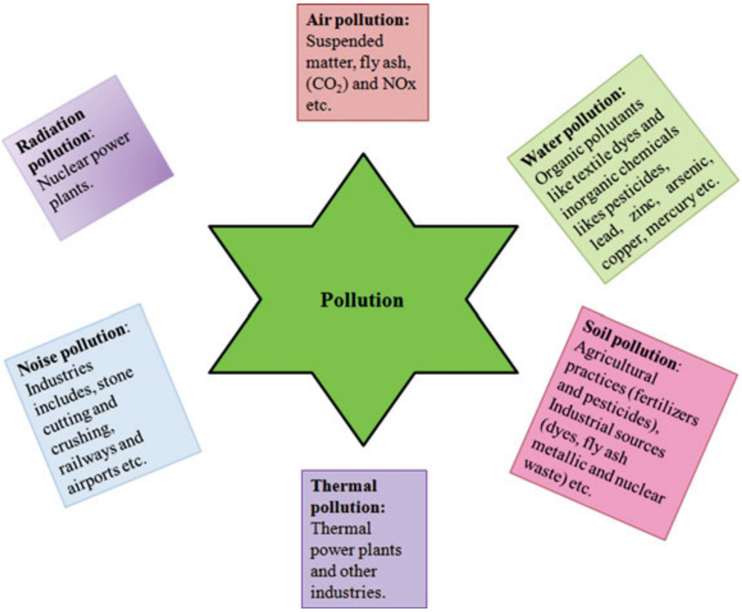

Fig. 8.1 Different types of environmental pollutions

detriment of the ecosystem in order to meet the demands of people. Environmental contaminants most prominently occur in terms of the type of liquids, solids, and gases, which exceed the agreed limits. There are six types of pollution as shown in Fig. 8.1. Water pollution is the second most pollutant after the air. Water is the substance necessary for every living organism to survive on the planet and to perform a normal routine function. Similarly, unpolluted fresh drinking water plays a censorious role in a healthy life.

However, water contamination is a big concern due to overpopulation and industrialization. The textile industry is one of those that commonly uses different coloring agents to display more appealing clothing. These industries use many types of coloring with complex aromatic structures that impart color to the fabrics and have different characteristics, such as solubility, speed, color, and content. In the dyeing process, it is necessary to have chromophore and auxochrome chemical groups.

8.2.1 Chromophore

It is an active atom possessing the capability to absorb light in the visible region (400–800 nm) which is responsible for giving color to the particular dye. There are different types of chromophores such as azo (–N=N–), carbon-nitrogen (>C=NH or –CH=N–), sulfur (>C=S), carbon (=C=C=), nitro (=NO–OH or –NO_2), nitroso (N–OH or –NO), and carbonyl (=C=O), respectively, referred to as a chromogen.

8.2.2 Auxochrome

Auxochrome is a group of atoms attached to a chromophore; eventually it changes the wavelength and absorption intensity of chromophores. The dye binding to the fabric should have a stable bond which is accomplished by the auxochromic groups; either it might be acidic (–OH, –S–OH, and –COOH) or basic (NH–R, NH, and N–R) in nature correspondingly. Dyes take the leading role in the global textile market until purple dye which was chemically synthesized by William Perkin, and thereafter in the twentieth century, synthetic dyes became dominant over natural dyes.

8.3 Classification of Dyes

Different types of dyes have unique properties like structure and bonding ability toward the specific fiber. Some of the dyes are firmly bound to the fabrics by chemical bonding, while others are bonded by van der Waal forces. Dyes are majorly classified concurring to their origin such as natural and synthetic dyes.

8.3.1 Natural Dye

Natural dyes are acquired from natural plant, animal, and mineral sources. According to its biochemical composition, natural dyes are classified as indigoid dyes obtained from a bush pea family, i.e., *Indigofera tinctoria*. Flavone dyes are isoflavones, and flavone derivatives, i.e., hydroxy- and methoxy-substituted groups, reveal yellow color possessing light fastness properties. Usually, anthraquinone-based dyes exhibit red color isolated from the plants and insects. Alpha-hydroxy-naphthoquinones are extracted from the *Lawsonia inermis* cultivated in Egypt and India and give an orange color shade. Carajurin and direct orange dye is a natural member of anthocyanidins isolated from the *Bignonia chica* leaves. Dihydropyran is closely related to the flavones and provides dark shade. Carotenoids have conjugated double bonds that are responsible for providing color including saffron and annatto.

8.3.2 Synthetic Dyes

Synthetic dyes are made from organic or inorganic sources. Depending on their chemical structure and dyeing process, different types of synthetic dyes include the following: Basic dyes possess positively charged chromophore, which are more attracted toward the oppositely charged substrate via electrostatic interaction. Acidic have one or more acidic groups liable for getting the negative charge on dye and include food colors. Direct dyes are water-soluble aromatic compounds also known as substantive dye and revealed bright shades on fabrics. Azoic dyes are made up of aromatic amines mostly naphthol or phenol or aniline and created with the aid of two chemical compounds reacted with each other which were diazo base or diazo salt or diazo compound and naphthol as a coupling compound. Dispersive dyes are water-insoluble, pursuing fine particle size possessing larger surface areas which are assisted to absorb by the substrates. Reactive dyes have chromophore groups possessing the ability to bind the fiber covalently. Vat dyes are produced from carbazole, anthraquinone, and indigo. It is an insoluble complex of polycyclic compound readily soluble in sodium hydrosulfide (Na-S-H) solution at 50 °C temperature with color fastness property. Mordant dyes are an organic or inorganic molecule which is required for the coloring agent to act as a dye. Solvent dyes are water-insoluble while soluble in an organic solvent such as alcohols. In sulfur dyes chromophore of these dyes contains sulfur as an integral part and sodium sulfide is used in dyeing process. Pigment dyes are azoic compounds with metal content and maintain the crystalline structure throughout the coloring process. Ingrain dyes (developed dyes) are directly synthesized on the fabrics. Commonly, phenol and naphthol are used as coupling reagents during the dyeing process.

8.4 Hazardous Effect of Textile Dyes

Usage of dyestuff in the textile industry is up to 80% which is largest than the other sectors. Approximately 30–50 L of water is needed to make 1 kg of fabric, depending on the type of dye used in the dyeing application. According to the World Bank, 17–20% of water pollution mainly arises from the textile dyeing industries as a huge amount of synthetic dyes are released into a water stream. Mainly in India, 55,000 million cubic meters of wastewater are discharged daily from the textile field, of which 68.5 million are wastewater directly mixed into the river without any pretreatment (*Government of India Ministry of Water Resources Annual Report 1999–2000 New Delhi* 2005) leading to immense toxicity (i.e., mutagenic, teratogenic, and carcinogenic) which is not only limited to mankind but also the flora, fauna, and livestock presented in the concerning environment.

Most of the azo dyes are harmful and have been reported to cause human cancer: hepatocarcinomas, sarcomas, and also chromosomal aberration in mammalian cells and ultimately owing to chromosomal breakage (Ratna and Padhi 2012). According to Chen (2006), the carcinogenic amines are increased by azo and nitro compounds eliminated in the sediments of marine animals. With this reactive dyes have also shown symptoms such as respiratory sensitization, itching, watery eyes, sneezing, coughing, and wheezing symptoms with carcinogenic properties (Rangabhashiyam et al. 2013). Dispersive and vat dyes are also familiar with skin sensitivity. Toxicity assessments of several types of dyes were tested on various model organisms for proving the toxic nature of dyes.

8.5 Remedial Technologies for Textile Dyes

Now, different methods are implemented to remove and neutralize the hazardous chemicals and colors from textile effluent on the basis of its efficacy which includes chemical, biological, physical, and some other technologies as shown in Fig. 8.2.

8.5.1 Chemical Methods

Chemical methods involve strong oxidizing agents such as H_2O_2, ozone which is a highly unstable gas, Fenton's reagent (H_2O_2-fe), and sodium hypochloride (NaOCL) to oxidize the organic-inorganic pollutants including the process of mineralization of textile dyes. H_2O_2 is a potent oxidizing agent, harmless since each organism has the ability to convert it to oxygen and water. However, this single compound is unable and needs composite with ferrous salt for the efficacious treatment of textile dyes. For the remediation purpose, ozonization process has been adopted (Kurbus et al. 2003) mostly against the drinking water for generating a clean and clear solution by generating a free radical which is extremely reactive against the substrate. But the process has some drawbacks such as higher equipment cost and duration time, and also it generates hazardous intermediate by-products. Among the advanced oxidation processes, Fenton reagent (H_2O_2-fe) is one of the best oxidation processes for the mineralization of numerous textile dyes and persistent organic pollutants presented in the wastewater bodies. Using Fenton reagent, i.e., H_2O_2 with $FeSO_4$, higher dye concentration containing effluent can be treated efficiently but requires the highest energy. However, this method is restricted due to the production of secondary pollutants, i.e., precipitate of $Fe(OH)_3$ promoting water pollution

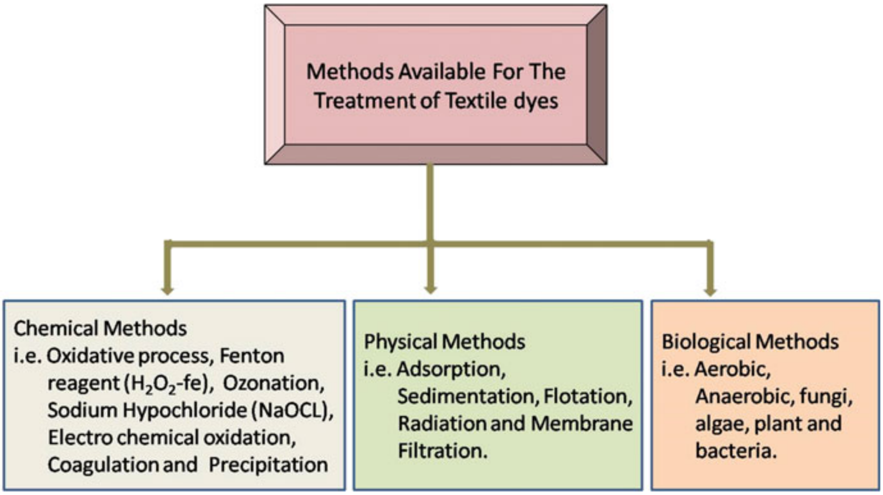

Fig. 8.2 Remedial technologies for the treatment of textile dyes and wastewater

problem. Similarly, sodium hypochloride (NaOCL) is a chemical method where effluent decolorization rate is directly proportional to the intensity of chlorine compound present in the reaction mixture. Commonly, those dyes comprising naphthalene ring having amino group are greatly favored for the successful chlorine decolorization process. In the electrochemical method, chloride of sodium, potassium, magnesium, and calcium are mostly used as an electrolyte. In this process, metal complexes are removed via the precipitation reaction with the electrode while applying an electric charge on it.

TiO_2 and UV radiation coupled photocatalysis has the ability to degrade toxic organic substrates or dyes as well. It works actively at lower temperature and pressure and doesn't require costly oxidants. However, this process also produces secondary by-products which might be extremely toxic than the maternal compound. Thus, the above chemical methods are restricted to use in the treatment of textile dyes because it possesses the following drawbacks such as chemical expensiveness and also it arises secondary pollution problem and some of them also create a disposal problem.

8.5.2 Biological Methods

A biological method is an eco-friendly approach extensively used for the treatment of textile effluent. Since 1970 efforts have been taken into consideration for the isolation of bacterial cultures, i.e., *Bacillus subtilis*, *Bacillus cereus*, and *Aeromonas hydrophila*, for the degradation of azo dyes. Several researchers have reported that the remediation of textile dyes is successfully achieved through microorganisms including bacteria (Pearce et al. 2003) and fungi (i.e., *Dichomitus squalens*, *Daedalea flavida*, *Irpex flavus*, *P. chrysosporium BKM-F-1767*, and *Polyporus sanguineus*) (Chander and Arora 2007).

The fungal system releases numerous enzymes like manganese-dependent peroxidases, lignin peroxidase, glucose-1-oxidase, phenol oxidase, and laccase playing a key role in the degradation of effluent containing azo dyes. At the present moment, bacterial-assisted color removal system has been extensively applied for the management of textile dyes. Some algae like *Chlorella* and *Oscillatoria* belonging to aquatic organism secrete azo reductase enzyme liable to interrupt the azo bond that existed in dye structure (Aksu 2005). Many plant systems include *Aster amellus* and *Zinnia angustifolia*, and some aquatic plants such as *Elodea canadensis*, *Elodea nuttallii*, *Ceratophyllum demersum*, and *Hydrilla verticillata* have been found to degrade the textile dyes (Khandare and Govindwar 2015). Plants secreted oxidoreductive class of enzymes like laccase, veratryl alcohol oxidase, azo reductase, riboflavin reductase, tyrosinase, lignin peroxidase, and dichlorophenolindophenol reductase which have ability to convert the complex structure of dyes into a simpler form. Common advantages and disadvantages of all these strategies are demonstrated in Table 8.1.

Table 8.1 Common advantages and disadvantages of different techniques available for the management of wastewater

	Advantages	Disadvantages
Chemical methods	It has ability to decolorize the soluble as well as insoluble colorants effectively Treated a wide range of pollutants	Chemicals used in this process exhibit their expensiveness Sludge disposal problem
Biological methods	At lower concentrations, it works efficiently. It also reduces COD levels	Require longer time (1–2 days). High sensitivity. Expensive cost for maintaining its culture. Very difficult to scale up this process
Physical methods	Eco-friendly approach and greater adsorption capacity Waste material into value-added material indicates its cost-effectiveness It can be regenerated with minimal loss of adsorbent Different pollutants can be treated successfully	Disposal problem Regeneration cost

8.5.3 Physical Methods

The physical methods include sedimentation, flotation, radiation, membrane filtration, and adsorption. In sedimentation, the suspended particles present in the aqueous solution are determined by the gravitational process. Consequently, reducing the consumption of chemicals is required in the process of coagulation.

Flotation is a simple process given an alternative to sedimentation to remove the total flocs. This process is basically applied to the mineral called froth flotation. Even various bubble generation methods have also been extensively used for the removal of the contaminants including dispersed air and dissolved air flotation (Kitchener and Gochin 1981). Different types of flotation processes are available on the basis of size and its mechanism, i.e., foam fractionation, foam flotation, ion flotation, and micro- and ultra-flotation used in industrial applications. Even several textile dyes were efficiently removed by the dispersed-air flotation process. However, these methods also come up with some drawbacks such as greater requirement of collector reagent, nonbiodegradable compound, and toxicological effects of generated by-products on the environment.

Radiation is a technique that originally comes from chemistry and showed promising results in wastewater treatment (organic pollutants). This process generates high energy flux significantly responsible for the radiolysis of water eventually forming highly reactive species to decompose the hazardous organic pollutants from the environment (Liau and Chiang 2007). A different type of radiation includes gamma-ray, X-rays, and electron beams which have been widely used for the management of wastewater pollutants. However, this technique also has a disadvantage; it is unable to treat a larger volume of effluent.

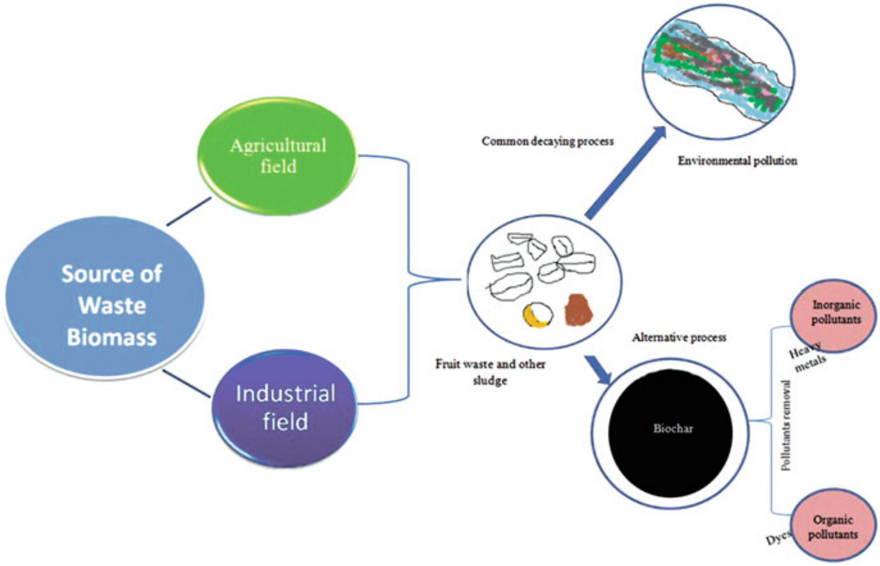

Fig. 8.3 Biomass source for the preparation of biochar

Membrane filtration is the method to evacuate dye particles from the water. Membrane pore size is a crucial parameter influence on the membrane. Membrane filtration includes reverse osmosis (<0.002 μm), ultrafiltration (0.2–0.02 μm), and nano-filtrations (<0.002 μm) which are commonly used in the industrial process for refining or purifying the final products. However, this method has major disadvantages like limited membrane life and expensive periodic replacement.

Owing to the above disadvantages in the abovementioned methods, adsorption is one of the viable methods for extracting dissolved contaminants from aqueous solution or effluent. Different adsorbents like ion exchangers, activated carbon, and inorganic materials with higher surfaces are used in adsorption applications. Among these, activated carbons and biochar are effective adsorbents demonstrating microporous properties and superior sorption ability. However, biochar is an excellent alternative adsorbent for the elimination of diverse organic-inorganic contaminants. Exploring diverse agro-industrial waste biomasses into the biochar is a cost-effective flourishing treatment for remediation of fabric dyes and effluent also. For the biochar preparation, various types of agro-industrial waste biomasses have been utilized which include plant waste biomass, animal manure, industrial waste and sewage sludge (sugar factory, paper mill, food processing waste, etc.), and forest biomasses as demonstrated in Fig. 8.3 (Ahmad et al. 2014; Vyavahare et al. 2021). The sorption capacity is totally dependent on the pyrolysis temperature and physiochemical properties of biochar. Thus, biochar has been recognized as an effective adsorbent significantly applied in the management of environmental pollutants (Ahmad et al. 2014). Currently, most biochar-assisted color removals practices have been done successfully which are demonstrated in Table 8.2. As

Table 8.2 Different biochars adopted for the treatment of organic and inorganic pollutants and wastewater

Sr. no.	Adsorbent	Pyrolysis temperature (°C)	Yield (%)	Moisture (%)	Ash (%)	pH	pHpzc	Surface area (m^2/g)	Targeted pollutants	Sorption percentage (%)/ capacity (mg/g)	Toxicity	References
1.	Pine needle biochar	700 (6 h)	14 ± 0.5	NA	2.20	NA	NA	490.8	Naphthalene (NAPH)	0.005	Hemoglobinuria	Chen et al. (2008)
2.	Sugarcane bagasse biochar	800 (1 h)	NA	NA	NA	NA	NA	382.89	Malachite green	99.98%	Carcinogenic, reduction in fertility rates	Vyavahare et al. (2018)
3.	Mango leaves biochar	800 (1 h)	37	NA	15.2	10.1	7.7	168.23	Crystal violet	99.88%	Carcinogenic, respiratory and gastrointestinal track irritation	Vyavahare et al. (2019)
4.	Pine needle biochar	700 (3 h)	24.95 ± 1.31	0.01 ± 0.00	18.74	NA	NA	390.52	Trichloroethylene	211.289	Kidney damage, nephrotoxicity	Ahmad et al. (2013)
5.	Palm bark biochar	400 (30 min)	NA	4.2	NA	7.10	NA	2.46	Methylene blue	99.3% (5 mg/L^a)	Increased heart rate, cyanosis, and tissue necrosis in humans	Sun et al. (2013)
6.	*Eucalyptus* biochar	400 (30 min)	NA	4.1	NA	7.47	NA	10.35	Methylene blue	86.1% (5 mg/L^a)	Increased heart rate, cyanosis, and tissue necrosis in humans	Sun et al. (2013)
7.	Peanut shells biochar	700 (3 h)	21.89 ± 2.47	0.35 ± 0.07	8.91 ± 0.08	10.57 ± 0.05	NA	448.2	Trichloroethylene	30.74	Kidney damage, nephrotoxicity	Ahmad et al. (2012)
8.	Macroalgae-derived biochar	800 (90 min)	22.62 ± 2.01	NA	53.59	12.31	2.4	133.2	Malachite green, crystal violet, and Congo red	5306.2, 1222.5, and 345.2	Mutagenic carcinogenic, teratogenic, and respiratory toxicity	Chen et al. (2018)
9.	Sewage sludge-derived biochar	550 (2 h)	43.61	NA	NA	7.5	NA	25	Methylene blue	98% (100 mg/L^a)	Increased heart rate, cyanosis, and tissue necrosis in humans	Fan et al. (2017)

(continued)

Table 8.2 (continued)

Sr. no.	Adsorbent	Pyrolysis temperature (°C)	Yield (%)	Moisture (%)	Ash (%)	pH	pHpzc	Surface area (m^2/g)	Targeted pollutants	Sorption percentage (%)/ capacity (mg/g)	Toxicity	References
10.	Korean cabbage biochar	500 (1 h)	34.19	NA	39.22 ± 0.18	9.18	NA	11.44	Congo red and crystal violet	95.81 and 1304	Mutagenic and carcinogenic	Sewu et al. (2017)
11.	Raw sludge-derived biochar	600 (1 h)	NA	NA	NA	8.1 ± 0.2	NA	62.651	Red X-GRL	47.6	Genotoxicity, mutagenicity, and carcinogenicity	Xiao et al. (2018)
12.	Pinewood sawdust	600 (3 h)	22.1 ± 0.3	NA	1.65 ± 0.05	NA	NA	337 ± 25	Tetracycline and sulfadiazine (6.0–48 mg/L)	5.53 and 1.27	Cytotoxicity via protein photooxidation and vomiting, mental confusion or leukopenia for sulfadiazine	Li et al. (2019)
		700 (3 h)	21.1 ± 0.8	NA	1.66 ± 0.07	NA	NA	369 ± 4		7.38 and 2.84		
		800 (3 h)	20.3 ± 0.6	NA	2.02 ± 0.08	NA	NA	431 ± 18		8.66 and 4.94		
13.	Pine wood	525 (2 min)	NA	1.53 ± 0.1	9.52 ± 0.8	NA	NA	198.03 ± 11.5 cm^2/cm^3	Methylene blue	7.9 ± 0.5	Increased heart rate, cyanosis, and tissue necrosis in humans	Lonappan et al. (2016)
	Pig manure biochar	400 (2 h)	NA	7.65 ± 0.4	65.48 ± 1.8	NA	NA	346.97 ± 18.4		NA		
	Paper-derived biochar	500 (2 h)	NA	4.99 ± 0.3	12.45 ± 1.1	NA	NA	310.82 ± 21.0		8.9 ± 0.9		
14.	Turbinaria conoides biomass (seaweed)-derived biochar	500 (20 min)	27.3	NA	NA	NA	NA	NA	Remazol brilliant blue R (reactive dye)	92.5% (1000 mg/L[a])	Carcinogenic	Vijayaraghavan and Ashokkumar (2019)
15.	*Miscanthus*	850 (30 min)	NA	NA	NA	7.6	NA	500	Wastewater	Turbidity (TSS 31%)/ *E. coli* (23%)	Nausea, cramps, headaches, diarrhea, and abdominal pain	Kaetzl et al. (2020)
16.	Forestry wood waste	700 (15 h)	NA	NA	NA	NA	NA	137	Wastewater	*E. coli* (92–99%)	Diarrhea and abdominal pain	Lau et al. (2017)

[a] Indicates initial dye concentration (mg/L) taking for the sorption reaction. *NA* not applicable

shown in Table 8.2, several laboratories and field studies have been performed to explore the biochar absorbency with different contaminants which involve organic pesticides, heavy metals, antibiotics, polycyclic aromatic hydrocarbons (PAHs), textile dyes, and wastewater.

8.6 Biochar Preparation

The different thermal processes include slow pyrolysis, fast pyrolysis, and flash pyrolysis which are mainly adopted for the preparation of biochar which depends on our interest in end products. Major differences in the above processes include heating rate, operating temperature, and residence time in which it was produced.

8.6.1 Slow Pyrolysis

Different feedstocks that have been adopted in the preparation of biochar for the remediations of various contaminants are shown in Table 8.2. The slow pyrolyzed process has a higher residence time (minutes to hours) with a heating rate <10 °C/min and temperature ranging from 350 to 800 °C favorable for greater yield (15–89%) of biochar (Ahmad et al. 2012). The thermal decomposition of biomass acquired from plant compounds is gradually increased with increases in pyrolytic temperature. Stages found in pyrolysis are dehydration, depolymerization, and decomposition of feedstock. At the initial stage, biomass dehydration is carried out, and some of the compounds get volatilized and subsequently decompose the hemicelluloses, cellulose, and lignin at 300, 500, and >700 °C temperature, respectively. The biochar yield obtained from the slow pyrolysis is higher than the fast and flash pyrolysis process.

8.6.2 Fast Pyrolysis

Usually, bio-oil production is accomplished in a fast pyrolysis process. Bio-oil arises from cellulose-, hemicellulose-, and lignin-containing biomass consisting of several compounds. Residence time for fast pyrolysis process is very short (<2 s) and has a higher heating rate (∼1000 °C/s) with 400–1000 °C temperature which ultimately reduces the yield of biochar (Shah et al. 2012). Higher heating rate of fast pyrolysis simulates a key part in rapid dehydration and volatilization of biomass by removing vapors, and thus condensation yields higher bio-oil as a main product.

8.6.3 Flash Pyrolysis

In the flash pyrolysis process, biomass is converted into a gaseous product at elevated pressure (1–12 MPa). Pyrolysis conditions for flash pyrolysis are <0.5 s residence time pyrolyzed at 800–1000 °C temperature. This pyrolysis process is mainly used to convert the biomass containing a long chain of carbon, oxygen, and hydrogen into the gaseous and oil as an end product. The process that occurred during flash pyrolysis is rapid devolatilization in the inert atmosphere by applying a high heating rate and temperature (500–1000 °C) and forming gas.

8.7 Properties of Biochar

Biochar is a carbon-rich solid material with an aromatic surface resulting after burning or pyrolyzing of biomass and waste material in a zero or low oxygenated environment. Every biomass has specific chemical functional groups in its structure indicating their desired properties depending on biomass type and process of its preparation conditions. Thus, below mentioned are the common physicochemical properties of biochar.

8.7.1 Physical Properties of Biochar

Biochar prepared under lower heating rates exhibited similar-sized particles compared to the feedstock. Grinding of feedstock prior to pyrolysis increases the heat transfer rate that inclines to be very fine particles (1–100 μm) of biochar, thus making it more porous (Brewer 2012).

According to the International Union of Pure and Applied Chemistry (IUPAC), pores are divided into three types on the basis of their size: micropores (internal diameter less than 2 nm), mesopores (internal diameter less than 2–50 nm), and macropores (internal diameter greater than 50 nm) correspondingly. Thus, larger-pore materials are responsible for increasing the water-holding ability of the soil. Biochar surface area is an important property that has a crucial role in the interaction of pollutants and their surfaces; higher surface area means the participation of biochar is higher in a chemical reaction per gram of biochar. If biochar has a higher surface area, it would possess better adsorption capacity (Chen et al. 2008). The biomass pyrolyzed at higher temperature along with long residence heating times encourages the formation of micropores structure in the material. Thus, it indicates that pyrolyzing temperature significantly affects the biochar surface area and its porosity.

8.7.2 Chemical Properties of Biochar

Mostly, the chemical properties of biochar are related to aromaticity and its surface functionality. Rise in pyrolysis temperature, hydrogen, oxygen, and some volatile compounds get extracted and form a new aromatic structure of biochar by carbon-carbon bonding that is gradually limited to oxidative breakdown.

Surface active groups of feedstock are generally carboxylic acids (–COOH), hydroxyls (–OH), and alkaline chains like methyl groups (–CH_3) that varied according to the type of raw material (Brewer 2012). After pyrolysis of feedstock, prepared biochar has different surface chemistry groups that highly contributed to increasing the cation exchange capacity of the biochar. Biochar pH is another important chemical property that significantly impacts the sorption mechanism. Generally, most of the biochar surface has a negative charge and alkaline pH; this negativity and alkalinity are increased with an increasing pyrolytic temperature (Ahmad et al. 2013). These negatively charged active groups can effectively attract positively charged environmental pollutants through cation exchange capacity.

8.8 Mechanism of Sorption

The sorption interaction between the adsorbate and adsorbent basically depends on the structural and chemical properties of adsorbate and adsorbent as well, and it will be varied with its type. Protonation and deprotonation of surface functional groups can facilitate a net charge of the biochar resulting in the formation of double-layer surfaces that significantly interacts with organic pollutants via coulombic attraction.

Interaction or sorption mechanism between the biochar and pollutants is classified as covalent bonding, electrostatic attraction, surface adsorption, hydrogen bonding, coulombic interaction, π-interaction, pore filling, ion exchange, precipitation, hydrophobic interaction, and other dipole interaction (Vithanage et al. 2016).

8.8.1 Covalent Bonding

In covalent bonding, electron pairs are shared and form an irreversible chemisorption reaction which is stronger than any other non-covalent interaction. However, non-covalent interaction is generally found in the physical sorption process (physisorption) of the adsorbent.

8.8.2 Electrostatic Interaction

This interaction mainly occurs among the cationic charged pollutants and negatively charged attributed biochar surfaces (Vyavahare et al. 2018). Generally, the surface of biochar has a negative charge, and it can be controlled using pH, i.e., when the pH of the solution below its isoelectric point attributes positively charged surface of biochar, whereas solution pH higher than the isoelectric point will occupy net negative charge.

Ionic strength and pH of solution also affect the sorption reaction; it can affect positively or negatively depending on the isoelectric point of biochar.

8.8.3 Hydrogen Bonding

This reaction is carried out where the hydrogen donor, acceptor pairs are present. Usually, hydrogen donors are bonded to acceptor atoms which include nitrogen (N), fluorine (F), and oxygen (O) in the form of $–NH_2$, –COOH, and –OH functional groups (Yang and Xing 2010; Kah et al. 2017). These donor-acceptor groups might have existed on the pollutants or biochar surfaces that facilitate hydrogen bond formation. According to Gilli et al. (2009), the charge-facilitated H-bonding has three classes: positive charge-assisted (+), negative charge-assisted (−), and double charge-assisted (±) H-bonding. The small change of pk_a values between pollutants and biochar surfaces encourages H-bond formation by sharing proton. Negative charge-assisted H-bonding has strong bonding capacity among proton donor and acceptor pairs in that base and acid were acted as a proton donor and acceptor, respectively (Gilli et al. 2009). Compared to π- or hydrophobic interaction, charge-assisted H-bonding plays a significant role in sorption of weak organic pollutants on oxygen possessing biochar surfaces.

8.8.4 Coulombic Interaction

Two charged moieties are involved in coulombic interaction; if adsorbate and adsorbent have opposite charges, eventually they will interact with each other via inducing the coulombic force.

8.8.5 π-Interaction

This interaction is weaker than hydrogen bonding. In this system, aromatic rings or C=C double bond could interact with polar molecules. This sorption system also includes π-π interaction where the intermolecular attractions between the π systems occurred. Oppositely polarized quadrapoles of the system also participate in the π-π interaction.

8.8.6 Pore Filling

Biochar surfaces have micropores and mesopores structures which reveal their applicability in pollutant sorption through the pore-filling mechanism (Hao et al. 2013). Pyrolysis temperature highly influenced the contaminant sorption properties of biochar. This indicates that higher heating rates increase the overall surface area and porosity of the biochar because of rapid depolymerization reaction and hence the sorption process. The sorption process of biochar is influenced by biochar porosity; if the biochar has higher pore volumes, it will sorb a greater amount of pollutants via the internal diffusion mechanism, whereas low pore volumes of biochar have fewer pollutant sorption efficiency. Polar, nonpolar contaminants can be sorbed via pore-filling mechanisms of the biochar, depending on its type and nature of biochar.

8.8.7 Ion Exchange

Ion exchange is another sorption mechanism where cation exchange capacity is considered as one of the essential parameters for measuring the ion exchange capacity of the adsorbent. Cation exchange capacity will vary with biochar type. This process comprises ionizable cations and protons of the biochar which are exchanged through the ion exchange mechanism. However, this process depends heavily on the scale of the pollutant and the functional groups of biochar surfaces. Biochar containing minerals control its cation exchange capacity. Higher pollutant sorption on the biochar via ion exchange mechanism specifies that this biochar has greater cation exchange capacity.

8.8.8 Surface Precipitation

This process has two main aspects: One is increased pH of solution from the biochar leads to reduce the mobility of pollutants and forms precipitate with hydroxide. The second aspect of precipitation is releasing of some soluble chemicals like carbonate and phosphate from the biochar prepared at a lower pyrolytic temperature which enables the formation of surface precipitation reaction with pollutants (Cao and Harris 2010). Precipitation of contaminants has certainly occurred with alkaline biochar after thermal degradation of cellulose and hemicelluloses at moderate pyrolytic temperature (>300 °C) (Cao and Harris 2010). Mostly, biochars made up of plant biomasses are executed in the surface precipitation reaction.

8.8.9 Hydrophobic Interaction

Hydrophobic interaction is a nonspecific interaction implying the aggregation of nonpolar groups which ultimately reduces the water molecules contact. For the hydrophobic interaction, term bond is irrelevant because unspecific interactions are not triggered by intermolecular forces with adsorbents (Meyer et al. 2006). Octanol-water distribution coefficient (K_{ow}) is a chromatographic method mainly adopted for the determination of hydrophobicity of the organic chemicals.

8.8.10 Other Dipole Interaction

Dipole-induced dipole interaction (Debye interactions), permanent dipole interactions (Keesom interactions), and fluctuating dipoles (dispersive forces or London forces) are included in the other dipole interaction. These forces might be useful for the polar functional groups (ether, nitrile and alkyl halide, etc.) of the adsorbate (Yang and Xing 2010; Kah et al. 2017).

8.9 Application of Biochar

Biochar has a wide range of applications such as animal farming, building sectors, food industries, and soil and water remediation due to its unique characteristics like high sorption capacity, surface area, microporosity, and ion exchange capacity (Ahmad et al. 2014; Schmidt and Wilson 2014). In animal farming, it is used as a silage agent and feed additive which increases the antibody level. Biochar added into the soil along with molasses, ash, or slurry can act as a soil conditioner and fertilizers (Schmidt and Wilson 2014). A small bowl of biochar stored in the refrigerator absorbs bad odors and prevents the post-maturation of fruits and vegetables from increasing the storage time (Schmidt and Wilson 2014). Biochar has the ability to perform effectively a decontaminator role in soil remediation after being added into the soil. It is widely used in the treatment of sewage plants to sorb broad varieties of organic and inorganic contaminants by acting as an adsorbent and reduces the malicious odor and color of aqueous solution (Ahmad et al. 2014; Amin et al. 2016). Continuing with abovementioned applications, biochar has also been reported for the treatment of lakes and ponds water by sorbing pesticides, fertilizers, and textile dyes and promotes the aeration of water. Thus, biochar worked as an active carbon filter and microfilters for the treatment of wastewater and drinking water correspondingly (Schmidt and Wilson 2014). Prevailingly, biochar is used in textile industries for the expulsion of noxious dyes, heavy metals, and recalcitrant chemicals certainly used in the dyeing method of cloths (Vyavahare et al. 2018).

8.10 Biochar-Assisted Textile Dye Removal

Several dyes are used in the textile industry for dyeing process and are destructive for the ecosystem and thus need to be removed from the industrial effluent prior to release into the common environment. Thus, different biochars derived from agro-industrial waste, kitchen waste, microalgae, and seaweeds have been reported to remove a variety of fabric dyes through the various sorption mechanisms (Sun et al. 2013; Sewu et al. 2017; Vyavahare et al. 2018, 2019, 2021).

Despite this, pigments-extracted macroalgae, bamboo shoot shells, cassava slag, and straw-based biochar have been reported for the maximum sorption of textile dyes (Chen et al. 2018; Hou et al. 2019; Wu et al. 2020). The N-doped microporous biochar synthesized from crop straws performs orange acid 7 dye sorption in presence of ammonia (Lian et al. 2016). In addition, Zhu et al. (2019) researched the rapid removal of acid orange 7 dye by wood-based biochar due to the porous nature of biochar. Several Remazol dyes were removed by algae-derived biochar (Gokulan et al. 2019). Pig manure biochar prepared at 800 °C showed efficacious removal of direct 23 dye (Liu et al. 2016) indicating weak electrostatic force present

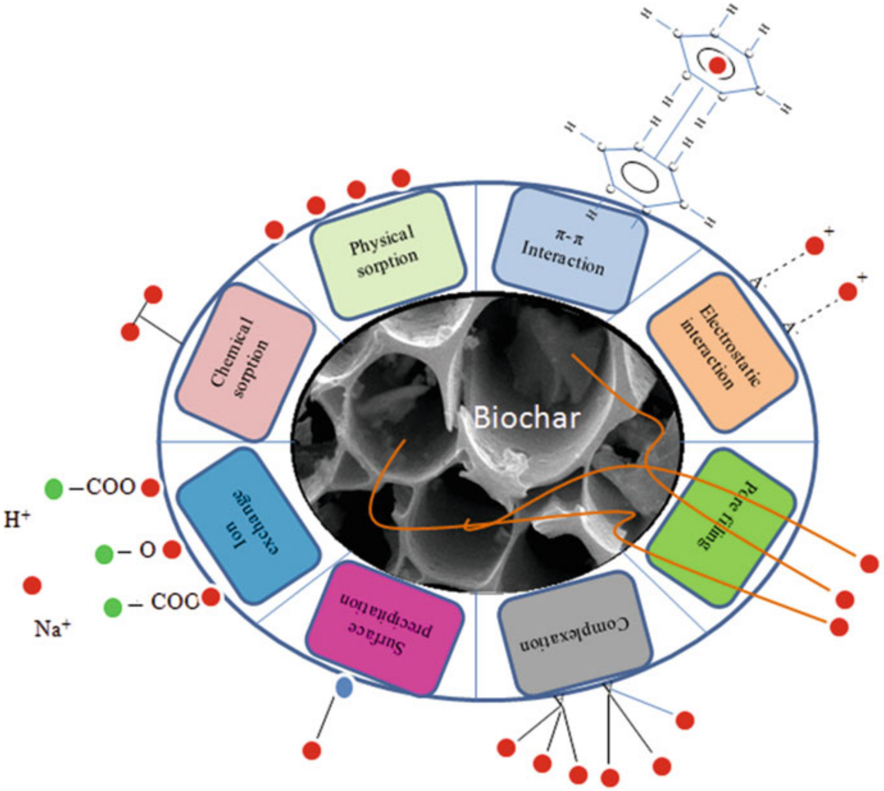

Fig. 8.4 A schematic demonstration of the sorption mechanism of pollutants

in between dye and active sites of the biochar (Fan et al. 2017). Further, Kelm et al. (2019) demonstrated the successful sorption of azo dye "Indosol Black NF1200" onto wood waste biochar via external mass transfer and electrostatic interactions. Thus, it indicates that several organic materials pyrolyzed at higher temperatures were effective in the removal of textile dyes. Recently, modified biochars attempts have been made for the sorption of higher concentrations of dyes. Sugarcane bagasse biochar composite with calcium alginate, magnetized nanocomposite biochar made up of seaweed, and banana peel biochar composite with iron sulfate were used in the exclusion of methylene blue dye (Zhang et al. 2020; Yao et al. 2020) with superior sorption capacity for five repetitive cycles. This shows that the chemicals used in modification are primarily attributed to the formation of pores (mesoporous and macroporous) and additional new functional groups on their surface that acts an important role in dye sorption (Islam et al. 2017; Fan et al. 2017). Sorptions of wide varieties of pollutants onto different biochars are demonstrated in Fig. 8.4. Thus, biochar-assisted environmental pollutants removal can be considered as a sustainable cost-effective remedial strategy.

8.11 Conclusion with Future Prospective

Most of the scientific works have offered better intuition, particularly on the environmental risk assessment for the management of toxicants especially emphasis on textile dyes. In this chapter, we have detailed the usage of different types of dyes and their hazardous impacts on environmental organisms. Usage of dyes is not only limited to the textile industry but also in the microbiological and medicinal field as a pH indicator and stain. However, most of these dyes are deadly poisonous to environmental organisms. Widely, these dyes are being enormously used in the world. Therefore, the removal of dyes from effluent is an imperative need. Sorption is an eco-friendly, cost-effective, and sustainable strategy for the removal of contaminants. We have taken efforts in order to review articles for the expulsion of textile dyes with the help of various biological, chemical, and physical methods. Expulsion of different organic and inorganic pollutants from the environment is remarkably perceived by using biochar as an adsorbent. Nevertheless, disposal of pollutants sorbed biochar is a major concern. Hence, future attention needs to be given to solve the disposal problem of biochar-sorbed noxious contaminants.

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Conflict of Interest The authors declare that they have no conflict of interest.

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9 Conversion of Agricultural Wastes into Biochar and Its Characteristics

Dibyajit Lahiri, Moupriya Nag, Sougata Ghosh, Dipro Mukherjee, and Rina Rani Ray

Abstract

Biomass, after thermal decomposition without the presence of O_2, is turned into biochar; hence, it is resulted from the thermochemical conversion of biomass. The quality and yield of biochar are dependent on the process parameters and the technology that is used for its production. Ever-increasing anthropogenic activities have resulted in continuous release of various types of wastes out of which on-farm crop residues and household peels of vegetables and fruits have resulted in serious environmental issues posing threats to human life. Biodegradable residues are considered to be important source for substantial production of energy. Various biodegradable substances like agricultural residues can be easily converted to biochar via various thermochemical routes that help in the sustainable management of biodegradable wastes. The production of biochar involves various processes that include gasification, pyrolysis, fast pyrolysis and torrefaction. The yield of biochar is significantly reduced with the increase in oxygen availability. It plays a significant role in the enhancement of soil quality by improving the physicochemical parameters of the soil. This chapter

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emphasizes on the mechanisms of conversion of various agro-wastes to biochar and different production parameters with special reference to their characteristic features.

Keywords

Agro-wastes · Biodegradable wastes · Crop residues · Biochar · Biochar preparation · Pyrolysis · Soil pollution · Remediation · Metal impregnation

9.1 Introduction

Biochar is produced through the process of pyrolysis of different types of organic compounds. Here, the biomass is supplied with continuous heat in the presence of minimum amount of oxygen. The various contaminating compounds are reduced to intermediate products, which are a simpler than their original forms. These conversions produce gaseous products like carbon dioxide (CO_2), carbon monoxide (CO), water vapour, hydrogen (H_2), methane (CH_4) and ethane (C_2H_6). This leads to the development of solid carbon residues that are also known as “char” (Leconte et al. 2011). The term “biochar” denotes that the components are produced from biomass, like hay, rice hulls, woodchips, animal manure, sewage sludge, corn stover, bagasse, switchgrass, etc. The main reason for the production is using them as a rich source of energy. A lot of these components are the byproducts of agricultural materials or components of the municipal waste management. These products are usually classified or treated as the waste materials those are required to be disposed. The reusage of the waste materials for the production of biochar is advantageous as they may often be used in the process of formation of agricultural crops and also used in animal farming. The utilization of biochar is a way of environmental protection through which carbon and energy may be recovered. The different characteristics of biochar rely on the type of the feedstock materials that further determines the parameters, such as the process of pyrolysis and heating (Brodie et al. 2000). The parameters like temperature and duration of pyrolysis are specially considered in this case. The various kinds of biomass yield of biochar have different types of properties. However, for almost every type of feedstock component, a rule is in its application. This rule states that, with increase in the temperature of pyrolysis, the formed biochar is accounted to have a high level of carbon content, bulk density, energy content, porosity and surface area with low levels of oxygen and hydrogen content. Increase in the process of pyrolysis time also increases the biochar surface area and the amount of carbon level. The usage of biochar in the process of farming and agriculture is a topic which is thoroughly administered through many research works throughout the last few decades (Lehmann et al. 2011). Many of these research works aim to use biochar for soil amendment. The different factors which are dependent on each other like the increased quality of the soil and different bacterial activities, the increase in crop yields and the decrease in the emissions of greenhouse gases, which is associated with the increased use of fertilizers, are considered as focal point of research. Biochar is rich in carbon and are comprised of products those are organic and undergoes some specific thermal combustion processes in the presence of minimum amount of oxygen. Different organic waste materials which may be considered as feedstock materials for the production of biochar, like the cultivational wastes and kitchen solid wastes, are extensively studied (Glaser et al. 2002).

9.2 Biochar Properties

The different characterizations of biochar are extensively discussed by research journals and review papers in the course of time. One of the main characteristics of biochar from the point of cultivation and production of livestock is studied the most and is the main topic of research. Biochar properties are dependent on its composition. Usually, it is dependent on the feedstock components which are necessary for the process of pyrolysis and the parameters used in the process (Thies and Rillig 2009). In the process of biochar formation, the most important factor is to get the maximum of the carbonaceous product which is in the solid state. The ideal time of pyrolysis and temperature required for the production of biochar usually varies between 1 and 4 h and from 300 to 700 °C, respectively. Torrefaction is said to be a certain temperature in the process of pyrolysis which is low and lies between 200 and 300 °C and is also referred to as "high-temperature drying" or "mild pyrolysis" (Sun et al. 2011). The ever-increasing demand in the process of formation of biochar has effects in high levels of product development with regulatory effect. The European Biochar Foundation, which is a non-profit organization, gives us some general instructions to ensure that the formation or production of biochar also gives a component which has well and good characteristics and a nicer environmental effect (Park et al. 2011). The International Biochar Initiative (IBI) is the type of institute that acts for the best industry practices, influencing the collaboration with stakeholders, other industrial processes, along with some ethical or environmental standards for supporting the process of biochar which is regarded as commercially viable and safe. The standards of biochar of the IBI give us some specific tools for maintenance of quality standards to ensure safer use. It also helps to maintain the required characteristics and several process parameters of biochar. It is an essential factor for the cultivational functions of biochar which may have been suffered from contamination with dioxins, heavy metals, polycyclic aromatic hydrocarbons, semi-volatile and volatile organic compounds like toxins. The biochar which suffers from their unknown origin, which is formed from waste components having contaminations, should be studied much, rather than the other types, which are the type of biochar whose substrates or origins are known.

These types include the agricultural types like the biochar originating from the pruning residues, poultry litter and corn stover (Steiner et al. 2008). Some studies convey that the findings in the effect of different pyrolysis conditions also affect the rate of biochar production. The rise in the level of temperature of pyrolysis and the time of heating of pyrolysis of the feedstock substances from approximately 350 to 550 °C and from 1 to 3 h show the results in the biochar, which have characterizations such as increase from 64.4 to 82.2% of carbon content, decrease from 6.67 to 12.62% of ash content and increase from 6.95 to 8.58 in the pH conditions. But between all these things, the yield of the biochar suffers a reduction from 45.18 to 20.94%. Some research studies also utilized pitch pine woodchips in a fast pyrolysis process, which takes approximately 2 min in various temperatures like 300, 400 and 500 °C as well as the elevated temperatures which will eventually form into a biochar with high carbon content which are about 63.9%, 70.7% and 90.5%, respectively (Verheijen et al. 2010). However, the reduced hydrogen margin remains 5.4%, 3.4% and 2.5%, respectively. The reduced oxygen margin remains 30.13, 25.625, and 7.78% of the total content. The various production rates of biochar which are also reduced with the increase in the process of pyrolysis temperatures, which ranges from 60.7% at 300 °C, 33.5% at 400 °C to 14.4% at 500 °C. Some specific studies however showed a comparison with the results of slow heating rate, ranging from 50 °C/min, when the total process accounts for 60 min. They also showed the results of the fast heating rate of 120 °C/min where the total process accounts for 20 min. The process of pyrolysis of sugarcane results in the slow pyrolysis and gives rise to fuel in a greater biochar percentage of production from the fuel which is received by similar components in the fast pyrolysis process. The fuel which is received from fast pyrolysis process is said to possess a larger fraction of the total amount of fluid which ranges from about 50.89% at 480 °C to 38.11% at 780 °C in comparison to the process of slow pyrolysis. In the slow pyrolysis process, the content of tar usually ranges from 27.11% at 390 °C to 19.20% at 980 °C (Sizmur et al. 2011). The amount of biochar is comparatively high through the process of slow pyrolysis and low through the process of quicker pyrolysis; however, an indirect relation exists among the amount of biochar, and the parameters like the temperature of pyrolysis may be explained. The larger the amount of biochar is, the slower the process is. This is actually likely towards the result of the secondary biochar production, which takes place in the different procedures slowly. But normal ways may be observed because, whatever the type of pyrolysis is, the rise in the pyrolysis temperature gives rise to reduction in the content of biochar. This again results in lowering in the yield of biochar. Some studies state that, when the temperature of wastewater sludge pyrolysis increases, this effects in reduction of the yields from 72.3% for pyrolysis at 300 °C down to 52.4% at 700 °C. But with the increase in the temperature of pyrolysis, the reduction in the content of carbon takes place from 25.6 to 20.2% between 300 and 400 °C which then remains stable. These changes in the content of carbon have an explanation which can be explained by the large amount of carbon high having volatile compounds in the components of feedstock, which was supplied with different gases quite easily when the temperature level increased. Hydrogen, nitrogen and oxygen levels reduced with the increased temperature ranging from 2.645% to 0.76%, 4.01% to 1.34% and 7.96% to ~0.001%, respectively (Beesley et al. 2011).

9.3 Modification and Preparation of Biochar

9.3.1 Preparation of Biochar

The different processes for the formation of biochar, which are usually grouped into carbonization and microwave carbonization, pyrolysis, HTC or hydrothermal, are very common. The various ways of formation effect the different properties which can be both chemical and physical characteristics present in biochar. These include specific surface area, yield, ash, pore structure, type, functional groups and cation exchange capacity (Bernal et al. 1998). In comparison to the pyrolysis process, in hydrothermal carbonization, drying is not required, and it possesses a larger yield of biochar. The positive sides of microwave carbonization are no hysteresis, controllable process, rapid convey of heat and efficiency of energy. But the biochar, which is formed by hydrothermal carbonization and also by a microwave carrying higher concentrations of organic compounds, is usually not required as a component of soil remediation (Ishii et al. 2000).

9.3.2 Pyrolysis

The process known as thermal decomposition or commonly known as pyrolysis is a process which is operated in cases where oxygen is not required and which is an easiest way for the preparation of the biochar. Usually, the process of pyrolysis contains the heating of organic compounds to temperatures which are higher than 400 °C in the different inert atmospheres, taking place by higher temperature medium or electric heating. Some of the parameters effecting the physicochemical characteristics of biochar include the raw materials, reaction conditions like heating rate, residence time and reaction temperature (Thies and Rillig 2009).

9.3.3 Characteristics of Pyrolysis Process

Normal substrates requiring information of biochar are innumerable. Usually, the use of various forms of organic compounds can undergo pyrolysis. Because of the high biomass output of resources of solid wastes, the biomass acts as a common raw component in biochar which is consisted of livestock and poultry manure, kitchen waste, sludge, fruit skin, melon seed shell, peanut shell, rice husk, wheat straw, corn straw, wood chips, etc. The produced biochar is usually formed of various components which possess several ratios of cellulose, hemicellulose and lignin (Pietikäinen et al. 2000). That's why, the yield of the composition and the portion of ash are different. Some studies have found out that the amount of ash in the straw biochar is comparatively larger than that of the rest of the types of biochar, especially those which are majorly resulting to large amount of Si in straw. The comparison of the physicochemical characteristics of the produced biochar having different feedstocks is done by many research articles. The feedstock materials are the components of soybean, peanut, canola and corn. The amount of produced ash in the biochar, produced from the straw and produced from the corn, is done in a temperature of 700 °C, and it gives the amount which is up to 73.30% in comparison to the peanut straw, canola and soybean biochar having production percentages of about 55%, 23.70% and 38.50%, respectively (Wardle et al. 2011). The temperature of reaction varies from higher hydrothermal synthesis, temperature anoxic and flash carbonization for preparing the BC which are 400 to 900 °C to 180 to 250 °C and 300 to 600 °C, respectively (Hua et al. 2009). Usually, when the temperature of pyrolysis increases the biochar yield and the number of acidic side chains like the –OH and –COOH are reduced ash content, pH and the alkaline functional groups are all risen up. Additionally, results of the process of temperature of pyrolysis on pore volume and the surface areas are very much important. Some of the studies have showed that the total pore volume and specific surface area of sesame straw BC rises from 44.7 to 276.2 $m^2 \cdot g^{-1}$ and 0.0654 to 0.1388 $cm^3 \cdot g^{-1}$ respectively, when the temperature of pyrolysis rises up from 500 to 600 °C. Based on the various heating rates, pyrolysis can be parted into slow pyrolysis or SP and FP or fast pyrolysis. Slow pyrolysis is shown by heating in a slow process which depends on minutes to hours (Dias et al. 2010). The slow heating of pyrolysis is in the organic components in the oxygen-less atmosphere and comparatively gas residence times and long solids. In the time of the process of slow pyrolysis, the liquid and solid components like the syngas, BC and bio-oil which are mainly H_2, CO_2 and CO are formed. The fast pyrolysis process consists of a blow of small particles in the different organic compounds in a thermal reactor and suffers an explanation towards the process of heat transfer in milliseconds to seconds. The newest fast pyrolysis normally occurs in some systems using ablative reactors, fluidized bed system and systems using polymerase chain reaction or which is otherwise known as centrifuge reactors for pyrolysis. Slow and fast pyrolysis processes give rise to biochar, having various physicochemical characteristics. This gives various effects on the application of soil and its different properties. In comparison to the biochar undergoing fast pyrolysis, it contains unpyrolyzed fraction of biomass (Klamer and Bååth 1998). However, the biochar formed from slow pyrolysis can experience a complete pyrolysis. Similarly, in the temperature of pyrolysis, the yield of biochar suffers a reduction with the rise in the residence time. Some studies provide a preparation from BC with orange peel with a temperature of pyrolysis for about 700 °C, the time of residence of 7 h approximately, and the yield of biochar was about 6.95%. The pores of BC and the specific surface area were with the extending of the residence time (Gaspard et al. 2007).

9.3.4 Metal Impregnation

The term “metal impregnation” means the process of adsorption of a few heteroatoms and ions of metals in the pores and surfaces of the BC. Again, there are instances, where the surface area is risen up, and additionally the ions of the metal are in a combination along with the adsorbent for the improvement of the performance of adsorption. Some of the usual metal ions are Fe, Mg, Ag, Zn, etc. From a few of the works, we come to know that there are certain advantages of the chemical reagents for having a better adsorption performance. Preparation of a novel biochar material is also done, which is the CMC–FeS biochar by the combination of CMC or carboxymethyl cellulose and FeS or iron sulphide. This has undergone a demonstration that the useful absorbent of CMC–FeS biochar has a composition for removal chromium (VI) (Frostegard et al. 1993a).

9.3.5 Other Methods

Along with the above-mentioned ways of modifying the methods like the low temperature plasma modification methods, organic matter grafting and ozone oxidation are very popular subjects of experimentation nowadays. The modification of temperature plasma which occurs on a very low temperature refers to the plasmas, which occur through the generation by glow, microwave and corona (Federle et al. 1986). All of these are collided with carbon-carbon bonds on the biochar surface and plasmas which have been oxidized to the functional group containing oxygen, and it also increased the polarity of biochar. But there are many ways which are not yet used on a large scale or experimented for a long time because of the high cost of it and its complicated operation (Rinnan and Baath 2009).

9.4 Removal Mechanism of Major Pollutants by Biochar

There are different types of processes of remediation against soil pollution, which are caused by biochar. Some of these are precipitation, electrostatic interaction, complexation, ion exchange and physical adsorption (Table 9.1).

9.4.1 Ion Exchange

The term ion exchange conveys the process in which the acidic functional groups that possess oxygen on the biochar surface like the hydroxyl groups, carbonyl groups and carboxyl groups possess the ability of ionizing the proton or the base ions on the surface like K^+, Mg^{2+}, Na^+, Ca^{2+}, etc., for the purpose of exchanging against the ions of heavy metal or the organic pollutants that are cationic (Benitez et al. 2005).

Table 9.1 Biochar in heavy metal pollution

Raw material	Tested soil	Pollutant	Remediation effect
Rice husk	Dryland and saturated soil	Cadmium	Adsorption of cadmium in the saturated soil risen up by 22–43%, and on soil of the dryland risen up by 39–53%
Gliricidia sp.	Soil from the shooting range	Lead and copper	Adding the biochar to the soil decreased the dissolution rates of lead and copper by 11.0–98.5% and 14.6–97.5%, respectively, and was able to hold the lead and copper when they are loosened by protons and ligands in the soil
Straw wheat	Acidic soil	Cadmium and copper	The concentration of copper inside wheat roots was decreased with most efficiency of 39.9% by biochar. The already present cadmium and copper inside the soil with an addition to the biochar reduced to 17.34 and 16.54%
Rice straw bamboo and Chinese walnut shell	Soil which is industrially contaminated	Copper	Copper taken from the roots was decreased by 14%, 33% and 23%, respectively. Biochar produced from the rice straw decreased the solubility of copper and lead
Sludge from the sewage	Soil of Brazil	Cadmium, lead and zinc	Biochar decreased the concentration and bioavailable ranges of cadmium, lead and zinc in the leachates
Litter from the poultry	Paddy soil near zinc and lead mines	Cadmium, lead, zinc and copper	Cadmium located in soils which are soluble by acids is involved in poultry litter biochar that was seen to have 9–12% reduction than in the polluted soil content
Cow manure, poultry manure and sheep manure	Soil from the farmland	Chromium (VI)	Poultry manure reduced to 63.58 $\text{mg}\cdot\text{kg}^{-1}$ chromium (VI) in soil having acid in it and 77.99 $\text{mg}\cdot\text{kg}^{-1}$ chromium (VI) in basic soil. Cow and sheep manure reduced by 63.61, 53.47, 55.61 and 63.17 $\text{mg}\cdot\text{kg}^{-1}$ chromium (VI) in both acid and base soil, respectively

9.4.2 Physical Adsorption

The mechanism of physical adsorption says that the biochar undergoes full utilization of its surface properties consisting of porousness and large specificity of the surface area. These factors result in different pollutants like the heavy metals or the organic substances which can undergo absorption over the biochar area or diffusion into the micropores. The heavy metal ion radius is always shorter than the mean pore radius of the biochar (Bligh and Dyer 1959). Usually, the lesser the radius of the heavy metal more are the number of pores present which undergo penetration inside the pores of the BC thereby increasing in the adsorption capacity. Intensity in the physical adsorption method is in close relation to the different characteristics and specific surface area of biochar, the characteristics and various concentrations of the temperature and the pollutants in which the procedure of adsorption is carried out. Again, the process of physical adsorption kinetics is basically used through the pseudo first-order and pseudo second-order models of chemical kinetics. Physical adsorption may have only one layer of adsorption or some multilayers of adsorption that is done by Freundlich and Langmuir model (Frostegard et al. 1993b).

9.4.3 Electrostatic Interaction

The process of electrostatic interaction means that the adsorption takes place electrostatically between the heavy ions of metal and the area charge of BC. While the value of pH in the solution is higher than that of point of charge of BC or the pHpzc, the −ve charge lying inside the biochar of the positive charge and surface on the heavy metals results in the process of electrostatic adsorption (Bardgett et al. 1996). The ions present in the heavy metals possess a positive charge on the biochar surface along with the functional groups containing oxygen like carboxyl, carbonyl and hydroxyl.

9.4.4 Precipitation

Various types of mineral compounds that are found within BC remain associated with OH^-, Cl^-, SO_4^{2-}, SO_3^{2-}, CO_3^{2-}, PO_4^{3-} and SiO_3^{4-}, when combined together with heavy metal ions for the production of water insoluble components (Eiland et al. 2001). The different water insoluble components are metal carbonates, metal phosphates and metal oxides, which carry the process of immobilization and adsorption of heavy metals. Some studies have proved that the adsorption of copper, zinc, cadmium, etc. by the biochar fertilizer is majorly done by the process of precipitation of PO_4^{3-} and CO_3^{2-}. During this process, the surface of electron complication by the functional side chains such as –OH groups or delocalized π is much less (Gómez-Brandón et al. 2011).

9.4.5 Complexation

The term complexation explains the level of interaction between functional groups possessing oxygen, which takes place in the surface of biochar and heavy metals for the production of various complexes that can be repurposed. Many research works have been conducted over the cow manure biochar, and its aluminum phytotoxicity for production of wheat and a conclusion can be drawn that the process of adsorption of Al by BC was because of the complication of carboxyl side chain with $[Al\ (OH)]^{2+}$ complex and the surface, which is a monomer compared to the attraction of Al^{3+} electrostatically with negative charge is distinctively proven (Beesley et al. 2010). Some studies have also conveyed that the oxytetracycline adsorption of biochar is majorly done through the formation of π and π bonds and bridge of metal along with the surface complication, which is the major property and also cation exchange, which may or may not exist. During this procedure of adsorption, there is not a single pathway, but there exists a summation of combinations of various processes of adsorption (Barje et al. 2008).

9.4.6 Biochar in the Sludge as well as Sludge Additive

It is of almost importance that the environment factors in the utilization of biochar are the biochar as a manure and the use of biochar as any other kind of compostable wastes or additive. The properties like high porosity and large surface area of biochar are considered to be a very good adsorbent agent. This retains the precious elements like nitrogen, carbon and sulphur which are typical and will not be found in the environment as pollutants which are not required (Bossio and Scow 1995). High surface area creates high aerated and spacious habitats for the different microbes which facilitates the microbial activities with and highly stimulated conditions and with a little high level of acidic and organic carbon content that is necessary for the microbes and which has a very strong and very positive effect on the different composting processes. Many research works conducted previously have a laboratory scale of experiment, which are conducted for the investigation on the different effects of biochar amendment for dairy cattle slurry for the necessity of preserving the slurry nutrients. The biochar produced from wood shavings at first underwent an addition with the slurry with a dosage, which almost equals 3.89 $m^3\ ha^{-1}$ and resulting in 76% NH_3, 64% N_2O and 81% CO_2 decrease of emissions (Gómez-Brandón et al. 2011). Other conducted research works also result in the application of pinewood biochar, apparently floating inside the surface of manure formed by swine by the treatment of gaseous emissions. Many research works also showed a 13–23% decrease in the ammonia emission, which takes place along with the largest experimented biochar application of dosage of 4.47 $kg{\cdot}m^{-2}$, a 14–32% decrease ammonium sulphate with a dosage of biochar of 2.28 $kg{\cdot}m^{-2}$ and up to a 26% reduction for indole, again along with the application of biochar dose of 2.28 $kg{\cdot}m^{-2}$ (Amir et al. 2010). But the different observations were mathematically and statistically insignificant. It should also be mentioned here that an applied dosage of 4.43 $kg{\cdot}m^{-2}$ is seen to have a very significant increase in the methane content, which is up to 24%. This may occur because of the extra availability and content of carbon, along with the other nutrients for the high methanogen content in the manure. Other research works also suggest that an extra 5–22% (w/w) of chips of pine from biochar to poultry litter goes through the process of composting. The process of biochar amendment fastens up the process of composting and the process of reduced emissions of hydrogen sulphate and ammonia by 72% and 54%, respectively. These were seen for the 22% biochar treatment, whether the 6% biochar for treating decreased the hydrogen sulphate emission by 58%. Some of the research works suggest that 6% production of biochar is produced by woody components to sludge from sewage like that of the woodchips mixture which is enriched with decomposition of organic matter and decreased ammonia emission by almost half during the course of the primary week of production of compost as seen in Table 9.2 (Steger et al. 2005).

Table 9.2 Application of biochar to soil

Biochar dose	Feedstock material	Effect	References
1.5 and 10 t·ha^{-1}	Poultry litter wheat straw	Various effects of biochar amendments in various variations of soil Reduced total biomass of plants in acid arenosol, larger biomass of plants in acid like ferralsol	Macdonald et al. (2011)
12–48 t·ha^{-1}	Poultry litter	Almost 96.32% rise in total dry matter of plants Rise in nitrogen, phosphorus, sulphur, sodium, calcium, magnesium concentrations in plants Rise of electrical conductivity of soil, the pH, total nitrogen, total carbon, calcium, magnesium, sodium, potassium and effective cation exchange capacity The reduction in soil exchangeable aluminium	Chan et al. (2010)
4% of mass of the soil	Wheat straw	Rise in pH, total nitrogen, total carbon and plant growth yield The reduction in leaching of nutrients	Muhammad et al. (2011)
2 g per 48 g of soil (~20 t·ha^{-1})	Pine woodchips	Ammonia rich in a bioavailable nitrogen origin for plants Almost three times rise in root dry matter Almost four times rise in leaf dry matter	Taghizadeh-Toosi et al. (2013)
1.8 and 4% of dry weight of the soil	Fir tree and manure pellets, pruning residues	Decrease in heavy metals' bioavailability Decrease in bioavailability of one element rises the bioavailability of the other	Fellet et al. (2010)
6 and 22% of the mass of poultry litter	Pine chips	55% NH_3 emission decrease 73% H_2S emission decrease	Steiner et al. (2008)
1.22–5.89 kg·m^{-2} of swine manure	Pinewood	Almost 24% NH_3 emission decrease Almost 29% H_2S emission decrease Almost 29% indole emission decrease Almost 22% CH_4 emission rise	Maurer et al. (2006)

(continued)

Table 9.2 (continued)

Biochar dose	Feedstock material	Effect	References
14% of volume of slurry of dairy cattle	Wood shavings	79% NH_3 emission decrease 62% N_2O emission decrease 83% CO_2 emission decrease	Brennan et al. (2011)
2% of mass of tomato stalk mixture poultry manure	Commercially manufactured	Increase of physiochemical characteristics of the compost mixture that allows promoting of microbial works in the compost	Wei et al. (2009)
6% of mass of woodchips mixture of sewage sludge	Wood	Almost 48% of ammonia emission decreases in the primary week of formation of compost. Increase in decomposition of organic matter	Malinska et al. (2004)
6 and 12% of mass of wheat straw mixture of poultry manure	Willow woodchips	Almost 42% decrease in ammonia emission	Janczak et al. (2009)
2–48% of mass of the byproducts of brewing process of beer	Brewer's spent grain	Biochar can give rise to biogas formation up to 33%	Dudek et al. (2010)
7 and 14% of mass of wheat straw mix in poultry manure	Wood	Forming short thermophilic phase and rise in temperature of compost mix Almost 7.78% rise in carbon dioxide emission	Czekała et al. (2017)
11% of dry mass of wheat straw mix in poultry manure	Green waste poultry litter	Almost 77.65% N_2O emission decrease Almost 39.8% of total nitrogen content in the compost mixture	Agyarko-Mintah et al. (2019)

9.5 Biochar in the Additive of Feed

Application of biochar in additive for the feed and in the animals of farm is seen since a long time. The results of these supplies in the various groups of animals are commonly seen. The meaning of this application of biochar indicates towards better digestion, feed, GHGs emission mitigation, conversion ratio, weight gain and used also in medicating in response to bacteriological diseases, intoxication and viral diseases. Also, various applications of biochar as a food option in the matter of nutrition in animals can be an alternative method of solution and so a lot of research is targeted in this area. Some of these research works are observed to give the introduction which wood from oak in biochar inside laying hens' and chicken broilers' diets may greatly affect the formation and the efficiency of the produced biochar (Beffa et al. 1996a, b) (Table 9.3).

Table 9.3 Functions of biochar in animal feed

Biochar dose	Feedstock material	Effect	References
Hen's feed mass from 1.5 to 4.2%	Woody green waste	Almost 5.5% rise up in eggs weight Almost 13.3% rise up in eggs yield Almost 7.1% decrease in feed intake Almost 13% better feed conversion ratio Almost 18% rise up in shell breaking strength Almost 25.5% decrease in N content in excreta	Prasai et al. (2009)
0.6 and 1.1 g of biochar per kg of body weight of goat	Bamboo	16.4% rise up in daily body mass gain 62.5% decrease in nitrogen content in urine	Thanh Van et al. (2010)
2–13% by the total chicken broilers' mass and feed of the laying hens'	Oakwood	Almost 8% better feed conversion ratio Almost 21% rise in body weight gain Almost 63% decrease in the number of cracked eggs	Kultu et al. (2011)
Up to 2% by mass of chicken broilers' feed	Canarium seed maize cob	Almost 13% rise in body weight gain Almost 118% rise in pancreas weight Almost 19% rise in intestine density Almost 83% rise in creatinine level Almost 27% rise in gizzard mass	Kana et al. (2013)
Almost 2 g of per cow daily charcoal	Charcoal	Almost 30% reduction in *C. botulinum* antibody levels	Gerlah et al. (2014)
Almost 6% of biochar mass of the feed of chicken broilers'	Poultry litter	Almost 8% rise up in feed intake Almost 2% reduction in body weight gain 11% decrease in feed conversion ratio	Evans et al. (2018)
2% of intake of dry matter of goats	Charcoal in activated state	Almost 75.3% decrease in excretion of aflatoxins No change in milk composition	Nageswara Rao et al. (2019)
3 and 5% of mass of feed of chicken broilers'	Poultry litter	Almost 7% rise up in conversion ratio Almost 9% reduction in body weight gain	Evans et al. (2017)

(continued)

Table 9.3 (continued)

Biochar dose	Feedstock material	Effect	References
5% mass of laying hens' feed	Waste like green and woody	Almost 1.2% rise in egg productivity Almost 3% rise in eggs weight Almost 8% rise in conversion ratio Almost 2% reduction in feed intake	Prasai et al. (2012)
Molasses of biochar mixed at a ratio 3:1 and then fed to cows	Jarrah wood	Sorption toxin Easy passing on of nutrition from the gut of the cow and its dung to the soil	Joseph et al. (2007)
2–5% by mass of chicken broilers' feed	Waste like green and woody	The reduced water content of excreta of laying hens Almost 27% reduction in excreta N content Almost 45% rise in C content in excreta Almost 47% rise in NH_3 emission	Prasai et al. (2008)
0.9 and 4% by feed mass	Whole pine trees	Improved digestion Almost 18.4% decrease in CH_4 emission Almost 9.7% decrease in CO_2 emission	Winders et al. (2011)

9.6 Conclusions

In the recent times, the usage of biochar in cultivation is actually based among the products based on biochar as an amendment of soil. But, here always lies ample number of possibilities for the investigation through the other applicable areas of biochar application (Downie et al. 2009). There are many strong relationships, which lie between many factors like the feedstock components of biochar, biochar dose, the different characteristics of biochar, the various types of soil, the various types of species of plants, the targeted elements or the experimental compounds, etc. The other factors of biochar development, which are exposed to experimentation in the last few years, include the biochar-enhanced composting methods and formation of the biochar by the process of pyrolysis of wastes produced out of cultivation. But the usual and known characteristics of biochar with their cultivation potentials have been utilized in the rest of the areas like the odour, providing nutrients to the animals, emitting the gases, the usage of biochar-containing manures made from animals used usually due to different types of fertilizers, etc. The process of composting the biochar contains an overall good result on the process of composting. But the decrease of few gaseous emissions can take up the other options (Glaser et al. 2009). Using the biochar as an additive of animal feed also possesses a good effect. Again, other studies also confront that the field of biochar utilization is a new one and needs to be experimented more, and also they are expected to produce useful results. Again, some research works prove that as in this area, the utilization of biochar can be low, but at the same time, it can also give useful results. The various types of feedstock components have a contribution in the various properties of the biochar, and the differences in the characteristics have an increased amount of substance by the various parameters of pyrolysis, especially the parameters like temperature and time. An optimum dosage of biochar should be studied when it is studied as an additive and when the influence and different characteristics of biochar should be taken into account (Kato and Miura 2008).

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Antiepileptic Drugs: From Public to Environmental Health Problem

10

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Abstract

Around 50 million people worldwide live with epilepsy, making it one of the most common neurological diseases globally. Affecting people of all ages, this chronic noncommunicable condition is mainly concentrated in low- and middle-income countries, becoming a public health problem. Besides, people with epilepsy suffer from stigma and discrimination, and this condition also requires therapeutical treatment with antiepileptic drugs for many years or a lifetime. This fact leads to the need for constant production and use of these pharmaceutical compounds globally, placing them among the four classes highly found in water, thus creating an environmental health problem. To fill gaps in social and environmental contexts, this chapter addresses understanding and perspectives on the topics (1) public awareness of epilepsy and its effects in society; (2) antiepileptic drugs occurrence and interaction with aquatic ecosystems; and (3) remediation processes for anticonvulsants in wastewater.

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10.1 Epilepsy Disease Effects in Society

Affecting approximately 50 million people globally of all ages, sexes, and races, epilepsy is one of the most prevalent neurological severe diseases. People with epilepsy (PWE) suffer from a brain disorder characterized by abnormal electrical activity, causing seizures, unusual behavior, sensations, and, in some cases, loss of awareness (WHO 2019). Despite it being the only severe and disabling chronic neurological condition fully treatable with antiepileptic drugs (AEDs) in most cases, PWE's life is negatively impacted in essential areas, such as education, employment, marriage, and social integration. This is due to stigma and discriminatory practices that remain in society for centuries (Braga et al. 2020).

Besides the social impacts, epilepsy carries neurological, cognitive, and psychological consequences, leading to a high risk of disability, psychiatric comorbidity, social isolation, and premature death. PWE has up to three times more chances to have a premature death than the general population, and in low- and middle-income countries, the risk of poor quality of life for people with this condition increases. This is due to high treatment gaps, exceeding 75% in low-income countries (LIC) and 50% in middle-income countries (MIC), despite the effectiveness and low cost of AEDs available in the market. The epilepsy occurrence in these countries is higher than in high-income countries (HIC), and the reason can be the lack of access to basic health facilities to prevent the disease.

Although the cause of some epilepsy cases remains unknown, this neurological condition can be attributed to genetic, metabolic, infectious, structural, and immune causes. Also, lesions such as birth injury, head trauma, and stroke can lead to an epilepsy case, justifying the predominance in children and people over 60 years old (WHO 2019). Significant progress has been made to improve epilepsy diagnosis and therapeutic approaches. However, the burden of epilepsy is still positively associated with social aspects, and it has severe implications in personal health and society functioning, including economic development (Jennum et al. 2021). From the social and treatment point of view, PWE's life's-related factors are highlighted in Fig. 10.1 and discussed in the sections below. It is important to emphasize that the treatment quality is directly linked to the epilepsy social aspects. Access to reliable medicines and control of the clinical condition will only be possible when epilepsy becomes part of the public health agendas worldwide.

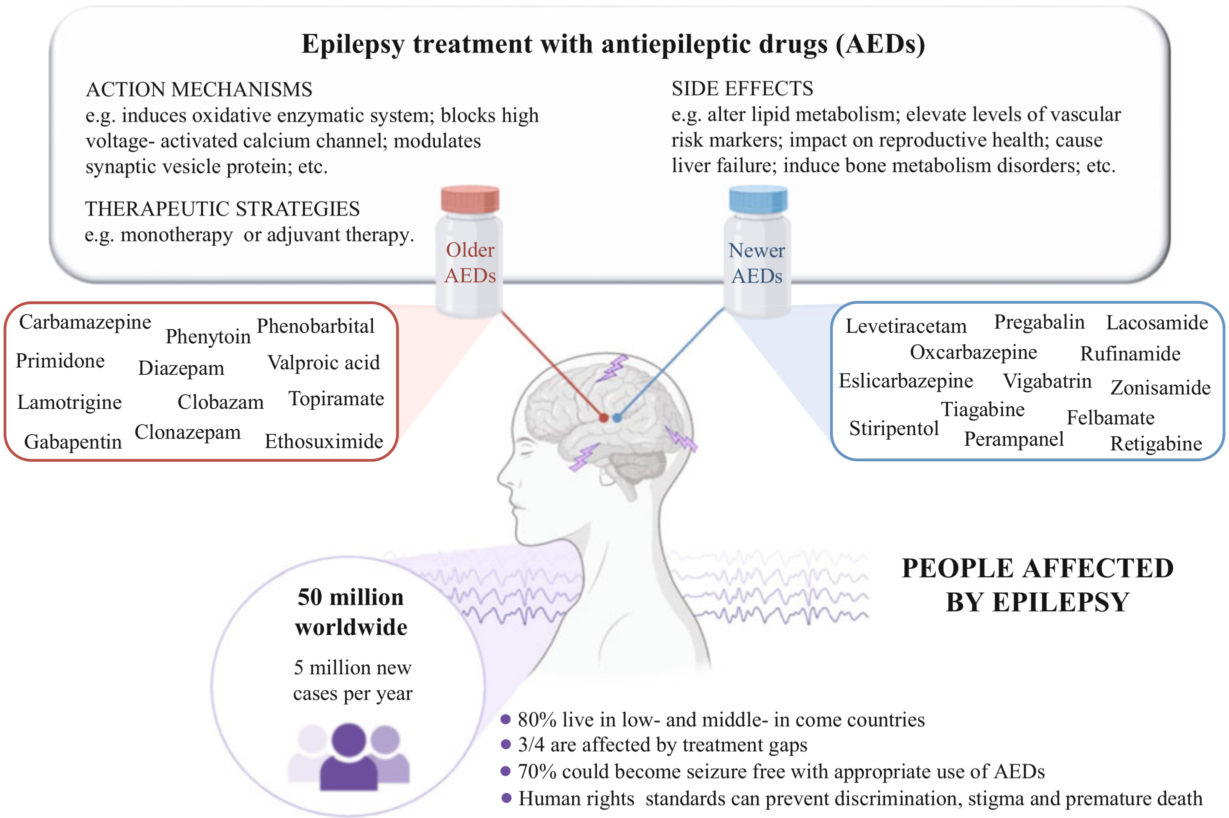

Fig. 10.1 Treatment and social aspects of epilepsy disease. Support data: “Epilepsy treatment with antiepileptic drugs” obtained from Brodie and Kwan (2012); Pickrell et al. (2014); McMillin and Krasowski (2016); Zabihollahpoor et al. (2020); and Fox et al. (2020); “People affected by epilepsy” obtained from World Health Organization report (WHO 2019)

10.1.1 Public Awareness

Due to rising life expectancy and healthcare services, avoiding several epilepsy-related deaths, the number of PWE is estimated to continuously increase worldwide, with a rate of 5 million new cases per year. Because it is treatable, this neurological condition can lead to a full and productive life. In 70% of the cases, the individual can become seizure-free through an appropriate therapeutic approach. The integration of epilepsy into primary health care and the guarantee that PWE has access to quality and affordable medical services has shown a promising way to achieve a quality of life and reduce the burden of epilepsy (WHO 2019).

The treatment and social gaps remain enormous and lead to a human rights violation scenario worldwide. The knowledge regarding epilepsy is still limited in the general population, both in HIC and LIC, leading to myths and misconceptions about this condition and an intrinsic undervaluation of PWE, both by the felt and institutionalized stigma (WHO 2019; Braga et al. 2020). The WHO report (2019) showed that only 20% of Latin America and the Caribbean countries has national legislation related to epilepsy and emphasizes that physical and social health can be improved with a multipronged strategy.

Almost 50% of adults with epilepsy have coexisting physical or psychiatric conditions, with depression and anxiety being the most prevalent. In children, epilepsy often coexists with intellectual disability, and the elderly with neurodegenerative diseases (WHO 2019). In a pandemic scenario, as in the SARS-CoV-2 (COVID-19) started in the late 2019, the implementation of several degrees of social distance and interventions can negatively impact the quality of life and medical care of PWE. Subotic et al. (2020) highlighted that a pandemic situation exacerbates negative feelings, such as social isolation, and brings more anxiety about the future, both in social and treatment aspects.

The long-term consequences of epilepsy could be ameliorated through management and research. However, the investments in epilepsy research remain insufficient, and even in HIC, only a small proportion of the efforts are directed to this disease. In the United States, for example, 0.09% of the total National Institutes of Health budget is dedicated to epilepsy, and it has stagnated over the last 3 years, according to WHO (2019). The WHO report mentions the even worst situation of the low- and middle-income countries, where research is majority financed by domestic organizations and is directed to other types of diseases.

To obtain a measure of epilepsy research in public awareness, we consulted the Web of Science and Scopus databases and found the disparity in scientific production worldwide. In both databases, the regions domaining publications on the subject are the United States, the United Kingdom, and, surprisingly, India. The last one goes against the expected comportment for two reasons: it is a LIC, and, according to WHO (2019), in 2016, India devoted only 3.6% of gross domestic product (GDP) to health care. On the other hand, the United States and the United Kingdom, both HIC, devoted 17.1% and 9.8%, respectively. The establishment of regional research priorities and agenda may be the case in India and is one of WHO suggestions because it facilitates the defense of research funding in regions of high need.

Public knowledge and awareness about epilepsy play an essential role in disease control because PWE requires therapeutic treatment with antiepileptic drugs for many years or a lifetime. Although there are many compounds available in the market to treat epilepsy, as shown in Fig. 10.1, and capable of reducing or eliminating the seizures in 70% of the cases, the medication non-adherence can reach up to 79% in some low- and middle-income countries, mainly due to a diagnosis lack and poor access to medicines (WHO 2019; Braga et al. 2020). Given the importance of antiseizure medicines in epilepsy treatment and control, the next section of this chapter is addressed to introduce this group of drugs and some therapeutic aspects of these compounds.

10.1.2 Antiepileptic Drugs

The pharmaceutical class known as antiepileptic, anticonvulsant, or antiseizure drugs has been widely used to manage seizure frequency in PWE. As shown in Fig. 10.1, there are many types of action mechanisms and therapeutic strategies to AEDs which prevent the brain disorders that cause epilepsy, making them a group of drugs structurally and pharmacologically diverse. The AEDs can be classified based on when the compound was accepted and approved as a medicine to treat epilepsy (McMillin and Krasowski 2016; Rani et al. 2016; Zabihollahpoor et al. 2020).

The AEDs known as older, first-generation, or classical were introduced before the 1990s and include the compounds carbamazepine, phenobarbital, phenytoin, primidone, valproic acid, lamotrigine, gabapentin, topiramate, clonazepam, diazepam, ethosuximide, and clobazam. They possess significant pharmacokinetic variability and high adverse effects and risk of toxicity (Brodie and Kwan 2012; Pickrell et al. 2014; McMillin and Krasowski 2016; Zabihollahpoor et al. 2020; Fox et al. 2020). Long-term use of these medicines may affect thyroid function and bone metabolism, increase the risk of vascular-related pathologies, and impact the patients' reproductive health (Fox et al. 2020; Markoula et al. 2020; Shi et al. 2020). Despite the use of older EADs trends to diminish, their utilization remains relatively common in PWE, mainly among elderly patients. This behavior is also seen in countries with limited health resources, where the use of older EADs represents a cost-effective strategy to guarantee access to treatment for the population (WHO 2019; Fox et al. 2020).

Driven by the necessity to reduce side effects and drug-drug interactions and cover drug-resistant epilepsy cases, affecting one-third of PWE (Brodie and Kwan 2012), the treatment with newer AEDs, also classified as the second and third generation of anticonvulsants, has been approved since the late 2000s. The newer compounds comprise levetiracetam, oxcarbazepine, lacosamide, pregabalin, rufinamide, zonisamide, eslicarbazepine, vigabatrin, felbamate, stiripentol, tiagabine, retigabine, and perampanel. Several of them have shown efficacy similar to the older, lower risk of adverse effects, and increased chances for patients to become seizure-free (Brodie and Kwan 2012; Pickrell et al. 2014; McMillin and Krasowski 2016; Zabihollahpoor et al. 2020). Clinical experience is limited for some of these compounds, and it is a concern among the medical community. Epilepsy research can be a powerful tool for increasing confidence in the newer AEDs and reducing the impacts that epilepsy treatment can have on the PWE's quality of life.

According to the WHO report (2019), besides the diverse availability of older and newer EADs worldwide, the quality aspect should be considered. Data indicate that over one out of ten medicines available in low- and middle-income countries are substandard or falsified. The use of these medicines has severe consequences because they may contain toxic compounds or impurities. In this sense, the standardization of AEDs production is a public concern. It has to become closely monitored to ensure security to patients and the environment since some drugs are not fully metabolized. In fact, up to 50% of the administered dose can be excreted unchanged (Habibi 2010).

10.2 Antiepileptic Drugs Interaction with Aquatic Ecosystems

The occurrence and detection of AEDs in environmental matrices, such as surface water and wastewater, brought a new perspective of environmental quality due to their low concentrations and hazardous aspect. The primary sources of pharmaceuticals such as AEDs in the environment are wastewater treatment plants (WWTPs) (Naghdi et al. 2018) and hospital effluents (Verlicchi et al. 2012). Global consumption of AEDs leads to an increase of these compounds' occurrence in water matrices since the active principles are not completely metabolized in the human body and, consequently, are excreted in metabolites form. For example, 25% of carbamazepine (CBZ) is excreted in urine after liver metabolization, where the primary metabolite is carbamazepine-10,11-epoxide (Bertilsson and Tomson 1986), while 40–50% of primidone (PMD) is excreted unchanged by urine (Habibi 2010).

Jjemba (2008) highlights that pharmaceuticals' half-life ($t_{1/2}$) on environmental matrices depends significantly on the pharmaceutical compound itself and on the medium, reaching up to 120 h. This parameter helps to estimate how long the pollutant will be present in the environment. Solubility is also an important physical-chemical property, indicating whether the contaminant has more affinity with water or with organic substrates. It is directly related to the distribution coefficient and the octanol-water partition coefficient (log K_{ow}). The $\mathrm{pK_a}$ is also relevant in environmental samples, which are usually acidified before the extractions and analysis of pharmaceuticals. In fact, the extractability is reduced for compounds exhibitig high $\mathrm{pK_a}$ values. The aspects mentioned above illustrate if the contaminant has more water or organic affinity, definitely impacting the wastewater treatment strategies.

Many studies have investigated these properties and the concentration of AEDs in water bodies, as presented in detail in Table 10.1. In addition to the occurrence in surface water and WWTPs, the AEDs have been found in other matrices either, as reported by Rezka et al. (2015), pointing concentrations of 2–2325 ng L^{-1} of CBZ in groundwater and 12–25 ng L^{-1} in drinking water. This compound is the most

Table 10.1 Antiepileptic drugs properties and occurrence in water bodies

Compound	Molecular formula	Chemical and physical properties				Concentration in water matrices (ng L^{-1})		References
		Water solubility (mg L^{-1})	pK_a	log K_{ow}	$t_{1/2}$ (h)	Surface water	Wastewater treatment plants	
Carbamazepine	$C_{15}H_{12}N_2O$	17.7	7.0	2.45	12–65	Germany: 110 Great Britain: 251–684 Italy: 345 Spain: 1110 Sri Lanka: 12.5	Belgium: inf[a] 227–1028 Brazil: inf 240–406/eff[b] 272–492 Germany: inf 1536/eff 1614 and 630 Greece: inf 800/eff 900 Italy: eff 280–1200 Norway: eff 3.4 10^6 Republic of Korea: eff 21,600 Spain: eff 1.8 10^4–1.7 10^7 United States: eff 38–1300	Kosma et al. (2010); Sim et al. (2011); Tarcomnicu et al. (2011); Verlicchi et al. (2012); Writer et al. (2013); Rezka et al. (2015); Gurke et al. (2015); Guruge et al. (2019); Keerthanan et al. (2020); Pivetta et al. (2020)
Clonazepam	$C_{15}H_{10}ClN_3O_3$	100.0	$pK_1 = 1.5$ $pK_2 = 10.5$	2.41	19–60	Brazil: 42–335	Not detected	Pivetta et al. (2020)
Diazepam	$C_{16}H_{13}ClN_2O$	50.0	3.4	2.82	24–120	Sri Lanka: 1.42	Belgium: inf 1–9 China: eff 1.1–16 Italy: eff 2–38	Tarcomnicu et al. (2011); Verlicchi et al. (2012); Rezka et al. (2015); Guruge et al. (2019)

(continued)

Table 10.1 (continued)

		Chemical and physical properties				Concentration in water matrices (ng L^{-1})		
Compound	Molecular formula	Water solubility (mg L^{-1})	pK_a	log K_{ow}	$t_{1/2}$ (h)	Surface water	Wastewater treatment plants	References
Lamotrigine	$C_9H_7Cl_2N$	170.0	5.7	1.19	24	United States: 108	Germany: inf 574/eff 862 The United States: eff 120–488 and 54–1200	Ferrer and Thurman (2010); Writer et al. (2013); Gurke et al. (2015); Bollmann et al. (2016)
Phenobarbital	$C_{12}H_{12}N_2O_3$	1110.0	7.3	1.47	53–118	Germany: 210 Italy: 13	Germany: eff 5 Italy: 270 (n.r.[c])	Verlicchi et al. (2012); Hass et al. (2012)
Phenytoin	$C_{15}H_{12}N_2O_2$	32.0	8.3	2.47	7–42	Japan >15 Sri Lanka: 6.44 United States: 480	United States: inf 250/eff 450	Yu et al. (2006); Hoshina et al. (2009); Guruge et al. (2019)
Primidone	$C_{12}H_{14}N_2O_2$	500.0	12.3	0.91	10	Germany: 180	Germany: inf 710 and 725/eff 665	Hass et al. (2012); Gurke et al. (2015); Keerthanan et al. (2020)
Oxcarbazepine	$C_{15}H_{12}N_2O_2$	300.0	13.7	1.11	2	Germany: 8–570	Germany: inf 337/eff 574 The United States: eff 23–290	Writer et al. (2013); Gurke et al. (2015); Brezina et al. (2017)

[a] *inf* influent
[b] *eff* effluent
[c] *n.r.* not reported

studied and monitored in several countries, with a wide range of concentrations found in surface water and in influent and effluent streams of WWTPs.

The findings in studies of Table 10.1 indicate the failure in existing treatment plants in AEDs removal, with higher concentrations of the compounds in effluent samples than in influent, in some cases. The high half-time of AEDs is also an indication that these substances persist in water bodies if the appropriate removal process is not applied. To date, the newer class of EADs is poorly monitored in the environment, and the literature available so far has been monitoring only the oxcarbazepine compound.

Pivetta et al. (2020) investigated psychotropic drugs in Brazilian surface water and wastewater treatment plants in addition to assessing their environmental risks. The presence of six of eight target compounds on wastewater samples supports the inefficiency of conventional treatment processes applied to remove contaminants of emerging concern. The risk assessment presented by the authors showed that the AEDs' detected concentrations pose no direct risk to the aquatic environment. Despite this, psychoactive drugs have a lack of reliable ecotoxicological data, highlighting the challenge of assessing the impact of these drugs.

The investigation of pharmaceuticals in environmental matrices faces a common challenge, with regard to the identification and quantification of compounds, due to their low concentrations and the inherent complexity of water matrices. Monitoring AEDs in the environment requires refined analytical techniques and, in most cases, pre-treatment procedures, such as liquid-liquid extraction and solid-phase extraction. The determination of several compounds in the same sample is also a challenge that has been explored, aiming at achieving sensitivity and accuracy in complex mixtures, such as in WWTP influents (Rani et al. 2016). Even though many analytical methodologies have been developed to quantify AEDs in water bodies, the search for fast and inexpensive techniques will go further to achieve the maximum number of analytes and best sensitivity. These challenges motivate new research and environmental policies worldwide.

10.2.1 Risk Assessment of AEDs

To assess and manage environmental risks of emerging contaminants, it is necessary to know their ecological exposure and associated hazards. Toxicological assessment is an important study field to understand the risks of AEDs release in the environment. Toxicological analyses are mainly based on lethal dose (LD_{50}) or lethal concentration (LC_{50}) indicators. In summary, the indicators represent the concentration that eliminates 50% of the evaluated organisms, considering ingestion or inhalation contact (Jjemba 2008).

For instance, carbamazepine, phenytoin, primidone, and valproic acid have been associated with changes in human lipid metabolism, leading to an increased risk of cardiovascular accidents (Fox et al. 2020) and an increase in the rate of congenital malformations when administered during pregnancy (Pickrell et al. 2014). From the environmental point of view, LD_{50} and LC_{50} indicators have been monitored in ecotoxicological studies with the microcrustacean *Daphnia similis*, confirming the effect of carbamazepine in mobility and reproduction health of the tested organism (Chen et al. 2019).

The potential risks of AEDs to the environment can be assessed using a procedure guideline from the European Medicines Agency. The procedure takes place by determining the capacity of drugs to bioaccumulate along the food chain, their mobility, and the predicted environmental concentration in the aquatic environment. However, most pharmaceutical compounds do not show toxicity under the conditions of traditional assays (which include tests, e.g., for acute and reproductive toxicity and carcinogenic effects), and most studies available in the literature are based on the mathematical prediction of no-effect concentrations (Cunha et al. 2019).

Another analysis used is the Hazard Quotient (HQ), or risk quotient (RQ), which considers the occurrence and ecotoxicological data to define the potential environmental risk caused by a contaminant. The purpose of this analysis is to assist environmental agencies in updating the lists of priority substances. Verlicchi et al. (2012) investigated the RQ of hospital and WWTP effluent samples containing 73 pharmaceutical compounds. The authors identified that the AEDs carbamazepine and diazepam have low environmental risk.

It is worth emphasizing that pharmaceutical compounds are designed to alter target organisms' biochemical, physiological, and behavioral functions. It is then possible that nontarget organisms in the aquatic ecosystem undergo functional and behavioral changes due to these compounds' presence (Cunha et al. 2019). Several toxic effects are observed in organisms in nonstandardized tests, which are often not considered in the risk assessment. In this sense, it is essential to consider the ecotoxicological data from nonstandardized trials to fill existing gaps in the literature and legislation, especially for AEDs increasingly used worldwide.

10.2.2 Ecotoxicity of AEDs

The persistence of AEDs in the environment, even in trace concentrations (ng L^{-1} to μg L^{-1}), has brought the necessity of understanding the contaminants' fate and transport and their effects on organisms in the environment. They can bioaccumulate in the tissues of living organisms through water absorption and ingestion (Naghdi et al. 2018), in addition to the possibility of bioaccumulation at different trophic levels, through the biomagnification of food chains (Wang et al. 2020).

It is essential to use organisms from different trophic levels to understand and evaluate pharmaceutical compounds' fate in the environment. The most-reported organisms in ecotoxicity assays are crustaceans (*Daphnia magna*), algae (*Pseudokirchneriella subcapitata*), and bacteria (*Vibrio fischeri*). In aquatic ecosystems, primary consumers can be considered the main bioaccumulators of pharmaceutical compounds.

Because CBZ has been on the market for years as a well-established and older AED, it is the most prescribed medication for epilepsy treatment and is, therefore, an essential indicator of the occurrence of drugs in the water. CBZ and its metabolites are widely detected in wastewater at concentrations equal or higher than the parent compound (Wang et al. 2020). For the reasons mentioned above, studies have been focused on its ecotoxicity.

Nkoom et al. (2019) analyzed *D. magna* exposure's effects to 5 and 100 μg L^{-1} of CBZ for 48 h and evaluated its bioconcentration capacity. At the end of the test, the CBZ concentrations in the medium were 4.5 and 94.8 μg L^{-1}, respectively, indicating its bioconcentration. The feeding and phototactic behavior were also evaluated by exposing to concentrations of 5, 15, 50, and 100 μg L^{-1}, for 5 h and 7 days. The results showed that the organisms were unable to feed properly and showed a decrease in negative phototactic behavior. The authors also conducted a biochemical experiment with 150 neonates exposed to the AED in the same concentrations as the feeding and phototactic behavior tests for 7 days. The activities of acetylcholinesterase (AChE), catalase (CAT), superoxide dismutase (SOD), and glutathione reductase (GR) were determined, and the results indicate the oxidative stress of the organism, caused by the accumulation of the compound and inhibition of the antioxidant enzymes mentioned above. In addition, activity inhibition of AChE was identified, indicating the potential for neurotoxicity.

Spirulina platensis was exposed to CBZ in Wang et al. (2020) study by adding the drug (varying from 1 to 100 mg L^{-1}) to the Zarrouk medium containing microalgae suspension. After 10 days of cultivation, there was a decrease in the algae growth compared to the control. At higher concentrations (50 and 100 mg L^{-1}), there was a significant decrease in the organism's biochemical characteristics and photosynthetic activity due to the change in antioxidant enzymes' activity.

Herrmann et al. (2015) studied the toxicity of the phototransformation products of gabapentin (GAB) through *V. fischeri* and *Salmonella typhimurium*. The first organism was applied to investigate the influence of GAB on the bacteria luminescence, and the second to study the effects of GAB by-products on genotoxicity. Twenty-seven phototransformation products were formed shortly after the start of photolysis. After 128 min of irradiation, inhibitory effects occurred, indicating an increase in short-term bacterial cytotoxicity and an even more pronounced long-term antibacterial activity for samples collected during photolysis. The results suggest that GAB phototransformation products may have a considerably higher toxic potential than the parent compound.

The ecotoxicity of transformation products (TPs) generated during wastewater treatment is paramount for choosing the appropriate treatment and avoiding environmental risks. Li et al. (2011) studied different processes for disinfecting synthetic wastewater and investigated the toxicity of oxcarbazepine TPs in *D. magna*. The solutions disinfected with UV, prepared in synthetic surface waters, exhibited an increase of acute toxicity to the organism due to acridine formation during the process.

Donner et al. (2013) investigated the toxicity of TPs (acridine and acridone) produced during UV photolysis of CBZ in wastewater effluents, using organisms of different trophic levels. The following standardized ecotoxicity tests were performed: inhibition of *V. fischeri* bioluminescence, inhibition of *P. subcapitata* growth, and immobilization of *D. magna*. There was 70% inhibition of *V. fischeri* bioluminescence after 25 min of treatment and 100% of *P. subcapitata* growth in 20 min. *D. magna* only demonstrated a measurable toxic effect after 45 min of treatment, indicating that this organism was the least sensitive to the CBZ exposure. These results suggest that TPs may be significantly more harmful than the parent contaminants.

10.3 Biochar-Based Process for Anticonvulsants Removal from Wastewater

Carbonaceous materials for drug removal in wastewater have shown significant advances over the past decade. Characteristics like high surface area and thermal and chemical stability make these materials adsorbing efficiencies greater than 90% in most cases (Cai and Larese-Casanova 2014). In this scenario, biochar has stood out among contaminant removal processes, mainly because it is a carbon-rich material, derived from biological residues, highly heterogeneous, porous, and with the presence of functional groups on the surface (Chu et al. 2019).

Pyrolysis of residual biomass is the main strategy for biochar production for remediation processes, whose characteristics will depend on the nature of the precursor material and the pyrolysis parameters (Nidheesh et al. 2021). The pyrolysis of biosolids to generate biochar as a micropollutant adsorbent is interesting since the biochar can be recycled back to the pyrolysis process after removing the pollutants, considering that the pyrolysis step will remove the compounds, as already observed for antibiotics and hormones. Consequently, residual biomass pyrolysis to produce biochar can offer a sustainable alternative to remove micropollutants from wastewater by adsorption (Tong et al. 2019).

The raw biochar's absorption capacity can be improved by functionalization processes, applying different chemicals to the material to increase the system's efficiency (Tan et al. 2016). As for the application of biochar in AEDs, a recent advance in research can be seen, however, mostly limited to carbamazepine remediation (Liang et al. 2020). Therefore, the adsorption mechanisms of this drug and others in biochar are still being discussed.

Biochar functionalized with copper oxide showed high specific surface area and pore volume associated with Cu^{2+} ions as a pore-forming agent, being able to remove twice the concentration of carbamazepine compared to crude biochar (Liang et al. 2020). Chen et al. (2017) described the dependence of adsorption mechanisms of carbamazepine in biochar with the presence of aromatic carbon in the structure, resulting from the increase in pyrolysis temperature, where the highest concentration was adsorbed. In amorphous carbon, the drug was adsorbed to a lower concentration but more quickly. The authors also addressed that hydrophobic and π-π interactions were probably the most prevalent in this system.

Recent studies have shown biochar application for the removal of other anticonvulsant drugs with promising results. Primidone was efficiently removed by three different biochar types, demonstrating that the modified biochar can significantly impact decontamination (Yanala and Pagilla 2020). In the same way, lamotrigine proved to be efficiently removed through biochar adsorption (Li et al. 2020). Considering the characteristics of biochar, many potential applications are targeted, mainly involving the removal of pollutants from wastewater, as it is a low-cost and abundant matrix, in addition to easy production (Tan et al. 2016). Even so, attention is drawn to the need to advance studies with AEDs in effluents, mainly aiming at the biochar production and optimization of adequate functionalization processes to remove these contaminants.

10.3.1 Hybrid Treatment Systems with Advanced Oxidation Processes

The combination of biochar with advanced oxidation processes (AOPs) has been considered an exciting alternative for the degradation of emerging contaminants. The versatility and sustainability of the carbonaceous material combined with aqueous phase oxidation show several advances (Nidheesh et al. 2021). AOPs use the power of highly reactive species, such as hydroxyl radicals ($HO^{\bullet}$), hydrogen radical ($H^{\bullet}$), hydrated electron (e_{aq}^{-}), sulfate radicals ($SO_4^{\bullet-}$), peroxymonosulfate radicals ($SO_5^{\bullet-}$), superoxide radicals ($O_2^{\bullet-}$), singlet oxygen ($^1O_2^{\bullet}$), and hydroperoxyl radials ($HO^{\bullet}_2$). The association of these processes in a hybrid system allows high efficiency in the degradation of several organic compounds with a low generation of residues during the treatment and potential mineralization of the pollutants.

The high degradation efficiency is due to the combination of chemical and physical properties of the biochar and to the possibility of using these materials as catalysts in AOPs to activate hydrogen peroxide (H_2O_2) and persulfate, or as a support material for metals and metal oxide composites. They can also act as a cathode for H_2O_2 generation in the electro-Fenton process and ensure electron transfer and separate photoexcited holes and electrons in photocatalysis. Additionally, the biochar structure contains free radicals necessary for reactive oxygen species (ROS) generation, thus playing an essential role in AOPs. However, it is necessary to note that the biochar suitable characteristics for application in hybrid systems with AOPs are strongly associated with the biomass preparation procedure (Nidheesh et al. 2021).

As a catalyst, biochar can be explored mainly for $HO^{\bullet}$ and less pronounced for $SO_4^{\bullet-}$-mediated degradation. This fact may be related to the highest standard reduction potential of $HO^{\bullet}$ compared to $SO_4^{\bullet-}$. Accordingly, hydrogen peroxide, an oxidant widely used in AOPs, can be decomposed through interaction with free radicals present in the biochar, with the generation of hydroxyl radicals (Nidheesh et al. 2021). Similarly, according to the authors, the mechanism behind the activation of persulfate forming $SO_4^{\bullet-}$ radicals depends on the hydroxyl groups present on the carbon surface and also on the π-π^* transitions in the biochar.

Furthermore, the presence of iron oxides in the biochar, obtained mainly from sources such as rice husks and coconut husks, can promote Fenton reactions without the need to use additional iron. Finally, as a cathode in electrochemical processes, biochar is a potential material for the working electrode in electro-Fenton reactions. The mechanism involved is related to highly perfect graphitization, porous nature, and functional groups containing oxygen on the biochar surface (Nidheesh et al. 2021).

Nidheesh et al. (2021) recently reviewed the role of biochar in AOPs, showing that around 25% of the hybrid system's target application was related to pharmaceutical removal (e.g., sulfamethazine, ciprofloxacin, tetracycline hydrochloride, gemifloxacin). At the same time, no studies with AEDs were mentioned. It is also observed that different configurations of hybrid systems can be effectively applied. Despite the several advantages of using this combined treatment approach, the authors emphasize that the biochar-based catalyst in AOPs in real field wastewater must be further evaluated. Design of more compact and simple reactors, which can accommodate biochar-based catalysts, is required for real field applications. Hence, pilot-scale studies have to be conducted to gain insight into the applicability at the industrial level.

Despite the effectiveness of the hybrid system in drug removal, few studies closely matched a combination of AOP and biochar for AEDs degradation. Liu et al. (2019) achieved 97% of carbamazepine removal by coupling a reductive process with zero valence iron and biochar. At the same time, AOPs have shown an essential role in the degradation of AEDs, especially carbamazepine (Huang et al. 2021), primidone (Sgroi et al. 2021), and diazepam (Yang et al. 2020), all of them belonging to the class of older AEDs.

As mentioned above, the biochar application for AEDs degradation has been focused on carbamazepine. Recent studies show excellent degradation efficiencies for different compounds, such as primidone (Yanala and Pagilla 2020) and lamotrigine (Li et al. 2020). Therefore, the literature validates the critical role of different non-combined AOPs and biochar for the effective treatment of wastewater containing AEDs. It is also observed that the coupling of processes has shown encouraging results for other classes of drugs, mainly with regard to the low biodegradability and high toxicity of these compounds.

In this regard, a good response is expected from the application of hybrid systems combining biochar and AOP to remove antiepileptics, since the behavior for most of the drugs already studied is quite impressive. In addition, the exploration of second- and third-generation AEDs is expected, as studies generally focus on older AEDs. Thus, an opportunity opens up for future investigations in this area.

10.3.2 Biochar as a Support Material in Enzymatic Biocatalysis

The degradation or transformation of emerging contaminants can be catalyzed biologically using a wide spectrum of enzymes and microorganisms. Enzymatic biocatalysis is an environmentally safe alternative, low energy consuming, and operated under moderate conditions. In this scenario, microorganisms and enzymes stand out as a promising pathway for the selective removal of contaminants in wastewater, including AEDs.

The biodegradation of drugs can be directly catalyzed by oxidoreductase enzymes or by applying microorganisms that produce a consortium of enzymes (Yang et al. 2021). Fungal enzymes, mainly produced by white-rot fungi, have been evaluated for this purpose due to their action on a wide spectrum of substrates (Naghdi et al. 2018). Other microorganisms have also been studied, such as the bacteria *Pseudomonas stutzeri* and *Shewanella putrefaciens* (Yang et al. 2021).

Although each enzyme has specificities and unique mechanisms of action resulting from different producing microorganisms and environmental conditions, the principle of all oxidoreductases is based on the generation of free radicals and ions, responsible for the biotransformation of compounds in subsequent reactions. The most-reported oxidoreductase enzymes for removing emerging compounds are lignin peroxidase (LiP), manganese peroxidase (MnP), versatile peroxidase, laccase (Lac), and tyrosinases (Bilal et al. 2019). Lac is the most used enzyme for drug removal, mainly because it has low specificity and uses oxygen as an electron acceptor. This allows the catalysis of a wide spectrum of compounds, making it relevant in wastewater treatment systems (Viancelli et al. 2020).

Reactions catalyzed by enzymes generally do not mineralize the substrate but form free radicals that can be disintegrated into fractions of transformation products, which may have less toxicity or be more biodegradable than the parent compounds. Therefore, oxidative enzymes for wastewater treatment are an attractive route for removing micropollutants (Unuofin et al. 2019). However, one of the significant challenges of the enzymatic process performance in WWTPs to remove recalcitrant compounds, such as AEDs, is the process's stability, which can be affected by variations in operational parameters. Besides, the use of enzymes in the free form is not viable, considering that the entire enzyme would be lost with each batch.

To improve the process feasibility, techniques for immobilizing microbial cells and enzymes have been widely evaluated. The immobilization process is carried out by adhering the microorganism cells or enzymes to support materials, making it advantageous due to easy handling, excellent stability, reuse potential, and greater ability to withstand adverse conditions, including variations in pH and temperature, and inhibitors' presence. The use of carbon-based materials (such as biochar) as a support material for immobilizing enzymes has demonstrated high efficiency, making them an important advance for these processes (Zdarta et al. 2018). Enzymes immobilized in biochar showed improved stability in relation to the free enzyme and recyclability with low loss of enzyme activity, which is of great relevance for the economic viability of wastewater treatment (Naghdi et al. 2017).

The adsorption method, conducted keeping the enzyme and biochar in contact, is widely used because it is simple and economical. However, it occurs through weak chemical bonds, thus facilitating enzyme leaching. The covalent bond immobilization process has the main advantage of enzyme slower release and greater stability. In continuous processes, immobilization by covalent bonds may be preferred (Lonappan et al. 2018).

The use of enzymes or microorganisms immobilized in biochar in drug biodegradation processes occurs through two main mechanisms: (1) enzymatic catalysis, where the compound occupies the active sites of the enzyme through adsorption, which are released following the enzymatic action; and (2) removal of compounds by adsorption in the pores of the biochar, without degradation (Naghdi et al. 2017). In the Naghdi et al. (2017) study, it was estimated that the first mechanism was responsible for more than 45% of carbamazepine removal from wastewater, while the second one removed less than 30%, highlighting the relevance of enzyme immobilization to increase efficiency and avoid rapid saturation of material adsorption sites, allowing for continuous treatment processes.

The functionalization of biochar through chemical processes is interesting for immobilization since it leads to functional groups' formation on the material surface. This functionalization favors the formation of anchor points, providing stronger connections between the support and the enzyme through electrostatic interactions (Naghdi et al. 2017). After biochar functionalization with nitric acid and sulfuric acid, the concentration of functional groups on the surface increased, and there was no change in the material structure. The use of laccase immobilized in functionalized biochar demonstrated the potential to reduce 86% of carbamazepine concentration on secondary effluent (Naghdi et al. 2017).

Advances related to biocatalysts immobilization to remove AEDs, whether by microorganisms or enzymes, are still very scarce. This demonstrates a research field with a large gap, especially considering the persistence of these compounds in the environment. In this scenario, it is essential to understand the biodegradation pathways of anticonvulsants and the already reported efficiency of enzymes and microorganisms to remediate these compounds.

When evaluating the drug lamotrigine in the biodegradation process with substrate colonized by the fungus *Pleorotus ostreatus* with laccase activity, a 73% reduction in the drug concentration was observed in just 5 min of incubation (Hultberg et al. 2020). Another recent study reported that it took 20 days for 93% lamotrigine biodegradation through the fungus *Pleorotus ostreatus*. The simultaneous presence of carbamazepine and lamotrigine in wastewater hindered the biological removal of the compounds, in which case the removal of carbamazepine was not affected. However, lamotrigine removal was slower, assuming that the fungus oxidation mechanism of both drugs was the same (Chefetz et al. 2019). Even in the absence of immobilization processes, these advances are relevant to the understanding of biodegradation pathways and to the development of new technologies from exploratory investigations with high efficiencies, as observed in these studies.

It is essential to highlight that the immobilization of enzymes in biochar concomitant with its potential to remove AEDs is an area that is still little explored. Some studies related to enzymatic immobilization in biochar with application purpose for other classes of drugs, such as antibiotics and anti-inflammatories (Lonappan et al. 2018; Yang et al. 2021), reinforce the need for advances in research to remove AEDs by enzymatic process combined with biochar. Also, the lack of newer AEDs exploration is enormous in this research area, opening an opportunity for further findings.

10.4 Conclusions and Future Perspectives

The perspectives explored in this chapter from the public to environmental health problem of epilepsy disease and antiepileptic drugs shows considerable gaps to be filled both in the pharmaceutical industry and in environmental sciences. Although the availability of several medicines in the market for epilepsy treatment, especially the older ones, just a few of them have been widely studied.

So far, the long-term consequences in people with epilepsy life treated by older AEDs are worrying. Still, there is a lack of global engagement to solve the epilepsy burden, from social to treatment aspects. This same gap has been seen to solve the problems of wastewater treatment plants containing these drugs, increasing the environmental risks caused by their disposal in water bodies.

The environmental regulation should be improved and reinforced to include more emerging contaminants as target compounds, motivating the use of new technologies in wastewater treatment. The lack of research on AEDs, especially from second and third generations, investigating their fate, occurrence, translocation, and biotransformation, emphasizes the task emergency. Efforts are required in order to understand the removal mechanisms and associated toxicity of novel degradation processes, such as hybrid systems combining biochar and advanced oxidation processes, or enzymatic biocatalysis using biochar as a support material. These treatment processes have great potential to fill gaps in the environmental health problem of anticonvulsants.

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Biochar: A Futuristic Tool to Remove Heavy Metals from Contaminated Soils

11

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Abstract

Biochar has seized interest due to its important impact on the remediation of heavy-metal-contaminated soil. Based on the research accomplishments of biochar remediation of heavy-metal-contaminated soils in recent years, a variety of important aspects, including development and properties of biochar, remediation processes, remediation effects, and influencing factors, are examined for research status and advancement in this sector. The following results have been obtained: (a) Biochar has the advantages of low price, good performance, greening, and enhancement of the soil. (b) Biomass materials and pyrolysis temperatures influence the physicochemical properties of biochars. The adsorption of heavy metals on biochar can be enhanced by activation, magnetization, oxidation, and digestion. (c) Two opposing factors are involved in the effects of biochar on heavy metal mobility and bioavailability: the immobilization of heavy metals to minimize bioavailability or the mobilization of heavy metals to improve bioavailability. (d) Biochar can be used to improve the quality of the treated soil with other solidifying materials. (e) Physical adsorption, ion exchange, electrostatic interaction, complexation, and precipitation comprise the adsorption processes of heavy metals on biochar. Finally, future research is proposed, including the development of a standardized biochar classification criterion; the investigation of the effectiveness of biochar in the remediation of multicontaminant sites; the illustration of the interactions between biochar and heavy metals in the diverse soil environment; and the extension of the research scale from laboratory- and small-scale in situ testing to large-scale and long-scale in situ testing.

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Keywords

Biochar · Pyrolysis · Remediation · Contaminated soil · Heavy metal

11.1 Introduction

The inefficient and intensive use of pesticides to manage crop pests and diseases led to infection of agricultural soils and related ecosystems (Chiari et al. 2017; Jallow et al. 2017; Mostafalou and Abdollahi 2017; Shahid et al. 2016; Tosi and Nieh 2019; Khalid et al. 2020). Heavy metals are discharged from different industries viz., mining, metallic finishing, electroplating, glass, textiles, ceramics, and garage batteries. Recently, there are growing considerations over water pollutants, which in the long run directly or indirectly combine with agricultural land. Soil pollutants with pesticides, herbicides, industrial water, and alternative practices (which contain heavy metallic ions) can also additionally stop up in fluctuations in physicochemical properties and microbial properties of agricultural soils. As a soil health and human health purpose of view it is essential to decrease the impact of heavy metal inside the soil. To manage the venturesome results and preferably repair the system offerings of infected soils, an array of in situ and ex situ remedy strategies are developed, as properly as surface capping, encapsulation, landfilling, soil flushing, soil washing, soil emanation (air sparing), vacuum ventilation (vapor extraction), thermal extraction, electro kinetic extraction, chemical degradation, stabilization, solidification, vitrification, bioremediation, and phytoremediation (Zhu et al. 2010; Liu et al. 2018). These strategies use physical, chemical, thermal, electrical, and biological strategies and tactics to contain, immobilize, and in the end cast off soil contaminants (Fig. 11.1). In the field, all of the available solutions highlight the benefits and drawbacks of treatment potency, cost effectiveness, and pertinence (Liu et al. 2018). Recently, biochar change has been investigated to relieve soil infection and facilitate soil remedy (Chai et al. 2012; Houben et al. 2013; Koltowski et al. 2016; Ippolito et al. 2017; Guo et al. 2020).

Biochar is a carbon-rich byproduct of pyrolyzing biomass at high temperatures and low oxygen levels for biofuel production (Lehmann 2007) and though it's type of like alternative charcoals, biochar is outlined through its intentional application to the soil for environmental applications (Lehmann and Joseph 2015). It contains extremely condensed aromatic structures that face up to decomposition in soil and therefore will correctly sequester some of the implemented carbon for lots of years to centuries (Lehmann et al. 2006; Novak et al. 2009; Wardle et al. 2008). One evaluation estimates that significant use of biochar might mitigate up to 12% of current anthropogenic CO_2 emissions (Woolf et al. 2010; Biederman and Harpole 2013).

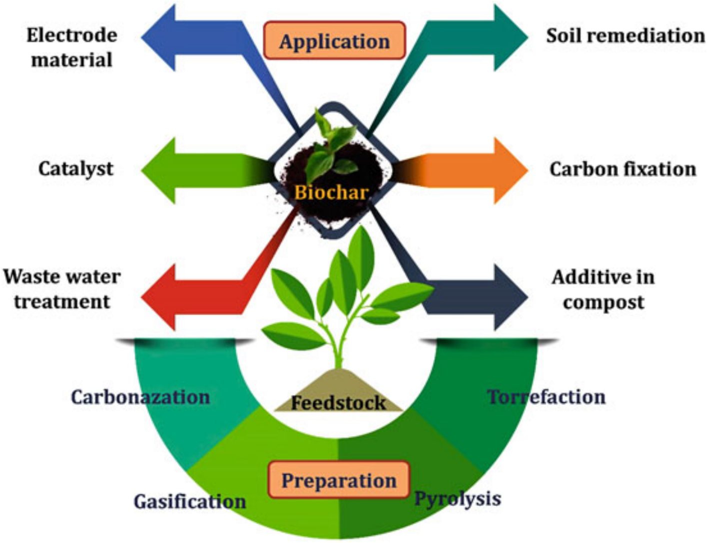

Fig. 11.1 Preparation and application of biochar

11.2 Preparations of Biochar

The physical and chemical residences of biochar rely absolutely on the categories of feedstock and pyrolysis situations, i.e., temperature, residence time, reactor kind, and heating rate. The most thermochemical procedures that are commonly used to generate biochar square measure slow carbonization, fast pyrolysis, flash carbonization, gasification, and microwave assisted pyrolysis (Manya 2012). It's true that biochar produced at high temperatures (600°C to 700°C) contains less H and O functional groups due to drying and deoxygenation of the biomass, but it also has a very aromatic character with well-organized C layers and lower ion exchange capacities (Uchimiya et al. 2011; Ahmad et al. 2014). On the opposite hand, the biochar created at decreased temperature (300–400 °C) suggests numerous natural characters, aliphatic and cellulose kind systems and contain additional C—H and C==C functional group (Glaser et al. 2002). It is this advanced and heterogenous physical and chemical composition of biochar that gives its wonderful properties of contamination elimination via activity (Vithanage et al. 2015; Godwin et al. 2019).

11.2.1 Feedstocks

The feedstocks for each conventional and microwave-aided pyrolysis is biomass. During pyrolysis the proportion of cellulose, hemi-cellulose, and lignin content determines the ratios of bio-oil, fueloline, and biochar in pyrolysis product. It has been incontestable that feedstocks with high lignin content produce the very best biochar yield once pyrolyzed at slight temperatures, viz. 500 °C (Fushimi et al. 2003). Therefore, selection of pyrolysis feedstocks is also decided by the required stability between the various pyrolysis products (biochar, bio-oil, fueloline). Biomass is any residing or lately residing organic material with the ability as a source of energy (Motasemi and Afzal 2013). Biomass is believed to possess the ability to become one of the foremost reasserts of energy in the subsequent century (Berndes et al. 2003). The biomass as a source of energy is carbon-neutral, renewable, promptly available in nature, comparatively decreased S (sulfur) content, and feature the ability to be the maximum effective different to fuel sources. Replacing fuel with biomass as a source of energy will reduce pollutants and global warming, alleviate the energy disaster, and make contributions toward property development (Hall 1997; Panwar et al. 2011). Biomass sources will be classified into three essential categories: (1) virgin sources, (2) residues, and (3) municipal solid waste (Motasemi and Afzal 2013). The virgin sources include forest sources and oilseed/cereal crops. The residues are also timber residues, agricultural residues, and wastes of livestock residues. Municipal stable waste may be residential or non-residential. With an acceptable conversion method those classes of biomass will be promising resets of energy for the longer term. The municipal stable wastes and forest and agricultural residues are promising substitutes for microwave pyrolysis processes. Extensive study has been conducted using those lingo-cellulosic feedstocks, as well as virgin sources and residues. wood, wood pellets, tea trash, coffee hulls, biodegradable sewage sludge, wheat straw, rice straw, macro and microalgae, maize fodder all have unquestionable fantastic potentials as pyrolysis feedstocks (Miura et al. 2004; Domínguez et al. 2007; Yagmur et al. 2008; Budarin et al. 2009, 2011; Huang et al. 2010; Godwin et al. 2019).

11.2.2 Conventional Pyrolysis

This is the standard heating system in which heat is transferred from an external supply to the biomass through conductivity, radiation, and convection. In this methodology, the heat/temperature on the floor of the feedstock is extremely excessive and reduces toward the center of the feedstock. In standard pyrolysis method the most important method variables are that (I) the heating is low and (II) the vapor residence time is long (Manya 2012). This methodology has been used to manufacture charcoal for many years. During this pyrolysis there are some known variables that decide performance and yield of the process. These parameters are strain and wet content material of the feedstock (Antal and Grønli 2003). The peak temperature is the highest temperature reached during the conventional pyrolysis procedure. It has been stated that a rise in the height temperature results in a rise in the biochar fixed-content material (Manya 2012). The operational strain of the pyrolysis method has vital effect on the properties of the produced biochar. A study on the pyrolysis of various biomass feedstocks (eucalyptus wood, radiata pine, sugar cane bagasse) (Cetin et al. 2004) discovered that increasing the operational strain leads to a decrease in the total expanse of the char. Similar results were conjointly reported during a slow pyrolysis of Miscanthus (Melligan et al. 2011). They observed a major decrease in BET expanse of char from 161.7 m^2/g at 0.1 MPa to 0.137 m^2/g at 2.6 MPa. The researchers attribute these findings to deposits of tar clogging the char pores as a result of high strain. According to studies on the effects of wet content material in biomass feedstocks, top moisture content material complements charcoal production when subjected to high pressures. As a result, maximal biomass with high moisture content is particularly appealing for biochar production via conventional pyrolysis (Manya 2012). This pyrolysis approach is inefficient and slow, and it is also dependent on the biomass thermal conductivity as well as the system's convection present day (Godwin et al. 2019).

11.2.3 Microwave-Assisted Pyrolysis

Pyrolysis of biomass using microwave entails strength conversion rather than mere heating. At some point of this approach, electromagnetic energy is regenerated into thermal energy by using dielectric heating (Motasemi and Afzal 2013). Furthermore, the heat is generated during the biomass volume as a substitute than an external supply. In contrast to typical pyrolysis, the temperature of the feedstock at its centre is higher than the temperature of the components.

The microwave-aided pyrolysis approach is among the foremost promising strategies of fast and improving chemical reactions. As an end result of the economical heat transfer profile, the chemical reactions are completed at a shorter time and efficiently in comparison with alternative thermo-chemical processes (Lidstrom et al. 2001; Salema et al. 2017; Nhuchhen et al. 2018). The advantages of this system over competing pyrolysis strategies are that it accelerates chemical reactions and shortens their duration, saving energy surface and time (Godwin et al. 2019).

11.2.4 Impregnation-Pyrolysis

The preparation of magnetic biochar by impregnation-pyrolysis is accomplished by impregnating biomass with a solution containing transition metal salts while removing the solvent. The dried residue muffle chamber is then pyrolyzed in an oxygen-depleted or inert atmosphere to generate funding for the magnetic biochar product. Thus, pyrolysis and magnetization are finished in a single step, thereby guaranteeing that the physicochemical properties and surface assimilation capability of the magnetic biochar are tightly managed by the operative parameters (e.g., pyrolysis temperature, inert gas, and pyrolysis time) (Li et al. 2017; Yang et al. 2019). For example, Liu et al. (2020) discovered that the Cr (VI)-adsorption capacities of magnetic biochar synthesized at varied temperatures (650–800 °C) ranged from 182.32 to 223.21 mg/g and have been proportional to the pyrolysis temperature. Furthermore, when the pyrolysis temperature rises, the species of iron oxides in magnetic biochar are reduced. For example, Wang et al. (2019a, b) discovered that the iron oxides present in magnetic biochar modified with a rise in pyrolysis temperature. Hematite, magnetite, wustite, and zero-valent iron are the oxides that develop as a function of temperature (Yi et al. 2019).

11.2.5 Co-precipitation

The synthesis of magnetic biochar by co-precipitation includes the dispersion of biochar into a solution containing transition metals, accompanied by the addition of sodium hydroxide or ammonium hydroxide solution at a particular temperature and the subsequent stirring of the aggregate for a period of time at pH scale 9–11. Next, the supernatant is removed and consequently the residue is washed and then dried to afford magnetic biochar. This methodology is more sophisticated than the impregnation-pyrolysis methodology; however it is more manageable, allowing the magnetic medium to be stably adhered to the biochar matrix. Recently, researchers have consistently compared the pollutant-adsorption capability of magnetic biochar synthesized by two strategies. As an example, Wang et al. (2015) demonstrated that magnetic biochar synthesized by co-precipitation had an adsorption capacity for arsenic that was sevenfold higher than that of magnetic biochar synthesized by impregnation-pyrolysis. Conversely, Zhou et al. (2019) demonstrated that the magnetic biochar prepared by impregnation-pyrolysis removed fluoride more efficaciously than did the magnetic biochar synthesized by co-precipitation. Therefore, target waste characteristics ought to be notion before the synthesis of magnetic biochar for pollutant removal, to modify the acceptable artificial synthetic to be elite (Yi et al. 2019).

11.2.6 Reductive Co-deposition

The subtractive co-deposition approach is similar to the co-precipitation technique, but it varies in that the transition metals are reduced in their mixture with biochar using lowering agents like as sodium borohydride or potassium borohydride. Once During the reaction, the supernatant is removed and consequently the residue is washed and vacuum dried to get magnetic biochar. Surprisingly, this substance contains nanoparticles and primarily zero-valent metals, which significantly reduces and increases the pollution removal performance of magnetic biochar. Zhu et al. (2018) determined that the adsorption ability of reductively co-precipitated magnetic biochar for Cr(VI) was 58.82 mg/g, in which maximum of the Cr(VI) turned into decreased to Cr(III). As a result, magnetic biochar with improved pollutant- elimination performance is frequently synthesized using this technique; however, the reluctant required is hazardous, and hydrogen is produced during the reduction process, implying that this technique has some capability protection risks, particularly if used at scale. (Yi et al., 2019).

11.2.7 Hydrothermal Carbonization

Hydrothermal carbonization is the heterogeneous reaction of biomass with a metal particle solution at a lower temperature (100–300°C) than pyrolysis, and at a pressure generated by the reaction itself. These are milder reaction situations than the previous ways, and besides the very fact that an alkali or a powerful reducer is not required, this synthesis is more enticing. For instance, Zhang et al. (2018) successfully synthesized magnetic biochar by this hydrothermal technique from iron-containing sludge and sludge at 473 K and used the ensuing product as a Fenton-like catalyst to fully degrade methylene blue. Similarly, Cai et al. (2017) observed that magnetic biochar synthesized by this technique had a maximum floor assimilation capability for Cr (VI) of as much as 142.86 mg/g, which was more than that of maximum magnetic biochars prepared by of co-precipitation (Shang et al. 2016), subtractive co-deposition (Zhou et al. 2018), or impregnation-pyrolysis (Yi et al. 2019).

11.2.8 Other Preparation Methods

In recent years, alternative preparation strategies are developed like ball-milling (solvent free mechanical combining of biochar and iron oxides) (Shang et al. 2016), direct pyrolysis of biomass/metal salts (also acknowledged as the molten salt method) (Dai et al. 2019), cross-linking of biochar and iron oxides (Mojiri et al. 2019), and microwave-assisted pyrolysis (Yap et al. 2017). For example, Shang et al. (2016) demonstrated that the surface assimilation capacities of magnetic biochar synthesized by ball-milling of biochar and iron oxide for the pharmaceuticals carbamazepine and tetracycline have been 62.7 mg/g and 94.2 mg/g, respectively. Additionally, Dai et al. (2019) found that the herbicides dichlorophenol and atrazine have been very efficiently eliminated by magnetic biochar synthesized by the molten salt technique. To further enhance the utility of magnetic biochar in environmental remediation, several researchers have treated it with alternative metals, or with acids and bases, or functionalized it with varied chemical moieties to enhance its surface assimilation property and capability. For example, Li et al. (2017) determined that the amendment of magnetic biochar with the linear polysaccharide chitosan yielded a material with advanced surface morphology and considerably improved surface assimilation capability for Cd (II). Similarly, Li et al. (2017) CeO2–MoS2 treated magnetic biochar showed a maximum surface assimilation capability for lead of 263.6 mg/g, which was several times higher than untreated magnetic biochar. The maximum ordinarily used strategies have been impregnation-pyrolysis (39%) and co-precipitation (30%). Hydrothermal carbonization, subtractive co-deposition, and other artificial strategies are alternative methods to get magnetic biochar. Therefore, the character of the stuff, the physicochemical properties of the pollutants, and consequently the technique operability ought to be rigorously thought about when choosing an artificial method to magnetic biochar (Yi et al. 2019).

11.2.9 Biochar Made Using from Nanoparticle

Metal nanoparticles of biochar will be produced by pretreating biomass mistreatment with metallic salt before pyrolysis. Firstly, the biomass is impregnated with metallic salts ($FeCl_3$, $Fe(NO_3)_3$, $AlCl_3$, $MgCl_2$, $MnCl_2$, $CaCl_2$, $ZnCl_2$, etc.), sulfur-based metallic salts, and natural primarily based totally metallic salts solutions in an electrical area or no electric powered area (Jung and Ahn 2016). Metallic ions from the solutions are deposited onto the surface or indoors of feedstocks. Secondly, the pretreated biomass is pyrolyzed at comparatively decreased temperature beginning from 400 to 800 °C in an O_2 limited or O_2-free surroundings when drying.

In the pyrolysis techniques, metallic ions are going to be reborn to metallic oxide nanoparticles (Fe_2O_3, Al_2O_3, MgO, MnO_2, CaO, ZnO, etc.) or zero valent ions on the surface of biochar. For instance, Fe_3O_4 in most cases primarily based totally magnetic biochar become ready with the aid of using the pyrolysis of $FeCl_3$ pretreated corn straw in an electrical field at 600 °C for 1 h (Yang et al. 2019). The presence of evenly dispersed rod-like Fe3O4 nanoparticles was confirmed by characterization of Fe3O4 on a fully magnetic biochar surface in the majority of cases. Additionally, the end result unconcealed that Fe_3O_4 primarily based magnetic biochar confirmed an impressive lead surface assimilation capability. A unique magnesium impregnated biochar was prepared through the pyrolysis of $MgCl_2$ pretreated biomass feedstock at 10 °C/min as much as 600 °C under O_2 limited situations for 1 h (Chen et al. 2018). The consequences confirmed that nano sized magnesium oxides were equally distributed on the surface of biochar with a thickness of over 4.3 nm and MgO biochar displayed a mesoporous shape with common pore length of 1.74μm. The MgO biochar composites exhibited excessive phosphate surface assimilation capability from solution. Thermal pyrolysis of bismuth oxide and hydrochloric acid pretreatment wheat straw at 400 to 600 °C with a heating rate of 10 °C/min in a highly nitrogen environment atmosphere for 1 hour produced bismuth impregnated biochar (Zhu et al. 2016). Morphology examination indicated that the flourishing pore shape with a diameter between 0.5 and 1μm become ascertained in bismuth impregnated biochar and consequently the white global debris have been firmly grafted in the internal and outer surface of biochar. For phosphorus, arsenic, and chromium, bismuth-modified biochar shown a high capacity for floor assimilation. A useful biochar supported magnetic $MnFe_2O_4$ nano composite become ready through the pyrolysis of Fe $(NO_3)_3$ and $Mn(NO_3)_2$ pretreated corn straw at 500 °C in a very element environment for 5 h (Zhang et al. 2019). Characterization consequences indicated that magnetic $MnFe_2O_4$ debris have been with success supported on surface of biochar and confirmed excessive dispersion at the floor of biochar. Furthermore, the composite confirmed wonderful overall performance in the elimination of Cd (II) and Pb (II) (Liu et al. 2020).

The second synthesis technique of metal nanoparticles of biochar is assisting metallic nanoparticles onto biochar. Firstly, the biomass become reborn to biochar by pyrolysis hydrothermal carbonization and gasification. Afterward, biochar become soaked inside the metallic salts solution and metallic ions have been adsorbable to the pores and surface of biochar. Finally, metallic nanoparticles have been brought about onto the surface of biochar to make the composites by using the reduction technique of pyrolysis adjustment of metallic salt solution pH and alternative ways (Liao et al. 2018). For example, Kim et al. (2019) studied that iron changed biochar and utilized it to get rid of arsenite from water. Miscanthus become foremost pyrolyzed to provide biochar at 500 °C with a rate of 10 °C/min for 1 h in a nitrogen present in environment. Iron ions have been precipitated onto biochar by the adjustment of pH to 9 with sodium hydroxide. Fe modified biochar exhibited advanced overall performance on the surface assimilation of arsenite. The sewage sludge become foremost pyrolyzed at 600 °C with a rate of 10 °C/min in a nitrogen present in atmosphere for 3 h to arrange sewage sludge derived biochar and afterward zero valent iron nanoparticles have been immobilized on biochar (Diao et al. 2018). Characterization effects confirmed that lots of porous systems have been ascertained and zero valent iron nanoparticles have been deposited on the surface of biochar. Pb^{2+} and Cr^{6+} may also be efficiently removed. Biochar supported iron nanoparticles are created and are utilized to remove heavy metals from aqueous solution (Zhu et al. 2016). The wetland plant become foremost pyrolyzed reed to arrange biochar at a temperature of 600 °C for 1.5 h under N_2 condition. Nanoscale zero valent iron become prepared via the chemical reduction technique and it had been supported onto the surface of biochar. Wan et al. (2017) used available biochar to support MgFe and MgAl double hydroxides for phosphate recovery from wastewater. Bamboo biochar become foremost ready by using slow pyrolysis of bamboo at 600 °C in nitrogen present in atmosphere for 2 h. The metallic hydroxide has been brought about onto biochar by adjusting solution pH. Characterization end result analysis confirmed biochar may also act as a good aid for MgFe and MgAl superimposed double hydroxides. The experimental consequences indicated that the composites displayed excessive phosphate surface assimilation (Liu et al. 2020).

The third synthesis technique reportable to arrange metal nanoparticles of biochar is when pyrolyzing the biomass enriching the goal metallic component (Dai et al. 2019; Cho et al. 2019; Mian et al. 2019). The metallic component inside the biomass is reborn to metallic nanoparticles by using thermal pyrolysis. For instance, a calcium wealthy biochar is created by direct carbonization of crab shell at 300–900 °C with the heating rate of 10 °C/min for 2 h and it had been used for phosphorus elimination (Dai et al. 2019). Characterization evaluation indicated the most metallic component calcium and consequently the formation of lime in crab shell biochar. The elimination experiments prompt that calcium wealthy biochar is used for the elimination of phosphate in water. An enriched magnesium biochar is created by direct carbonization of magnesium wealthy tomato tissues at 600 °C for 2 h in nitrogen surroundings (Yao et al. 2013). Scanning electron microcopy, X-ray photoelectron spectroscopy, and X-ray diffraction confirmed a mass of nanoscale periclase and magnesium hydroxide particles existed in the built biochar. The material exhibited a higher elimination capacity to phosphate from wastewater. Crayfish shell become at once pyrolyzed at 600 °C with a heating rate of 15 °C/min for 2 h to arrange a calcium rich biochar for lead surface assimilation (Zhang et al. 2019). Scanning electron microcopy, X-ray diffraction, and Fourier transform infrared spectrometry evaluation confirmed that crayfish shell biochar had a mass of

$CaCO_3$ particles on its surface. Calcium enrich crayfish shell biochar may also be extremely powerful for lead elimination from water. A built biochar is created by direct carbonization of magnesium-rich tomato tissues at 600 °C in nitrogen surroundings to get better phosphorus from waste water (Yao et al. 2013). Characterization consequences indicated that the novel built biochar had an oversized variety of magnesium oxide and magnesium hydroxide nanoparticles. This biochar derived from magnesium-enriched tomato tissues displayed robust phosphate surface assimilation capacity. In the artificial techniques of metallic nanoparticles of biochar a few factors like the feedstocks varieties, pyrolysis temperature, ratio of biochar and metallic nanoparticles, and pyrolytic response media have an impact on the properties and overall performance of metallic nanoparticles of biochar. Initially, different feedstock varieties result in different compositions, such as cellulose, hemicellulose, lignin, and inorganic salt (Liu et al. 2020).

11.3 Properties of Biochar

Biochar is often used not only as a soil amendment with the goal of improving soil physical, chemical, and biological properties, but additionally as an adsorbent to remove organic and inorganic pollutants. The capabilities and applications of biochars largely depend on their structural and physicochemical properties; so, it is vital to represent the structural and physicochemical properties of biochar before its use. Various types of biomass (wood, agricultural wastes, dairy farm manure, sewage sludge, and so on) are used to produce biochars under a variety of pyrolysis conditions. Different feedstock reassets and pyrolysis method situations contribute to different structural and physical traits of biochar, including structural complexity, extent, porosity, particle size distribution, density, and mechanical strength (Lehmann and Joseph 2015; Plaimart et al. 2020). During pyrolysis, biomass undergoes a variety of physical, chemical, and molecular changes. Pyrolysis circumstance and feedstock type considerably affect the structural and physicochemical traits of the ensuing biochar product (Zhao et al. 2017).

Biochar is porous, displaying a tough morphological surface with honeycomb like anatomical or different abnormal structures under the microscope. The inherent micropores (diameter in the range of 0.8–235μm and mostly large, with average at 10μm; Hardie et al. 2014) engender the material a comparatively excessive intrapore volume (e.g., 0.9–1 cm^3 g^{-1}; Batista et al. 2018) and low envelope density (e.g., 0.2–0.6 g cm^{-3}; Joseph et al. 2019). Biochar consists frequently of amorphous, aromatic carbon and possesses over abundant oxygen containing surface functional groups (e.g., –C=O, –COOH, and –OH). A disorderly stacked graphene sheet shape has been projected for biochar. The aromaticity of biochar usually will increase whereas the surface practicality decreases due to the fact that the pyrolysis temperature is elevated (Song and Guo 2012; Zhao et al. 2016). That is often an outcome of the innovative losses of aliphatic C–H, olefinic C=C, carbonyl, carboxyl, and hydroxyl groups at a higher temperature (Fu et al. 2012; Tan et al. 2015; Guo et al. 2020).

Biochar will play a crucial position in improving nutrient retention in soil largely due to its surface charge density (Kongthod et al. 2015). Biochar largely has negatively charged surfaces that will increase the surface assimilation capability of cation species (Lou et al. 2016). Biochar has gained interest in the multidisciplinary areas of global warming mitigation, soil amendment, crop production enhancement, and carbon sequestration (Glaser et al. 2002; Laird 2008; Tan et al. 2015). Biochar has good capacity for increasing soil fertility (Ahmad et al. 2014). This could be partly attributed to effects on soil microbiology that scale back fertilizer losses via leaching (Atkinson et al. 2010; Tan et al. 2015; Plaimart et al. 2020). Generally, woody biomass provides a plenty of carbon-rich biochar as compared to other feedstocks because it contains variable quantities of hemicellulose, cellulose, lignin, and tiny portions of different natural extractives and inorganic compounds. Xu and Chen (2013) recommend that better lignin and mineral content result in a higher yield of biochar. Therefore, woody biomass is one of the vital sources for biochar production. The structural and physicochemical properties of biochar, like extent, pore structures, surface functional groups, and element composition, may be influenced by varying the pyrolysis circumstance, like pyrolysis temperature, heating rate, and keeping time. The pyrolysis temperature is reported to considerably influence the ultimate structural and physicochemical properties of biochar due to the discharge of volatiles and the formation and volatilization of intermediate melts. Previous research indicated that better temperature resulted in a very better C content material, whereas the losses of nitrogen (N), hydrogen (H), and oxygen (O) were additionally recorded. Additionally, increasing the temperature causes a rise in the ash and stuck carbon contents and lowers the content material of unstable materials. Furthermore, the rise in pyrolysis temperature influences H/C and O/C ratios, porosity, surface area, surface functional groups, cation exchange capability (CEC), and so on (Zhao et al. 2017).

11.4 Remediation of Biochar

Biochar has been explored for mitigating soil heavy metal contamination. Reported analysis using laboratory vessel, greenhouse pot, and subject plot experiments indicates that biochar is capable of efficaciously sorbing heavy metallic cations from water and immobilizing heavy metallic elements in soil and thus serves as a promising amendment for decreasing the eco-toxicity of heavy metal contaminated soils (Guo et al. 2010, 2020; Ahmad et al. 2014; Tan et al. 2015; O'Connor et al. 2018).

Biochar is often used for the correction of soils (or sediments) that are contaminated by inorganic and organic compounds. It is high sorption capability together with its high surface area applicable to immobilize contaminants. Thus, the contaminants will not be eliminated from the matrix however sequestered. It is assumed that the contaminants will not be freed into the matrix until the biochar is degraded. A close discussion concerning the steadiness of biochar over the years is the primary target of this paper. However, the average residence times of pyrogenic organic memories examined under various field settings varied widely, ranging from 6 to 5448 years (Lehmann et al. 2015). A component of this variability owes to the real fact that the models to calculate the mean residence times differed, or that pyrogenic organic matter properties or experimental tactics were completely different (Lehmann et al. 2015; Hilber et al. 2017).

11.4.1 Biochar for Remediation of Soils Contaminated with Organic Compounds

Biochars used for remediation were better suited to immobilize organic than inorganic contaminants (Xie et al. 2015) and activated charcoal reduced organic contaminants more effectively than biochar (Hale et al. 2015). The biochars' comparatively low KD (Soil and sediment solid/liquid partition coefficients) values compared to in situ KOC caused the modest end outcome. As compared to these, the KOC (tendency of a chemical to bind to soils) values no longer contain carbonaceous geosorbents like black carbon, coal, or kerogen that clearly arise in organic matter and exhibit a 10–100 times higher sorption capability than amorphous OC (Cornelissen et al. 2001). None of the char amendments decreased DDT uptake in plants. The C free was assessed by the polyoxymethylene (POM) passive sampler proxy and correlated well with the availability of the earthworms, but no longer with the phytoavailability (Denyes et al. 2016). So, completely different endpoints (earthworms, plants, proxy) under globe situations indicated contradicting results and consequently the form and kind of char influences the end result. The restricted data of only field study with biochar leads to inconclusive results. Equilibrium times are, besides the weathering of biochars in soils or sediments, important and need to be taken into consideration before deciding over success or failure of remedy of contaminated sites with biochar (or activated charcoal). Positive or immobilization effects cannot be anticipated to be reached at once, as equilibration instances are also terribly lengthy for biochar or AC modification. A polychlorinated biphenyl-contaminated sediment that was amended with 2% AC reached equilibrium after about 2000–2500 days (Werner et al. 2006). When the batch experiment was mixed, the C free was decreased to a tenth of its original concentration after only 50 days; however once it had been left unmixed, the same result was reached not until about 900 days (Werner et al. 2006; Hilber et al. 2017).

11.4.2 Biochar for Remediation of Soil Contaminated with Heavy Metals

The sorption characteristics of biochar may scale back the bioavailability of unsought elements and reduce ecotoxic outcomes (Karer et al. 2015). Nutrients from organic soil additives together with biochar may enhance the productivity of marginal lands with contaminated soils. As for other soil remediation technologies, it is necessary to survey the site-specific soil and contaminant situations and to check the efficacy of the meant remediation technology at small scale. Different combinations of contaminants might also additionally require bespoke biochars or combinations of biochars with different sorption characteristics. The dominance of the superb or the poor face of biochar for remediation functions relies upon the component and its speciation. Whereas metals occurring predominantly in cationic form are bound by biochar, anionic metals and metalloids won't be immobilized by biochar and display a frowny. Elements like As, B, and Mo that predominantly arise in anionic form are rather mobilized due to negative surface charges of biochar, pH outcomes, and opposition with DOC for binding sites (Beesley et al. 2014). In the following we pay attention on current subject research concerning remediation of heavy metal contaminated sites. The foremost investigated heavy metals are Cd and Pb in paddy rice soils (Cui et al. 2011; Chen et al. 2016) or Zn and Ni (Shen et al. 2016). The uptake of Cd by rice grain was reduced by 57–86% over two seasons (Chen et al. 2016) and by 17–62% over 2 years (Cui et al. 2011). The study of Shen et al. (2016) described that 0.5–2% biochar amendment confirmed reduced acid leachates of Ni and Zn by 83–98% over 3 years, which was comparable to the cement-based treatment performed at constant site in parallel. Despite the fact that the contaminant's absorption into plants was reduced in the preceding study, plants react differentially to the biochar amendment, for example, various rice cultivars reacted differently to Cd uptake. (Chen et al. 2016) or no grass may be planted on the subject (Shen et al. 2016). These results suggest that though biochar has wonderful sorption capacities for heavy metals, other factors like the plant species, the contaminant itself, and the impact of the biochar on soil conditions like pH, available nutrients, earthworm habitats, etc. (Beesley et al. 2014) are required for a site-specific self-reclamation. Shaheen and Rinklebe (2015) compared the immobilisation of Cd and Pb by biochar, chitosan, nanohydroxyapatite, and organoclay to low-cost alternative materials such as limestone, zeolite, bentonite, and others. n research lab and field tests, they discovered that in rapeseed, the availability of elements from soil to soil solutions was altered for Cd and Pb flood plain in response to biochar additions. 100% shows that same elemental means in soils with and while without biochar. 50% implies that in soils with biochar the elements have been only half as available as in soils while without biochar. 200% implies that in soils with biochar the elements had double the provision as compared to soil while without biochar. The decreased availability can be a positive impact. All research that confirmed increased availabilities of heavy metals after biochar amendments have been marked with a frowny. The biochar and chitosan amendments decreased the Cd concentrations in the plant, and thus did zeolite and bentonite. In contrast, the amendment with limestone increased the Cd concentration in B. napus. Limestone increased the carbonate fraction ($CaCO_3$ content material in limestone is 98.5%), which induced Cd precipitation and complexation with carbonates, and was then mobilized inside the acid *rhizosphere* zone and brought up into the plant (Shaheen and Rinklebe 2015). The researchers proposed to take benefit of this increased phyto-extraction for Cd for the utilization of rapeseed as bioenergy crop. Biochar might indirectly remediate Cd-contaminated soils by phytoremediation. The consequences of the rising amendments, besides organoclay, confirmed also a minimized uptake of Pb into the plant, so did all low value amendments besides zeolite. It has been concluded that subject and long-term study with biochar and contaminated soils are extremely limited for both natural pollutants and heavy metals, implying future research needs (Zhang et al. 2013). Another aspect of biochar amendment can be the decreased mineralization as opposed to the immobilization and occasional bioavailability and accessibility of the contaminants. These outcomes of contrary directions, immobilization, and microbial degradation of biochar or activated charcoal amendment need to be rigorously and consistently evaluated (Gouliarmou et al. 2013; Zhang et al. 2015; Hilber et al. 2017).

Heavy metals in soil will be degraded, posing a risk to the ecosystem. They will enter the food chain through plants and move into bodies of water (Nathanail and Bardos (2005) used the source pathway receptor model to simplify the interaction between organisms and heavy metals, indicating that heavy metal-infected locations may be remediated by removing sources, removing the pathway, or modifying the publicity to the receiver (Fig. 11.2) (Wang et al. 2019a, b).

Biochar can immobilize heavy metals in the soil, thereby decreasing their mobility and bioavailability. At the same time, addition of biochar to the soil reduces the strength of the soil. Therefore, in this section, the outcomes of biochar on heavy metal contaminated soils are reviewed from the aspects of mobility, bioavailability and strength (Wang et al. 2019a, b).

Biochar will sorb heavy metals and scale back their environmental dangers in soil. Batch experiments (e.g., toxicity characteristic leaching procedure (TCLP) and column leaching) are useful to measure the leachability of heavy metals in biochar treated with contaminated soils. Properties of biochar created from different biomass feedstocks are usually different, which influences the mobility of heavy metals in the soil. Conversely, biochar can also mobilize the heavy metals from soil particles to soil solutions. For instance, arsenic and phosphorus have competitive adsorption on the surface of biochar. The addition of biochar increased phosphorus in the soil and thus forced additional arsenic to be leached out due to the competitive adsorption (Hartley et al. 2009; Wang et al. 2019a, b).

Biochar can also immobilize heavy metals through reduction. For example, in the environment, Cr exists in two main forms: trivalent (chromium (III)) and hexavalent (chromium (III)). Chromium (III) is usually non-toxic and tightly attached to soil particles, whereas chromium (VI) is very poisonous and mobile. Cr (VI) hazards can frequently be reduced by lowering Cr (III) levels (Choppala et al. 2012). The oxygen functional group on the surface of biochar reduces the mobility of Cr (VI) in the soil via influencing its redox response. Choppala et al. (2015) investigated two carbon substances (chicken manure biochar and black carbon) for their effects on the reduction of hexavalent Cr (chromium (VI)) in two spiked (600 mg Cr (VI)/kg) and one tannery waste-contaminated (454 mg Cr (VI)/kg) soils. The results confirmed that the addition of carbon substances enhanced the reduction of Cr and the subsequent immobilization of chromium (III) in soils. The reduction rate of Cr (VI) in the black loam-recovery sandy loam was up to 75%. Under aerobic conditions, the quality and toxicity of arsenic (III) in soil is better than those of

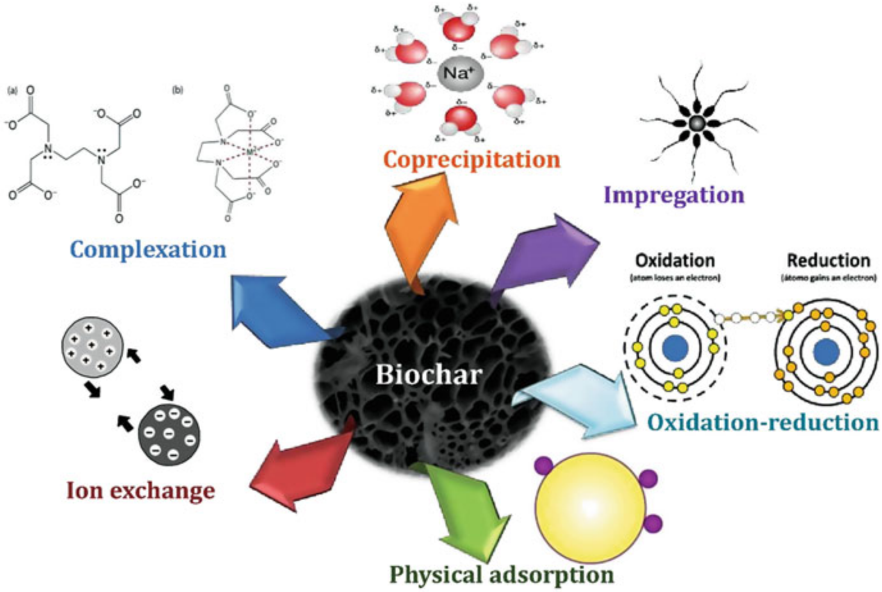

Fig. 11.2 Mechanism of biochar for removal of heavy metals from soil

arsenic (V). Biochar might reduce arsenic (V) to arsenic (III), thereby improving arsenic mobility (Ahmad et al. 2014). The application of biochar might cause increased mobility of arsenic. Therefore, different amendments are required to offset this negative effect. Studies have determined that the application of iron oxide magnetizes biochar and decreases the mobility of arsenic in soil by anion exchange (Warren et al. 2003). It can be seen that biochar might immobilize or mobilize heavy metals in soil, depending on the categories of heavy metals and biochar properties (Wu et al. 2012). The type of soil significantly influences the effectiveness of biochar. Shen et al. (2016) implemented a hardwood biochar to a sandy contaminated soil (95% sand) and discovered a significant decrease in leached nickel and zinc (Zn) from the soil 3 years after the remedy. In contrast, they implemented a similar biochar to a lead (Pb)-contaminated kaolin (35% clay) (Shen et al. 2016) and consequently the remedy confirmed no significant influence on the lead mobility in the soil. Likewise, Shen et al. (2018) implemented a wheat straw biochar to a clay rich contaminated soil. Although the addition of biochar reduced the amount of significant metals (cadmium, copper (Cu), and lead) leached by TCLP, this immobilisation deteriorated with increased ageing. As a result, the efficacy of biochar in immobilising metals in soils is highly dependent on soil type (Wang et al. 2019a, b).

Heavy metals in soil and sediment have the dangers to be absorbed by flora. A pot research is usually used to confirm the bioavailability of heavy metals in soil (Lai et al. 2008). Additionally, the fate of heavy metals in soil determines their bioavailability and environmental risks. At present, the common analytical ways for soil heavy metal forms are the Tessier sequential extraction method and the Community Bureau of Reference consecutive extraction technique. Tessier et al. (1979) developed an analytical process involving consecutive chemical extractions for the partitioning of particulate trace metals (cadmium, cobalt (Co), copper, nickel, lead, zinc, iron and manganese (Mn)) into five fractions: exchangeable, bound to carbonates, bound to iron manganese oxides, bound to organic matter, and residual. The iron manganese oxide bound and also the organic matter bound fractions are usually non-bioavailable. The residual fraction is available inside the crystal lattice of primary or secondary minerals and thus is the maximum stable fraction with very cheap bioavailability. The fate and fractions of heavy metals represent absolutely specific bioavailabilities and effect at the surroundings (Wang et al. 2019a, b).

The combination remediation of biochar and other materials will minimize the bioavailability of heavy metals in soil. Gao (2013) compared the effects of biochar, lime, and biochar and lime-mixed curing agents on pH and cadmium in cadmium-contaminated meadow soil. The experimental results show that the pH of the soil is significantly increased when applying the aforementioned curing agents, and therefore the content of exchangeable cadmium in the soil is decreased to a few extent; the reduction is in the order of biochar and lime mixed > lime > biochar. The concentration of various kinds of cadmium also rose, resulting in a decrease in cadmium bioavailability. At the same time, regression analysis revealed that there is a strong negative connection between soil exchangeable cadmium concentration and pH value. Beesley and Marmiroli (2011) studied the effect of fruit tree biochar and compost on the restoration of naturally infected ore. A pot experiment was conducted to measure the dissolved concentration of heavy metals in pore water and soil extract. Heavy metal migration is influenced by the dissolved organic carbon concentration in compost. Heavy metal bioavailability will be reduced significantly with combined repair. Biochar can reduce the bioavailability of heavy metals, reduce the absorption of heavy metals by flora, and therefore greatly lower the toxicity of heavy metals (Wang et al. 2019a, b).

The density and pore shape of biochar affect the mechanical properties of treated soil. Zhang et al. (2014) studied the effects of three varieties of biochar on the mechanical properties of red soil and carried out experiments on unconfined compressive strength (UCS) and shear strength of soil. The results show that the application of biochar significantly reduces the UCS and shear strength of the soil and a rise in the quantity of biochar implemented results in a rise in compressive strength, but has no significant result on the inner friction angle. As a result of the application of biochar, the soil's macrospores will increase, and the connection between the soil particles will alter, reducing the soil's compressive strength. The findings of the pot experiment reveal a decrease in tensile strength with higher rates of biochar application (Chan et al. 2007; O'Kelly and Som 2014; Wang et al. 2019a, b).

The decrease in soil strength by biochar might aid crop production in agriculture; but, in the context of soil solidification, a diminished soil strength was not expected. There biochar is usually applied with specific alternative materials in solidification/ stabilization to boost the mechanical properties of the soil. Haque et al. (2014)

conducted laboratory UCS tests on biochar mixed clays (BMCs) treated with lime and ground coarse blast furnace slag (GGBS), combined with scanning electron microscopy (SEM) and X-ray diffraction (XRD). It was determined that a rise in GGBS content led to a significant increase in soil strength and an extended curing time will aid the development of the compressive strength. The application of biochar offset the development of soil strength at the initial stage of curing (90 days), resulting in a decrease in compressive strength; however this end result diminished in the long run (after 180 days of curing). SEM and XRD findings revealed three distinct forms of microstructural interactions between biochar and soil particles: interface cementation, surface deposition, and pore area space by cementations minerals, all of which are responsible for the improvement of UCS with curing. Reducing lime content by incorporating biochar and GGBS into soils would create the soil combining a more environmental friendly and sustainable technique. In practical projects, the determination of the remediation plan should consider heavy metal type in soil, environmental conditions, curing age, and the physical and chemical properties of biochar. Akhtar and Sarmah's (2018) studied biochar, a carbonaceous solid material produced from three different waste sources (poultry litter, rice husk and pulp and paper mill sludge), was utilized to exchange cement content up to a quarter of the whole volume and the result of individual biochar mixed with cement on the mechanical properties of concrete was investigated through absolutely specific characterization techniques (thermo gravimetric analysis, XRD, etc.). Biochar has the potential to improve the concrete properties while substituting the cement in minor fractions in typical concrete applications (Wang et al. 2019a, b).

11.5 Modification Methods of Biochar Remediation

The use of biochar as a way of remediating polluted soil and water has been advocated. Standard biochar's practical uses for pollutant immobilisation and removal require further improvements in order to be successful in remedial needs. To increase biochar's remediation effectiveness, physical and chemical methods such as activation, magnetization, oxidation, and digestion are commonly used (Wang et al. 2019a, b).

11.5.1 Steam Activation

Steam activation is an efficient activation technique. During activation, the biochar surface consists lots of advanced pore structure and a bigger pore volume. Hass et al. (2012) investigated the impact of pyrolysis temperature and steam activation on the properties of biochar. It was discovered that steam activation will increase the ssa and pH scale of biochar. The steam activation of biochar made at 350 °C includes a comparable liming impact to soil with that made at 700 °C (Wang et al. 2019a, b).

11.5.2 Magnetization

Magnetization is additionally a way for improving the sorption capability of biochar. Magnetic biochar has strong ferromagnetic capacity and the exhausted/spent biochar can be easily separated and picked up through magnetic separation. Chen et al. (2011) studied three magnetic biochars made through chemical co-precipitation of iron (III) (Fe^{3+})/iron (II) (Fe^{2+}) on orange peel powder and discovered that magnetized biochar includes a large pore diameter and a more potent ability to remove organic contaminants and phosphate from water. Additionally, the g-iron (III) oxide (g-Fe_2O_3) particles at the carbon surface served as sorption sites through electrostatic interactions. Magnetized biochar is simply isolated and eliminated with outside magnets; it is employed in numerous arsenic (As) contaminant elimination applications (Wang et al. 2015).

11.5.3 Oxidation

Oxidation of biochar is accomplished through adding different oxidants such as nitric acid (HNO3), potassium permanganate (KMnO4) (Li et al. 2014), and hydrogen peroxide (H2O2) (Xue et al. 2012) to enhance the adsorption capacities of biochar. Studies have proven that the surface of biochar during oxidation treatment contains a large number of acidic functional groups, and nitric acid is extra effective than potassium permanganate (Li et al. 2014; Wang et al. 2019a, b).

11.5.4 Digestion

Digestion treatment can also enhance the adsorption capacity of biochar. The adsorption capability of biochar made from biomass feedstocks like bagasse (Inyang et al. 2010), beetroot (Yao et al. 2011), and dairy manure (Inyang et al. 2012) treated through anaerobic digestion is far above that without digestion remedy and its adsorption capability is comparable to that of commercially activated carbon. Inyang et al. (2010) discovered that digestible bagasse biochar had higher pH, surface area, CEC, and hydrophobicity and more of negative surface charge (Wang et al. 2019a, b).

At the ssa, functional groups, CEC, pH scale, and alternate physical chemical characteristics of biochar, it can be observed that the varied have diverse outcomes. These modifications are closely associated with the remediation of heavy metal contaminated soil. The alkaline, porous structure and surface O_2 functional groups of biochar are the best indicators for comparing its remediation capability for heavy metals (Wang et al. 2019a, b).

11.6 Remediation Mechanisms of Biochar

11.6.1 Heavy Metal Remediation Mechanisms

Biochar has a porous structure, comparatively high pH values, aromatic components, and active surface functional groups. These properties play a crucial role in the remediation mechanisms of heavy metals in soil, collectively with physical adsorption, ion exchange, electrostatic interaction, complication, and precipitation (Wang et al. 2019a, b).

11.6.2 Physical Adsorption

Physical adsorption, also mentioned as van der Waals adsorption, arises from interactions among the adsorbate and also the adsorbent molecules. As physical adsorption is principally a result of the intermolecular force, the adsorption is mostly reversible. The physical adsorption of heavy metals on biochar is mainly affected by the specific surface area, surface energy, and pore quantity of biochar (Xie et al. 2011; Zhang et al. 2009). A rise in the pyrolysis temperature of biochar will increase its specific surface area and pore quantity, which can significantly increase the contact area among biochar and heavy metallic ions and enhance the physical sorption of biochar. For example, biochar produced from pine wood (700 °C) and switch grass (300 °C) will correctly immobilize copper and uranium (U) by physical adsorption (Liu et al. 2010). Beesley et al. (2014) confirmed that heavy metallic ions like arsenic, cadmium, and Zn are immobilized at the surface of biochar by physical adsorption (Wang et al. 2019a, b).

11.6.3 Ion Exchange

Ion exchange is the selective exchange of exchangeable metal ions/ionizable protons (e.g., sodium (Na^+), potassium (K^+), Calcium (Ca^{2+}) and magnesium (Mg^{2+})) on the biochar surface by heavy steel ions. The efficiency of ion exchange principally relies on surface chemical properties of the biochar. High CEC of biochar will enhance the ion exchange effect between biochar particles and metal cations (Wang et al. 2019a, b).

The biggest CEC of biochar has been found in pyrolysis temperatures of 250–300 °C, because a higher pyrolysis temperature leads to a decrease in the number of acidic oxygen functional groups and oxygen/carbon, which reduces the CEC of biochar (Lee et al. 2010). El-Shafey (2010) investigated the remediation mechanisms of zinc and mercury (Hg) by husk biochar created at 175–180 °C. The results confirmed that acidic oxygen functional groups at the biochar surface like –COOH and –OH will exchange with zinc (Zn^{2+}) and mercury (II) (Hg^+). The cation exchange capability of biochar is closely associated with the pH of soil solution. Once pH values of soil solution are below the pH of biochar at point of zero charge, a lot of heavy metal ions are attracted to the biochar surface via the ion-exchange method. Liu et al. (2010) determined that hydrothermal biochar has abundant oxygen functional groups, whereas pyrolysis biochar have excessive specific surface area that aid the adsorption of copper (II) ions (Cu^{2+}) by ion exchange and physical adsorption, respectively. Additionally, the adsorption capability of hydrothermal biochar was larger than that of pyrolysis biochar, indicating that ion exchange is more effective than physical adsorption (Wang et al. 2019a, b).

11.6.4 Electrostatic Interactions

A high negative charge of biochar will enhance the electrostatic interactions between soil particles and metallic cations to immobilize heavy metals through electrostatic attraction. The biochar metallic electrostatic interaction is principally dependent on soil solution pH, the valence and ionic radius of the heavy metallic and the PZC of biochar (Dong et al. 2011; Mukherjee et al. 2011). Applying biochar to soils will increase the CEC and pH of soil and so increases electrostatic interactions between heavy metallic ions and soil particles (Peng et al. 2011). According to Qiu et al. (2008), wheat and rice straw biochar have a stronger rectification effect than electrostatic interactions between lead (II) ions (Pb2+) and electrostatic biochar. Therefore, electricity interaction is a mechanism for biochar to immobilize heavy metals in soil (Wang et al. 2019a, b).

11.6.5 Complexation

The surface of biomass carbon is rich in oxygen-containing functional groups like –COOH, –COH, and –OH, which complex with heavy metallic ions to make stable complexes (Park et al. 2011). Biochar, when produced in significant quantities, includes an unusually high amount of oxygen functional groups, which efficiently immobilise heavy metals by metallic complexation. The number of oxygen functional groups within biochar will increase over time, which can be caused by oxidation of the biochar surface and carboxyl formation (Harvey et al. 2011). Complexation will be generated between the undoubtedly charged metallic cation and the C=O ligand of the oxygen functional group, like surface complexation of lead (II) ions with free carboxyl and hydroxyl functional groups and inner-sphere complexation of lead (II) ions with free hydroxyl functional groups of mineral oxides (Cao et al. 2009; Lu et al. 2012). The oxygen functional groups of biochar significantly increase the ligands on the soil surface to immobilize more heavy metals by forming ligand–heavy metallic complexes (Tong et al. 2014; Uchimiya et al. 2011). Dong et al. (2011) looked into the mechanisms of Cr correction by sugar beet tailing biochar. Complexation is the most important process for Cr cleanup, according to the results (Wang et al. 2019a, b).

11.6.6 Precipitation

Biochar will co-precipitate with metal cations to create insoluble phosphates and carbonates, thereby immobilizing heavy metals in soil (Shen et al. 2016, 2018). The high-temperature (>300 °C) pyrolysis of cellulose and hemicellulose in plant biomass sometimes produces alkaline biochar to create metal precipitates in soil (Cao and Harris 2010). Animal biochar generally has more ash content, like sodium, potassium, calcium, magnesium, phosphorus, sulfur (S), and silicon (Si), which may react with heavy metals to create insoluble minerals. For example, Cao et al. (2011) observed that cow manure biochar contains a large quantity of phosphate, which may immobilize lead in soil by forming insoluble pyromorphite ($Pb_5(PO_4)_3(OH)$). Additionally, research have proven that dairy-manure-derived biochar adsorbs lead from aqueous solution via precipitation (84–87%) and surface sorption (13–16%) (Cao et al. 2009). Xu et al. (2013) compared the effects and mechanisms of lead, copper, zinc, and cadmium adsorption by rice husk biochar and cow manure biochar and observed that main adsorption mechanism is the precipitation between phosphate or carbonate and metals. The results recommend that precipitation will correctly immobilize heavy metals (Wang et al. 2019a, b).

11.7 Conclusion

Because of significant segment pressure, at a time when the environment is changing and human demands are projected to increase. Biochar treatment is a crucial step in restoring soil fertility. If the pollution of the soil by toxic natural mixtures and heavy metals worsens, the condition of the soil must be improved to minimize environmental change, ensure food protection, power availability, and water accessibility for future generations. Using suitable parent material and fair arrangement techniques for biochar shift not only increases biochar properties, but also increases remediation components such as real adsorption, particle trade, electrostatic partnerships, complexity, and precipitation, all of which are useful in the remediation of soil polluted with natural mixtures and heavy metals.

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Conversion of Agricultural Wastes into Biochar and Its Characteristics

12

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Abstract

This chapter provides an elaboration on the agricultural productivity, resources, and waste management of Asian countries particularly on its high-value crops such as rice, corn, pineapple, coconut, sugarcane, and oil palm. It presents a comprehensive detail on the biomass waste generation from the various crops, its characteristics, and the different thermal conversion processes of agricultural wastes into biochar. The authors aim to provide an effective way to efficiently utilize the agricultural wastes into value-added products as current state of the art in bioenergy generation and utilization for sustainable and green technology innovation.

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Biomass · Biochar · Agricultural waste management · Sustainability · Green technology · Energy generation

12.1 Introduction

Majority of the North Asian countries are equatorial with various weathers, i.e. rainy, winter and summer seasons, which help to have an agricultural diversity. Two of the major crops in India and neighbouring countries are rice and corn, whereas Southeast Asian countries have a tropical climatic region that differs the cropping pattern. Crop selectivity depends on the specific climatic region such as Malaysia has sugarcane as a native perennial crop and oil palm as a commodity crop, and in the Philippines, majority of the agricultural practices are pivoted around fruit farming like pineapple, coconut, etc. A large amount of agricultural productivity revolves around rice, corn, oil palm, sugarcane, coconut and pineapple farming in the Asian region. Figure 12.1 shows the production (million tonnes) of the selected crops in different Asian countries.

Waste generated through all the agricultural activities contributes to the generation of biomass. Biomass is a lignocellulosic energy dense compound, which can be used for energy recovery processes, and it is considered as a renewable resource of energy. Different biomass has different physical and chemical properties due to its diversified origin and species. Also, the same biomass at a different location, geographical condition, age, climate and soil conditions would have different chemical compositions (Kerkeni et al. 2016). Study shows that only 10% of these natural fibres from agricultural wastes are used as alternative raw materials for biocomposites, automotive component, biomedical and other similar industries.

12.1.1 Biomass Waste Generation from Various Crops

Rice (*Oryza sativa*) is considered to be a robust crop that can grow in any soil. The residues from this crop consist of rice husk and rice straw. In India, based on the straw to grain ratio of 1.2, around 4.2 tonnes/ha rice straw is produced, and 200 kg of rice husk is generated for every ton of paddy processed (Soam et al. 2017). These residues are incorporated in the field by open burning, used as animal fodder, or used for the generation of electricity or biogas. Agricultural residues generated from corn (*Zea mays*) include corn cob, corn straw and corn stover. The major end use of corn residues is poultry farming, brewery industries and energy productions (owing to high energy content) (Ficci 2014). The conversion process of oil palm fresh fruit bunch in palm oil mills will produce crude palm oil (CPO) and oil palm biomass such as oil palm trunks (OPT), palm oil sludge (POS), oil palm fronds (OPF), empty fruit bunches (EFB) and palm pressed fibres (PPF), palm kernel shells (PKS) and palm oil mill effluent palm (POME) (Hambali and Rivai 2017). In Indonesia, the oil

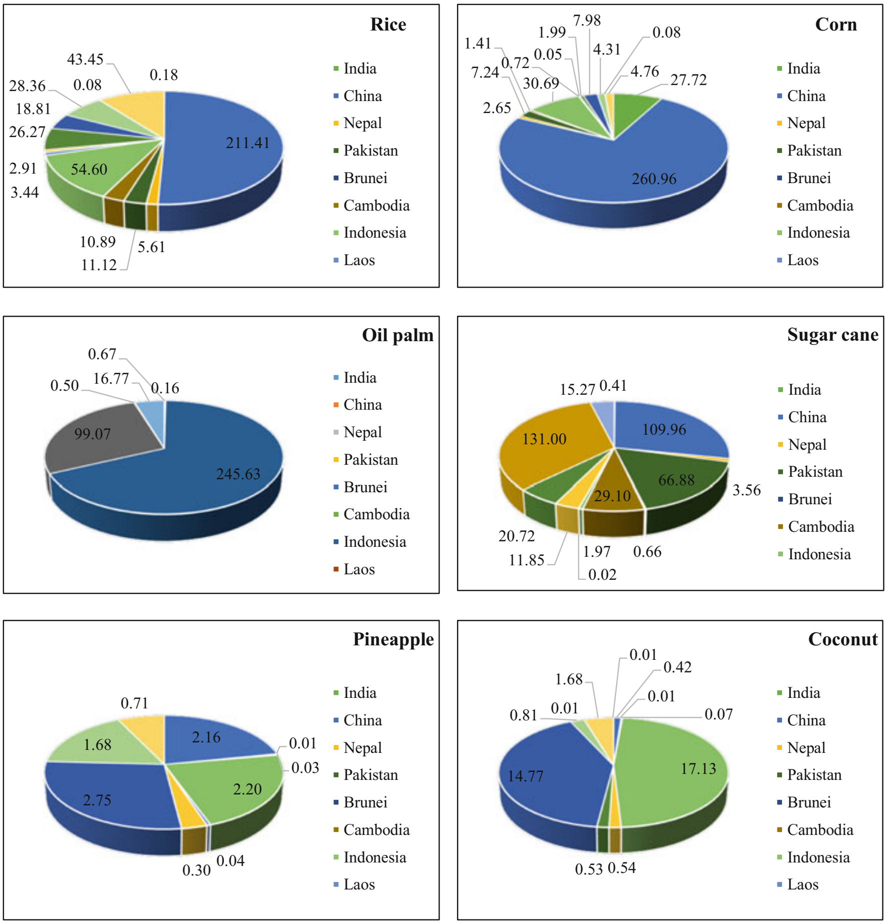

Fig. 12.1 Annual crop production in various Southeast Asian countries in tonnes (FAO 2019)

palm biomass has been estimated at 418 million tonnes by palm oil mills by 2030 (Hambali and Rivai 2017). However, 85–110 million tonnes of biomass, dry solid and liquid are expected to be generated by Malaysia's oil palm industry by 2020 (Onoja et al. 2019). Sugarcane (*Saccharum officinarum L.*) is a perennial grass native to Southeast Asia's tropical climates and now is grown in different countries around the world (El Chami et al. 2020). It is an essential crop to produce sugar (sucrose) and ethanol. It is transferred to the sugar processing mill to extract raw juice after harvesting from the sugarcane farm. The major by-product generated after processing is sugarcane bagasse. For example, 540 million metric tonnes of sugarcane bagasse is generated every year globally from the top ten sugarcane-producing countries (Kumar et al. 2021). The common reuse method for the sugarcane bagasse is to generate energy through burning (Aruna et al. 2021). Pineapple (*Ananas comosus* (*L.*) *Merr*) is one of the most well-known tropical fruits in the world, particularly in Asia. The residues of pineapple are reported to account for 50% of its weight and generate ~10 tonnes/year quantity of fresh fibre. Insoluble dietary fibre is the main fibre fraction found in the residues of pineapple which is 56–65% of the total dietary fibre content. Pineapple residues which include leaf bracts, shell and core are composed mainly of cellulose microfibrils containing hemicellulose and lignin (Elena et al. 2014). Coconut (*Cocos nucifera*) has several main products which include coconut oil, desiccated coconut, coconut water, coconut milk, coconut sap sugar and refined glycerin, not excluding coco coir, coco lumber and other food and non-food products. Its shell is generally identified as one of the agricultural wastes with the potential to serve as the base material to be utilized for the development of activated carbon (Muzarpar et al. 2020).

12.2 Characteristics of Agricultural Wastes

12.2.1 Proximate, Ultimate Analysis and Biomass Composition

Agricultural waste (biomass) can be characterized using proximate, ultimate and compositional analysis. Proximate analysis provides values of volatile matter (VM), ash content (AC) and fixed carbon content (FC); ultimate or elemental analysis determines carbon (C), hydrogen (H), oxygen (O), nitrogen (N) and sulphur (S) elements present in the biomass; biomass composition analysis specifies the cellulose, hemicellulose and lignin content. Table 12.1 enlists the proximate, ultimate and biomass composition analysis of various biomass.

VM of biomass is a significant parameter affecting the biomass conversion process, and it is the major source for gaseous and liquid yield from the thermochemical process (Vassilev et al. 2010). Compounds having weak chemical bonds get dissociated into simpler hydrocarbons like aliphatic hydrocarbons and phenols and acids which evaporate due to heat and end up in condensable gases. Whereas molecules dissociated extensively form CO_2, H_2, CO, CH_4, etc., VM of the selected biomass varied from 45.2 to 82.13% (Table 12.1). Inorganic compounds in biomass like silica, oxides of calcium or magnesium or aluminium contribute to the AC. These inorganic contents are not generally influenced by the heating process but can alter the rate of the thermochemical conversion process. Higher AC was observed in rice straw, rice husk, corn straw and oil palm sludge, whereas AC was $<10\%$ in the other selected biomass (Table 12.1). The carbon content that remains in the solid structure after the VM is driven off is referred to as FC. The FC content of raw biomass varied from 7.7 to 39% (Table 12.1). AC and FC present in biomass define char properties after the conversion process (Vassilev et al. 2010; Weber and Quicker 2018).

Ultimate analysis is used for determining the element composition of carbon, hydrogen, oxygen, nitrogen and sulphur in percentages. Ultimate analysis helps in analysing the biomass quality and to predict the biomass yield. Table 12.1 enlists the ultimate analysis of the selected biomass. C, H, O, N and S varied in the range of 34.2–49.36%, 5–6.57%, 39–48.1%, 0.4–1.23 and 0.07–1.1%, respectively (Table 12.1).

Table 12.1 Proximate, ultimate and compositional characteristics of various agricultural wastes

	Proximate analysis			Ultimate analysis					Biomass composition			
Biomass type	VM (%)	AC (%)	FC (%)	C (%)	H (%)	O (%)	N (%)	S (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	References
Rice straw	51.4	36.5	12.1	40.09	5.34	42.27	1.07	–	36.72	26.81	14.53	Wang et al. (2018)
Rice husk	60.2	23.5	16.3	45.1	6.4	48.1	0.4	–	37	24	14	Rajasekhar Reddy and Vinu (2018)
Corn straw	73.1	19.2	7.7	44.73	5.37	42.47	0.6	0.07	–	–	–	Tortosa Masiá et al. (2007)
Corn stover	77.9	5.7	13.7	48.7	6.4	44.1	0.7	0.08	38	26	19	Ravikumar et al. (2017)
Corn cob	79.9	1.8	16.4	–	–	–	–	–	44.4	38.8	11.9	Ravikumar et al. (2017)
EFB	60	6	30	43	6	41	10	–	–	–	–	Liew et al. (2017)
OPT	47	8	39	46	5	39	10	–	–	–	–	
Mesocarp fibre	60	3	30	46	7	9	38	0	–	–	–	
OPF	51	4	33	46	6	7	41	0	–	–	–	
Dermal tissue of OPF	79.95	0.12	13.18	41.63	5.31	1.72	51.34	–	–	–	–	
PKS	58	4	34	51	7	39	3	–	–	–	–	
POS	45.2	26.2	16.4	34.2	6.4		5.3	1.1	–	–	–	Goh et al. (2019)
Sugarcane bagasse	–	–	–	41.48	5.14	51.1	0.36	0.06	–	–	–	Zaichenko et al. (2020)
Sugarcane straw	–	–	–	45.44	6.45	40.53	0.32	0.08	–	–	–	
Filter mud	35.67	6.45	3.31	22.52	3.36	2.06	64.82	0.79				Bernardino et al. (2017)
Pineapple leaf bracts waste	–	7.37	–	–	–	–	–	–	43.53	21.88	13.88	Elena et al. (2014)

(continued)

Table 12.1 (continued)

Biomass type	Proximate analysis			Ultimate analysis					Biomass composition			References
	VM (%)	AC (%)	FC (%)	C (%)	H (%)	O (%)	N (%)	S (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	
Pineapple peel/ shell waste	–	1.5		41.02	6.05	48.17	0.79	–	40.55	28.69	10.01	Elena et al. (2014); Fu et al. (2016)
Pineapple core waste	–	1.3	–	–	–	–	–	–	24.53	28.53	5.78	Elena et al. (2014)
Coconut shell waste	66.71	3.63	18.63	–	–	–	–	–	–	–	–	Iloabachie et al. (2018)
Coconut fibre	82.13	4.05	13.82	49.36	6.57	42.7	1.23	0.14	–	–	–	Dhar et al. (2020)

Biomass is mainly composed of cellulose, hemicellulose and lignin which are naturally occurring complex organic polymers along with trace amount of pectins, starch, etc. Biomass composition is an influencing factor for thermochemical conversion of biomass as it affects the heating rate and thus the quality of generated biomass. The degradation of cellulose, hemicellulose and lignin occurs at different temperatures. Lignin is considered to be the binding material of biomass which starts degrading above the temperature of 200 °C. Hemicellulose is thermally degraded before cellulose at a temperature of 350 °C, whereas cellulose is degraded at comparatively higher temperatures (Huang et al. 2012). Higher cellulose to lignin ratio ensures a higher heating rate of biomass and vice versa (Gani and Naruse 2007). Generally, all the biomass samples constitute a higher percentage of cellulose and hemicellulose and comparatively lower percentages of lignin. The composition of biomass varies according to seasonal variation, region, climatic conditions, age of crop, species, growth stage, etc. (Bajpai 2019). Cellulose and hemicellulose in all the selected biomass were $>20\%$, whereas the lignin content of 19% was observed in corn stover (Table 12.1).

12.3 Methods for Biochar Production

For biochar production, different thermochemical conversion techniques are adopted. The selected conversion technique and the operating parameters (amount of oxygen, heating rate, reaction temperature, etc.) of the conversion technique determine the yield and quality of biochar obtained from particular biomass. Generally, the yield of biochar decreases with a faster heating rate or more oxygen available. Biochar production is achieved through various traditional and modern approaches.

12.3.1 Traditional Approaches

The early approach of biomass conversion is the burning of biomass in a pit covered by soil to prevent oxygen supply, burning of biomass in open space, covering half-burned biomass immediately with soil, etc. The process is carried out in handmade reactors such as firebrick pits, clay burners, brick kilns and iron retorts. Pyrolysis is the common traditional approach used for biomass conversion to biochar. It is a process by which biomass is subjected to thermal degradation under a limited/minimal supply of oxygen yielding solid residue (biochar) along with liquid and gaseous end products. Based on the heating rate, pyrolysis is classified as slow and fast pyrolysis. In slow pyrolysis or conventional pyrolysis, biomass is heated to 300–600 °C at a heating rate of 5–7 °C/min for hours to yield biochar. Fast pyrolysis is carried out at a temperature greater than 500 °C with a heating rate of 300 °C/min for a shorter time (REILLY 1925; Thines et al. 2017). Fast pyrolysis yields more liquid and gaseous products compared to biochar.

12.3.2 Modern Approaches

Modern approaches of biomass conversion include gasification, torrefaction, flash pyrolysis, vacuum pyrolysis, hydrothermal carbonization (HTC), microwave pyrolysis, electro-modified biochar and magnetic biochar. Gasification is carried out at a high temperature, usually greater than 700 °C, under a limited or controlled supply of oxygen and steam. The main product is hydrogen, with a considerable amount of biochar which can also be produced during the process (Al-Rahbi and Williams 2017; González et al. 2008). The torrefaction process improves the biomass properties at relatively low temperatures such as 230–300 °C and is carried out in the absence of oxygen under atmospheric pressure (Pentananunt et al. 1990). Flash pyrolysis is an improved process of fast pyrolysis wherein biomass is heated to 900–1200 °C for around less than 1 min, employing a heating rate of 1000 °C/s (Demirbas and Arin 2002). Vacuum pyrolysis is conducted in the absence of oxygen where biomass is subjected to thermal degradation under vacuum or low pressure with the range of 0.05 and 0.20 MPa and at a temperature range of 450–600 °C. In the HTC process, wet biomass is processed at a temperature range of 220–240 °C under high-pressure (2–10 MPa) reactor for several hours (Hu et al. 2010; Lynam et al. 2011; Titirici et al. 2007). The process eliminates pre-drying of biomass to reduce moisture content. The end product is usually transformed into brown coal or remains in its dissolved form. Microwave pyrolysis is an advanced technique, where the biomass is heated by the dielectric heating of microwave (Arafat Hossain et al. 2017; Huang et al. 2012; Menéndez et al. 2004). Electro-modified biochar production employs modification of biochar by chemical treatment such as mixing it in Fe, Mg or Al for 2–12 h in the presence of electric current that might change the functional groups on the surface of pores and eventually improves specific adsorption (Jung et al. 2015; Zhang and Gao 2013). Production of magnetic biochar intends the production of biochar with good magnetic property along with other surface characteristics. For example, magnetic biochar can be prepared with iron (Fe) ions on the surface of biochar through the help of a binding agent such as chestnut shell at a temperature 450 °C under microwave heating (Thines et al. 2017; Zhou et al. 2017). The magnetic biochar exhibited tremendous adsorption capacity of pollutants with complete separation and recovery of the biochar from aqueous phase after the treatment process. The biochar produced in these methods is mainly used as a soil amendment to improve soil property or adsorbent for the removal of aqueous pollutants (Table 12.2).

12.4 Biochar Yield from Various Production Methods

Biochar yield from particular biomass varied based on the conversion techniques and the operating parameters such as heating rate, the temperature of the reaction, inert gas (N_2/Ar/H_2) purging, etc. Biochar yield decreased with an increase in temperature and residence time in the thermochemical conversion process. Table 12.3 enlists the biochar yield from various biomass at different operating conditions. MW pyrolysis

Table 12.2 Biochar production using different traditional and modern approaches

Biochar production techniques	Biochar production conditions	Applications	References
Traditional approaches			
Early approach	Burning of biomass in a pit or handmade reactors such as firebrick pits, clay burners, brick kilns and iron retorts	Soil amendment, liquid product as preservation for dead bodies and meat, house painting, caulking or sealing wood barrels, ship-building and to attach arrowheads to spear shaft, etc.	REILLY (1925); Thines et al. (2017)
Slow pyrolysis	Temperature, 300–600 °C; heating rate, 5–7 °C/min	Soil amendment, bio-oil, syngas as an energy fuel	Lai et al. (2013); Verma et al. (2012)
Fast pyrolysis	Temperature, >500 °C; heating rate, 300 °C/min	Adsorbent, soil amendment, bio-oil, syngas	Dai et al. (2017); Essandoh et al. (2015); Huang et al. (2017); Menéndez et al. (2004)
Modern approaches			
Gasification	Temperature, >700 °C with gasifying agents (steam)	Dye removal, adsorbent, carbon sequestration, soil amendments, syngas	Al-Rahbi and Williams (2017); González et al. (2008)
Torrefaction	Temperature, 230–300 °C	Regarded as a pretreatment step to improve the physical, chemical and biochemical characteristics of raw biomass	Pentananunt et al. (1990)
Flash pyrolysis	Temperature, 900–1200 °C; heating rate, 800–1000 °C/s	Soil amendment, bio-oil, syngas	Demirbas and Arin (2002)
Vacuum pyrolysis	Pressure, 0.05–0.20 MPa; temperature, 450–600 °C; heating rate, 300 °C/min	High porosity biochar, adsorption of mineral, soil amendment	Tripathi et al. (2015); Uras et al. (2012)
Hydrothermal carbonization	Pressure, 2–10 MPa and temperature, 220–240 °C	Retention of nutrients, high calorific value fuel, better grindability, improved hydrophobicity	Hu et al. (2010); Lynam et al. (2011); Titirici et al. (2007)
Microwave pyrolysis	Temperature, 450–800 °C; microwave power, 400–600 W; and microwave frequency, 2450 MHz	Soil amendment, bio-oil, syngas	Arafat Hossain et al. (2017); Huang et al. (2012); Menéndez et al. (2004)

(continued)

Table 12.2 (continued)

Biochar production techniques	Biochar production conditions	Applications	References
Electro-modified biochar production	Current supply, 0–100 V and 0–12 A for 5 min; pyrolysis temperature, 400–500 °C; heating rate, 5 °C/min in the absence of oxygen	Adsorbent for pollutant removal from aqueous phase	Jung et al. (2015); Zhang and Gao (2013)
Magnetic biochar production	Material soaked with a solution of Fe_2O_3, $FeSO_4.7H_2O$ or $FeCl_3.6H_2O$ before pyrolysis, pyrolysis temperature: 450–1000 °C	Adsorbent for pollutant removal from aqueous phase	Thines et al. (2017); Zhou et al. (2017)

of rice husk yielded 62.9% biochar with MW power, temperature and residence time of 800 W, 500 °C and 10 min in a continuous reactor (Table 12.3). MW pyrolysis of rice husk and rice straw resulted in comparable biochar yield under similar operating conditions (Table 12.3).

Conversion of agricultural wastes to biochar offers several end uses of the obtained biochar, along with agronomic benefit of crop residue handling and management. Biochar is one of only a few technologies with good carbon sequestration potential (Castilla-caballero et al. 2020; Dhar 2020). Besides, biochar produced from different agricultural wastes is extensively used as an adsorbent for the removal of pollutants such as heavy metals, nutrients and pharmaceutical compounds from wastewater (Dhar 2020; Goh et al. 2019; Lo et al. 2017; Rajasekhar Reddy and Vinu 2018; Ravikumar et al. 2017; Wang et al. 2018). The incorporation of biochar as soil amendment improved soil fertility, microbial activity and soil nutrient retention capacity thus resulting in enhanced crop productivity (Castilla-caballero et al. 2020; Dhar 2020; Lo et al. 2017; Wang et al. 2018). Biochar is also used in biocomposites and bioremediation process (Castilla-caballero et al. 2020; Dhar 2020). The comparable heating value of biochar with conventional fuels like coal enables its use as a solid fuel (Castilla-caballero et al. 2020; Dhar 2020).

12.5 Biochar Characteristics

Biochar is majorly used as an adsorbent in wastewater treatment, soil amendment for improved soil property and crop productivity, solid fuel to replace conventional coal, etc. The end use of biochar depends on the characteristics of biochar obtained from different biomass employing various conversion techniques. Table 12.4 enlists the proximate and ultimate analysis characterizations of various biomass along with surface area and heating value. The carbon content of various biochars varied from

Table 12.3 Biochar production from biomass using various conversion techniques

Biomass	Biomass part	Biochar production method	Inert gas purged	Sample weight (g)	Operating conditions				Biochar yield (wt %)	References
					MW power (W)	Temperature (°C)	Heating rate (°C/min)	Residence time (min)		
Rice	Rice straw	MW pyrolysis (batch)	N_2	100	800	500	–	10	62.9	Ravikumar et al. (2017)
		MW pyrolysis (batch)		5	500	–	–	30	20	Lo et al. (2017)
		MW pyrolysis (continuous)		24	–	400	–	–	37.41	Wang et al. (2018)
					–	500	–	–	32.44	
					–	600	–	–	31.27	
				45	–	400	–	–	38.67	
					–	500	–	–	34.83	
					–	600	–	–	33.14	
				66	–	400	–	–	39.15	
					–	500	–	–	41.96	
					–	600	–	–	34.52	
	Rice husk	MW pyrolysis (batch)		20	450	600	–	10.3	40.1	Suriapparao et al. (2018)
		MW pyrolysis (batch)		40	420	800	–	8.5	38.3	Rajasekhar Reddy and Vinu (2018)
					560		–	7	35.1	
					420		–	6.5	36.7	
					560		–	6.5	34.8	

(continued)

Table 12.3 (continued)

Biomass	Biomass part	Biochar production method	Inert gas purged	Sample weight (g)	Operating conditions				Biochar yield (wt %)	References
					MW power (W)	Temperature (°C)	Heating rate (°C/min)	Residence time (min)		
		MW pyrolysis (batch)		5	500	–	–	30	22	Lo et al. (2017)
Corn	Corn cob	MW pyrolysis (batch)	N_2	100	800	500	–	10	32	Ravikumar et al. (2017)
	Corn stover	MW pyrolysis (batch)	N_2	100	800	500	–	10	34.4	Lo et al. (2017)
				5	500		–	30	20	
Oil palm tree	POS char	Pyrolysis	N_2	–	–	200	15	90	92.1	Goh et al. (2019)
						300			82.2	
						400			64.2	
						500			53.3	
						600			47.4	
	PKS char	Pyrolysis	N_2	–	–	500	10	60	37.07	Lee et al. (2017)
	EFB char			–	–	500	10	60	35.14	
	POS char			–	–	500	10	60	79.16	
Sugarcane	Bagasse char	Pyrolysis	Ar –	–	–	1000	–	–	26.46	Bernardino et al. (2017); Zaichenko et al. (2020)
	Straw char			–	–	1000	–	–	29.9	
	Bagasse char			–	–	500	10	30	25	

Coconut	Coconut shell wastes	Pyrolysis	N_2 and O_2	–	–	280	10	60	36.17	Castilla-caballero et al. (2020)
				–	–	304		60	33	
				–	–	350		60	30.43	
				–	–	396		60	28.14	
				–	–	420		60	27.13	
	Coconut fibre	Slow pyrolysis	–	–	–	350	10	60	48.13	Dhar (2020)
			–	–	–	400			40.26	
			–	–	–	450			37.55	
			–	–	–	500			34.09	
			–	–	–	550			32.65	
			–	–	–	600			29.34	

Table 12.4 Biochar characteristics

Biomass	Biomass parts	Method	Ultimate analysis (wt.%)					Proximate analysis (wt.%)				BET surface area (m^2/g)	Heating value (MJ/kg)	References
			C	H	N	O	S	Fixed carbon	Volatile matter	Moisture content	Ash			
Rice	Rice husk	Microwave pyrolysis	59.6	4.21	0.71	39.45	0.003	52.2	18.5	31.05	19.9	190	25.46	Sahoo and Remya (2020)
	Rice straw	Pyrolysis @300 °C	72.1	5.03	1.55	21.3	–	36.9	40.2	–	22.9	–	–	Wu et al. (2012)
		Pyrolysis @400 °C	77.2	4.01	1.74	17.1	–	46	25.2	–	28.8	–	–	
		Pyrolysis @500 °C	82.8	3.25	1.77	12.1	–	44.9	23.3	–	31.8	–	–	
		Pyrolysis @600 °C	87.1	2.51	1.52	8.8	–	57.5	14.9	–	27.6	–	–	
		Torrefaction	75.16	3.7	2.45	18.7	–	2.86	69.82	–	27.32	–	21	Huang et al. (2012)
Corn	Corn straw	Slow pyrolysis	35.88	1.64	0.43	1.86	–	–	–	4.76	60.19	13.08	–	Chen et al. (2011)
	Corn stover	MW pyrolysis	68.01	1.84	0.74	5.94	0.05	–	–	–	23.42	18.3	–	Zhu et al. (2015)
	Corn cob	Slow pyrolysis	67.21	4.49	0.67	27.63	–	49.1	43.6	2.4	4.9	61.8	–	Liu et al. (2014)
Oil palm tree	POS char	Pyrolysis	33.7	7.7	5.3	–	1.6	17.8	44.2	11.2	26.7	8.5	–	Goh et al. (2019)
			32.6	6.1	5.5	–	0.9	21.3	39.3	9.6	29.8	10.2	–	
			31.9	4.6	4.4	–	0.7	26.6	26.7	8.4	38.2	16.3	–	
			29.2	3.3	3.7	–	0.6	31.2	15.2	7.8	45.8	20.8	–	
			28.3	1.8	3.4	–	0.4	33.5	9.3	6.1	51.2	19	–	
	PKS char	MW pyrolysis	70	3	1	26	0	84	10	3	3	270	–	Adibah et al. (2020)

	PKS char	Pyrolysis	73.11	–	–	25.88	–	59.92	30.26	2.24	7.56	–	27.50	Lee et al. (2017)
	EFB char		54.5	–	–	32.94	–	53.78	27.46	1.03	17.73	–	26.18	
	POS char		72.34	–	–	20.91	0.41	21.37	24.05	5.86	48.70	–	9.80	
Sugarcane	Bagasse char	Pyrolysis	90.15	0.15	0.27	2.13	0.27	–	–	–	7.03	–	30.51	Zaichenko et al. (2020)
	Straw char		74.62	0.66	0.59	0.29	0.19	–	–	–	23.65	–	25.97	
	Bagasse char	Pyrolysis	74.9	2.3	–	5.3	–	–	–	5.7	4.7	148.23	–	Vimal et al. (2019)
	Bagasse char	Pyrolysis	69.5	4.2	0.9	24.36	–	–	–	–	–	5.2	–	Creamer et al. (2014)
			78.6	3.52	0.92	15.45	–	–	–	–	–	13.6	–	
			76.45	2.93	0.79	18.32	–	–	–	–	–	388.3	–	
	Bagasse char	Pyrolysis	–	–	–	–	–	48.16	41.79	5.82	4.23	224.07	–	Mubarik et al. (2015)
			–	–	–	–	–	50.47	38.62	5.71	4.17	361.77	–	
			–	–	–	–	–	49.97	37.71	6.73	4.08	291.37	–	
Pineapple	Pineapple peel waste	Pyrolysis	72.95	3.36	1.23	12.05	–	–	–	–	10.41	0.82	33.94	Fu et al. (2016)
			73.9	2.21	1.08	10.23	–	–	–	–	12.58	2.73	25.74	
			74.53	1.37	0.99	9.88	–	–	–	–	13.23	6.64	23.74	
	Pineapple peel waste	Slow pyrolysis	62.54	4.12	1.83	23.59		42.49	45.79	4.14	7.93	5.55	46.95	Shakya and Agarwal (2019)
			64.87	3.83	1.73	18.84		62.71	23.41	2.49	10.73	3.37	37.17	
			68.87	3.17	2.53	13.81		68.52	16.65	3.22	11.61	11.11	32.05	
			73.55	2.11	2.26	10.01		71.03	15.47	1.76	12.08	6.39	30.68	
	Pineapple stump	Pyrolysis	52.04	4.27	1.27	32.96	–	–	–	–	–	24.46	–	Cheah et al. (2013)
	Pineapple crown leaf waste	Microwave pyrolysis	–	–	–	–	–	–	–	–	–	17.03	27	Astuti et al. (2019)

(continued)

Table 12.4 (continued)

Biomass	Biomass parts	Method	Ultimate analysis (wt.%)					Proximate analysis (wt.%)				BET surface area (m^2/g)	Heating value (MJ/kg)	References
			C	H	N	O	S	Fixed carbon	Volatile matter	Moisture content	Ash			
Coconut	Coconut shell wastes	Pyrolysis	53.35	–	0.49	2.5	451.31	–	–	–	–	13.28	–	Castilla-caballero et al. (2020)
			45.6	–	0.45	0.85	508.26	–	–	–	–	10.93	–	
			36.7	–	0.41	2.5	401.03	–	–	–	–	15.57	–	
			42.47	–	0.42	4.14	512.7	–	–	–	–	15.75	–	
			43.42	–	0.41	2.5	498.56	–	–	–	–	9.85	–	
	Coconut fibre	Slow pyrolysis	68.36	4.24	1.75	25.31	0.34	35.38	58.5	–	6.12	8.2	23.73	Dhar (2020)
			71.7	4.14	1.61	22.18	0.37	54.17	37.26	–	8.57	58.59	25.97	
			76.76	3.97	2.15	16.84	0.28	60.43	29.12	–	10.45	193.7	25.48	
			78.33	2.71	2.37	16.4	0.19	68.87	19.79	–	11.34	278.58	22.33	
			81.47	1.92	1.43	14.91	0.27	70.24	17.61	–	12.15	295.57	21.65	
			84.93	1.81	1.71	11.36	0.19	71.09	16.72	–	12.19	286.68	21.64	
	Coconut shell	Pyrolysis	73.92	5.6	3	13.98	3.5	48.81	44.77	3.65	2.77	–	–	Priya et al. (2020)

28.3 to 90.15%. The carbon content of the biochar was highest (90.15%) in bagasse biochar obtained through conventional pyrolysis process, whereas POS biochar obtained through pyrolysis process resulted in the lowest carbon content (Table 12.4). Proximate analysis of biochar shows FC and VM which majorly defines the activity of biochar. For different biochars, obtained FC ranges from 2.86 to 71.03% and VM ranges from 9.3 to 69.82%. The highest FC is observed in pineapple peel waste biochar obtained through conventional pyrolysis process, and the lowest VM is obtained in POS biochar obtained through pyrolysis process (Table 12.4).

For adsorption and nutrient retention in soil with biochar, it should have a considerably high specific surface area (SSA). The SSA obtained by Brauner-Emmett-Teller (BET) Technique after thermochemical conversion process majorly showed an increase in value, compared to parent biomass. The highest SSA obtained, considering the selected biomass, is 361.77 m^2/g for sugarcane bagasse biochar (Table 12.4).

Heating value is one of the important characteristics of biochar. If the heating value of biochar is good enough to compete with conventional fuel, then the obtained biochar can be considered as a good fuel alternative considering its production cost. The average heating value obtained via pyrolysis lies in 20–30 MJ/kg. The maximum heating value obtained is 46.95 MJ/kg (Table 12.4). This shows promising results of heating value comparable to conventional fuels like coal which has a heating value around 22–25 MJ/kg.

12.6 Summary

With an increase in agricultural productivity, the generation of agricultural residues and wastes is among rising problems all over the world. Rice, corn or maize, oil palm tree, sugarcane, coconut and pineapple are the six major crops produced in Asian countries. India and China are major producers of rice and corn; oil palm crops are cultivated majorly in Malaysia and Indonesia; coconuts are mainly produced in Singapore and other coastal Asian countries. The crop production and post-processing techniques generate enormous quantity of residue as agricultural waste (biomass) such as rice husk, rice straw, corn cob, corn straw and corn stover, crude palm oil, oil palm biomass, sugarcane bagasse, pineapple leaf bracts, coconut shell, etc.

Based on proximate analysis, volatile matter content of the selected biomass varied from 45.2 to 82.13%. Higher ash content (AC) was observed in rice straw, rice husk, corn straw and oil palm sludge, whereas AC was $<10\%$ in the other selected biomass. The fixed carbon (FC) content of raw biomass varied from 7.7 to 39%. The ultimate analysis of biomass indicated C, H, O, N and S of the biomass in the range of 34.2–49.36%, 5–6.57%, 39–48.1%, 0.4–1.23 and 0.07–1.1%, respectively. Traditional approaches of thermal conversion techniques like combustion, pyrolysis, etc. and advanced approaches such as torrefaction, gasification, microwave thermal conversion techniques, vacuum pyrolysis, magnetic biochar production, etc. are employed for the conversion of biomass into biochar. The characteristics of biomass, type of conversion process and operating conditions affected the yield and property of the obtained biochar. Among the selected biomass, the highest biochar yield of 92.1% was obtained from pyrolysis of POS and average yield of biochar from various biomass was observed between 30 and 50%. Sugarcane bagasse biochar obtained through pyrolysis indicated the highest specific surface area of 361.77 m^2/g. The average heating value biochar is observed to be 20–30 MJ/kg.

Biochar produced from biomass posed good carbon sequestration potential. Besides, biochar produced from different agricultural wastes is extensively used as an adsorbent for the removal of pollutants such as heavy metals, nutrients and pharmaceutical compounds from wastewater. The incorporation of biochar as soil amendment improved soil fertility, microbial activity and soil nutrient retention capacity thus resulting in enhanced crop productivity. Biochar is also used in biocomposites and bioremediation process. The comparable heating value of biochar with conventional fuels like coal enables its use as a solid fuel. Thermal conversion processes of different feedstocks are efficient value-adding techniques and getting great attention from researches as well as industry experts, considering their lower operation time and high scale-up potential. These technologies definitely will become part of industrial activities in the near future.

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Biochar as a Tool for the Remediation of Agricultural Soils

13

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Abstract

Biochar is a carbon-rich solid produced by heating biomass with little or no oxygen. It can be produced from vegetable biomass or animal wastes from agro-industrial processes, reducing the volume of residues to be disposed of and adding value to these materials. Biochar presents a porous structure with a high surface area containing many functional groups. These characteristics allow the use of biochar in many applications, such as a remediation tool for degraded agricultural soils. Intense use of the soil can cause a decrease in the nutrient content and accumulation of pesticides, negatively affecting the soil ecosystem and the crop yields. The application of biochar in degraded soil can change the physicochemical properties of the soil, increase the nutrient availability by reducing nutrient leaching, and promote the chemical and/or biological degradation of pesticide residues. Thus, this chapter aims to approach the main aspects of biochar production and its application as a remediation tool in degraded soils, including the increase in nutrient availability and the promotion of pesticides

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degradation. The chapter is organized in five sections: introduction, biochar production, biochar role in the promotion of pesticides degradation, increasing nutrients availability through the use of biochar, conclusions, and future trends.

Keywords

Waste biomass · Degraded soil · Soil nutrients · Pesticide residues

13.1 Introduction

Healthy soils are essential to keep human life on Earth since they are directly connected with the provision of food, wood, and raw materials, besides acting as a gigantic filter, accumulating nutrients, regulating greenhouse gases concentrations, decontaminating the water, and minimizing floods (Kopittke et al. 2019). However, with the intense human population growth and the consequent increase in the demand for consumer goods, soils and all the services they provide are being subjected to huge pressure. The global human population was 6.5 billion in 2005, 7.7 in 2019, and is expected to reach 9.7 billion by 2050 (United Nations 2019). Based on this, the Economics of Land Degradation Initiative estimated that food production must increase by 70% between 2005 and 2050, which will directly impact the use of the soil (ELD Initiative 2015).

Conventional agriculture already impacts soil properties and functions leading to different processes of unsustainable soil degradation, such as erosion, desertification, loss of organic matter, contamination by overapplication of agrochemicals, acidification, salinization, and loss of biodiversity (Kopittke et al. 2019). With an increasing demand for food and other commodities, the expansion of conventional agriculture is expected, as well as the intensification of soil degradation, reducing the long-term capacity of soils to provide the complex net of services from which humanity is dependent (Kopittke et al. 2019). To solve this paradox (increasing demand ↔ intensive use of the soil ↔ decreasing soil productivity), the focus of the decision-making processes must change from the immediate benefits of intensive agricultural systems to the long-term sustainability of the soil. For this, it is important to understand that soil degradation directly leads to economic losses. It is estimated that 52% of agricultural land is already moderately or severely degraded, which costs the world US$400 billion per year due to lower productivity and increased food prices (ELD Initiative 2015).

Intensive agriculture impacts on soil mainly include harmful effects on soil nutrients cycling, soil biodiversity, and increased soil contamination by agrochemicals. These impacts result in a reduction of soil quality, which contributes to short-term and long-term productivity loss, income reduction, a drop in the price of agricultural land, leading to farmers vulnerability, food insecurity, and migration (Asfaw et al. 2020).

The availability of nutrients in the soil is negatively affected by erosion processes, loss of soil microbiota and organic matter, and reduction of pH and porosity, which are all caused by non-sustainable agricultural practices (Zalidis et al. 2002). When the quantities of nutrients removed from the soil by the harvest products and the impacts caused by intensive agriculture surpass the quantities of nutrients being applied, the soil fertility decreases, resulting in a reduction of plant growth and yield. Thus, more fertilizer is needed to meet the demands of the crops. Therefore, increasing the efficiency of the fertilizers is essential to reduce the farming costs, decrease the exploration of nonrenewable resources for the production of fertilizers (such as phosphorus reserves), and create more sustainable agriculture.

Another environmental problem caused by intensive agriculture is the accumulation of pesticide residues in the soil due to the extensive and inefficient use of these agrochemicals (Liu et al. 2018). Despite decreasing soil quality, the pesticide residues can run off to surface water bodies and leach to groundwater, contaminating the aquatic ecosystems and compromising human health, since some pesticides are known to be toxic, mutagens, carcinogens, immunosuppressants, etc. (Hassaan and El Nemr 2020). Moreover, the intense degradation of agricultural soils can have global impacts, such as the enhancement of climate change (due to increased deforestation in the search for new fertile lands), water regime changes, and water contamination. Thus, the sustainable use of soil resources, restoration of degraded areas, management of land use, and conservation of soil quality is essential to preserve the agricultural yields as well as the balance of the global ecosystem (Zeraatpisheh et al. 2020).

Several strategies have been employed to increase agricultural soil sustainability, and many more are being developed. The use of biochar, for example, has shown to be a promising alternative to increase the nutrient retention in the soil by decreasing nutrient loss through gaseous emissions or leaching and enhance pesticide degradation by modifying the physicochemical properties of the soil and improving soil microbial abundance, activity, and associations (Ding et al. 2017). Biochar is a carbon-rich porous solid produced by heating biomass in the absence of oxygen (Ding et al. 2017). It presents several functional groups and can be made using agricultural wastes such as corn cob (Mensah and Frimpong 2018), rice straw (Si et al. 2018), grass and beet residues (Isakovski et al. 2020), pig manure (Zhang et al. 2013), and many others. The use of biochar produced from agricultural waste to enhance crop yield is an environmentally friendly technique since it turns residues into useful agricultural additives, being a sustainable strategy for the management of agro-residues. Moreover, it can promote a circular economy in the agriculture sector since the application of biochar in the soil can be integrated into conventional fertilization practice (Jindo et al. 2020).

Based on this, this chapter approaches the use of biochar in agriculture as an alternative to increasing the sustainability of the agricultural system and as a tool for the remediation of degraded soils. First, a general overview of the production process of biochar and its main characteristics are addressed, and then its use to promote nutrient availability in the soil and pesticide degradation is discussed.

13.2 Biochar Production

Biochar is a solid carbonaceous material produced from carbon-rich raw materials (Yaashikaa et al. 2020; El-Naggar et al. 2019). The most common sources for obtaining biochar are the solid biomass composing the different types of organic waste (Kim et al. 2012). Some of the most used wastes for the production of biochar are from crops, municipal organic waste, industrial organic waste, animal waste (manure/feces), and waste from forest biomass (leaves, branches, wood, and roots) (Yaashikaa et al. 2020). The use of organic residues for biochar generation is justified because it is a highly economical way of obtaining it and, in general, presents a high production yield (Yaashikaa et al. 2020; Chi et al. 2021; Babu and Chaurasia 2003). Moreover, the use of waste promotes the circular economy and meets the search for sustainable social development, through the reduction of waste through reuse and recycling (Yaashikaa et al. 2020). Besides biochar, other products are obtained in the biorefinery, such as syngas and bio-oil, which can be considered a form of renewable energy and can be used in several steps of the biochar production cycle, reducing the costs and the demand for fossil fuels. Figure 13.1 illustrates the main steps of biochar production and application.

For the reasons mentioned above, the focus of this topic is on obtaining biochar derived from biomass. In this context, the biochar production conditions are the main determinants of the biomass yield (Babu and Chaurasia 2003). These parameters include, basically, the type of biomass, synthesis temperature, synthesis time, heating rate, and pressure (Yaashikaa et al. 2020; Babu and Chaurasia 2003). Among all parameters, the temperature is the one that most affects the biochar characteristics; for example, it can make it hydrophobic or hydrophilic (Chi et al. 2021), more porous or less porous (Manyà 2012), etc. For biomass-derived biochar, thermochemical methods of production are the most widely used. Among them, it is

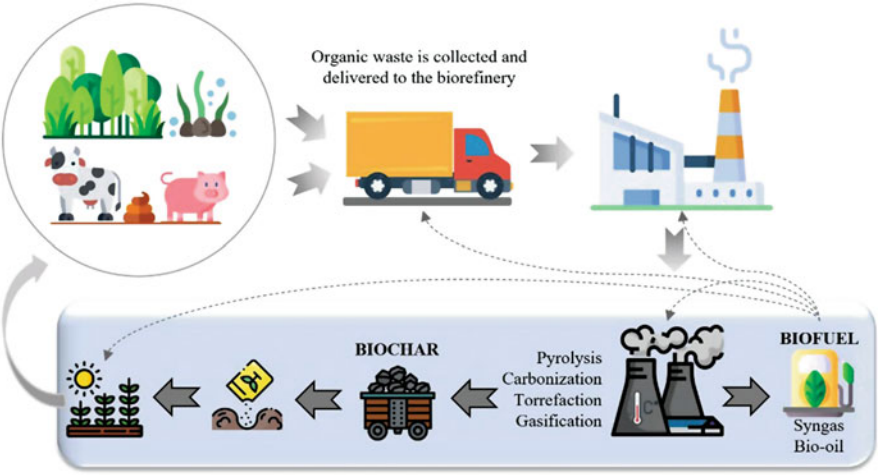

Fig. 13.1 Biochar production cycle: From organic waste to biochar and biofuel

worth mentioning the pyrolysis, carbonization, torrefaction, and gasification methods. Pyrolysis is the most commonly used method among all the others (Yaashikaa et al. 2020; Manyà 2012; Chi et al. 2021).

The most appropriate thermochemical method must be chosen according to the biomass type, as well as the process parameters, to guarantee the highest biochar yield (Yaashikaa et al. 2020; Babu and Chaurasia 2003). In general, the thermochemical transformation processes start with the dehydration of biomass (close to 100 °C), which loses weight by removing the high structural water content; subsequently, with the rise in temperature (from 220 °C), the degradation of cellulose, hemicellulose and lignin begins. Finally, after the decomposition and burning of the carbonaceous residues, a remaining material is obtained. This material of carbonaceous and thermally stable nature is called biochar (Yaashikaa et al. 2020; Babu and Chaurasia 2003). The main biochar production methods are described in the sub-items below.

13.2.1 Pyrolysis

Pyrolysis is a thermal process in which materials (usually organic) are subjected to a high temperature (250–750 °C) under an oxygen-free or low-oxygen atmosphere (Yaashikaa et al. 2020; Chi et al. 2021). This process promotes a physical and chemical transformation of biomass, converting it into solid (biochar) (Kim et al. 2012), liquid (bio-oil) (Brindhadevi et al. 2021), and gaseous (syngas) (Zhou et al. 2021) products with high added value. Pyrolysis can be classified as slow or fast, depending on the process conditions used, such as temperature, heating rate, residence time, and pressure (Manyà 2012). The process is carried out in reactors, such as wagon reactor, paddle kiln, bubbling fluidized bed, and agitated sand rotating kilns, which are quite suitable for the production of biochar (Yaashikaa et al. 2020). In a simplified way, pyrolysis occurs in basically three stages (Kim et al. 2012): first, with the gradual increase in temperature, the biomass is dehydrated; subsequently, primary char is formed, and as a result of the initial temperatures of thermal degradation in this phase, part of the mass is converted into volatile compounds (pyrolytic gases) (de Oliveira et al. 2021); the continuation of the process promotes the slow degradation of primary char, which ultimately results in a secondary carbon with high carbon content, that is, biochar (Kim et al. 2012).

During pyrolysis, the biomass cellulose undergoes depolymerization (Manyà 2012; de Oliveira et al. 2021). The cellulose fragmentation in chemical species of lower molecular weight during the slow pyrolysis favors the char formation (de Oliveira et al. 2021). However, under fast pyrolysis, cellulose undergoes rapid degradation with the immediate release of volatiles, which leads to the formation of levoglucosan (Yaashikaa et al. 2020; Zhang et al. 2012). Levoglucosan also undergoes a dehydration process, which leads to the formation of hydroxymethylfurfural. The latter can decompose and originate liquid (bio-oil) and gaseous (syngas) products, as well as undergo aromatization, condensation, and polymerization reactions, forming biochar (Yaashikaa et al. 2020; Zhang et al.

2012). Hemicellulose decomposes similarly to cellulose to form oligosaccharides. Depending on the pyrolysis temperature, hemicellulose may undergo different reactions that lead to the formation of biochar or even decomposition in bio-oil and syngas (Huang et al. 2012). The lignin present in the biomass undergoes molecular breaks in the β-O-4 bonds caused by hydrolysis and dealkylation reactions, resulting in the formation of free radicals and phenolic products. At the end of the reactions, biochar is obtained by repolymerizing/cross-linking intermediate compounds (Jain et al. 2016).

Pyrolysis can be performed under different temperatures, generally ranging from 100 to 800 °C (Hassan et al. 2020). At higher temperatures (500–800 °C), the biochar yield tends to be lower. However, the material has a higher fixed carbon content, greater surface area, and increased microporosity (Ding et al. 2017; Manyà 2012). Huang et al. (2020) produced biochar from sewage sludge using different pyrolysis temperatures, and the biochar surface area increased from 7.26 to 81.26 m^2/g when the temperature changed from 300 to 700 °C. This increase can be due to the release of biochar volatiles as the pyrolysis temperature rises (Liu et al. 2014a). Besides temperature, the biochar characteristics also depend on the raw material used. Hassan et al. (2020) analyzed 533 publications and concluded that, generally, biochar from hardwood and softwood has greater surface area than biochar derived from manure and grass, for example.

Another feature influenced by the pyrolysis temperature used in the process is the biochar pH. Biochar produced at higher temperatures presents higher pH due to the release of alkali salts from the organic raw material used. Domingues et al. (2017) demonstrated that biochar produced from different feedstocks (chicken manure, eucalyptus sawdust, sugarcane bagasse, and pine bark) showed a significant increase in pH as a consequence of increased pyrolysis temperature. For example, the pH of eucalyptus sawdust biochar increased from 5.9 to 9.7 when the temperature changed from 350 to 750 °C (Domingues et al. 2017).

The biochar obtained from pyrolysis under lower or moderate temperatures (100–500 °C) may have a more hydrophilic characteristic; the opposite is true for high-temperature pyrolysis processes, in which the produced biochar is thermally more stable and hydrophobic (Chi et al. 2021). In processes where the temperature is higher, the biomass undergoes more chemical transformations and rearrangements, as aromatization, giving rise to new functional surface groups, such as carboxyl, pyridine, phenol, lactone, etc. (Manyà 2012). However, polar functional groups (such as -OH and C-O) are removed when a high pyrolysis temperature is used, turning the biochar surface more hydrophobic, which can hinder water retention within the biochar particle (Ding et al. 2017). The reduction in the concentration of O and H results in lower surface reactivity and, therefore, higher biochar stability. The stability is also dependent on the feedstock used in the process. As demonstrated by Cross and Sohi (2013), biomasses containing more recalcitrant carbon lead to more stable biochar: for example, wood-derived biochar showed higher stability in comparison to biochar produced from sugarcane bagasse, which in turn was more stable than chicken manure biochar. The production of biochar with great stability is

Table 13.1 Effects of pyrolysis temperature in some biochar characteristics: (+) indicates an increase and (−) indicates a decrease in the characteristic value

Biochar characteristic	Low temperature	High temperature
Hydrophilicity	+	−
Stability	−	+
Biochar yield	+	−
Surface area	−	+
Porosity	−	+
pH	−	+
Cation exchange capacity	+	−

important to maintain the potential positive effects of biochar application in the soil over longer periods.

Another characteristic influenced by the pyrolysis temperature is the cation exchange capacity (CEC) of the biochar. The CEC is an important feature since it indicates the biochar capacity to adsorb cations such as ammonium and calcium ions, which are vital nutrients for the crops, reducing nutrient losses from the soil (Hodges 2010; Ding et al. 2017). Some studies indicate that biochar produced at higher pyrolysis temperatures has lower CEC. This was demonstrated by Domingues et al. (2017) using biochar derived from chicken manure: when pyrolysis temperature of 350 and 450 °C was used, biochar had a CEC of ~40 cmol_c/kg; however, when the biochar was produced at 750 °C, its CEC reduced to ~20 cmol_c/kg. The decrease of CEC value when high pyrolysis temperature is applied has been attributed to the biochar aromatization and the loss of negative functional groups, mainly oxygen-containing groups (Ding et al. 2017; Domingues et al. 2017).

As can be noticed in the discussions above, several biochar characteristics are influenced by the temperature used during the pyrolysis process. Table 13.1 summarizes the effects of low and high temperature on the main characteristics of biochar that must be considered when choosing the process parameters. These characteristics dictate whether or not the produced biochar will be suitable as a remediation tool in the target soil.

13.2.1.1 Fast Pyrolysis

Fast pyrolysis is considered a direct thermochemical treatment, capable of liquefying solid biomass to obtain bio-oil, mainly used for energy generation (Yaashikaa et al. 2020; Chi et al. 2021; Manyà 2012). Although its application is more suitable for obtaining bio-oil, some studies have shown good biochar yields derived from biomass from fast pyrolysis. This process is characterized by the high heating rate of the biomass (above 100 °C/min) and very short synthesis time (exposure of the biomass to heat between 0.5 and 2 s) under high temperatures (about 400–600 °C) (Yaashikaa et al. 2020; Chi et al. 2021; Manyà 2012). Due to the processing speed, the biochar obtained by fast pyrolysis tends to have lower surface areas and porosities concerning the biochar obtained from slow pyrolysis (Manyà 2012). Some studies have shown that the presence of alkali and alkaline earth metals during the pyrolysis, such as sodium, potassium, and magnesium salts or hydroxides, can catalyze the reaction by increasing the yield of pyrolysis products, in this case, bio-oil and biochar (Manyà 2012).

13.2.1.2 Slow Pyrolysis

Slow pyrolysis has a better char yield when compared to fast pyrolysis and carbonization methods. This process is characterized by the low heating rate of the biomass (from 5 to 7 °C/min) and synthesis times of hours and even days depending on the objective (Yaashikaa et al. 2020; Chi et al. 2021; Manyà 2012). The slow heating and the long residence time of the biomass favor the formation of char, much more than of bio-oil and syngas. For this reason, slow pyrolysis is the process most commonly employed in the production of biochar. Studies have shown that processes under high pressure (1.0–3.0 MPa) tend to increase the yield of biochar. However, some research reports that, with the increase in pressure, a decrease in the biochar surface area can be observed (Yaashikaa et al. 2020; Chi et al. 2021; Manyà 2012). Moreover, the moisture content present in the biomass can influence the biochar yield; some studies showed that high moisture content (42–62%) can increase the production yield (Manyà 2012).

13.2.2 Carbonization

Carbonization is a thermochemical process in which incomplete combustion of solid organic-based materials occurs when they are exposed to extreme temperatures. During the carbonization reaction, heat removes hydrogen and oxygen from the solid; so the residual matter is composed mostly of carbon, which we call char. In this case, the residual biomass processing by the carbonization gives rise to biochar (Chi et al. 2021). Carbonization can be performed using the conventional hydrothermal process or by a method known as flash carbonization, which is described in the next items.

13.2.2.1 Hydrothermal Carbonization (HTC)

Classic hydrothermal carbonization (HTC) is also known as wet torrefaction, and it is a biochar production method that occurs at pressures of around 10–15 bar and lower temperatures (150–300 °C) compared to the pyrolysis process. This process was developed by Friedrich Bergius in 1913 in Germany and aims to use wet biomass (mixed with water) or with a high moisture content (food residues, algae, animal waste, etc.) (Yaashikaa et al. 2020; Libra et al. 2011). During the process, the biomass is usually mixed with water in a closed reactor. The temperature is increased slowly to ensure the process stability, which lasts, on average, from 30 min to 16 h. The HTC process can also be used to obtain different products depending on the temperature used. Up to 250 °C hydrothermal carbonization takes place, through which wet char, called hydrochar (paste composed of a carbonized solid phase and a liquid phase), or dry char, i.e., biochar can be obtained (Zhang et al. 2017). Between 250 and 400 °C, hydrothermal liquefaction occurs and bio-oil is produced. Above

400 °C hydrothermal gasification takes place, and syngas (CO, CO_2, H_2, and CH_4) is formed (Yaashikaa et al. 2020). In this process, the reactions of biomass decomposition and char formation occur mainly by hydrolysis, decarboxylation, aromatization, and reconditioning (Libra et al. 2011).

13.2.2.2 Flash Carbonization (Flash)

The flash carbonization process (Flash) was developed at the University of Hawaii by professor Michael J. Antal, and its main characteristics are described in the US Patent No. 6,790,317 B2 (Antal Jr 2004). The Flash production method is a process of converting biomass to char that has shown higher efficiencies than slow pyrolysis and hydrothermal carbonization. This process consists of a compacted bed of biomass inside an air-pressurized vessel (1.0–2.0 MPa) (Manyà 2012). A heated air (300–600 °C) is forced through the biomass, which is converted into char. The processing time is usually less than 30 min. The bed temperature profile is influenced by several factors, including the type of raw material, the heating time, and the amount of heated air supplied (Manyà 2012).

13.2.3 Torrefaction

Torrefaction is an emerging thermochemical process and occurs in milder conditions than traditional pyrolysis (Yu et al. 2017). This process uses much lower heating rates (less than 50 °C/min), residence time (less than 1.0 h), and temperatures (150–300 °C); for this reason, it is also called mild pyrolysis (Yaashikaa et al. 2020; Yu et al. 2017). Torrefaction can be performed in a closed reactor which atmosphere is inertized by the removal of all internal air and oxygen through the injection of N_2 (Yaashikaa et al. 2020; Yu et al. 2017). The process phases can include drying, torrefaction, and cooling. Through torrefaction, it is possible to produce biochar of high calorific value capable of being used as an alternative raw material in the production of clean energy (Yu et al. 2017). The torrefaction can be carried out as (1) wet torrefaction, also called hydrothermal carbonization (explained above), which is usually carried out in the presence of water at a temperature between 180 and 260 °C for about 5–240 min depending on the type of raw material and objective; (2) steam torrefaction, in which the biomass is treated under steam for about 10 min at a temperature not exceeding 260 °C; and (3) oxidative torrefaction, carried out under classical process conditions but in an atmosphere containing oxidizing gases (air, oxygen, etc.) (Yaashikaa et al. 2020; Yu et al. 2017).

13.2.4 Gasification

Gasification is a thermal method of decomposing carbonaceous material (biomass, charcoal, or a mixture of both) into gaseous (non-condensable) products called syngas, which is basically composed of CO, CO_2, H_2, CH_4, and traces of low-molecular-weight hydrocarbons (Yaashikaa et al. 2020). The process is normally operated at high temperatures (above 800 °C). In the same way, the temperature is the most important parameter in the gasification process, capable of determining the yield of syngas production and composition (Manyà 2012). Some studies have shown that, at higher temperatures, the production of CO and H_2 is favored, with a reduction in the fraction of the other chemical species (Yaashikaa et al. 2020; Manyà 2012). In this process, syngas is the main product formed, with biochar being the secondary product of the reaction, presenting, then, lower yields (5–10%) (Brewer et al. 2009). The biochar obtained from gasification can contain high levels of metals and minerals, depending on the ash content and the composition of the raw material used. This characteristic is not desirable for applications of the material in soil due to the toxicity and bioaccumulation of metals and the high content of minerals (Manyà 2012).

The classic gasification process comprises of the stages of drying, pyrolysis, oxidation/combustion, and gasification (Yaashikaa et al. 2020). Drying takes place between 100 and 150 °C and is carried out separately when the raw material has high humidity; in this stage, the substrate dehydration occurs. With the gradual increase in temperature, the biomass undergoes a pyrolysis process between 200 and 500 °C; in this stage, thermal decomposition, char formation, and release of pyrolytic gases take place (Yaashikaa et al. 2020; Manyà 2012; Zhang et al. 2010). The rise in temperature leads to the oxidation/combustion of char and generated gases, which happens between 800 and 1200 °C. In this stage, gasification occurs, where oxidation agents (air, steam, among others) react with the combustible gases present in the gasifier (reactor system) to produce CO_2, CO, and water (Yaashikaa et al. 2020; Manyà 2012; Zhang et al. 2010).

The partial gasification process (controlled with air, steam, or CO_2 as an oxidizing agent) can be used to improve the textural properties of biochar previously obtained by other processes (Manyà 2012). In this case, gasification is not used for production, but for the physical activation of char, which can be applied in adsorption and catalysis processes (Zhang et al. 2004). The obtaining of activated char by gasification is carried out with a burning percentage between 30 and 50% and constant temperature between 700 and 850 °C (Zhang et al. 2004).

Each production technique produces biochar with different characteristics, such as porosity, hydrophilicity, surface functional groups, among others. These characteristics influence the biochar performance as a soil remediation tool. The next sections discuss the use of biochar to increase nutrient availability in the soil and increase pesticide degradation, showing how the process parameters can help in obtaining biochar capable of remediating the soil based on the needs of the land to be treated.

13.3 Increasing Nutrient Availability Through the Use of Biochar

During development, plants need at least 16 elements to complete their life cycle. A few are made available by air and rainwater (carbon, oxygen, and hydrogen), while the rest of the elements are absorbed by the plants through the roots, being acquired exclusively through the soil. The elements consumed in greater quantities are nitrogen (N), phosphorus (P), and potassium (K), being called macronutrients. In addition to these, calcium (Ca), magnesium (Mg), and sulfur (S) are also essential. Micronutrients are needed in smaller quantities, but equally crucial for the normal development of plants, such as boron, copper, chlorine, iron, manganese, molybdenum, and zinc (Hodges 2010).

During soil formation, the base material for each soil type undergoes many physical and chemical changes. There is a reduction of soil particles and dissolution of minerals, forming new clay minerals. These tiny particles are called colloids and due to their large surface area in relation to the volume, they are extremely reactive. They are of organic or mineral origin and are responsible for basically all the charge and chemical reactivity of the soils, having an essential role in the availability of nutrients. The extent and type of charges on soil colloids determine their ability to retain essential nutrients for plants, preventing the leaching of nutrients with water. This ability to retain cations increases with the increase of negative charges on the soil, acting as a magnet, being able to make these cations available when another cation takes its place. The nutrients attached to the soil in this way are called "exchangeable cations." Thus, the negative charge of the soil is called cation exchange capacity (CEC), and it is responsible for the availability of nutrients for the soil solution, becoming accessible to plants (Hodges 2010). A summary of the cation exchange process is shown in Fig. 13.2.

Other factors such as pH and soil type affect CEC and, therefore, soil fertility. The application of biochar has the potential to modify the chemical and physical properties of the soil (Guo 2020). The acidic pH in the soil is detrimental to the growth of plants because it makes available normally toxic metals like aluminum (Al). The potential of biochar to increase the pH of the soil is related to its alkalinity and retention of cations. Mensah and Frimpong (2018) found that the application of biochar in acidic soils (pH 4.7 and 5.0) resulted in a significant increase in pH (5.8 and 6.1, respectively). This increase may be related to the high pH of the biochar used (7.0). Thus, biochar can be used as an alternative to limestone to correct soil pH.

The increase in soil pH facilitates the release of nutrients into the soil solution, allowing them to be absorbed by the plants' roots. Studies have shown that the addition of biochar can increase soil CEC. Jien and Wang (2013) observed an increase from 7.41 to 10.8 cmol/kg in the CEC of the soil after the application of biochar. Laird et al. (2010) observed an increase of up to 30% in relation to the control after the application of biochar, demonstrating an improvement in nutrient retention and general soil fertility. The improvement in soil CEC after the application

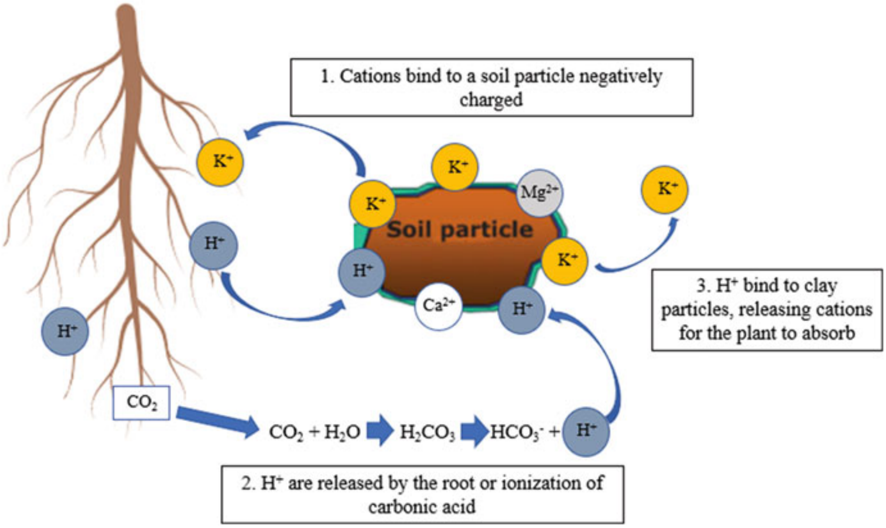

Fig. 13.2 Cation exchange capacity in soil

of the biochar may be related to its high specific surface area and the number of biochar carboxylic groups (Ding et al. 2016).

In addition to the influence on pH and CEC, the biochar has other positive effects on soil, improving the structure and capacity of water retention, besides reducing the loss of nutrients through volatilization or leaching (Van Zwieten et al. 2010). When applying biochar from paper mills to two different soil types (ferrosol and calcarosol) in greenhouse experiments, Van Zwieten et al. (2010) found that the application of biochar was beneficial for the agronomic performance of the studied crops (radish, wheat, and soybean). At the rate of 10 t/ha application, the biochar significantly increased the pH, CEC, and calcium (Ca) exchangeable in ferrosol, while in calcarosol, it also increased exchangeable potassium (K). These effects on the soil increased crop productivity. Other examples of studies that observed an increase in crop productivity and biomass after biochar application are presented in Table 13.2.

Ding et al. (2016) indicate four ways in which the biochar can improve soil fertility: (1) Biochar can be used as a source of nutrients. The nutrient content present in the biochar depends on the temperature and the raw material used; lower temperatures of pyrolysis release more N, while higher temperatures release more P, K, and Ca. Thus, the biochar could be produced for specific situations depending on the soil needs. (2) Biochar can improve the physical and chemical characteristics of the soil, mainly due to its porosity, specific surface area, and water retention capacity. Due to its ability to improve CEC, aggregation, and pH, it can enhance soil fertility by increasing the content and availability of nutrients in the soil, also preventing its leaching. However, long-term experiments must be carried out to assess the performance of the biochar over time. (3) Biochar could store nutrients.

Table 13.2 Effect of biochar on crop productivity and biomass

Biochar type	Application rate (t/ha)	Crop	Soil type	Yield/biomass increased over control (%)	References
Corn straw	20	Cotton	Inceptisol	21	Tian et al. (2018)
Corn straw	10	Cotton	Inceptisol	18	Tian et al. (2018)
Rice straw	2.25	Rice	Silt loam	7	Si et al. (2018)
Willow wood	25	Maize	Ferralsol	29	Agegnehu et al. (2016a)
Acacia wood	10	Barley	Clay loam	60	Agegnehu et al. (2016b)
Hardwood	38	Maize	Midwestern mollisols	17	Rogovska et al. (2014)
Hardwood	58	Maize	Midwestern mollisols	48	Rogovska et al. (2014)
Wheat straw	40	Rapeseed	Red soil	36	Liu et al. (2014b)
Secondary forest wood	68	Cowpea	Xanthic ferralsol	20	Glaser et al. (2002)
Secondary forest wood	68	Rice	Xanthic ferralsol	50	Glaser et al. (2002)
Charcoal	0.5	Moong	Delhi soil	22	Glaser et al. (2002)

Source: Adapted from Ding et al. (2016) and Shaaban et al. (2018)

Due to its porosity and functional groups, surplus nutrients can be stored on the surface of the biochar, being made available slowly over time. (4) Biochar can improve the activity, structure, and abundance of the soil microbiota. This improvement in soil microbiology may be due to increased availability of nutrients, shelter, and improved living conditions. The increase in microbial activity makes it possible to improve nutrient cycling, improving the general fertility of the soil.

Despite demonstrating the potential for plant production, negative effects on plant development have also been reported in the literature. Aguilar-Chávez et al. (2012) found that the application of oak biochar hindered the development of wheat plants, with no increase in production being observed. Nzanza et al. (2012) observed that the application of eucalyptus biochar resulted in a 13% decrease in the dry mass of the tomato root, in addition to a reduction in the P content in the leaves. Thus, the application of biochar can have adverse effects, which may be related to the type of biochar in a specific type of soil. Further studies on the effects of biochar on crops should be performed, especially in the long term, since crops are the main interest of the farmers (Shaaban et al. 2018).

Thus, the application of biochar in degraded soils could be a way to recover these soils. Its capacity for water retention, increase soil pH and ECC, and improvement of the soil structure makes it an interesting alternative for recovery processes. However, the source material and the production method of the biochar must be carefully selected to produce specific biochar considering the type and necessities of the soil to be remediated and the crops intended to be planted.

13.4 Biochar Role in the Promotion of Pesticide Degradation

Over the years, the overuse of pesticides in agricultural fields has caused harmful effects on the environment, especially on soils. Despite the capacity for self-purification of the soil, it is now perceived that the accumulation of these toxic agents is above the limit of natural and spontaneous degradation of nature, requiring efficient and sustainable interventions/strategies to promote the remediation of the deteriorated soils (Zhen et al. 2018). Besides, the application of low-cost alternatives that allow large-scale use in crops should be considered when proposing procedures (Sanchez-Hernandez et al. 2019). In this context, biochar is an effective option, widely studied for this purpose and eco-friendly. The role of biochar in promoting the degradation of pesticides is closely correlated with the properties of the material itself, the soil to be treated, and the form (combined or not) in which it is applied in the crop. Therefore, it is essential to have full knowledge about the biochar-soil-plant interaction mechanisms when using it as an ally in the degradation of pesticides. Also, biochar can act as a stimulator for microbial biodegradation of pesticides since it can change the chemical composition and pH of the soil, providing energy, water, and structure suitable for microorganisms (Ren et al. 2018).

The process of degradation of pesticides in the soil can happen through different mechanisms, such as hydrolysis, photolysis, oxidation, biodegradation, among others (Liu et al. 2018). Table 13.3 shows some works reported in the literature, highlighting the feedstocks used for the production of biochar and the degradation mechanisms of different pesticides. The degradation of most products of this class of agrochemicals occurs due to the action of microorganisms, such as fungi, bacteria, and others. However, the excessive application of pesticides in the crop can cause adverse effects to the soil's natural microbiota, such as the increase and/or reduction of the presence of microorganisms through the availability of nutrients (carbon, nitrogen, phosphorus, sulfur, and others). These disturbances in the soil microbiota can cause the accumulation of pesticides in the area, which consequently deteriorates the soil even more, besides contaminating rivers and aquifers by leaching. Furthermore, the degradation of different pesticides in the soil only happens under specific/appropriate conditions, such as, for example, in the presence of little or no oxygen and at a certain pH (Varjani et al. 2019). Therefore, the use of biochar in conjunction with microorganisms or some chemical process can provide excellent results in the

Table 13.3 Different precursors of biochars used in the degradation of pesticides

Biomass	Pesticide	Degradation mechanism	References
Miscanthus × giganteus and pieces of beet	Chlorpyrifos, chlorpyrifos-methyl, and chlorfenvinphos	Biodegradation	Isakovski et al. (2020)
Sewage sludge	Carbendazim	Adsorption and biodegradation	Huang et al. (2020)
Empty bunches of palm oil and rice husks	Imazapic, Onduty®, and imazapyr	Biodegradation and photodegradation	Yavari et al. (2019)
Corn straw and pig manure	Thiaclopride	Adsorption and chemical/biological degradation	Zhang et al. (2018)
Pig manure	Carbaryl and atrazine	Adsorption and catalytic hydrolysis	Zhang et al. (2013)
Pine wood	*p*-nitrophenol	Generation of free radicals	Yang et al. (2016)

(bio)degradation of pesticides in the soil. For instance, the biochar can act as a support for microorganisms or in changing the pH of the soil to provide an increase in the biodegradation activity. Also, biochar application in the soil can increase the amount of organic matter and water available, reducing competition between microorganisms for supplies. Another phenomenon involved in promoting the process of degradation of pesticides when using biochar is adsorption, and its study (biochar-pesticide interaction) must be carried out previously so that it does not cause problems in the application phase, as the biochar can adsorb the agrochemical, interfering in the chemical/biological process of breaking the agrochemical and/or combating the respective pests (Vijayaraghavan 2019).

Nowadays, most of the developed pesticides are easily degraded, mainly by hydrolysis. Thus, the biochar can assist in the chemical degradation of these compounds, due to the synergy between the materials, ions present in the soil, and the pH. However, the degradation of pesticides by microorganisms is still dominant in the environment. Biochars produced from *Miscanthus × giganteus* biomass and pieces of beet were used to investigate its potential as a remediation technique to prevent the leaching of organophosphate pesticides (chlorpyrifos, chlorpyrifos-methyl, and chlorfenvinphos) into groundwater (Isakovski et al. 2020). The process of synthesis of the materials was through slow pyrolysis at a temperature of 400 °C, chosen based on the chemical composition of the raw materials used (cellulose and hemicellulose). In the study, they used alluvial sediment from the banks of the Danube River to test pesticide biodegradation and found, from the isolation of strains and phylogenetic analysis, that *Bacillus megaterium* was the microorganism responsible for the breakdown of the compounds. From the results obtained from the biodegradation tests with the presence of biochar, they observed that there was an increase in the delay of up to 18 times the pesticides leaching to groundwater. Also, they listed the main positive points of the aid of biochar in the biodegradation of agrochemicals present in the sediment, since it can act as support for bacteria due to its microstructural properties, promoting the multiplication of the microorganisms, besides acting as an adsorbent for the pesticides. In general, the research demonstrated the potential of biochar as a remediation tool to inhibit pollutant leaching into groundwater and to act in synergy with microorganisms in the biodegradation of organophosphate pesticides.

The influence of the biochar production variables and the composition of the carbon precursor are reported in several studies that evaluated the role of carbonaceous material in the degradation of pesticides. Biochars synthesized from pyrolysis of sewage sludge at different temperatures (300, 500, and 700 °C) were used to evaluate the degradation of carbendazim in clay soils from different locations in China (Huang et al. 2020). The results showed that the degradation of the pesticide occurred quickly in the presence of biochar produced at 700 °C (BC 700) in comparison to other temperatures. One reason may be related to the higher surface area of the biochar (81.26 m^2/g), since more adsorption sites are available for the pesticide and/or nutrients to the microorganisms that degrade carbendazim. Also, the sorption power of the biochar is intrinsically correlated with the surface functional groups, which are strongly affected by the pyrolysis temperature. The BC 700 presented aromatic compounds and a higher degree of aromatization than the biochars synthesized at milder temperatures, which may be one of the reasons for the higher percentage of adsorption of the agrochemical. Also, the degradation of the pesticide in the presence of BC 700 can be linked to the increase in soil pH and the generation of free radicals, which can facilitate the chemical degradation of carbendazim.

Another mechanism of degradation of agrochemicals in the soil is through photolysis, commonly called photodegradation. Biochars synthesized from empty bunches of palm oil and rice husks were applied to the degradation of imazapic, Onduty®, and imazapyr herbicides in rice paddy soil (Yavari et al. 2019). The biochars were used in herbicide biodegradation and photodegradation experiments. Samples were collected and analyzed at intervals of 0, 7, 14, 28, 42, 56, and 70 days after the application of the chemical agents. The results demonstrated that the use of biochar in the soil has great potential to influence the herbicides' half-lives. In the photodegradation experiments, a decrease in the rate of photolysis was observed when the biochar was applied in the soil, demonstrating an increase in the half-life of the agrochemicals. On the other hand, the biodegradation was improved with the presence of biochar, mainly with the material coming from the rice husk biomass, since the results demonstrated a reduction by half of the half-lives of the herbicides.

Another topic of great interest to the scientific community is to unravel the mechanisms involved in the degradation of pesticides in the soil. As a result, more research is focused on adsorption-desorption processes, bioaccumulation, transformation, among others. There are different alternatives to base/elucidate the studies of the phenomena involved in the degradation process of agrochemicals. The use of biochar, for example, can provide numerous advantages for the mechanistic study of the degradation of pesticides since it is widely known that it can act as an adsorbent of chemicals/metals in contact with the soil and also help in the chemical and/or biological degradation of the pesticides.

Zhang et al. (2018) used corn straw and pig manure for biochar production to systematically study the degradation mechanisms of thiacloprid (THI) in black soil, such as sorption and chemical and/or biological degradation. The biochar was synthesized via pyrolysis at different temperatures (300, 500, and 700 °C) and was tested in different proportions in the soil to analyze the degradation of the agrochemical. The results proved that the presence of biochar in the black soil influenced the degradation of thiacloprid, and the changes were associated with the physical-chemical and biological interferences of the material. Also, other advantages attributed to the biochar are that it improved the pH, the electrical conductivity, bioavailability of phosphorus, the contents of organic matter and hydrogen in the soil, and the availability of shelter (pores of the material) for the microorganisms. The biochar produced at a temperature of 300 °C (300-TC) was the one with the best values regarding the increase in dissolved organic carbon and the biodegradation of the pesticide. The excellent biodegradation performance in the presence of 300-TC was attributed to the increase in the number of microorganisms and to the improvement of the activity of nitrile hydratase (NHase). However, biochar manufactured at 500 and 700 °C inhibited the pesticide biodegradation, due to the amount of dissolved free thiacloprid and adverse effects on NHase. Regarding the sorption of the pesticide, the increase in temperature in the biochar synthesis favored the adsorption of the agrochemical. This trend can be explained by the increase in the surface area of the material and the decrease in the hydrogen to carbon ratio. Therefore, based on the results of this study, pyrolysis temperature in the synthesis of biochar can affect the degradation mechanism of the pesticide: low temperatures can improve biodegradation, whereas high temperatures favor adsorption. In the chemical degradation of THI, the authors observed that, as the pH became more alkaline with the correction of the soil with the biochar, the degradation of the pesticide increased, which can also be influenced by the active groups of the biochar surface and the generation of hydroxyl radicals.

The use of biochar from pig manure biomass has shown excellent results in the degradation of carbaryl and atrazine (Zhang et al. 2013). Adsorption and catalytic hydrolysis were the two phenomena studied. The materials synthesized at different temperatures (350 and 700 °C) were evaluated with and without the ash removal process (deashing). The adsorption results of the pesticides were higher with the biochar manufactured at 700 °C after the deashing process since the presence of ash in the biochar can interfere in the sorption of the compounds. Both pesticides were hydrolyzed more rapidly in the presence of biochar. In the study of carbaryl hydrolysis, it was observed that the degradation increased with the biochar suspensions due to the catalytic effects of the alkaline pH, the release of metal ions, and the high surface area. The hydrolysis of atrazine was potentiated mainly due to the high pH and biochar surface. Carbaryl and atrazine were broken down by 71.8% and 27.9% in 12 h, respectively.

The generation of free radicals by biochar is another mechanism that has been studied for the promotion of pesticide degradation in soils. However, little is known about the behavior of these free radicals in contact with agrochemicals. Yang et al. (2016) investigated the degradation of *p*-nitrophenol (PNP) using biochar seeking to systematically assess the role of persistent free radicals in the process. Biochar was produced from five different biomasses (pine wood, corn stalks, peanut shells, rice, and wheat straw) using a programmed temperature method (kept at 100 °C for 30 min and then pyrolyzed for 4 h in 200, 350, 500, and 700 °C, separately). Biochar obtained at temperatures above 200 °C, except 700 °C, showed satisfactory results of degradation of PNP, mainly from the system with biochar produced from biomass of pine wood at 500 °C (PI-500). In the sorption experiment using PI-500, they found that after 7 days of reaction, the nitrate concentration (intermediate of the PNP break) proportionally increased with higher concentrations of PNP but fixed biochar amount. However, nitrate concentration decreased when the biochar amount was reduced, demonstrating that the nitrate was originated from PNP degradation. Also, the nitrate concentration kept increasing with time, showing that the degradation of PNP in the presence of biochar was accelerated. The authors used electron paramagnetic resonance (EPR) to detect the presence of free radicals at the biochar surface. Strong signs of free radicals were detected in the samples, and the signal intensity showed an excellent correlation with the extent of the degradation of PNP. In the raw material, no sign of free radicals was detected, while for the biochar produced at 200, 300, and 500 °C, the signal increased significantly and proportionally to the temperature. On the other hand, the sign of free radicals at the biochar produced at 700 °C was very low. According to the authors, elevated temperatures can cause the collapse and reorganization of the organic structures, resulting in a significant decrease or even disappearance of free radicals. Therefore, the study concluded that biochar produced at the right pyrolysis temperature can generate free radicals and is capable of promoting the degradation of organic contaminants in the environment through these radicals.

In general, it is observed that biochar plays a fundamental role in promoting the degradation of pesticides, and there are numerous advantages of its use in the (bio)degradation of these compounds: (1) it can serve as a soil additive to provide a habitat optimized for microorganisms, where nutrients, water, and shelter are available; (2) biochar can cause an increase/decrease in soil pH depending on the soil needs; (3) it can release free radicals capable of degrading the pesticides; (4) increase organic matter in the soil; (5) enhance the retention of agrochemicals due to the adsorption phenomenon; among others. Figure 13.3 summarizes the role of biochar in pesticide degradation in the soil. In the discussion of this topic, positive points of biochar were reported in the chemical and/or biological degradation of pesticides. However, new research addressing the behavior of this material in the ecosystem in the long-term and cytotoxicity studies is necessary, so that the use of biochar today does not become an environmental problem in the future.

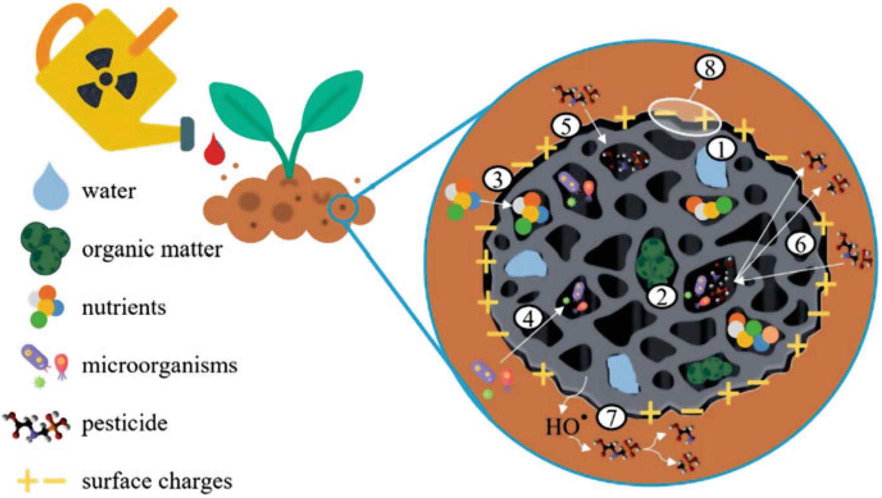

Fig. 13.3 Main effects of biochar application in pesticide-contaminated soil: (1) water and (2) organic matter retention; (3) soil nutrient retention and prevention of nutrient loss by leaching or evaporation; (4) the biochar pores serve as shelters for microorganisms that are attracted to the solid due to the high availability of nutrients, water, and organic matter; (5) pesticide molecules can adsorb on the biochar, preventing the leaching of pesticides to water bodies; (6) the microorganisms present in the biochar can act on the degradation of pesticide molecules; (7) the biochar can release free radicals able to degrade the pesticides present on the soil; (8) biochar surface charges can modify soil properties, such as pH

13.5 Conclusions and Future Trends

The recovering of degraded soils is an important task, and human beings must take total responsibility for it in order to ensure food security for the present and future generations. The search for remediation techniques using low-cost, renewable, and highly available resources must be one of the priorities in this area. In this sense, the use of biochar in agriculture as an alternative for the remediation of degraded soils has great potential. The use of waste, both from agricultural and industrial activities, for the production of biochar makes it economically viable and environmentally friendly.

Due to its physicochemical characteristics, the application of biochar to the soil shows numerous advantages, such as beneficial changes in pH, increased cation exchange capacity, improved soil structure and porosity, improved water retention capacity, reduced nutrient losses due to leaching and volatilization, and favoring the activity of microorganisms.

The biochar also shows great potential for promoting the degradation of pesticide residues in the soil, mainly due to its ability to provide a favorable microenvironment for the activity of the soil microbiota, which is the main responsible for the degradation of these compounds. Also, biochar can promote the degradation of pesticides through changes in soil pH, free radical release, and adsorption.

However, further studies are needed regarding the use of biochar in soils. Despite the good results obtained so far, studies on the performance of this compound and possible consequences for long periods are necessary. In addition, experiments involving the combination of different raw materials and production methods can be interesting for applications in specific situations.

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Removal of Contaminants by Modified Biochar-Based Material

14

Khushboo Dasauni, Divya, and Tapan K. Nailwal

Abstract

Biochar (BC) is a low-cost sustainable adsorption material. Due to its broad application prospects, it has attracted a lot of research attention recently. Having several functional groups available on the surface, biochar treated by several methods can be modified and used as a catalyst or catalyst support. Functional groups attached to the surface of biochar can trigger active free radical species to play an important role, thereby causing destruction of pollutants as catalysts and removal of adsorbents by involving electron transfer or redox processes. Biochar-based materials can be used to remove inorganic contaminants, such as heavy metal, nitrate or phosphate. Biochar-based materials can also be used to repair eutrophic water by releasing compounds containing N or P. This chapter reviews more feasible and sustainable biochar-based materials, which effectively remove environmental pollutants as catalysts or carriers, and discusses the use of biochar-based materials as catalysts.

Keywords

Biochar-based materials · Pollutants · Heavy metals · Functional groups · Sustainable adsorption material

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14.1 Introduction

The world is currently facing environmental and climatic crisis such as increase in atmospheric CO_2, global warming, contamination of water bodies and decline in soil organic carbon and drought. Biochar could be considered as a promising material to help mitigate global environmental changes as well as elimination of contaminants from water bodies. Biochar is a complex carbon-rich material, whose properties vary along with production conditions and feedstock used. Scientific studies have recently demonstrated that application of biochar or biochar-based materials to agricultural soil increases crop production and contributes to carbon sequestration, hence reducing emission of greenhouse gases. Biochar obtained from pyrolysis of biomass is widely used in soil management, as a precursor for biofuel production, health and sanitation and water purification. In recent years, biochar has drawn attention as a potential source of bioremediation or removal of contaminants from polluted water bodies, therefore, helping in reducing the clean water availability crisis. Biochar usage has another advantage, i.e. invasive plant management, thereby protecting environment by converting invasive plant biomass into biochar which is a win-win situation. A wide range of feedstock forestry remains, wood, agricultural waste, grasses, animal waste, municipal sludge, etc. is employed for the production of sustainable and nonhazardous biochar. This is considered to be a potential absorbent for highly toxic emerging contaminants. pH, volatile matter (VM) content and recalcitrance, total carbon content, cation exchange capacity, mineral content and oxygen-containing surface functional groups contribute to the adsorption, catalytic oxidation and reduction properties of biochar. These characteristics are attributes of pyrolysis such as temperature, pyrolysis time, etc. Other alternatives to pyrolysis are hydrothermal carbonization, torrefaction, fast pyrolysis, and gasification. This chapter deals with the physico-chemical properties of biochar and mechanisms involved in eradication of emerging organic/inorganic and heavy metal pollutants (Yang et al. 2016).

14.2 Biochar: A Promising Biomaterial

Biochar is a carbon-rich sustainable and inexpensive renewable material. It is a product of thermal degradation (300–700 °C) via the process of pyrolysis under an oxygen-limited environment. Pyrolysis of biomass converts precursor into various products, viz. solid (biochar, tar), gas (syngas) and liquid (bio-oil). Yield and quality of biochar depend on diverse factors like feedstock, pyrolysis temperature, duration, heating rate, pressure and oxygen-limiting environment. A wide range of feedstock is used for production of biochar like rice straw, canola straw, soybean straw, apple wood, pine sawdust, manure pellets, alfalfa, wheat straw, multiple sludges, digested sludge, etc. Activated carbon is considered the most common and efficient sorbent for elimination of pollutants from aqueous solutions, but production procedure of activated carbon demands additional activation processes besides high temperature. On the other hand, biochar is a sustainable low-cost adsorbent. Additionally, its production is cheaper with low energy requirements as compared to activated carbon (Huang et al. 2020).

14.2.1 Properties

Carbon-rich biochar is a surface decorated with oxygen-containing functional groups and aromatic groups. Its varying physicochemical properties depend on feedstock and different parameters of pyrolysis technology. With an increase in treatment temperature during pyrolysis, biochar production decreases. This induces a favourable change in biochar structure. While the total carbon content, cation exchange capacity and mineral content are attributes of the type of feedstock used, the reported pH of most biochar is alkaline; though, frequently, biochar exhibiting pH range of neutral to slightly acidic has also been reported. This can be seen in case of biochar produced from pinewood or black locust wood. pH of biochar increases with an increase in pyrolytic temperature due to release of alkaline salts from feedstock. In other words, high pyrolysis temperature is associated with loss of acidic surface functional groups (oxygen-containing moieties). Therefore, it decreases cation exchange capacity (CEC) of biochar. As mentioned earlier, CEC is property of feedstock used for biochar production. Crop straw biochar shows greater CEC than biochar derived from manure. Various elements present in feedstock such as K, Na, Ca, Mg and P contribute to the formation of O-containing surface functional groups that enhance the value of CEC of biochar. Biochar obtained from poultry waste or animal manure exhibits higher ash content which is associated with greater mineral content in biomass. Another important property of biochar, the electrical conductivity (EC), is higher for manure-derived biochar than agricultural waste and woody feedstock. EC is defined as the capacity to conduct electricity. Higher EC of biochar is attributed to a higher concentration of Na, K, Mg, SO_4 and PO_4. EC does demonstrate hype with pyrolysis temperature but mainly depends on the types of biomass used for biochar production (Tan et al. 2015). Surface area is a key property of biochar, and it increases with an increase in pyrolytic temperature as a result of escape of volatile substances (cellulose and hemicelluloses) and promotes formation of pore or channel structure. Large specific surface area, porous structure, enriched surface functional groups as well as mineral components contribute to biochar's adsorption property. Adsorption by biochar can be successfully applied in pollutant removal from an aqueous solution (Chintala et al. 2013).

14.2.2 Production Methods

Various thermochemical processes that can be employed for production of biochar are slow pyrolysis, fast pyrolysis, hydrothermal carbonization (HTC), flash carbonization, torrefaction and gasification. Conventional processes of pyrolysis are slow pyrolysis system and fast pyrolysis system. Slow pyrolysis system involves slow rate of heating (5–20 °C min^{-1}) with residence time of more than an hour. Moisture content of the feedstock greatly affects pyrolysis process, and studies indicated that feedstock moisture content must be less than 10% to be pyrolyzed into biochar. Feedstock used for biochar production is composed of cellulose, hemicellulose, and lignin, where lignin is the most recalcitrant as compared to hemicellulose and cellulose. Pyrolysis sequentially follows four main steps:

1. Partial hemicellulose decomposition
2. Complete hemicellulose to partial cellulose decomposition
3. Full cellulose and partial lignin decomposition
4. Complete decomposition with high degree of carbonization

Weight loss in biochar becomes gradual with further increase of temperature up to 70 °C. When various feedstocks are slow pyrolyzed, product yield falls in the range of 15–90%. Increased pyrolytic temperature changes elemental composition of resulting biochar. It has been reported that the increase in pyrolytic temperature enhances carbon content of biochar and reduces concentration of nitrogen, hydrogen and oxygen. However, Kim et al. (2013) observed that nitrogen content of biochar largely depends on the feedstock used during pyrolysis. This observation indicates a decrease in H/C, O/C and N + O/C molar ratio with increasing pyrolysis temperature. High O/C ratio indicates the presence of more hydrophilic surface, while low O/C ratio indicates the presence of more aromatic groups (higher extent of carbonization). The higher the O/C ratio, the more are the functional groups (hydroxyl, carboxyl, carbonyl) present on surface leading to higher CEC value. H/C ratio represents degree of carbonization or loss of polar groups at higher temperature. With an increase in temperature, O + N/C ratio reduces; this indicates a loss of polar group. Therefore, this surface chemistry contributes to adsorption property of biochar (Kim et al. 2013).

Hydrothermal carbonization (HTC) involves conversion of biomass into biochar at 180–300 °C in water for 30 min to 16 h. HTC shows biochar yield of 36–72%. Biochar production through HTC is gaining more attention, and HTC makes use of wet feedstock. HTC promotes formation of biochar with irregular surface (higher surface area) and abundant oxygen-containing groups along with higher CEC value than biochar formed by slow pyrolysis. HTC provides few advantages over pyrolysis such as the use of unconventional wet biomass (sewage sludge, city waste, animal remains), which are readily biodegradable and have high carbon sequestration potential. The presence of acidic functional group on surface of biochar such as carboxyl, lactone, and phenol makes the HTC-derived biochar an adsorbent of choice (Kalderis et al. 2014). Torrefaction is another slow heating process at temperature range of 250–300 °C resulting in release of CO_2 and water accompanied with formation of solid fuel. Gasification process favours formation of gas at temperature range of 700–800 °C with elevated pressure in gasification chamber. It is a promising and renewable pathway for mass production of syngas (Table 14.1).

Table 14.1 Application of biochar produced from different feedstocks

Biomass feedstock	Pyrolytic temperature (°C)	Pyrolysis techniques	Contaminants	References
Bamboo	450, 600	Slow pyrolysis	Sulfamethoxazole	Yao et al. (2013)
Hardwood	450	Fast pyrolysis	Cu, Zn	Chen et al. (2011)
Pine wood	300	Hydrothermal carbonization	Pb	Liu and Zhang (2009)
Rice husk	350	Slow pyrolysis	Pb, Zn, Cu and Cd	Xu et al. (2013)
Dairy manure	200, 350	Slow pyrolysis	Pb and atrazine	Cao et al. (2009)
Orange peel	300, 700	Slow pyrolysis	Hydrophobic organic compounds	Chen et al. (2012a, b)
Peanut shells	300, 700	Slow pyrolysis	Trichloroethylene	Ahmad et al. (2012)

14.3 Biochar-Based Materials: Application in Contaminant/Pollutant Removal

Properties of biochar that contribute in the eradication of contaminants (nutrients from eutrophic bodies):

14.3.1 Surface Area

The critical parameter governing adsorption capacity of biochar (carbonaceous material) is the specific surface area. Increase in surface area leads to higher adsorption of adsorbate, as surface is directly associated with density of adsorption sites. Observation from studies conducted by Zeng et al. (2016) using ammonium and phosphates as adsorbates concludes that increase in pyrolysis temperature (500–700 °C) enhances the surface area which elevates adsorption capacity of biochar multiple folds. In a similar study, Chintala et al. (2013) reported that biochar treated with hydrochloric acid has tenfold greater surface area which significantly improves adsorption abilities for nitrates. As surface area of biochar is generally negatively charged, it may not perform same level of adsorption for anionic compounds (Wang et al. 2015; Yao et al. 2013; Zeng et al. 2016).

14.3.2 Ion Exchange

It is a well-known fact that negatively charged surface of biochar adsorbs cationic compounds. It is known that biochar produced from slow pyrolysis (at low temperature) exhibits higher value for cation exchange capacity (CEC), and this leads to greater adsorption capacity for NH^{+4} in eutrophic water where NH^{+4} is adsorbed on the anionic surface by replacing another cation that shows week interaction with the same surface anion. Gai et al. (2014) made an observation that CEC value is higher for low-temperature biochar than high-temperature biochar (fast pyrolysis). Besides pyrolysis temperature, biochar CEC is a feature associated with the type of feedstock used. Gai et al. (2014) in their experimental studies found out that straw-derived biochar shows greater value for CEC which leads to efficient removal of NH^{+4} when compared to biochar derived from peanut shell or wheat straw at all temperatures. Surface modification with metals enhances CEC, promoting greater adsorption for NH^{+4}. For example, magnesium-modified *Phragmites australis* biochar undergo ion exchange between NH^{+4} and Mg^{+2} (Gai et al. 2014).

14.3.3 Surface Functional Group

The surface of biochar made by higher pyrolysis temperatures is commonly characterized by hydrophobicity, and lower temperature leads to generation of negatively charged surface functional groups (oxygen-containing groups such as hydroxyl group or carboxyl group). The absence of functional group carrying net positive charge or the presence of net negative charge leads to minimum electrostatic attraction or maximum electrostatic repulsion, respectively. The solution pH has a key impact on protonation/deprotonation status of surface functional groups. This influences the electrostatic interaction between oxygen functional group and ammonium ion. Kizito et al. (2015) worked on wood- and rice husk-derived biochar (at 600 °C) at lower pH and observed poor removal efficiency of NH^{+4}. This poor interaction is attributed to protonation of functional groups ($C{=}O$, COO^{-}) on biochar surface (Yang et al. 2018).

14.3.4 Precipitation

Primary mechanism for removal of PO_4^{-3} from polluted water is the formation of magnesium and calcium phosphates (Cui et al. 2016; Yao et al. 2013). Jung et al. (2015) in their study explained that the high PO_4^{-3} adsorption capacity is a result of high ratio of magnesium and calcium to phosphorus ($Mg/P = 3.46$ and $Ca/P = 47.6$, respectively) on peanut shell-derived biochar (at 700 °C). There are several modification strategies for improving adsorption capacity of biochar. This includes physical activation (gas, microwave), acid, alkaline and oxidant oxidation, compositing (that involves mineral impregnation or loading with nanoparticles). This can be successfully applied for removal of heavy metals such as Pb, Cd and Zn from polluted water (Yang et al. 2019a, b; Wang and Wang 2019; Li et al. 2020) used engineering method of ball milling which greatly enhanced adsorption capacity for tetracycline and mercury ions. They synthesized Fe_3O_4/wheat straw biochar composites which used multiple combined adsorption mechanisms during removal

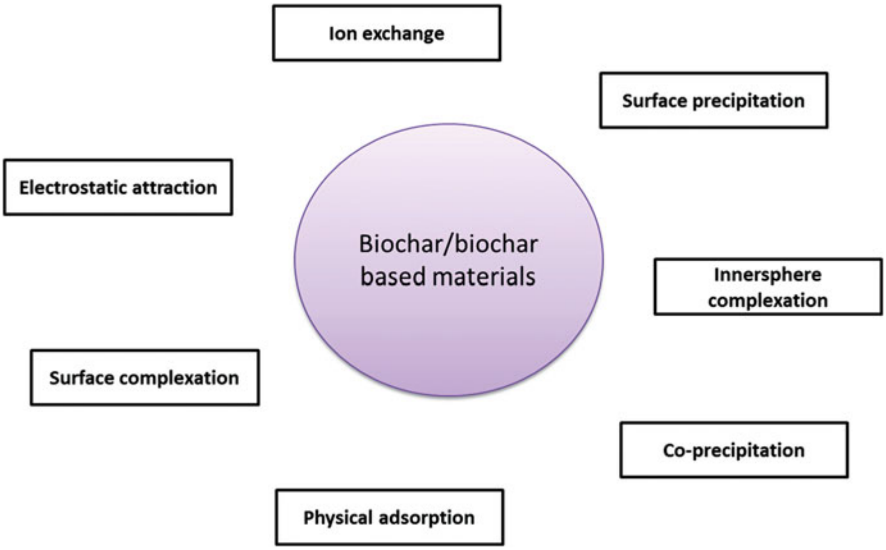

Fig. 14.1 Mechanisms of adsorption of heavy metal on biochar

process. It has been reported that that the magnetic biochar holds potential to effectively adsorb inorganic anionic pollutants (phosphate and nitrate), organic pollutants (organic dye and antibiotics), and radioactive matters, while Yi et al. (2020) reported that the N-doped biochar can be used to eradicate organic pollutants from contaminated water bodies or industrial untreated effluents. A number of adsorption mechanisms are involved during heavy metal removal via biochar such as electrostatic attraction, ion exchange, physical adsorption, surface complexation and precipitation (Li et al. 2020) (Fig. 14.1).

The oxygen-containing surface functional groups (such as carboxylate and hydroxyl) are responsible for interactions during removal of heavy metals. For instance, Lu et al. (2012) proposed that Pb adsorption on a sludge-derived biochar includes metal exchange with K^+ and Na^+ due to electrostatic outer-sphere complexation, surface complexation with free carboxyl functional groups and free hydroxyl functional groups and inner-sphere complexation with free hydroxyl groups. Similar mechanism is involved in adsorption of Hg (II) on biochar derived from soybean stalk as well as in case of adsorption of Cd (II) on corn straw biochar (Sun et al. 2014). Removal mechanism also depends on biochar feedstock source and mineral components such as CO_2 and $PO_4{}^{-3}$. Xu et al. (2013) tried simultaneous removal of Pb, Cu, Zn and Cd from aqueous solution using rice husk biochar and dairy manure biochar. Here the mineral components serve as additional adsorption site, therefore, enhancing further the adsorption capacity of biochar for heavy metals. Cao et al. (2009) also observed removal of lead by dairy-manure-based biochar through adsorption. Dairy manure is rich in $PO_4{}^{-3}$ and $CO_3{}^{-2}$ which leads to formation of Pb-phosphate precipitate $Pb_9(PO_4)_6$ and Pb-carbonate precipitate $Pb_3(CO_3)_2(OH)_2$.

Surface organic groups of biochar (hydroxyl and carboxyl) exhibit complexation with aluminium. Surface adsorption and co-precipitation of aluminium with silicate particles promote aluminium adsorption on biochar. According to the literature, surface area and porous structure of biochar seem to have less effect on heavy metal adsorption than oxygen-containing functional groups. Ding et al. (2014) reported that for high Pb adsorption on low-temperature biochar (250–400 °C) oxygen functional group was responsible whereas, for Pb adsorption on high-temperature (500–600 °C) biochar was mainly due to intra-particle diffusion. Oil palm biochar and rice husk biochar show adsorption for different heavy metals where the former has higher adsorption capacity for heavy metals with lower surface area compared to later. This indicates that the surface is not as important as the presence of oxygen-containing functional groups (Samsuri et al. 2014).

For removal of organic pollutants from aqueous solution, adsorption mechanisms can be successfully employed. These involve electrostatic interaction, hydrophobic effect, hydrogen bonds, and pore-filling phenomena of biochar with organic pollutants. Biochar surface is heterogeneous due to the presence of carbonized as well as non-carbonized fraction both having different adsorption mechanisms. Studies suggest that dominant adsorption mechanism is electrostatic attraction. Qiu et al. (2009) demonstrated the mechanism of dye adsorption on a straw-based biochar. They proposed that the mechanisms of dye adsorption involved π-π interactions (electrostatic attraction/repulsion and intermolecular hydrogen bonding) between dye molecules and graphene layers of biochar.

Zhang et al. (2013a, b) pointed out that the adsorption capacity of pig manure-derived biochar for insecticide carbaryl is attributed to hydrophobic effect, pore-filling together with pi-pi electron donor-acceptor interactions. Another report suggests that the degree of graphitization influences adsorption of sulphonamide on different biochar. Here the main mechanism of adsorption is also contributed by π-π electron donor-acceptor interaction. Pore filling is considered to be an important mechanism for removal of organic compounds by biochar via adsorption. Adsorption capacity here is majorly associated with surface properties of biochar. Adsorption capacity is proportional to surface area of micropores (Han et al. 2013). Therefore, pore volume and high surface area of carbonaceous material favour adsorption of organic pollutants as a result of significant pore-filling effect (Zhu et al. 2014).

14.4 Mechanisms That Drive Removal/Degradation of Contaminants

14.4.1 Catalysis

Recent scientific advances have made it possible to explore catalytic property of biochar and biochar-based material and their application in removal/degradation of contaminants. Biochar can also behave as electron acceptor to enhance photodegradation capacity of catalyst. Adsorption property of biochar is widely used for removal of contaminant; still adsorption is considered to be a non-destructive process, where toxic/refractory contaminant is transformed from one form to another, which still persists in the environment. Therefore, biochar-derived catalytic degradation technology has become a useful means for remediation of polluted environment. Commonly used catalyst includes titanium dioxide (TiO_2), zinc oxide (ZnO), tin oxide (SnO_2), zirconium dioxide (ZrO_2), and cadmium sulphide. Biochar acts as catalyst due to the presence of surface functional group and external transition metal. Both possess ability to degrade contaminant. Biochar can also be used as supporting material for photocatalysis. Biochar as support material can enhance photodegradation ability of the catalyst. Biochar surface contains environmental persistent free radical (EPFR) which reacts with oxygen to generate (OH) or sulphate radical (SO_4) catalysed by hydrogen peroxide or persulfate. These radicals are reported to degrade organic contaminant orange II, 2-chlorobiphenyl, and sulfamethoxazole.

Parameters that influence biochar's catalytic activity include pyrolysis temperature, pyrolysis time and transition metals. Yang et al. (2016) found out that higher pyrolysis temperature (200–500 °C) favours formation of free radicals which ultimately enhances catalytic degradation capacity. Temperature above 700 °C resulted in loss of free radicals, hence, reducing the catalytic activity. They checked the degradative role of biochar on *p*-nitrophenol, and feedstock used was pine wood, corn stalk, peanut shell, rice and wheat.

Another factor that affects the catalytic activity of biochar is pyrolysis time; with prolonged pyrolysis, a gradual decline in catalytic capacity can be observed. This decline happens due to the decomposition of phenolic compounds that play role in catalysis. Fang et al. (2015) demonstrated that for the generation of free radicals at low temperatures (less than 500 °C), the optimum pyrolysis time required is 12 h. For pyrolysis temperature greater than 500 °C, the required time is 1 h. In another study, Wang and Wang (2019) checked the efficiency of biochar/Fe(III)/persulfate system for catalytic degradation of sulfamethoxazole. The rate constant for biochar/Fe/persulfate system was found to be 31.3 times of biochar/persulfate system and 8.2 times that of Fe (III)/persulfate system (Fig. 14.2).

In this study, biochar preparation was undertaken at 500 °C for 2 h. The mass ratio of biomass to water too affects the catalytic ability of hydrocarbon. Greater value of biomass to water ratio favours formation of environmental persistent free radicals (EPFRs). It is concluded that catalytic activity of biochar/hydrocarbon is mainly based on pyrolysis temperature, transition metals, mass ratio of biomass to water and pyrolysis time.

Transition metal affects the catalytic capacity of biochar as it accounts for the generation of persistent free radicals. Mechanism involves the transfer of electron from phenol or quinone to metal oxides (e.g. Fe_2O_3) and later promoting the generation of persistent free radicals (PFRs). Here metal (transition metals) possesses higher redox potential. Fang et al. (2014) from his studies on degradation of contaminants reported that Fe reacts with H_2O_2 to produce OH radicals; further H_2O_2 reacts with hydroxyl radicals to generate superoxide ions (O^{-2}) that can

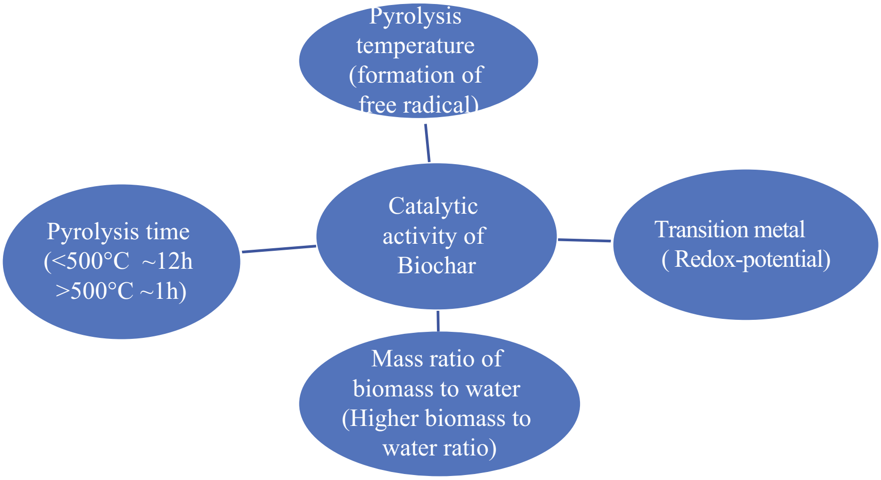

Fig. 14.2 Factors affecting the catalytic activity of biochar

degrade recalcitrant contaminants. Fe (III) is reported to possess the highest redox potential which helps achieve fast EPFR formation.

In the studies done by Lyu et al. (2019), they prepared biochar via ball milling. Ball-milled biochar exhibited greater electrocatalytic activity for reduction of $Fe(CN)_6^{-3}$. They reported that ball milling enhanced oxygen-containing functional group content from 0.8 to 2.9 to 2.2–2.4 m mol/g. Altogether it can be concluded that ball milling is a great engineering technique to enhance external and internal surface area together with good amount of surface functional group, and also exposing the graphitic structure, hence, increasing the catalytic capacity of biochar. Recently, the immobilizations of metal photocatalyst on biochar have paved another potential way for degradation of highly toxic emerging contaminants. It involves cooperation of adsorption and photocatalysis. Conventional catalysts such as TiO_2, ZnO, SnO_2 and ZrO_2 possess high catalytic activity with good chemical stability but possess limitations due to their large band gap width and difficulty in separation from aqueous solution and undergo photodissolution.

14.4.2 Adsorption

Properties that influence the adsorption efficiency of biochar are de-ashing treatment, pH, dosage of adsorbent, competitive anions and temperature.

Chen et al. (2008) analysed the combined desorption and distribution effects of biochar derived from pine needle at various temperatures (100–700 °C). Study revealed that the pyrolysis temperature has a significant impact on the structural change of biochar and greatly influences adsorption capacity for numerous organic pollutants. Degree of adsorption increases in the order of increasing temperature, consistent with their specific surface area (Chen et al. 2008). Chen et al. (2012a, b) noted that the pyrolysis temperature of biomass affects the rate of adsorption of compounds by biochar as it is proportionally associated with degree of carbonization of biochar. Higher temperature results in complete carbonization of the organic matter of biomass; this greatly increases the surface area. Beside this, more nanopores are generated which enhance the adsorption rate of naphthalene.

Ahmad et al. (2013) pointed out that the presence of more carbonized matter in biochar generated at higher temperature leads to greater adsorption of trichloroethylene. At higher treatment temperature, hydrophobicity of biochar increases with the loss of oxygen and hydrogen functional groups. Hence, this leads to higher adsorption of hydrophobic compounds such as trichloroethylene. Kim et al. (2013) reported that the pyrolysis temperature has impact on structure, elemental composition and morphological properties of biochar. In this study, the pH and surface area of biochar enhanced with pyrolysis temperature of greater than 500 °C. As a result, increase in Cd adsorption onto biochar was observed. Composition of feedstock also affects adsorption capacity of biochar (Sun et al. 2014). Value of adsorption capacity for pollutants differs with the type of original biomass or feedstock, even under the same pyrolysis conditions. Mineral composition of feedstock plays important role in the adsorption performance of biochar (Cao et al. 2009). Biochar derived from co-pyrolysis could also be used to eradicate contaminants from aqueous solution. Bernardo et al. (2013) checked removal efficiency of Pb by biochar derived from co-pyrolysis of pine, used tires and plastic waste. Researchers further investigated and compared adsorption properties of biochar derived from various biochar production methods, besides the commonly used pyrolysis method. Liu et al. (2010) reported that the hydrothermal treatment has potential to create more oxygen-containing groups on biochar surface than pyrolysis process. Kumar et al. (2011) showed that the biochar derived from hydrothermal carbonization (HTC) exhibits better adsorption properties for Cu from wastewater. There is limited adsorption of contaminants from water, when demineralization or de-ashing treatment is performed on biochar. De-ashing greatly influences the composition and surface characteristics of biochar as it decreases the elemental composition of surface except for carbon. Zhang et al. (2013a, b) pointed out that after de-ashing, adsorption capacity of biochar increases since inorganic compounds are removed which are supposed to prevent access to organic adsorption sites in biochar. Sun et al. (2013a, b) studied the effects on structural performance and adsorption performance of phenanthrene biochar after de-ashing treatment. After decarbonization, biochar had more hydrophobic domains and couple of polar functional groups. As a result, favourable and hydrophobic organic adsorption sites increased. This ultimately enhanced adsorption of phenanthrene (Fig. 14.3).

14.4.2.1 pH of the Solution

During optimization of adsorption process, pH of the solution is one of the crucial parameters. The role of pH on adsorption depends on the type of biochar and the target pollutants. It not only influences the surface charge of the absorbent but also affects the degree of ionization as well as morphology of adsorbate (Li et al. 2013). Therefore, most studies involving the adsorption of organic or inorganic pollutants

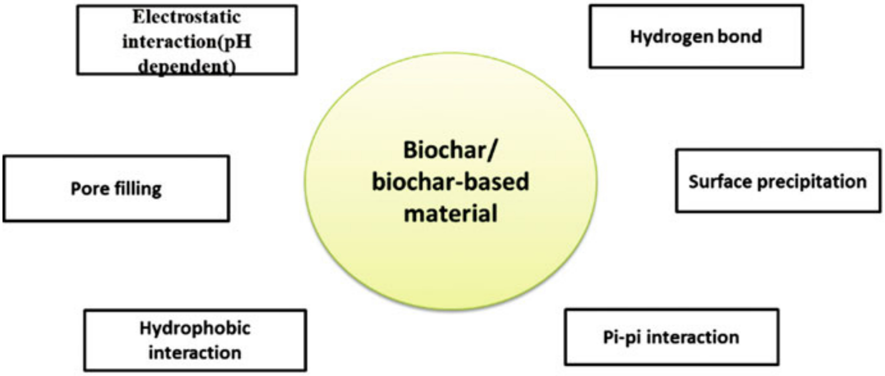

Fig. 14.3 Mechanisms of adsorption of organic contaminant on biochar/biochar-based materials (Tan et al. 2015)

consider the effect of pH. Biochar is enriched with number of functional groups such as carboxylate and hydroxyl. As pH of the functional group increases, behaviour of functional group alters. The surface of biochar is enriched with protonated functional groups at low pH. For pH less than pHpzc (point of zero charge), biochar surface exhibits positively charged functional groups; this facilitates the adsorption of negatively charged organic pollutants (anions) (Abdel-Fattah et al. 2015). In addition, the presence of large amounts of H^+ and H_3O^+ in aqueous solution may compete with cations available on adsorption sites. Therefore, at low pH value, electrostatic repulsion occurs between cationic contaminants and cationic functional groups present on the surface of biochar. With gradual increase in pH value, deprotonation of functional group occurs, and the competition between metal ions and proton for binding site declines and more binding sites are free. When biochar pH is greater than pHpzc (point of zero charge), the surface of biochar is negatively charged, and increased binding of cationic compounds on biochar surface was observed increasing its adsorption capacity. These trends have been observed in studies on the adsorption of different heavy metals by various biochar. Oh et al. (2012) investigated the effect of pH on fluoride adsorption by water treatment sludge biochar, which can also be explained on the basis of pHpzc (point of zero charge).

Chen et al. (2011) demonstrated that the biochar derived from hardwood and corn straw indicates higher adsorption capacity for copper and zinc at high pH and peaked at pH 5. Further hype in pH value resulted in decline of adsorption capacity. Formation of hydroxide complexes might be responsible for this decline in adsorption capacity. Parshetti et al. (2014) in their study reported that the food waste biochar show adsorption of textile dyes. The effect on adsorption was evaluated for pH range of 3.0–9.0. Highest dye adsorption was observed at alkaline pH because of the electrostatic interaction between cationic dye molecules and negatively charged surface. At acidic pH, the low adsorption efficiency is a result of dye protonation and excess H^+ ions in the solution that compete with cationic dye molecules for available adsorption sites. Tsai and Chen (2013) reported that the adsorption capacity of paraquat onto biochar significantly increased when pH of aqueous solution changed from 4.5 to 7.5 due to increased number of negatively charged sites. Similar trends were observed with the adsorption of methyl violet and oxytetracycline (Jia et al. 2013).

14.4.2.2 Co-existed Ions

For real-world application of biochar in actual water system, co-existence of ions has a crucial impact on the equilibrium adsorption capacity. As in the environment, the complex pollutants co-exist and have an interaction with adsorption efficiency. In a study by Jia et al. (2013), they observed the effect of corn stover biochar on adsorption of oxytetracycline involving interaction with metal ions. Results indicated that the presence of heavy metals has different effects on oxytetracycline adsorption on biochar. For example, Cd^{+2} has no obvious adsorption effect on it; Zn^{+2} promotes small level of adsorption; Pb^{+2} carries small inhibition effect; and Cu^{+2} at all pH values promotes adsorption of oxytetracycline on biochar. In another study on adsorption of co-existing pollutant in real environment by Zhang et al. (2011), they observed a significant reduction in adsorption capacity of biochar in the presence of more than one pollutant, for instance, the co-existence of diazine and azine. On the other hand, co-existing compounds sometimes show competitive adsorption where they inhibit adsorption of each other on to biochar. Kong et al. (2011) observed the same inhibition of adsorption or total reduction of adsorption scenario for phenanthrene (PHE) and Hg (II) in aqueous solution. However, co-existence of humic acid and cations enhanced the adsorption of polychlorinated-biphenyl (PCBs) on biochar.

14.4.2.3 Dosage of Adsorbent

Adsorption efficiency of biochar for organic or heavy metal pollutants is significantly influenced by dosage of adsorbent. It was observed in a study that the increase in concentration of adsorbent/biochar for the contaminant's removal reduces the total adsorption capacity of biochar (Chen et al. 2011). A study by Tsai and Chen (2013) pointed out that adsorption sites increase in line together with the increase in adsorbent dosage (i.e. 0.10–0.30 g/L). However, there was reduction of adsorption efficiency of biochar as its mass increased. In yet another study, it was reported that at constant concentration of methylene blue, the dye adsorption increases with increase in biochar dosage from 2 to 8 g/L. This characteristic can be attributed to the increase in adsorption surface resulting in availability of more adsorption sites (Sun et al. 2013a, b).

14.4.2.4 Temperature

Adsorption of contaminants on biochar is an endothermic process and with increase in temperature, adsorption capacity increases. For example, Pb ion adsorption on pinewood and rice husk biochar is more favourable at high temperature. This high temperature provides energy for capturing lead ions onto the interior structure (Liu and Zhang 2009; Zhang et al. 2013a, b). To test the rise in temperature adsorption capacity of biochar, Sun et al. (2013a, b) investigated the effect of temperatures at

30, 40 and 50 °C on adsorption capacity for methylene blue dye (cationic in nature). Significant enhancement in adsorption efficiency of methylene blue at 50 °C was observed for biochar derived from eucalyptus as rise in temperature increased the rate of diffusion of methylene blue.

14.4.3 Biochar as Gas Absorbent

Many scientific studies have proposed biochar as feasible low-cost gas adsorbent compared to CO_2 adsorbents as well as activated carbon. Surface chemistry of biochar shows better adsorption capacity of CO_2, benzene and methyl ethyl ketones (MEK) in air. Zhang et al. (2019) shows adsorption performance of different feedstock materials like rice straw pyrolyzed at 300–500 °C for heavy metal ions including Pb, Cd and Hg. These biochars are suitable for large-scale remediation of environmental pollutants. Gao et al. (2019) demonstrated that the adsorption capacity of rice husk biochar for Cd^{+2} is greater than sewage sludge biochar. Adsorption phenomenon here is the result of precipitation and cation exchange mechanism. Cao et al. (2019) used wheat straw biochar to analyse the adsorption efficiencies of carbonization and ball milling for removal of Pb form waste or polluted water. At lower adsorption dosage, both efficiently promoted Pb^{+2} adsorption due to enhanced ion exchange capacity. Dai et al. (2020) used *Auricularia auricular* drugs-derived biochar for tetracycline removal, and with increase in pyrolysis temperature, adsorption capacity increased. This adsorption possibly involved pore-filling effects, hydrogen bonding, electrostatic repulsion and π-π EDA interaction.

14.5 Reduction

Biochar catalyst reduces the toxicity of contaminants through their reduction, especially in case of heavy metals. Heavy metal, chromium (Cr (VI)), is a top priority hazardous pollutant, whereas Cr (III) is quite less toxic to environment. Therefore, reduction of Cr (VI) to Cr (III) has gathered much attention. Oxygen-containing functional groups on biochar surface are involved in Cr reduction making it less toxic (Xu et al. 2019). Cr (VI) reduction by biochar in the presence of orange G irradiated with UV was investigated. Here orange G oxidation produces organic acid which acts as electron donor to carry out reduction of Cr (VI). Further addition of persulfate into the system enhances the reduction efficiency of Cr (VI). Hence, it can be concluded that biochar plays a key role in reduction and oxidation of inorganic/heavy metal contaminants (Jeon et al. 2017).

14.6 Oxidation

Biochar and biochar-based catalysts remove organic pollutants via oxidation with or without the addition of oxidants. Fang et al. (2015) stated that organic pollutants can be oxidized by biochar with the use of external oxidants. Qin et al. (2017) carried out a study to figure out the effectiveness of degradation of 1,3-dichloropropene (1,3-D) by biochar at various temperatures 300, 400, 500, 600 and 700 °C. Moisture content of biochar plays a crucial role in removal of 1,3-D, and they concluded that the higher the moisture content, the greater the adsorption performance of biochar (Huang et al. 2015). With the rise in pyrolysis temperature from 300 to 500 °C, a decline in the rate of degradation of 1,3-D can be observed; this is due to decrease in concentration of OH radicals. However, further increase in pyrolysis temperature from 500 to 700 °C shows a rise in degradation rate, as a consequence of increase in pore size of biochar, thus, suggesting the effect of porosity selective adsorption. Its worthy to note that the concentration of EPFR of biochar has an inverse relation with the rate of degradation of 1,3-D; for instance, biochar at 500 °C carries the highest EPFR concentration, while at the same time the rate of degradation is the lowest. This indicates that EPFRs of biochar contained external radicals as well as internal radicals. Only the surface exposed external EPFRs participate in reaction with oxygen and induce formation of hydroxyl radicals, catalysing the degradation of 1,3-D. Hydrogen peroxide, persulfate and peroxymonophosphate are some of the oxidants which when added to biochar generate ROS that helps degrade organic contaminants (Kemmou et al. 2018; Huang et al. 2020). Wang and Wang (2019) found that triclosan is significantly decomposed when biochar-activated peroxymonosulfate were induced to produce ROS.

14.6.1 Advanced Oxidation Process

Advanced oxidation processes are widely applied in wastewater treatment and production of potable or reusable water to combat the clean water crisis. Advanced oxidation process works by generation of free radicals such as hydroxyl, sulphate-free radicals or chlorine radicals to oxidize or degrade toxic or recalcitrant compounds. In case of biochar, they during production generate and have environment persistent free radicals on their surface which react with oxygen gas to produce hydroxyl radicals without the use of external oxidant (Lyu et al. 2020). These hydroxyl radicals further oxidize the reduced organic or emerging contaminants (Yu et al. 2020). Ruan et al. (2019) described biochar as a source of free radical for such reaction as EPFR have longer lifetime. EPFR are also known to catalyse oxidants to generate ROS for further oxidation of reduced compound. Chemical compounds such as catechol, phenol, endocrine-disrupting compounds, etc. can be oxidized by free radical processes. Zhu et al. (2018) demonstrated that some biochars could possess higher catalytic activity than popular metal and nanocarbon catalysts by utilizing the N-doped graphitic *Phragmites australis* biochar to activate peroxydisulfate. Sun et al. (2019) produced multiple iron biochar composites

(Fe-BC) with varying ratio of Fe/BC mass ratio used for eradication of different pollutants from hydraulic fracturing wastewater. Fe-BC composite at ratio of 1:1 performed the best for simultaneous removal of 1,1,2-TCA as well as organic compounds present in high salinity hydraulic fracturing wastewater. In another study, Yang et al. (2019a, b) prepared corn stalk biochar composites featured with different layered double hydroxide (LDHs) and observed that incorporation of LDHs improves the adsorption capacity for phosphate many times. Here, the interlayer anion exchange and surface complexation are the dominant phenomenon among other adsorption mechanisms. An interesting study conducted by Zhang et al. (2020) used green synthesis method to produce banana peel biochar/iron oxide composites. These composites showed enhanced adsorption capacity for methylene blue and were reusable after five cycles. Bamboo sawdust derived biochar pretreated with phytic acid may enhance the surface area along with pore volumes and phosphorous contents (Hu et al. 2020).

14.6.2 Biochar and Biochar-Based Catalysts for Photocatalysis

Besides the use of oxidants for degradation of organic contaminants, biochar and biochar-based composites also show the property of photocatalysis for degradation of contaminants. Photocatalysis involves either the use of ultraviolet or visible light or in combination. Lu et al. (2019) investigated the degradation ability of TiO_2/biochar catalyst for methyl orange solution under the influence of UV irradiation. At a biochar to Ti weight ratio of 0.2, 0.25 g/L/TiO_2/biochar removed 96.88% of 20 mg/L methyl orange solution in 140 min. Hydroxyl radicals and superoxide anion radicals are responsible for oxidation of methyl orange. Among these, hydroxyl radicals played the dominant role.

Pi et al. (2015) noted that biochar acts as co-catalysts to provide sufficient catalytic sites for graphite carbon nitride (g-C_3N_4) under LED light irradiation. Biochar-based photocatalyst works as follows: electrons move from valence band to conduction band upon irradiation, formation of electron-hole pair takes place, followed by the formation of OH and O radicals, and then degradation of contaminants takes place on the photocatalyst surface.

14.7 Biochar in Environmental Remediation and Wastewater Treatment

Carbon, hydrogen, oxygen, nitrogen and phosphorus are the most essential elements required for structure and functions of living organisms. Nitrogen is required for synthesis of protein and nitrogenous bases, whereas phosphorus is a crucial part of structures such as cell membranes, genetic material and energy-carrying molecules (Marschner 2012). Anthropogenically generated organic waste, plant remains and untreated industrial discharge often lead to accumulation of nutrient into aquatic systems, which leads to eutrophication in rivers, lakes, reservoirs and estuaries worldwide. Eutrophication results in formation of algal blooms. This causes threat to drinking water safety as well as biodiversity of aqueous systems. In water bodies, elements responsible for causing eutrophication are inorganic nitrogen and phosphorus, generally existing in the form of ammonium (NH^{+4}), nitrate (NO^{-3}) and phosphate ($PO_4{}^{-3}$). Algal bloom is caused by simultaneous presence of N and P (NH^{+4} and $PO_4{}^{-3}$, NO^{-3} and $PO_4{}^{-3}$), whereas the presence of N alone does not result in the formation of algal bloom (Zeng et al. 2016). To tackle the problem of eutrophication, a dual-nutrient-reduction strategy can be used for removal of both N- and P-rich compounds. Additionally, atmospheric precipitation, biological nitrogen fixation and decomposition of organic matters also contribute to the total N and P concentration in aquatic ecosystems.

Phosphate-accumulating organisms are one of the ways of removing P-rich compounds in polluted or wastewater where phosphate-accumulating organisms store and release phosphates (Nielsen et al. 2019). As a supplementary method to biological processes, the chemical precipitation processes can be employed, which involve metal and metaloxides to precipitate phosphate (Ye et al. 2017). Depending on adsorbent properties and ambient electrolyte conditions, adsorption is considered an effective and rapid process to remove contaminants from the aqueous systems. Zeolites, bentonite, polymeric ion exchangers, nanoparticles and aluminium oxides have been evaluated for their effectiveness in eradication of N- and P-rich compounds (Alshameri et al. 2018; Angar et al. 2017; Xu et al. 2018). Because of the easy availability of feedstock and its low cost, biochar is a material of interest for environmental remediation. Metallic elements in biochar might help in binding of soil nutrients NO^{-3}, $PO_4{}^{-3}$ and NH^{+4} via specific and nonspecific adsorption. So, these can act as N- and P-enriched input where undesirable contaminants can be transformed into desirable nutrients in the agricultural system (Hale et al. 2013). Taghizadeh-Toosi et al. (2012) reported that biochar sequestered ammonia in stable form for a duration of 12 days which is considered to be available for plant uptake. In a number of studies, biochar has been used for individual as well as simultaneous removal of N (NH^{+4}, NO^{-3}) and P ($PO_4{}^{-3}$) from aqueous solution (Yang et al. 2018; Gao et al. 2015).

14.7.1 Ammonium Removal by Biochar

In aqueous solution, ammonium is one of the main inorganic forms of nitrogen. pH and temperature influence the inter-conversion of ammonium and ammonia. According to Emerson et al. (1975) in most of the aqueous environment, ammonium serves as main source of ammonia at pH less than 8.2 and temperature less than 28 °C. To evaluate the removal efficiency of ammonium nitrogen (NH_4-N) by biochar, extensive batch adsorption studies have been conducted by Yang et al. (2018) particularly with pine sawdust biochar and wheat straw biochar, whereas Gao et al. (2015) and Liu et al. (2016) conducted the same for peanut shell biochar, corn cob biochar and cotton stalk biochar. Throughout the literature, Qmax value of biochar varies with a mean value of 11.19 mg N/g. For pine sawdust biochar which pyrolyzed at temperatures 300 and 500 °C, the Qmax values for NH4-N were 5.38 and 3.37 mg N/g, respectively (Yang et al. 2018). For giant reed-based biochar pyrolyzed at 500 °C, Qmax value is 1.21–1.49 mg N/g (Hou et al. 2016).

14.7.2 Ammonium Removal by Modified Biochar

Alteration in biochar surface functional group and increase in CEC value together with enhanced chemical precipitation could improve total adsorption capacity of ammonium by biochar. For instance, to enhance Qmax value of ammonium, materials with high CEC can be added into char feedstocks (such as bentonite). Similarly, Gong et al. (2017) used Mg-modified *Phragmites australis* biochar where adsorption isotherm for NH^{+4} was observed to be linear. This indicates unsaturated adsorption capacities and with rising concentration of NH^{-4}-N, Qmax value was found to be 32 mg N/g within the tested concentration range. This result attributes to the property of cationic exchange that took place between Mg^{+2} and NH^{+4}. Phosphate-rich biochar shows higher adsorption capacity for NH^{+4} in the presence of Mg^{+2} as a result of precipitation of $MgNH_4PO_4$ (Struvite) (Fan et al. 2019).

14.7.3 Nitrate Removal by Biochar

Due to complete dissociation of HNO_3, nitrate is mostly present in anionic form (NO^{-3}) in aquatic phase. One of the significant barriers for nitrate adsorption on biochar is contributed by electrostatic repulsion between nitrates and negatively charged surface constituents existing on biochar.

14.7.4 Nitrate Removal by Unmodified Biochar

A number of studies have shown that the unmodified biochar had minimal adsorption capacity for nitrate. Gai et al. (2014) investigated 12 biochars pyrolyzed from 3 different feedstocks in batch adsorption tests. They observed no removal of nitrate from aqueous solution, even in some cases biochar released rather than adsorbing nitrate. These results are explainable by taking into consideration higher pyrolysis temperature ($\geq$600 °C) which leads to changes in physiochemical properties such as higher surface area and oxygen-containing functional groups (Ahmad et al. 2014). Reduction in oxygen-containing functional group minimizes electrostatic repulsion between biochar and nitrate, whereas increase in surface area enhances number of biochar sorption sites.

14.7.5 Nitrate Removal by Modified Biochar

Significant modification of biochar positively facilitates nitrate adsorption, especially the modifications that provide hindrance to electrostatic interaction between biochar and nitrate ions. Protonation of anionic functional groups and impregnation of metal/metal oxide on biochar are commonly used modification strategies. For instance, hydrochloric acid-treated biochar shows greater adsorption capacity for nitrate (Chintala et al. 2013). HCl-modified ponderosa pine wood residue-based biochar achieved highest level of adsorption for nitrate (9.74 mg N/g) when compared to untreated biochar that showed adsorption of 2.58 mg N/g. Here, enhanced adsorption attributes to rise in surface area by tenfold after HCl modification. Lanthanum-immersed sawdust pyrolyzed to biochar also enhances nitrate adsorption capacity of unmodified oak sawdust biochar from 2.02 to 22.58 mg N/g. This observation is also attributed to the increase in functional groups in lanthanum-modified biochar (Wang et al. 2015). In another study, Zhang et al. (2012) repeated the same method by immersing biomass feedstocks in $MgCl_2$ solution prior to pyrolysis treatment resulting in increase in adsorption capacity of MgO-modified biochar nanocomposites for nitrate. The observations showed adsorption capacity of this MgO-modified biochar as high as 95 mg N/g.

14.7.6 Removal of Phosphate by Unmodified Biochar

Depending on the environmental pH $H_2PO_4^{-1}$, HPO_4^{-2} and PO_4^{-3} are some of the forms in which inorganic P is found in aqueous solution or contaminated water bodies. Phosphate anions show repulsion to the negatively charged surface functional groups of biochar. Therefore, for inorganic phosphate, adsorption capacity of biochar is poor. In a study (Gong et al. 2017) with 22 unmodified biochars, adsorption capacity of PO_4-P was tested from which only 4 biochars exhibited positive results for PO_4-P removal. This indicates weak interaction between most of the wetland-derived biochar and PO_4-P. Gong et al. (2017) pointed out that the biochar of *Phragmites australis* (600 °C) provides little interaction with total phosphorus (TP) levels in a sample derived from eutrophic lake. The ability of biochar towards sorption of PO_4-P also shows biomass dependence. Biochar derived from peanut shells at 700 °C shows greater PO_4-P removal capacity than oak, soybean and bamboo pyrolyzed at same temperature (Jung et al. 2015).

14.7.7 Phosphate Removal by Modified Biochar

Scientific communities have strategically attempted to increase phosphate adsorption capacity of biochar via addition of metals and metal oxides to feedstock. A large number of studies involved the use of Mg to promote PO_4-P adsorption to biochar. Here the strong divalent cation promotes binding between Mg and P (Wang et al. 2020). P-sorption is associated with the concentration of intrinsic Mg present in biochar feedstock. *Thalia dealbata*-derived biochar shows greater adsorption capacity (2.54–4.96 mg P/g) when compared to three other phytoremediation plants. This increase in adsorption capacity by Mg-modification can be attributed to factors such as concentration of Mg, pyrolysis parameters and differences in intrinsic properties of biochar.

14.8 Conclusion and Future Prospects

A survey of number of literatures on application as well as production processes of biochar reveals the use of wide variety of biomass materials. The properties (adsorption and catalysis) are profoundly affected by parameters of pyrolysis, feedstock used and modifying agents used. This catalytic property of biochar and biochar-based composites holds potential future in environmental remediation and wastewater treatment. It is carried out in three ways: first, EPFRs of biochar react with oxygen to generate hydroxyl radicals, second, activation using hydrogen peroxide or persulfate generate hydroxyl or sulphate radicals, and third, act as electron acceptor to improve photodegradation capacity of catalysts. However, the current application of biochar as catalysts is limited to laboratory scale. An analysis of adsorption mechanisms reveals that different kinds of interactions including electrostatic attraction, ion exchange, physical adsorption and chemical bonding (complexation and/or precipitation) are predominantly responsible for binding water pollutants. Therefore, large-scale assessment and technical and economic applications should be encouraged.

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Application of Biochar for Removal of Heavy Metals, Pathogens, and Emerging Contaminants from Wastewater

15

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Abstract

Wastewater treatment is the key point to improve environmental and health quality. In fact, providing clean water and sanitation for everyone is featured as goal number 6 in the list of the Sustainable Development Goals (SDG) established by the United Nations. In this context, biochar application has emerged as an efficient, cost-effective, and eco-friendly option to wastewater contaminant removal. Considering the importance of highlighting some successful studies applied worldwide, this chapter will address the most relevant and diverse biochar materials used on the removal of pathogens, heavy metals, pharmaceuticals, and emergent contaminants from wastewater. Additionally, it brings a critical review of current research updates in this issue, especially considering that biochar application is in accordance with the circular economy concept.

Keywords

Wood · Circular economy · Alternative treatment · Biomass feedstock

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15.1 Introduction

One of the consequences of population growth is the increase on demand of foods such as cereal and animal protein. This increase leads to a greater volume of wastewater being generated, in an estimated world annual volume of 1000 km^3 of effluent produced (Lu et al. 2018). After proper treatment, wastewater is commonly disposed through incineration or applied as fertilizer on crops (Wang et al. 2017). Over the last decades, it has been proposed that wastewater be reused on irrigation, once that it is a rich source of nutrients and water for plants (Perez-Mercado et al. 2019). However, it is important to highlight the necessity of biosecurity protocols for the reuse of this material, once that wastewater could also be source of contaminants such as pathogens, residues of heavy metals, pharmaceutical, endocrine disruptors, and dyes from textile industries (Li et al. 2019).

The lack of proper wastewater treatment is a problem that affects people all around the world; as a consequence, thousands of contaminants reach the environment every day. This lead to the United Nations (UN) establishing the Sustainable Development Goals (SDG), a list of 17 goals created with the intention of encouraging research on key points related to sustainability and environmental preservation. Goal number 6 is about “clean water and sanitation for all” by 2030 (Gwenzi et al. 2017).

To achieve this goal, it is necessary to look for practical and efficient treatment methods to manage wastewaters. Among the low-cost methods to remove physical, chemical, and biological contaminants from aqueous solutions, biochar has presented itself as a promising option (Gwenzi et al. 2017); more than 6934 publications have been made on this topic from 1998 to 2018 (Wu et al. 2019). However, the first biochar application on wastewater treatment only happened in 2009 (Wu and Wu 2019).

The main steps of the transformation of residues into biochar by pyrolysis or gasification and its possible application to wastewater treatment are presented in Fig. 15.1. These processes can generate three different products: biochar, gas, and oil (Scholz et al. 2014). The pyrolysis system produces more biochar than the gasification, due to less oxygen present in the process. However, depending on the material composition, the amount of biochar generated can change, for instance, the silica content (such as rice husk), which prevents total carbonization, and consequently preserves the biochar structure, resulting in a bigger volume of biochar (Scholz et al. 2014).

One of the advantages of biochar is that it could be produced from a huge diversity of feedstock, enabling the use of local materials (natural and waste) available where the treatment will be implemented, such as agricultural residues (cereal plant parts), wood, and so on (Kaetzl et al. 2020).

Biochar mainly removes organic and inorganic pollutants through adsorption. The nature of the feedstock material, the contaminant target and the pyrolysis conditions, as well as surface area, chemical functional groups, and pore size are factors that can alter its removal efficiency (Tan et al. 2015).

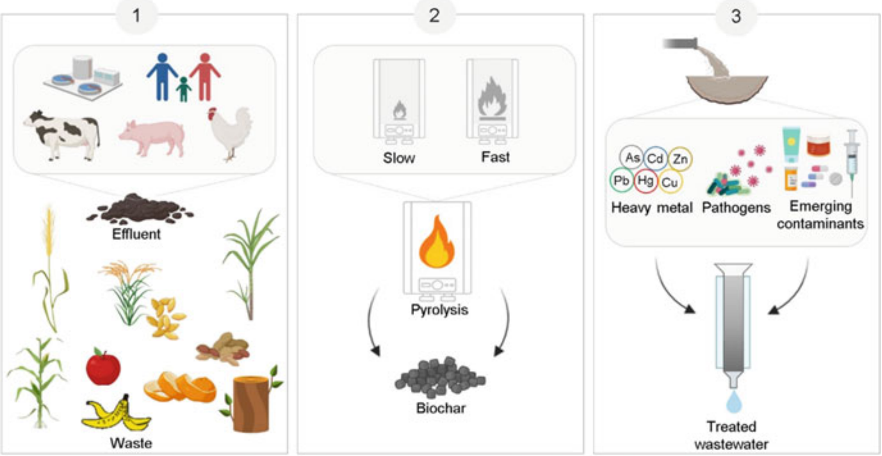

Fig. 15.1 Schematic representation of the main steps associated with biochar application: selection of residual materials (1); biochar production by pyrolysis (2); and application on wastewater treatment (3)

Biochar produced at high temperatures (above 500 °C) usually presents hydrophobic surface areas, which favor the adsorption of organic pollutants, while at low temperatures, a smaller pore size and oxygen-containing functional groups favor the adsorption of inorganic pollutants (Tang et al. 2015). Additionally, adsorption capacity can be improved by using chemical pretreatment techniques (Tang et al. 2015), such as applying alkali solutions which increase pore abundance, contact surface areas, and functional groups (Pokharel et al. 2020). Considering the nature of the binding and the ligation of the pollutant and the biochar, another important parameter is the contact time between these two elements (Sforza et al. 2020). Therefore, understanding these adsorption mechanisms is of essential importance to determine the treatment system layout and the operational conditions in order to achieve the highest removal rates.

15.1.1 Biochar Application in the Circular Economy Approach

Among the various advantages associated with biochar, one of them is the huge options of materials that can be transformed by the pyrolysis process (Table 15.1). It is worth to note that all of them are residues from other processes, mainly from agriculture and forest activities such as crops or forest residues, and so on (Fytili and Zabaniotou 2018). The practice of reusing residues in new production systems has been utilized over the last decades, especially for being in accordance with the concept of circular economy, which aims to close the loop of material utilization, especially considering the value aggregations and sustainability approaches (Fytili and Zabaniotou 2018).

Table 15.1 Summary of feedstock materials and pyrolysis condition, for removal of different contaminants from wastewater

Feedstock	Pyrolysis temperature/ time	Contaminant	Removal	References
Rice husk	350 °C/4 h	Pb	78–100%	Xu et al. (2013)
		Cu	25.6–62.4%	
		Zn	12.3–49.4%	
		Cd	0–51.1%	
Dairy manure	350 °C/4 h	Pb	10.6–17.7%	Xu et al. (2013)
		Cu	0.03–11.8%	
		Zn	0.4–10.9%	
		Cd	0–9.6%	
Digested dairy waste	600 °C/2 h	Pb	99%	Inyang et al. (2012)
		Cu	98%	
		Ni	26%	
		Cd	57%	
Digested sugar beet	600 °C/2 h	Pb	>97%	Inyang et al. (2012)
		Cu	>97%	
		Ni	>97%	
		Cd	>97%	
Sulfurized wood	600 °C/4 h	Hg	10.4–44.4%	Park et al. (2019)
Wood	600 °C/4 h	Hg	17.7–81.4%	
Bagasse waste	300 ± 10 °C/ 2.5 h	Pb	64.8–75.4%	Bharti and Kumar (2018)
Palm oil mill sludge	400 °C/1.5 h	Cd	98.0%	Goh et al. (2019)
		Cu	93.0%	
Raw corn straw	200 °C/2 h	Cd	73.9%	Chi et al. (2017)
		Pb	68.5%	
	300 °C/2 h	Cd	85.3%	
		Pb	81.2%	
	400 °C/2 h	Cd	99.2%	
		Pb	98.6%	
	500 °C/2 h	Cd	99.4%	
		Pb	98.8%	
	600 °C/2 h	Cd	99.4%	
		Pb	99%	
	700 °C/2 h	Cd	99.5%	
		Pb	99.8%	
Scots pine	400–700 °C/ 45–120 h	Cd	≈25%	Komkiene and Baltrenaite (2016)
		Pb	≈28%	
		Cu	≈22%	
		Zn	≈26%	

(continued)

Table 15.1 (continued)

Feedstock	Pyrolysis temperature/ time	Contaminant	Removal	References
Silver birch	400–700 °C/ 45–120 h	Cd	≈37%	Komkiene and Baltrenaite (2016)
		Pb	≈33%	
		Cu	≈24%	
		Zn	≈34%	
Sewage sludge	300 °C/ 30 min	As	30%	Agrafioti et al. (2013)
		Cr	70.0%	
Banana peel	600 °C/ 30 min	Cu	80%	Amin et al. (2018)
		Pb	55%	
Hardwood	–	*Escherichia coli*	~1 log 10 CFU	Perez-Mercado et al. (2019)
		Enterococcus spp.	~1 log 10 CFU	
		Saccharomyces cerevisiae	>1 log 10 CFU	
		Bacteriophages (ϕX174 and MS2)	~1 log 10 PFU	
Sand (70%) + Softwood (30%)	815–1315 °C/1–3 s	*Escherichia coli*	95%	Mohanty and Boehm (2014)
Miscanthus	850 ± 20 °C/ 0.5 h	*Escherichia coli*	1.35 ± 0.27 log 10 NMP 100 mL^{-1}	Kaetzl et al. (2020)
Wood pellets	520 °C	*Escherichia coli*	27%	Reddy et al. (2014)
Wood waste	700 °C/15 h	*Escherichia coli*	92.1–98.7%	Lau et al. (2017)
Wheat straw	500–560 °C	*Escherichia coli*	84%	Guan et al. (2020)
Willow wood	500–550 °C	*Escherichia coli*	79%	Guan et al. (2020)
Dairy manure	200 °C/4 h	Atrazine	0.02 mg g^{-1}	Cao et al. (2009)
Rice straw	450 °C/2 h	Diazinon	99%	Taha et al. (2014)
		Oxamyl	99%	
Wood pellets	520 °C	Naphthalene	76%	Reddy et al. (2014)
		Phenanthrene	100%	
Loblolly pine chips	300 °C/ 15 min	Diclofenac	70%	Jung et al. (2013)
		Ibuprofen	<30%	
		Carbamazepine	80%	
Rice husk	30 °C/24 h	Tetracycline	58.8 mg g^{-1}	Liu et al. (2012)
Poultry litter	400 °C/2–7 h	Ethinylestradiol	0.001 mg g^{-1}	Sun et al. (2011)
		Bisphenol A	10 mg g^{-1}	
Pine needles	550 °C/1.5 h	2,4,4′-Trichlorobiphenyl	0.4 mg g^{-1}	Wang et al. (2013)

(continued)

Table 15.1 (continued)

Feedstock	Pyrolysis temperature/time	Contaminant	Removal	References
Swine manure	400 °C/2 h	Dibutyl phthalate	20–80%	Jin et al. (2014)
Litchi peel	650–850 °C/1 h	Congo red	404.4 mg g^{-1}	Wu et al. (2020)
		Malachite green	2468 mg g^{-1}	
Crab shell	300–900 °C/2 h	Congo red	20,317 mg g^{-1}	Dai et al. (2018)
		Malachite green	12,502 mg g^{-1}	
Peanut straw	350 °C/4 h	Methyl violet	104.4 mg g^{-1}	Xu et al. (2011)

Additionally, there can be economic and social advantages indirectly associated with biochar production. Fytili and Zabaniotou (2018) have proposed the construction of a collective thermochemical system for bioenergy production, where residues generated on small rural properties could be gathered and used to produce energy, provide waste management, generate income for farmers, and, consequently, improve living conditions. After that, the biochar produced could be sold to be used as soil additive or in water and wastewater treatment.

Wastewater treatment materials have been the research subject for thousands of scientists around the world for a long time, for reasons such as the nutrient richness, and the reuse of wastewater liquid fraction on irrigation. However, these practices are of special concern once that, when unproperly treated, this material offers a very high pollution potential through the spread of pathogens, the presence of heavy metals, natural and artificial bioactive residues (hormones, pharmaceuticals), and other pollutants directly related to the activity which generated the wastewater.

Treatment methods always present disadvantages, especially when the pilot is left in the hands of large-scale plants (Li et al. 2019). Therefore, it is fair to say there is no perfect treatment that fits perfectly on the premises of being 100% efficient, eco-friendly, low-cost, and applicable to any type of contaminant removal.

Biochar presents versatile surface characteristics and has been proven to successfully remove a large amount of pollutants. Thus, its application has been pointed out as an opportunity to improve treatment systems maintaining eco-properties and avoiding the need for modification on the actual layout.

15.2 Biochar Application for Wastewater Treatment

15.2.1 Removal of Pathogens

Many studies have pointed wastewater as a potential sink for human and animal pathogens, such as bacteria, viruses, and several protozoa species, which have been responsible for approximately 1.4 million deaths of children associated with waterborne diseases worldwide annually (Sinclair et al. 2008). As an example, there are more than 150 identified types of enteric viruses transmitted by the fecal-oral route, thought water contamination by wastewater (animal or human) discharge or runoff (Sinclair et al. 2008).

Pathogen removal happens mainly through attachment and physical straining in small pore spaces (Torkzaban and Bradford 2016). This interaction can be influenced by physical and chemical factors such as pH, temperature, the presence of organic matter, metal oxides, and so on (Wong et al. 2013). Changes in these factors can lead to changes in the removal rate, for instance, an increase in pH levels can lead to higher electrostatic repulsion of bacteria cells, and consequently, to such pathogens not binding to the biochar (Mosley et al. 2015). Additionally, biochar properties can also influence pathogen removal rates (Sasidharan et al. 2016), such as the low-velocity areas created by small porous on the surface, which can lead to a higher retention of microbes (Mohanty and Boehm 2014).

The design of the treatment system can also influence the removal rate of pathogens, as studies have suggested that column systems are better to attach microbes than the batch systems (Torkzaban and Bradford 2016). Also, the use of biochar-amended materials such as sand filters has been reported as a better alternative than materials without it (Chung et al. 2014). Mohanty and Boehm (2014) have reported improved rates of removal efficiency of up to 96% using these materials. However, the same study reported that biochar with particles smaller than 125 μm decreased the removal efficiency from 95 to 62%. Ghavanloughajar et al. (2020) previously proposed that this phenomenon could be associated with the deposition of small particles, blocking the natural flow paths of the wastewater. These particles might even be generated over time by a natural process of biochar degradation (Ghavanloughajar et al. 2020). Because of this, some studies have suggested the need for developing a prediction model that could estimate and avoid the clogging of compacted biofilters (Le et al. 2020).

Additionally, in some situations, a biofilm might grow in the biochar surface, decreasing the contaminant removal efficiency, once it changes biochar characteristics (Mohanty and Boehm 2015). Chemical modifications on biochar have been recommended to increase the removal of virus particles through the formation of a surface with positive charge (Sasidharan et al. 2016).

In bath treatments, microbes retained during one cycle might be carried into the next, increasing the contamination instead of remove, and that in longer hydraulic retention time cycles, the removal efficiency decrease due to the detachment showing the importance of system careful maintenance (Mohanty et al. 2013).

Similarly, Guan et al. (2020) evaluated a biosand laboratory-modified filtering system with two biochars (one produced from wheat straw and the other one from willow wood) on *E. coli* removal. The filter containing wheat straw biochar presented the higher *E. coli* removal efficiency (84%) when compared to the willow wood biochar filter (79%), and both biochars showed adsorption capacities of 5.7 $\log_{10}$ CFU g^{-1}.

However, it is important to highlight that surface area from the wheat straw biochar was 55.24 (m^2 g^{-1}), while the one from willow wood was 380.00

(m^2 g^{-1}). This demonstrates that other properties could be involved on bacteria adsorption.

Bacteriophages, such as MS2 and ϕX174, are recognized as model (markers) organisms for virus behavior on environmental samples for being nonpathogenic to human and easy to analyze. Besides, MS2 bacteriophage presents characteristics such as low isoelectric point and low inactivation, while ϕX174 bacteriophages have low hydrophobicity and electrostatic interaction (Perez-Mercado et al. 2019).

Considering this, Perez-Mercado et al. (2019) used these markers to evaluate their removal by the application of a filter (60 cm depth, 7.5 cm diameter, 70 cm height) containing biochar derived from hardwood. The results showed that the biofilter did not remove the viruses. However, the same filter was successfully applied on the removal of protozoan-like biomarkers (Perez-Mercado et al. 2019).

Miscanthus biochar was used as wastewater filtration media as compared with sand filter. The removal of chemical oxygen demand of *Miscanthus* biochar was 74%, significantly higher than the 61% observed on sand filters. The biochar also presented higher results for *E. coli* removal, with a reduction of 1.35 log units (and even higher with increased contact time (Kaetzl et al. 2020)) when compared to 1.18 log units for the sand filters. On the other hand, biochar produced from wood pellets was not efficient in removing *E. coli* (Reddy et al. 2014).

Lau et al. (2017) investigated *E. coli* removal by wood modified-biochar (with $H_2SO_4^-$, $H_3PO_4^-$, and KOH^-) from synthetic media under intermittent flow. The results with $H_2SO_4^-$ modified biochar showed approximately double the surface area (234.7 m^2 g^{-1}) when compared to the original biochar. *E. coli* removal by modified biochar was around 98%, with an initial concentration of 10^6 CFU mL^{-1}. This removal rate was mainly attributed to the surface characteristics (area, hydrophobicity, and functional groups) and porous structure.

Even with the huge amount of studies about biochar applications on filtering systems, bacterial removal mechanisms are still not fully understood, and even less is known about viruses removal mechanisms (Sasidharan et al. 2016).

15.2.2 Removal of Heavy Metals

Heavy metal residues can reach the environment and water bodies mainly through anthropogenic industrial activities (Li et al. 2017). The most common ones are chromium, cadmium, lead, copper, nickel, mercury, and zinc (Krabbenhoft and Sunderland 2013). These residues are of special concern for their nondegradability and, consequently, long persistence on environmental matrices and bioaccumulation through the food chain (Masindi and Muedi 2018). This characteristic, together with carcinogenicity and high toxicity, has made heavy metals be classified as extremely dangerous for animals and plants, even in low concentrations (Masindi and Muedi 2018). The toxicity classification of heavy metals puts them in the following order: Hg > Cu > Zn > Ni > Pb > Cd > Cr > Sn > Fe > Mn > Al (Filipiak-Szok et al. 2015).

In humans, contamination by these metals can cause nausea, diarrhea, skin allergy, hearth kidney, liver and brain damage, mutations, teratogenicity, and congenital disorders, depending on metal type, concentration, and exposition time (Masindi and Muedi 2018). In this sense, many countries have considered heavy metals to be a priority concern when it comes to water quality processes (Calderón et al. 2020).

Heavy metal removal by biochar is based on various mechanisms such as precipitation, complexation, ion exchange, electrostatic interaction, and sorption. Sorption capacity depends mainly on biochar surface pore area, abundance size, and distribution (Mukherjee et al. 2011). A common characteristic of biochar is having a negative charge surface, which attracts positively charged metals. Additionally, the presence of functional groups can form complexes with metals, once biochar presents minerals such as calcium, potassium, magnesium, and sodium (Dong et al. 2011). The mineral content may vary according to the material used on the production of the biochar. For example, biochar derived from crop residue contains less mineral fractions; therefore, sorption occurs by functional groups, while in biochar derived from manure, which possess high mineral content, sorption happens based on mineral-metal complexation and precipitation (Zhang et al. 2013).

Xu et al. (2013) reported that biochar produced from dairy manure was more efficient than that produced from rice husk waste on removing heavy metals (Pb, Cu, Zn, and Cd). The authors reported that manure biochar removes these metals through precipitation with CO_3^{2-} and PO_4^{3-}, whereas rice husk biochar does so through the complexation of heavy metals and phenolic –OH present in the material surface.

Another study has reported that the application of biochar produced from digestate of dairy waste and sugar beet residues was effective on removing heavy metals through precipitation (Inyang et al. 2012). The authors also observed that waste treated by anaerobic digestion process and then transformed in biochar presented a higher sorption capacity (Inyang et al. 2012).

Corn straw biochar removed Cd and Pb through surface complexation with functional groups (–OH, –COO–), precipitation (CO_3^{2-}, SO_4^{2-}), and coordination with π electrons (C=C, C=O) (Chi et al. 2017). Wood pristine biochar removed Hg through interactions with C=C, COH, and COO (Park et al. 2019).

Goh et al. (2019) showed that biochar from palm oil mill sludge predominantly removes Cu and Cd through monolayer adsorption mechanism. The same study concluded that when biochar was produced by fast pyrolysis (ranging from 425 to 550 °C for <2 s), the resulting product mainly removes heavy metals through surface contact area, while surface functional groups were the main removing factor on the one produced by slow pyrolysis (ranging from 350 to 800 °C for minutes or days). Similar results were observed by Agrafioti et al. (2013) during biochar production with sewage sludge, where there was a larger surface area with high temperature of pyrolysis (500 °C), while low temperature pyrolysis (300 °C) increased biochar yield.

The removal rate of Cu^{2+} and Pb^{2+} ions with the application of banana peel biochar had its efficiency increased by approximately 45% when the pH of the solution was increased from 3 to 9; however, this process also increases the pH of the eluate (Amin et al. 2018). In this context, special attention must be given to highly alkaline biochars, once the disposal of treated solutions and biochar should respect legislation limits for environmental disposal (Komkiene and Baltrenaite 2016).

A study conducted by Sforza et al. (2020) compared the effect of exposition time on the removal of 3 mg L^{-1} Cr(III) from real tannery wastewater using 5 g L^{-1} pinewood biochar. The results showed that after 5 min of exposition, approximately 34% of the contaminant was removed; however, increasing the exposition time did not improve the removal rate. The same study also observed that increasing biochar concentration from 5 to 50 g L^{-1} did not increase the Cr(III) removal rate. The authors attributed these findings to the wastewater matrix complexity (Sforza et al. 2020).

15.2.3 Removal of Pharmaceuticals, Dyes, and Emergent Contaminants

The emerging contaminants, also called endocrine disruptors, are chemical compounds present in medicines, pharmaceuticals, pesticides, beauty and personal care products, plasticizers, food additives, cleaning products, and so on (Li et al. 2019). These compounds present bioactive effects on living organisms which, depending on the time and dose of exposure, can cause reproductive disorders and cancer (Li et al. 2019), even at very small concentrations. Additionally, these compounds have been found in bioaccumulative food chains and have therefore become a global concern (Rout et al. 2021). The removal of these compounds needs to be deeply analyzed due to the fact that some treatment methodologies generate by-products that are more toxic than the parent compound (Rout et al. 2021).

About pharmaceuticals, special attention has been given to antibiotic use, once it can lead to the creation of antibiotic resistant bacterial strains/genes (Rout et al. 2021). Besides, such residues in water bodies can influence natural microbial communities and consequently the limnology cycles (Rout et al. 2021). Biochar predominantly removes emerging contaminants from wastewater through adsorption, which depends on chemical bond, polarity charges, ash content, pore filling, and volume (Li et al. 2019). The mechanism is also dependent of the physicochemical properties of these organic compounds, such as molecular size, aromaticity, and hydrophobicity (Jung et al. 2013).

Biochar produced from agricultural crop waste has been recognized as an effective material for the adsorption of organic contaminants; Cao et al. (2009) investigated the application of biochar derived from dairy manure to removal of atrazine from wastewater, for example. In this study, the authors compared the use of dairy manure biochar with commercial activated carbon and reported that the first one presented higher removal rates, and removal happened mainly through adsorption (Cao et al. 2009).

Taha et al. (2014) evaluated the removal of 15 different pesticides (atrazine, azinphos-methyl, acetamiprid, boscalid, carbaryl, chlorfenvinphos, diazinon, imidacloprid, flutolanil, flusilazole, malathion, oxamyl, phosmet, propiconazole, and triadimenol) by the application of rice straw biochar pretreated with acid solution. They found that the pretreated biochar was more efficient in the removal of the pesticides after an exposition time of 2 h to a solution with pH 7. The authors proposed that the process happened through Van der Waals forces, primary π–π dispersive interactions and H-bonding (via highly polar bonds, nitro-group oxygen, and carbonyl group oxygen) (Taha et al. 2014). Wood pellet biochar was successful in removing phenanthrene (100%) and naphthalene (76%); it was not efficient on the removal of benzo(a)pyren (Reddy et al. 2014), however.

Emergent contaminants such as bisphenol A and 17α-ethinylestradiol are the most frequent compounds studied on environmental matrices, mainly because of the solubility of these compounds on water/wastewater (Sun et al. 2011). Sun et al. (2011) evaluated the removal of emerging contaminants by the application of biochar produced hydrothermally from organic waste/biomass. One advantage of this process is the little amount of energy required to transform the wet feedstock into biochar. This biochar was efficient on bisphenol A and 17α-ethinylestradiol removal through adsorption, which the authors attributed to the specific interaction of the compounds with the biochar functional groups (Sun et al. 2011).

Biochars produced from loblolly pine chips (15 mm × 6 mm) under oxygenated and oxygen-free conditions were applied to the removal of emergent contaminants (atrazine, bisphenol A, and 17 α-ethinylestradiol) and pharmaceutical active compounds (carbamazepine, diclofenac, ibuprofen, and sulfamethoxazole) (Sun et al. 2011). Biochar produced in oxygen-free conditions showed polarity due to the presence of alkyl, carboxyl carbon, methoxyl, and O-alkyl, while biochar produced in oxygenated conditions showed characteristics of aromaticity. Biochar produced in oxygen-free conditions showed better adsorption capacity in the removal of emergent contaminants and pharmaceuticals, suggesting that this material is a promising sorbent for environmental and agricultural applications (Jung et al. 2013).

Rice husk biochar produced in fast pyrolysis (450–500 °C) by a Chinese industry (1 ton per hour) was used by Liu et al. (2012) to evaluate tetracycline removal. The adsorption mechanism was attributed mainly to hydrogen bonding and π–π interactions, once the biochar was obtained from an oxygen-rich biomass, possessing many functional groups, such as OH, CO_2H, C=O, and C–O (Liu et al. 2012).

Biochars produced with pine needles and wheat straw under different temperatures (350–550 °C) and oxygen-free conditions were tested on removal of 2,4,4′-trichlorobiphenyl and displayed high adsorption capacity. The same study also investigated the 2,4,4′-trichlorobiphenyl removal by both biochars in the presence of metals (K^+, Mg^{2+}, Al^{3+}, and Fe^{3+}), which resulted in an increased sorption capacity (Wang et al. 2013). The same phenomena was investigated by Jin et al. (2014) using biochar derived from plant and manure to remove phenanthrene and dibutyl phthalate in the presence of Cd^{2+}, which resulted in an increased adsorption capacity (Jin et al. 2014).

A low-cost biochar was produced from crab shell through a simple pyrolysis without any modification. It showed an adsorption capacity of >2000 mg g^{-1} to anionic Congo red and >1200 mg g^{-1} to cationic malachite green dyes. Removal was mainly attributed to hydrogen bonding electrostatic attraction and π-π interaction (Dai et al. 2018).

15.3 Biochar Disposal

Despite the fact that biochar applications to wastewater treatment have numerous advantages, some of these applications may produce undesirable results which must be taken into consideration, such as the phytotoxicity observed by Gell et al. (2011) in greenery vegetables exposed to biochar produced from pig co-digestate, which presented high soluble salt content and organic compounds. Beesley et al. (2015) reported a decrease on tomato germination rates when orchard prune biochar content was increased on nutrient solution given to the plants. These findings indicate that biochar may be toxic by itself when used in high doses and that this toxicity could be potentialized by compounds immobilized in it after application on a treatment process (Beesley et al. 2015).

Additionally, it is important to remember that, after application, all the contaminants are concentrated on the biochar material, which makes correct disposal a very important issue. Biochar used to remove nutrients such as ammonium, nitrate, and phosphate from wastewater without heavy metals could be used in soil for fertilization purposes (Tan et al. 2015). However, further studies are required to understand its effects on soil natural biota, erosion, as well as biochar spreading and environmental health over time (Montanarella and Lugato 2013).

Considering contaminant desorption possibility, some studies have been conducted aiming to evaluate the possibility of "cleaning" biochar and its reuse on subsequent removal processes. Successful results have been observed on the removal of uranium and dyes by washing cycles with HCl and ethanol, respectively, from food waste biochar (Tan et al. 2015). There have also been studies on the regeneration of biochar by heat treatment at 100–300 °C to recuperate the surface capacity of adsorption (Zeng et al. 2021). Nevertheless, it is important to evaluate the economic feasibility of such cleaning processes, given that there is a wide range of materials from which biochar can be produced (Tan et al. 2015).

In general, the safe disposal of biochar is not completely established, and proper legislation needs to be written, as the contaminants present on used biochar are of special concern (Tan et al. 2015). EU regulations recommend that, in the absence of proper regulation, biochar not originated from pyrolysis processes should be considered waste and be managed according to waste protocols, such as those applied to sewage sludge (Montanarella and Lugato 2013).

15.4 Conclusion

This review showed many studies where the modification of pyrolysis conditions produced important changes on biochar characteristics and also the differences that can be observed when different types of feedstock are used to produce it. Results showed biochar as a viable and effective option to improve environmental quality by removing harmful contaminants.

Full-scale biochar application will be consolidated in a near future, and consequently, the industry of biochar production will be established in the circular economy concept. However, it is important to highlight the need of constant monitoring of wastewater after treatment with biochar, once that changes on the load of contaminants present in the wastewater can influence the efficiency of the process.

As for large-scale industries of biochar production, further studies are needed to evaluate the economic feasibility of the process, for a successful procedure should harmonically associate environmental and economic investments.

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A Unique Collaborative Perspective on the Utilisation of Biochar in Accelerated Biodegradation of Discharge from Factories

16

Anwesha Bhattacharjee and Subhasish Dutta

Abstract

Nowadays, discharge from the factories is an environmental hazard for the aquatic flora and fauna due to rapid industrialisation. The primary components of industrial effluents are heavy metals, lubricants, surfactants, tannery effluents, minerals, etc., which causes biomagnification within aquatic life. However, utilisation of biochar has proved to be very useful, sustainable and eco-friendly compared with other rheological processes. The present book chapter mainly focuses on various synergistic perspectives of biochar for effective biodegradation of industrial effluents. Emphasis has also been given on the use of plant endophytes like *Brachiaria mutica* along with specific bacterial stain for the bioremediation of tannery effluents showing the reduction of 94% BOD (biological oxygen demand). Hence, the use of biochar could turn out to be an excellent remedy for treating the industrial effluents due to its eco-friendly behaviour, which enhances soil fertility, thus stimulating the growth of the plants.

Keywords

Biochar · Bioremediation · Effluents · Plant endophyte · *Brachiaria mutica*

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16.1 Introduction

Since past few years of industrialisation, effluents from the factories are really an environmental hazard for the aquatic life. The toxic chemicals present in the effluents enter the food chain of the aquatic biota resulting in biomagnification or bioamplification in the food chain. Biomagnification is basically the increase in the concentration of the toxin in the tissues of organisms at successively higher levels. So in order to overcome this dreadful situation, biochar proves to be an eco-friendly and sustainable remedy compared with other rheological or chemical processes, because the inherent properties of biochar make it suitable for recovering the nutrients from the effluents or discharge from factories. Biochar is nothing but a dense solid carbon, which is basically produced via the pyrolysis of organic materials that occurs spontaneously at temperatures usually below 700 °C. Now when this biochar undergoes thermal degradation, it basically yields liquid bio-oil, tars, gaseous syngas and solid char. Since most of the industrial effluents often contains heavy metals like Ni(II), Zn(II), Cd(II) and Cu(II), they are traditionally eliminated by some or the other rheological or physicochemical processes like adsorption and chemical precipitation, but it doesn't produce any valorisable product, and these methods are very much exorbitant. So in this case, interaction between biochar and certain kinds of microalgae and macroalgae proves to be very beneficial for removing heavy metal ions present in the effluents. Now, some additional advantages that were also mentioned by some of the researchers are that they had possibly lower executing expenses, the soaring efficaciousness in rectifying heavy metals that were present in lesser concentration, and it required less quantity of biosorbent that were actually worthless (He and Chen 2014). Now among the industrial effluents, tannery is one of the leading causes for degrading the quality of water due to the increase in the level of BOD (biological oxygen demand).

Hence, plant-endophyte synergism in a constructed wetland can help in the bioremediation of such kind of tannery effluents. In order to utilise the natural processes in a more controlled environment, certain kind of specialised systems called constructed wetlands are established. In the twenty-first century, treatment of wastewater in constructed wetlands was characterised in many ways, for example, treatment of specific compounds present in wastewaters and identification of certain kind of bacteria, which assisted in the treatment processes as mentioned by scientist (Vymazal 2011). Since plants interact with a lot of microbial communities, some of them reside in the plant tissues without having any negative impact on the plant that they have mutualistic relationship. The word 'endophyte' means 'inner', and 'phyton' means 'plant' by Puri (2020). Endophytes seem promising in increase the rate of crop yield, producing fixed nitrogen or novel substances, inhibiting pathogens as pointed out by scientists (Rosenblueth and Martínez-Romero 2006). So basically in some constructed wetlands, the effluents are passed, and with it, some specific bacteria or fungi are also inoculated to help the plants to combat the toxicity of the pollutants present in the effluents as described by some of the researchers (Yousaf et al. 2010; Desta et al. 2014; Mitter et al. 2013; Ijaz et al. 2016). Here, plants provide nourishment for the bacterial growth, and in return, bacteria detoxify the harmful pollutants present in the effluents. But the wastewater treatment in the tannery industries experiences frequent problems but they are often dealing with adequacy due to poor plan or to expand production (Calheiros et al. (2007). So the choice of plants and the bacteria is also an important issue because they should have the potential to survive in the toxic effects of the effluents. Therefore, in this book chapter, an effort has been made in discussing the various synergistic perspectives for bioremediation of the industrial effluents by using biochar and microbes.

16.2 Biochar and Its Uses

The word ‘biochar’ is obtained from the Greek word ‘bios’, which means ‘life’, and ‘char’, which means ‘charcoal’. So basically, biochar is nothing but a charcoal that is generated via the pyrolysis of biomass in the absence of oxygen and is used for improving the soil quality and carbon sequestration. During ancient period, biochar was produced from smouldered agricultural offscourings in the pits by the Pre-Columbians Amazonians. Biochar plays a great role in influencing the density, porosity, particle-size distribution and the texture of the soil. In other words, we can tell that biochar plays a significant role in influencing the physical nature of the soil.

Now, biochar is manufactured via the pyrolysis of biomass at a temperature below 700 °C. During pyrolysis, most of the mass is lost in the volatile form, and due to this, there is a reduction in the volume. But the physical features of the biochar depend not only upon the biomass but also on the pyrolysis (i.e., pre- and post-management of biochar and biomass) and also on carbonisation. Now, certain processing condition can result in sintering (or fusion of ashes), which causes a drastic change in the structural composition of biochar. Scientists Wildman and Derbyshire (1991) found that the presence of leftover cellular framework of botanical origin that was identified in biochar of coals and woods causes the macroporosity in the biochar.

Heating rate, temperature and residence are some of the factors in pyrolysis on which the specific yield depends. At temperature around 400–500 °C, more char is produced, but when the temperature is above 700 °C, then in most of the cases, liquid and gas fuel components are produced. In such cases, 20% biochar, 20% syngas, and 60% bio-oils are produced. But when slow pyrolysis occurs, then more amount of char is produced (approximately 35%), which contributes in the soil fertility of Terra preta. Terra preta is a fertile, anthropogenic and dark soil, which is basically found in the amazon basin. It gets its characteristics dark colour due to the weathered charcoal content present in it. It is usually made on addition of a mixture of compost, bone, charcoal, etc. Researchers Lehmann and Joseph (2015) and Sohi et al. (2010) said that the ‘Terra Preta De Indio’ has stable organic matter (OM) in higher content and has higher pH and excellent crop productivity compared to other low fertile soils. So certain biochar production techniques like centralised and decentralised, and thermocatalytic degradation serves as an efficacious way for waste management and increases the efficiency of resources in the bioeconomy. In a centralised system, for processing of biochar, all the biomass is brought to a central plant, and then, the lower tech kiln is operated. Then, a pyrolyser is put on a vehicle or a truck so that it could be carried from place to place for pyrolysing the biomass. *Pennisetum purpureum Schum.* or napier grass is phenomenally efficient for the atmospheric CO_2 fixation and generating biomass around 60 t ha^{-1} in a very short period of time according to researchers Rafaela et al. (2016). In case of thermocatalytic depolymerisation, the organic matter is converted to biochar by using microwaves. On an industrial scale, approximately 50% char is produced.

Now, there are several methods for producing biochar other than the pyrolysis. So some of the methods of biochar production are as follows:

16.2.1 Hydrothermal Carbonisation

In hydrothermal carbonisation process, the biomass is kept in a closed reactor, and then, it is mixed with water. Now, in order to maintain the stability, the temperature is gradually increased. The biochar, which is formed at a temperature less than 250 °C, is called hydrothermal carbonisation, and hydrothermal liquefaction is the bio-oil formed within 250–400 °C temperature. At a temperature beyond 400 °C, some gaseous products like CH_4, CO, H_2 and CO_2 are formed, which is called hydrothermal gasification (Khorram et al. 2016). Then the hydrolysed product goes through a sequence of reactions like isomerisation, desiccation and fractionation. At last, the char is prepared by cross-linking of the intermediates and its repolymerisation.

16.2.2 Gasification

Gasification is the process of degradation of the carbonaceous material to syngas. In this process, the temperature of the reaction is a very important factor for deciding the syngas production. Researchers found that production of hydrogen and carbon monoxide increased as soon as the temperature increased but other components like carbon dioxide, hydrocarbons and methane depleted. Now, gasification includes certain processes like drying where the moisture is fully evaporated from biomass without the recovery of energy. Another process is oxidation and combustion. The important sources of energy are the combustion and oxidation reactions of the gasification agents. So carbon dioxide, carbon monoxide and water are produced when gasification agents react with combustible agents.

16.2.3 Torrefaction

Torrefaction procedure is also called as mild pyrolysis due to low heating rate. This process changes some of the characteristics of biomass like energy density, heating rate, particle size and surface area. There are several types of torrefaction such as in steam torrefaction, the biomass is treated with steam around 260 °C temperature and

10 min of residence time. But in case of wet torrefaction and oxidative torrefaction, the former biomass is treated with water at 180–260 °C, and in case of the latter one, the biomass is treated with certain kind of oxidising agents like gases used in combustion.

The several uses of biochar are as follows:

16.2.3.1 Biochar as a Soil Conditioner

In certain regions, the quality of soil is so poor that they are not suitable for crop cultivation. On applying untreated biochar, it has shown a positive effects by increasing the soil fertility. It helps the soil by increasing the water holding capacity and release of vital nutrients by increasing the pH of the soil.

16.2.3.2 Biochar as a Catalyst

Biochar has certain characteristics, which makes it suitable as an excellent catalyst. First of all, biochar has a greater surface area for the catalytic activity as many functional groups are present on it. For example, ketone groups are suitable for the adsorption of ammonium ions. So as a catalyst, it has various applications like production of syngas and tar removal.

16.2.3.3 Biochar in Wastewater Treatment

Since biochar is very much porous due to this property, it makes a very good substitute for treating the wastewater. As biochar has high adsorption capacity and greater porosity; it allows the poisons to cluster on its surfaces making the effluent clean.

16.2.3.4 Biochar Used as an Insulation in the Buildings

Since the thermal conductivity in biochar is very nominal, so it has greater water absorption capacity. Due to these characteristics, it acts as a perfect material for insulating the buildings and controlling the humidity. It also prevents air condensing and wetness on the wall.

16.2.3.5 Use of Biochar in Conservation of Food

Biochar prevents the post-ripening of fruits and vegetables by absorbing. It can act as an excellent packaging stuff for packaging of food. It absorbs humidity, thus preventing the growth of fungus in the food.

16.3 Various Synergistic Methods for Bioremediation of Industrial Effluents

As we know, industrial effluents are contaminated with toxic chemicals and heavy metals. So instead of using expensive wastewater treatment, we can use various synergistic methods for treating industrial effluents. Synergism is basically the cooperation between two or more organisms, which produces a collaborating effect greater than the summation of individual effects. So some of the synergistic methods are as follows:

16.3.1 Fungi–Bacteria Synergism for Treating Reactive Red X-3B Dye in the Effluents

The most important constituent in the effluents of textile industries are dyes, and nowadays, a large number of dyes and certain kind of chemical are used for producing quality products, but this has really created a havoc in our environment. But these dyes could be identified visually. Since most of the dyes used in textile industries have an intricate aromatic structure, due to the cleavage of the azo groups, the non-ionic and anionic azo dyes release certain toxic amines, which is resistant to light or any kind of biological activity. Since most of the industrial effluents are highly alkaline, it has greater BOD (biological oxygen demand) and TDS (total dissolved solids). So the textile dye wastewater could be treated by microbial decolourisation process, and this method is eventually very cost-effective. It was found that fungus had substantiated to be an appropriate organism for removing dyes and treating the textile wastewater. One additional benefit of fungal mycelia over unicellular organisms is that by producing extracellular enzymes, it solubilises the insoluble substrates. Fungus has substantial enzymatic and physical contact with the environment due to an increased cell-to-surface ratios (Kaushik and Malik 2009). The extracellular nature of fungal enzymes has several benefits like it can endure high concentration of the toxicants. Scientist (Hatakka 1994) found that in order to endure the toxicity of dyes, fungi produce certain kind of enzymes like manganese peroxidase and laccase.

The decolourisation mechanism of the reactive red X-3B dye occurring in the bacteria and the fungi group is attributed to both biodegradation and bioadsorption (Zhou et al. 2014). For fungi group decolourisation, bioadsorption played a crucial role because 70% of the decolourisation occurred in just 5 min as told by researchers (Zhou et al. 2014). For treating this, azo-dye wastewater from textile industries, near about 15 bacteria and two fungi have been secluded from the activated sludge. Researchers (Zhou et al. 2014) observed that the 18SrRNA sequence was homologous to *Geotrichum candidum* and *Candida pseudolambica* around 99%, and most of the 16SrDNA bacterial sequences come under the proteobacteria group, which include *Sphingobacteriia*, *Flavobacteriia*, *Bacteroidia*, *Nitrospirales* and *Phycisphaerae*. Due to the presence of large number of binding sites, the fungi have greater potential for the adsorption of azo dyes (Fu and Viraraghavan 2002). But the bacteria group has several other advantages compared with the fungi group because the biodegradation potential of the bacteria group is much stronger than the fungi group. The maximum absorption peak of reactive red X-3B dye was obtained at 538 nm, and when the bacteria started biodegradation, the peak almost got vanished (Zhou et al. 2014). The other chromogenic groups start originating as soon as the chromogenic group of X-3B starts splitting. The fungi group has better bioadsorption potential when it attains equilibrium at 5 min. But the bacteria group undergoes radical biodegradation for decolourisation. So for checking the clustering or aggregation potential of the microorganisms, the aggregation index is used. Therefore, for treating azo-dye wastewater, we could see a synergistic relationship that occurs between the fungi and bacteria group. The former plays a key role in the separation of biomass and effluent, whereas the latter contributes in improving the effluent quality.

16.3.2 Algae–Bacterial Synergism for Treating the Effluents of Wine Factories

One of the major problems faced by most of the wine factories is the mismanagement of large volumes of the effluents produced by the factories. Since most of the wastewater from wine factories has high amount of organic materials, lower pH and salinity of the water are variable, which poses a threat to the environment.

According to a recent study, it was found that most of the effluents from wine factories were rich in certain sugars (like maltose and fructose), organic acids (like tartaric acid and malic acid), esters, ethanol, etc. The organic substances in winery effluent mainly come from the wine material and grapes. In addition to this, winery effluents also contain sodium, potassium, calcium and magnesium ions. So due to the presence of organic and inorganic substances in the winery effluents, it becomes a bit difficult for treating winery wastewater. Now, there are various methods for treating this effluent, and some of them are physicochemical method, ion exchange method, biological method, etc. In physicochemical method, at first, the large solid substances like leaves and grape seeds get settled down; this step is very useful; it basically impedes other treatment machineries from being obstructed by these solid substances. But in ion-exchange method, ions are basically exchanged between the immobilised resin and solution. Now comes the biological treatment; it is very effective for treating winery wastewater as most of the organic substances present in the effluent are easily biodegradable. The consequences of culturing green algae with the native winery effluent abolishes nutrient pollutants and chemical oxygen demand (COD) from the effluents. The microbial community utilises the remaining organic substances, for example, the photosynthate that is secreted by the green algae. The photosynthate that is secreted by the algae assists the growth of the bacteria, which expands the bacterial population size. So here two strains of green algae that is *Auxenochlorella protothecoides* and *Chlorella sorokiniana* are cultured in a photobioreactor containing the sterile-filtered winery wastewater collected at different grape crush season (Higgins et al. 2015).

It was found that both the algae, which were cultured in the sterile-filtered wastewater medium, had the efficiency of removing nitrogen more than 90%. And more than 50% of phosphate was removed effectively. The detectable phosphate and nitrogen could easily be eliminated from the post-crush and pre-crush wastewaters from the wine factories with the help of *Chlorella sorokiniana* in just 4 days, whereas an elevation in chemical oxygen demand (COD) was found in the post-crush and pre-crush wastewaters after the *Auxenochlorella protothecoides* (algae) were grown in the sterile-filtered winery wastewater. After the experiment, it was found that the bacterial community was proficient in consuming the photosynthate produced by the algae *A. protothecoides.* There was a deterioration in the growth of *Chlorella sorokiniana* around 23% due to the existence of bacterial cells in raw effluents, but it had no impact on the growth of *Auxenochlorella protothecoides* compared with sterile filtered wastewater. Now there were plenty of *Bacteroidetes*, but actinobacteria was greater than the bioreactor-adapted community in the absence of algae when *Auxenochlorella protothecoides* cultured in wastewater with the bacterial community. So algal photosynthate endows organic substances in the wastewater, and the bacterial community lowers the chemical oxygen demand (COD) loads. The photosynthate secreted by the alga delivers organic carbon that assists the growth of the bacteria. So in other words, we can say that the bacterial community and algae are reconcilable with each other.

16.4 Constructed Wetland and Its Functioning for Treating the Effluents from Factories

Constructed wetlands are specially designed systems, which are built to use the natural processes like soil and microbial accumulation for the treatment of wastewater in a regulated environment. Besides wastewater treatment, the constructed wetlands have many objectives like it enhances the biodiversity and improves the quality of river water. Wetlands gives many ecological benefits to the human community. Constructed wetlands take the help of natural processes to eradicate pollutants from the wastewater without using chemicals. In fact, constructed wetlands are very eco-friendly and cost-effective.

Now, the most essential designing parameters on which the design of constructed wetlands depends are hydrology, macrophytic growth and flow direction (Vymazal 2011). Under hydrology comes (subsurface flow and open surface flow). Free floating, submerged and emergent comes under the category of macrophytic growth. According to the direction of flow inside the constructed wetland, it can be vertical or horizontal. So the types of constructed wetland are given below:

16.4.1 Free Water Surface Constructed Wetlands (FWS)

They are also called as wetland with surface flow. Many floating, emergent and submerged plants are found in areas having open water (Kadlec 2009). Researchers Crites et al. (2006) said that due to the presence of plant stalks, less velocity of water flow and litter controls the flow of the water in narrow channels, which actually assures the plug-flow conditions. Low depth of the water also assures the plug-flow condition. Now basically the FWS (free water surface) constructed wetlands permits the wastewater to flow above ground so that it could be exposed to sunlight. These beds are usually planted with aquatic flora. Now when the wastewater flows through the wetland, it goes through various proceedings like biological, chemical and physical proceedings. Here, the organic substances undergo biodegradation, certain solids are filtered, and nutrients are also removed from the water. In this type of wetlands, the microbes degrade the organic substances in a very efficacious manner, and suspended solid substances are removed with the help of sedimentation and filtration. Scientist (Vymazal 2011) told that with the help of nitrification in the aerobic region of the water column, the ammonia is efficaciously removed. Here, the nitrate undergoes denitrification in the anaerobic region of the litter layer presented below for the removal of ammonia. Now the FWS (free water surface) constructed wetlands have several merits such as it does not require any electrical energy, the operational cost is very less, and BOD (biological oxygen demand) of wastewater is eliminated at a higher rate. But there are several demerits of this wetland such as the open surface facilitates the breeding ground for the mosquitoes, large area of land is needed, and the rate of elimination process can be slowed down to ice formation in winter.

16.4.2 Horizontal Subsurface Flow Systems

In such kind of constructed wetland, the water column is directly not exposed to the atmosphere, and the wetland is generally saturated. Scientist Jan Vymazal (2011) told that the wastewater is fed at the inlet, and at a very slow pace, the wastewater moves through the porous medium under the bed surface where emergent vegetation is planted to the outlet. Now most of the bed is anaerobic or anoxic because the saturation of the bed is durable, but the aerobic region is basically found around the rhizomes, which leak oxygen into substrate. This type of wetlands has the filtration bed, which provides high resistance during the winter season. In horizontal subsurface flow constructed wetland (HFCW), basically, the municipal wastewater undergoes the secondary treatment. This type of wetlands is very much efficient in the elimination of suspended solids, heavy metals, etc. Scientists Brix (1990) and Vymazal and Kröpfelová (2008) found that the anaerobic process imparts a vital role in horizontal subsurface flow constructed wetland (HFCW), but the oxygen transport capacity present in the system is inadequate to establish the aerobic decomposition.

The oxygen from air is basically transferred through the leaves and stems of plants in rhizosphere in the presence of an aerobic–anoxic microcosm (Brix and Schierup 1990). Now the horizontal subsurface flow constructed wetlands have several advantages such as this type of wetlands does not require any electric power, the flow of wastewater is assisted by the gravity, the maintenance cost is very less, they require very less surface area, and these type of wetlands can treat the diluted wastewaters from the wastewaters, which cannot be treated using the traditional wastewater treatment technologies. But in the inlet region, there are high chances of obstruction, which is a major drawback in this type of constructed wetland systems.

16.4.3 Vertical Flow Systems

In these type of constructed wetland, it basically consists of a flatbed on which graded gravels are kept, and it is covered with sand on which the macrophytes are planted. Scientist Jan Vymazal (2011) said that this type of constructed wetland has large batches, which are fed at irregular intervals, thus flooding of the surface takes place. Here, the wastewater enters the bed through seepage, and at the bottom, there is a drainage system where the water gets accumulated. In this system, the suspended solids and organic substances are removed in larger amount. The vertical flow system needs very less surface area around 1–3 m^2 PE[1] (Cooper 2005). Researcher (Vymazal and Kröpfelová 2008) said that for treating sewage, industrial effluents and run-off storm water, generally VFCW, are used. In case of tidal flow systems, with the help of aeration pipes, the water is brought to the bottom, then the water percolates in upper direction till the surface is flooded. The pump automatically gets turn off when the surface is fully flooded and the wastewater in the bed comes in contact with certain kind of microbes, which grows in that medium. Then the water is drained after a certain time interval. The filtration substrates get obstructed in vertical flow constructed wetland, which is a major drawback in this type of wetlands.

The constructed wetland undergoes various kinds of processes like sedimentation, precipitation, sorption and microbial degradation for the elimination of toxic pollutants from the wastewater. The figure of constructed wetland showing various kinds of processes is shown below (Fig. 16.1):

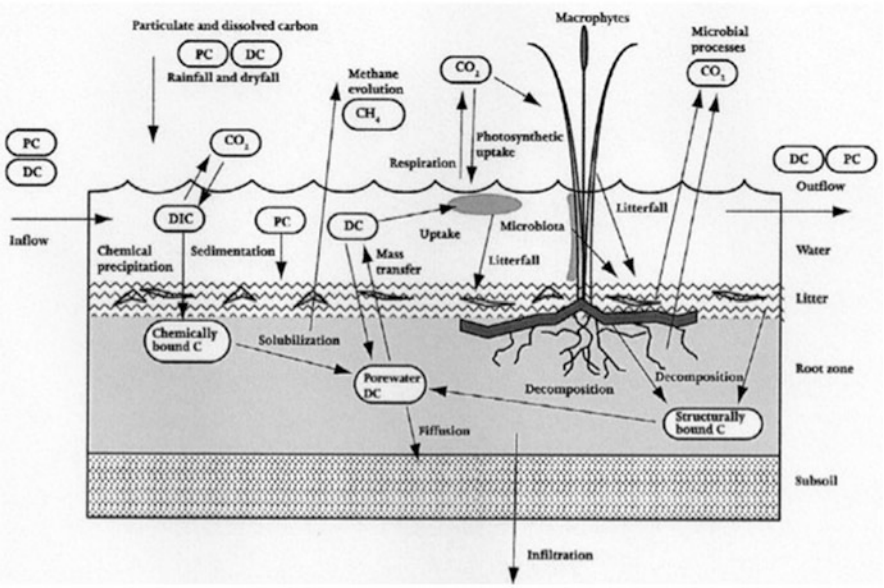

Fig. 16.1 A simplified figure of constructed wetland [http://www.courses.online.org]

The solid pollutants in constructed wetlands are eliminated by various physical processes such as filtration and sedimentation. The inlet zone of horizontal subsurface flow system and vertical flow system undergoes the elimination of solid pollutants. The organic pollutants are hydrolysed into simpler substrates, which are later absorbed by the facultative and anaerobic bacteria. The heavy metals in constructed wetlands are removed by metal sulphides precipitation in anaerobic environment. Nitrification and denitrification are some of the major processes for the elimination of nitrogen from wastewater in constructed wetland. Nitrification is the process in which the ammonia is oxidised to nitrite and nitrate in presence of certain kind of autotrophic bacteria. It is basically an aerobic process. In vertical flow constructed wetlands, oxidation of ammonia into nitrate is mainly dependent on the organic surface loads. In the tidal flow constructed wetlands when the wetland cells are completely flooded, then adsorption of ammonium ions takes place in the pores and matrix. Some other nitrogen elimination processes include volatilisation, nitrate dissimilatory reduction and assimilation of the biomass. Volatilisation is the process in which the dissolved substances changes to vapour. Plants play a crucial role in constructed wetlands. The wetland plants enhance the elimination of the nutrients. It transforms the nutrients into gaseous forms. So this shows that constructed wetlands are very effective in treating wastewater from dairy industries, food factories, wine factories and various kinds of other industries. The most amazing feature of constructed wetland is that it can work in any kind of weather conditions if the wetlands are designed in a proper way. So for treating industrial effluents or wastewater, these sustainable systems can replace many expensive technologies.

16.5 Plant-Endophyte Synergism: A Boon for Treating Industrial Effluents

As the world develops, rapid urbanisation and industrialisation increases the release of many toxic chemicals, which are dumped into the water bodies, thus hampering the aquatic biota. However, constructed wetlands have been proved very effective in treating the industrial effluents and improving the quality of contaminated water as it was discussed earlier. But vegetation choice, which is done according to the nature of the wastewater and climatic condition in a particular area, plays a crucial role in building a constructed wetland. It was found that effluents from the tannery industries are one of the main causes for the contamination of water. Moreover, when plant-endophyte synergism was established in a constructed wetland, it decontaminates the tannery effluents very effectively. Endophytes are basically the endosymbiont, which is often a fungi or a bacteria that resides inside the stems or leaves of a plant without causing any negative impact on the plant. They are often called as mycorrhizal fungi because they possess an external hyphae, which arises from the soil and surrounds the infected tips of the roots of the plants. According to scientist, Puri (2020) many endophytic bacteria, for example, *Pseudomonas, Bacillus and Azospirillum*, belong to the soil bacterial genera.

So here we would basically discuss the plant endophytic synergism between plant *Brachiaria mutica* and the endophytic bacterial strains (*Microbacterium arborescens* HU33, *Pantoea stewartii* ASI11 and *Enterobacter* sp. HU38) in a vertical flow constructed wetland. *Brachiaria mutica* is commonly known as buffalo grass, which is generally found in central Africa and parts of middle east where it is generally cultivated for the fodder for ruminant animals. It is basically a monocot plant and it belongs to the family Poaceae. Buffalo grass or *Brachiaria mutica* is a perennial grass in which the creeping stolons can reach up to a height of 5 m. The nodes found in the stem are a bit hairy. The bacteria *Pantoea stewartii* is a gram-negative bacteria. The shape of the bacteria is rod shape. It belongs to the phylum Proteobacteria and family Enterobacteriaceae. But *Enterobacter* sp. *HU38* is also a gram-negative bacteria. It is a rod-shaped bacterium, but it does not form spores. This bacteria also belongs to the family Enterobacteriaceae.

At first, the sample tannery effluent was collected from the major sewerage of tannery industry. The effluent contained Cr, Cu, Pb, Cd and Ni in higher amount. It also contained higher amounts of ammonia, nitrate, sulphide, chloride, phosphate, etc. So for treating this effluent, the vertical flow constructed wetlands were built in a small scale. According to researchers Ashraf et al. (2018), the wetlands were covered with a layer of pebbles, sand and loamy soil on top of it as shown in (Fig. 16.2). All these materials were placed one after another in a netted basket. Then approximately hundred number of stem cuttings of buffalo grass or *Brachiaria mutica* were cut (at least having one node in each stem) and grown in soil and then placed in certain containers, which were filled by tap water so that they were well-rooted. Since there were 12 systems of vertical flow constructed wetland. These systems were divided by four different treatments in which treatment 1 includes well-rooted *Brachiaria mutica* plants provided with tap water; treatment 2 includes *Brachiaria mutica* plants provided with tannery effluent; treatment 3 includes *Brachiaria mutica* plants having bacterial inoculation, which were provided with tannery effluent; treatment 4 includes *Brachiaria mutica* plants without bacterial inoculation and was provided with tannery effluent as performed by the researchers Ashraf et al. (2018). Regulation of the constructed wetlands was done batch wise so that each of the wetlands was subjected to tannery wastewater (after 27 days). Then root and shoot length of buffalo grasses were measured. As described by the researchers. Yoon et al. (2006) and Li et al. (2007), the translocation factor or (TF) is basically the ratio of heavy metals detected in the shoot of the plants divided by heavy metals detected in the root of the plants. It was found that in the presence of the endophytes, *Brachiaria mutica* or buffalo grass showed significant increase in growth in contrast to plants growing in other constructed wetlands. Although in case of second treatment, an upgradation was found in the quality of tannery effluents in constructed wetlands when buffalo grasses vegetated. But in case of third treatment when the *Brachiaria mutica* plants were inoculated with the endophytes in constructed wetland, it exhibited maximum eradication of the pollutants while minimum elimination of the pollutants were found in the fourth treatment, which didn't have any bacterial inoculation or *Brachiaria mutica* plants.

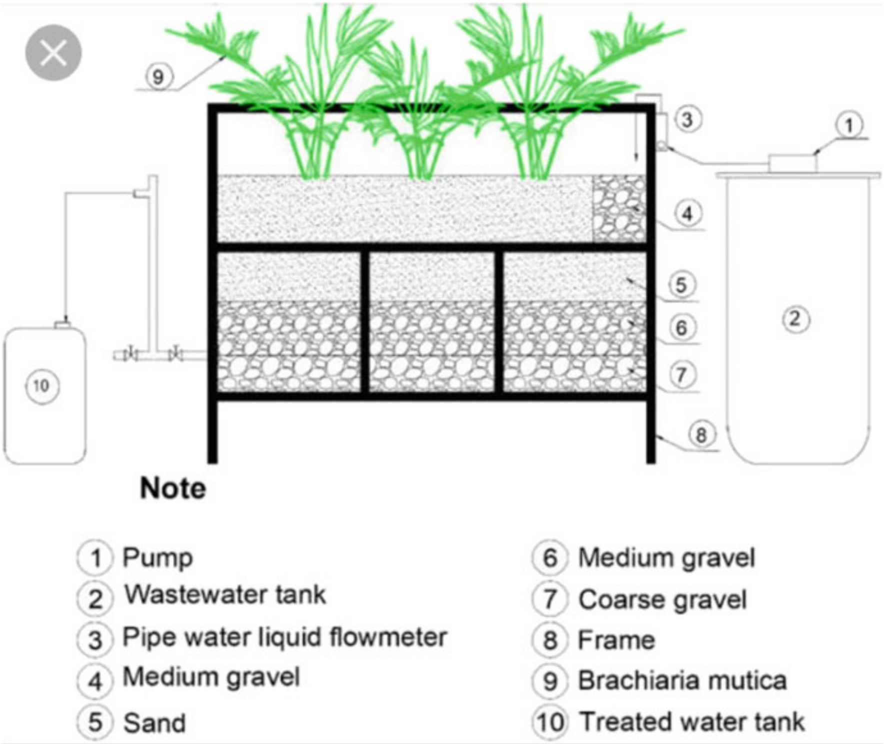

Fig. 16.2 An experimental setup showing *Brachiaria mutica* treating industrial effluent in a well-designed constructed wetland (Van Thanh Ho et al. 2020)

So this proves that the *Brachiaria mutica* plant and the endophytic bacteria experiences a symbiotic relationship. In a symbiotic relationship, plants provide nourishment and habitation to the endophytic bacteria but in return the endophytic bacteria degrade the harmful pollutants present in the tannery effluents and take care of the plant's health. Researchers Ashraf et al. (2018) found that the depletion of chemical oxygen demand (COD) and biological oxygen demand (BOD) was highest in case of third treatment. The COD and BOD depletion was around 82 and 94%. In other words when the organic pollutants in the tannery effluents were depleted, there was a significant increase in the oxygen concentration by the vegetation. In the vertical flow constructed wetland when the buffalo grass in collaboration with the endophytic bacteria were vegetated in the wetland, there was larger depletion in chemical oxygen demand (COD) and biological oxygen demand (BOD). So, similar kind of plant-endophyte synergism was also listed in the given table below (Table 16.1).

Brachiaria mutica was also efficient in the eradication of heavy metals like Cr, Mn, Ni, Co and Pb that are present in the effluent. The bacteria possess excellent potential for sorbing metal ions in its cell wall. In other words the availability of

Table 16.1 List of some plant and endophytic bacteria in degrading certain kind of pollutants

Plant	Bacterial strain	Pollutant	Reference
Hordeum vulgare	*Burkholderia cepacia*	2,4-Dichlorophenoxyacetic acid	Jacobsen (1997)
Triticum aestivum	*Burkholderia cepacian or Pseudomonas strain*	2,4-Dichlorophenoxyacetic acid	Kingsley et al. (1994)
Zea mays	*Pseudomonas putida*	3-Methyl benzoate	Ronchel and Ramos (2001)
Astragalus sinicus	*Mesorhizobium huakii*	Cadmium	Sriprang et al. (2002)

metal ions by plants is intensified by the inoculation of bacteria. Maximum uptake of Cr was found in case of third treatment. It was found that vegetation in collaboration with the endophytes showed maximum eradication of Cr (around 96%) in the wetlands. This can also be determined using the bioconcentration factor (BCF), which shows that a part of the metal ion found in the wastewater shifted to the stems and roots of the plants collected in larger amounts in the roots.

According to scientists Ashraf et al. (2018), the restriction fragment length polymorphism (RELP) interpretation showed that most of the bacteria (around 66%) were the members of inoculated endophytes in stems and roots of the plants of third treatment, but other endophytic bacterial strains were native to the effluent or *Brachiaria mutica*. So this proves that plant-endophyte synergism remediates the tannery wastewater. This is the most eco-friendly method compared to other high-tech machineries and chemical treatment. In this method, the biodiversity is maintained. In plant-bacterial synergism, a huge number of bacteria live inside the rhizosphere of the host plant, and the root and shoot of the plant helps in bacterial colonisation. So with this method, pollution is controlled, and a balance is maintained in our ecosystem.

16.6 Conclusion

As we all know, environmental pollutants enter the environment by means of both artificial (man-made) or natural sources, which leads to the pollution in water, soil and air. It degrades the condition of air and wastage of many non-renewable sources like fossil fuels (Sebiomo et al. 2010; Janbandhu and Fulekar 2011; Prince et al. 2013; Shabir et al. 2013). As we all are so much dependent on the fossil fuels (like petrol, diesel), due to this reason, it will get exhausted very soon. So for that reason, we should think for some alternative source of energy, which is cheap, easy to operate and is eco-friendly. So as we have discussed earlier, biochar can act as a very good source of energy. As explained by the researchers (El-Naggar et al. (2019a, b); Hu et al. 2017), the solid biomass mainly contains organic substances, and due to this, it has tremendous capability to produce biochar. So instead of dumping this solid waste, we can change it to biochar making a good use out of it. As we have discussed earlier that biochar has many properties like eradication of some toxic pollutants from soil, it helps in treating the industrial effluents. Nowadays the leftover of agricultural products like wheat straw are used to make biochar as experimented by researchers (Qian et al. 2019). Scientists (Yargicoglu et al. 2015) found that waste wood could also be used to make biochar. Corn cob was also used by the scientists to prepare the biochar as done by (Duan et al. 2019). So biochar appears as a promising alternative for the eradication of many toxic pollutants from the environment.

As we have also discussed, constructed wetlands are efficient in the elimination of pollutants from the industrial effluents. It is efficient in removing the pathogens from the wastewater. In other, words we can say that it is a kind of biofilter. Since it is a self-sustaining system, so it is very easy to operate, and the cost is very low. It uses the natural functions like soil, plants and microbes for treating the wastewater. As we have seen, certain factories discharge their wastewater directly into the bodies of water, which, really disturbs the aquatic ecosystem, so instead of doing that, if these effluents are discharged in respective engineered systems like constructed wetland, the water pollution (which is a burning problem for our environment) could be prevented easily. It was proved that the plant-endophyte synergism increased the efficiency of constructed wetland. It is totally eco-friendly. The plants provide habitation and nourishment to the endophytes so that the endophytes could grow properly, and in return, the endophytes degrade the toxic pollutants in the wastewater, which could hamper the health of the plants.

So constructed wetland with plant-endophyte synergism seems to be a promising technique for eradication of pollutants from the industrial effluents, thus preventing the water from being polluted. Therefore, the balance in our ecosystem is also maintained.

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Application of Biochar for Wastewater Treatment

17

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Abstract

The issues of wastewater containing different contaminants are insurmountable, as they cause major threats to aquatic ecosystems. The stages of treatment technologies may consist of or a combination of chemical, biological, or physical processes, depending on the wastewater characteristics, the climate, and the resources available. Among all, due to its simple operation in high volume with high performance, easy to functional sorbent preparation and reuse, the removal of contaminants by adsorption gains more interest. Biochar, a durable, low-cost carbon-rich material, is a promising agent for evacuating various organic and inorganic pollutants in wastewater due to its high adsorption properties. Functionally modified surface biochar is currently being developed to improve its ability to remove contaminants in wastewater and other bioremediation applications. This chapter offers clear information about the wastewater treatment process using biochar and knowledge gaps in biochar-based remediation of wastewater.

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Biochar · Wastewater · Adsorption · Pollutant removal · Biochar surface modification · Bioremediation

17.1 Introduction

An increase in population growth causes the demand for limited resources like water and affects the environment and aquatic system. In order to resolve this problem, wastewater from various human activities such as pharmaceutical, leather, tanning, pulp and paper industry, kitchen, agriculture, mining, and cosmetics is treated and used for various applications. Wastewater can be classified into three categories:

1. **Domestic wastewater or municipal wastewater:** Wastewater discharged from institutions, residences, and similar facilities. It is classified into gray water, such as liquid waste from the bathroom, laundry, and kitchen, and black water, such as wastewater discharged from the toilet.
2. **Industrial wastewater:** Wastewater discharged from factories and production units.
3. **Stormwater runoff**: Resulting from flood due to rainfall that enters the sewer system.

Recent studies explain that nearly 1.1 billion people starve for clean drinking water due to water contamination. Industries release wastewater containing many organic pollutants like chemicals, phosphorus, nitrates, pathogens, dyes, and inorganic pollutants as heavy metals such as Cu, Cd, Ni, and Pb. There are two types of pollutants: (1) primary pollutants such as CO_2 and NO_2 directly affect the environment, and (2) secondary pollutants are acid rain and global warming caused due to primary pollutants (Sörme and Lagerkvist 2002; Tahir et al. 2020). Wastewater characteristics are varying upon its source, and some wastewater does not need pretreatment to remove contaminants. Understanding the characteristics of wastewater is a critical step in properly managing it. Physical, chemical, and biological features of wastewater are the most common classifications. Total dissolved solids, suspended solids, electrical conductivity, temperature, and color are all physical characteristics. Dissolved oxygen (DO), chemical oxygen demand (COD), biological oxygen demand (BOD), nitrogen, and phosphorus are chemical characteristics, while biological characteristics include microbial population and biochemical oxygen demand.

Many contaminants present in wastewater are toxic to fishes in the stream and other aquatic organisms. For example, colorants are used to make an attractive product used in many industries like plastics, ceramics, cosmetics, and leather industries. The cosmetics industry uses some chemicals to improve the product, such as sodium laurel, a surfactant that causes the allergy, rashes, and eye irritation and affects the immune system. The dye industry using paraphenylenediamine is permanent hair dyes that cause skin irritation and redness. Plants up take some heavy metals available in wastewater through food chains entering into human and animal bodies. They cause numerous diseases such as carcinogenic and eye disorders, mercury such as nervous disorders, rheumatoid arthritis, depression, lethargy, ataxia, nervous diseases, liver damage, and insomnia (Sörme and Lagerkvist 2002; Burakov et al. 2018). Casein precipitation from the dairy industry is toxic to fish, and the deposited water may lead to mosquito breeding that causes dengue fever, malaria, chikungunya, and other diseases such as non-Hodgkin's lymphoma, cancer, typhoid, giardiasis, amoebiasis, Alzheimer's disease, respiratory problems, and hepatitis (Shete and Shinkar 2013).

The number of pollutants and contaminants in water keeps on increasing due to factories and similar units. To remove these pollutants, specific treatment methods are required. Researchers have reported many treatment methods. Those treatment levels are classified into four categories. Firstly, pretreatment or preliminary treatment is performed to remove the suspended solids and reduces clogging. Secondly, primary treatments are subjected to remove suspended inorganic and organic solids due to gravity, such as flotation and nanofiltration. Thirdly, the secondary treatment is used to remove dissolved solids in primary effluent using methods like membrane bioreactor, anaerobic filters, activated sludge processes, coagulation–flocculation, and chemical precipitation. Finally, the tertiary treatment is used to remove micropollutants using adsorption, reverse osmosis, and distillation techniques.

Recent studies show biochar as the best adsorbent to sorb heavy metals in wastewater (Pavithra and Jaikumar 2019). Biochar is a carbon-rich product produced during the thermochemical decomposition of biomass with or without oxygen. Biochar feedstocks are bamboo wood, pomelo peel, pinewood, paper mill sludge, rice husk, green waste, peanut shell, marine macroalgae, banana peels, maple wood, peanut hull, pecan nutshell, cauliflower leaves, etc. Physical and chemical characteristics of biochar depend on the biomass and thermochemical methods conditions such as temperature, reactor type, and heating rate. Pyrolysis, hydrothermal liquefaction, carbonization, gasification, and torrefaction are included in methods of thermochemical decomposition. Temperature is the only difference between all these processes.

Biochar acts as an adsorbent and has a high potential for sorption of organic and inorganic substances from the water system. Their great sorption capacity is associated with porous structure and their functional groups such as hydroxyl and carboxyl on the surface area. Biochar has various advantages such as effective and cheap, acts as a fertilizer to increase soil fertility and crop growth, is an eco-friendly adsorbent, and prevents the discharge of greenhouse gas emissions. It has a strong affinity for heavy metals (Xiang et al. 2020).

17.2 General Characteristics of Wastewater

Water is a vital natural resource, and wastewater is defined as any water negatively affected by its quality due to human activities. Water is scarce in most countries, and hence, it has become mandatory to reuse the wastewater in a productive manner to replenish the water resources of the country. Wastewater is obtained from domestic, industrial, commercial, and agricultural activities that contain physical, chemical, and biological pollutants. Due to the expansion of population at a higher rate, this wastewater is utilized for irrigation in agriculture. The nutrients and microorganisms in wastewater conserve valuable water resources by taking advantage of the nutrients in sewage to grow crops, algae, and bacteria for further application (Rajesh Banu et al. 2020; Dhandayuthapani et al. 2021). For example, the nitrogen content of sewage eliminates the requirement of commercial fertilizers in agricultural soil.

Wastewater released into the environment without proper treatment causes water and soil pollution. Hence, it is very important to know about the characteristics of wastewater for the effective usage of the wastewater for numerous applications. In the forthcoming section, some of the common characteristics of wastewater discharged from various industries are indicated in Table 17.1.

17.2.1 Physical Characteristics

Wastewater has various physical characteristics like color, temperature, solids, oil, odor, and grease, as listed in Table 17.1. The color in the wastewater is the first and foremost characteristic for indicating the age of wastewater. The color varies based on the period when it is generated and based on the wastewater source. Freshly discharged wastewater appears to be gray in color, which on visual appearance looks black. Industrial effluents take the color of the type of product produced or based on the industry type. Wastewater from the dairy industry is white in color (Shete and Shinkar 2013).

In contrast, purple, blue, violet, and black colors are observed in the case of the textile industry (Chowdhury et al. 2015). Effluent from the tannery industry is in yellowish-brown color with the average color range at the first monitoring point to be 1820 ± 5.5 Platinum–Cobalt Scale (Pt-/Co) units, which were 122 times higher than

Table 17.1 The physical, chemical, and biological characteristics of wastewater

Physical characteristics	Chemical characteristics	Biological characteristics
• Turbidity • Color • Odor • Total solids • Temperature	• Chemical oxygen demand • Total organic carbon • Nitrogen, phosphorus, chlorides, and sulfate • Alkalinity • pH • Heavy metals	• Biochemical oxygen demand • Oxygen required for nitrification • Microbial population

the recommended values of standard limits (15 Pt/Co units) (Noukeu et al. 2016). During alcohol production, residual liquid waste generated is called distillery spent wash, also called stillage (Piccin et al. 2016). Thus, the color of the wastewater changes based on the toxicity of the wastewater. In the case of dairy industry effluent, it is nontoxic, and the leather industry uses several dyes during their processing, making it more toxic (Bisschops and Spanjers 2003).

The odor is another important criterion for assessing the nature of wastewater. Gases produced by the decomposition of organic matter cause an offensive odor. When the sewage waste becomes devoid of oxygen, anaerobic microorganisms reduce sulfate to sulfides liberating hydrogen sulfide gas. Industrial and domestic wastewater has distinct odor based on the source from which raw material they are generated. Both decomposing wastewater and industrial wastes are sources of odor.

The temperature of waste products has an abnormal impact on aquatic life, chemical reaction rate, biological reaction rate, and gas solubility limitations like element depletion. The mean annual temperature of the waste product depends on the geographic location, from 10 to 21 °C. The high temperature of waste products will increase undesirable species and fungi, and low temperatures increase the treatment time and plant size.

The presence of solid content is another notable characteristic of wastewater. The solids can also be classified into organic (volatile) and inorganic fractions. In anaerobic conditions, the suspended solids can lead to sludge deposits in the aquatic environment when untreated wastewater is discharged. The filtration process is used to remove these suspended soils from the wastewater. Due to the nutritional availability in the suspended solids used for various applications (Selvakumar and Sivashanmugam 2017, 2018a). Wastewater generated in the tanning industry produced total dissolved solids at 21,300 mg/L concentration and total suspended solids at a concentration of 1250 mg/L, whereas the limit suggested by WHO is 2100 and 600 mg/L, respectively (Massoudinejad et al. 2015). Cotton textile industry effluent has total solids of about 28,900–49,300 mg/L because of the sourcing process. Most of the solid content comes under suspended solids in the wool textile industry with a concentration of about 1000–26,200 mg/L (Hubbe et al. 2016). The rubber industry produces wastewater with 560 mg/L where the standard is to be less than 50 mg/L and in the strict sense not to exceed 150 mg/L (Pillai and Girish 2014).

17.2.2 Chemical Characteristics

Chemical characteristics are determined by different constituents given in Table 17.1 as COD, TOC, pH, and alkalinity, and the amount of certain chemical components (nitrogen, phosphorus, chlorides, and sulfate contents) is present in the wastewater. Mostly organic and inorganic materials are included in these chemical characteristics. Chemical oxygen demand is to quantify the organic and inorganic materials present in wastewater, which is the amount of oxygen required to oxidize both compounds. It is measured by using strong oxidizing agents like potassium dichromate. The mean chemical oxygen demand of the effluents at different manufacturing units of the tannery industries ranges from 7200 ± 20 to 71,040 ± 40 mg/L, respectively. The tanning and dyeing effluent has a higher chemical oxygen demand level of 71,040 ± 40 mg/L because of the adding up of many organic vegetable tanning materials and inorganic chemicals (Piccin et al. 2016). The paper and pulp industry observed the chemical oxygen demand level of 7000 mg/L (Shankar et al. 2014). The chemical oxygen demand of rubber industry effluent was 5613 mg/L (Pillai and Girish 2014). A higher chemical oxygen demand level means a greater amount of oxidizable organic material in the sample, which will reduce dissolved oxygen (DO) levels (Bisschops and Spanjers 2003). A reduction in dissolved oxygen can cause a harmful effect on higher aquatic life forms. Therefore, it is mandatory to have a deep understanding of each chemical characteristics that have several destructive impacts. The pH of the effluent is an important characteristic of wastewater. The pH of the effluent depends upon the unit operations or process involved in the industry. The pH of paper and pulp industry effluent is 11.68; rubber industry mixed effluent is 8.3, whereas effluent of water boilers is 10.3 and effluent of boiler blowdown is 2.2. The pH values of the effluents at different leather manufacturing stages ranged from 3.8 ± 0.2 to 12.5 ± 0.5 (Hubbe et al. 2016; Pillai and Girish 2014). To avoid the harmful impacts of wastewater, the chemical characteristics have to be properly analyzed before using it for various purposes.

17.2.3 Biological Characteristics

Biological characteristics of wastewater are mainly determined by the different organisms that develop in the wastewater like bacteria, fungi, archaea, viruses, protozoa, algae, and helminths. It also includes biological oxygen demand and the oxygen necessary for the nitrification process. The BOD is the amount of oxygen needed to stabilize organic matter using microorganisms. It is similar to chemical oxygen demand, but it takes at least 5 days of testing, whereas chemical oxygen demand can be estimated within 1–2 h. Usually, BOD is estimated at 3 and 5 days, which gives BOD_3 and BOD_5, respectively. The mean BOD_5 of the effluents at diverse leather processing industry manufacturing units was in the range of 7200 ± 20 to 71,040 ± 40 mg/L. The higher value, 71,040 ± 40 mg/L, corresponds to leftover remains, and dyeing effluents were due to the accrual of many organic vegetable tanning materials and inorganic chemicals (Jahan et al. 2014). In dairy effluent, the BOD varies from 200 to 3500 mg/L, and rubber industry effluent has BOD at a level of about 1340 mg/L. The biological oxygen demand level of the paper mill effluent was 5279 mg/L. The effluent analysis of six different textile industries shows that the BOD varies from 500 to 1010 mg/L. The biological characteristics of various sources of water treatment are critically analyzed.

17.3 Different Stages in Wastewater Treatment

The removal of pollutants from the effluent to attain the standard quality of discharge requires different treatment levels. Here, the solids in wastewater are partially removed by decomposition from highly complex organic solids to stable organic solids. Various treatment methods treat those wastewaters. These treatment methods can be classified into four types: (1) pretreatment or preliminary treatment, which includes physical and mechanical processes to remove coarse suspended solids; (2) primary treatment, which includes physicochemical processes to remove suspended solids and organic matters such as biological oxygen demand due to gravity; (3) Secondary treatment or purification, which includes biological and chemical processes to remove soluble biological oxygen demanding primary waste; and (4) tertiary treatment, which includes physical and chemical processes for metals ions, dissolved solids, pathogens, and color (Crini and Lichtfouse 2019; Ullah et al. 2020).

Preliminary treatment is the first step in the wastewater treatment process for removing large and coarse suspended solids in untreated wastewater to reduce large-sized particles such as plastics, clothes, and wood. To avoid clogging and for easy operation, grit, grinders and screens are used. Treated wastewater flows to the next step for primary treatment. Primary treatment is done to remove suspended organic and inorganic solids by physicochemical processes. This is done after the preliminary treatment. In this process, wastewater is passed through several tanks and filters, including flotation, primary sedimentation tank, neutralization tank, and equalization tank. Sedimentation, an important process in wastewater treatment and its operation, depends upon the properties of suspended solids. Sedimentation tanks are classified into primary and secondary. Primary sedimentation tank is used to remove solid deposition and is easy to operate (Shahrokhi et al. 2012). Next, floatation is a separation process used to remove suspended solids from the liquid phase by air bubbles. Mostly dissolved air flotation is used to remove heavy metals, which require less time, but further treatment must be made to improve removal efficiency. Finally, the neutralization tank utilizes the chemical process to neutralize or balance pH. It also requires a high cost for chemicals (Zhou et al. 2019; Ullah et al. 2020). The secondary treatment is used to remove the residual organic and suspended solids in primary effluent by biological and chemical processes. This organic nutrient-rich sludge is used for different applications, including microbial cultivation and energy production (Selvakumar and Sivashanmugam 2018b; Selvakumar et al. 2019). In aerobic processes, membrane bioreactor treatment removes micropollutants in primary effluent, improving effluent quality. These are removed from the wastewater with the physical retention technique by membrane, sorption, biodegradation, and air stripping method.

It has several disadvantages like easily contaminated and expensive, and an experienced person needs to handle it (Grandclément et al. 2017). Activated sludge processes are used for the removal of biological oxygen demand in suspended solids. Lesser removal of pathogen and high power requirement is its limitations. Biological treatment could not be an effective method for removing effluent in all cases.

Therefore, the researchers are using the chemical process rather than biological treatment. Coagulation–flocculation removes the colloidal particles by adding a coagulant and flocculant that are formed. It requires lesser time to settle, but the operational cost is high (Durai and Rajasimman 2011; Crini and Lichtfouse 2019). Finally, the treated water is transferred to the final treatment tank for further handling.

Tertiary treatment is the final step to improving water quality by physical and chemical methods to reduce organic and inorganic substances such as nitrogen, phosphorus, and micropollutants in wastewater by ~80%. Adsorption is simple, which contain both chemical and physical process. Chemisorption is described as a chemical reaction between the adsorbate and the surface of adsorbents that results in a covalent or ionic bond formation. Physisorption is the sticking of particles on the surface through van der Waals' force. Adsorption has several disadvantages, as operating and maintenance cost are high as well as deposition of active sites (Burakov et al. 2018). Distillation, reverse osmosis, ion exchange, electrodialysis, and freeze desalination are five techniques used to remove soluble solids in water. Desalination is the method used to remove dissolved minerals from brackish water, which is an expensive method that requires high energy. Sludge is formed at the end and is further treated by incineration and recycling (Crini and Lichtfouse 2019; Ullah et al. 2020).

Although many materials and methods are used for wastewater treatment, the treatment process aims to find the best and efficient method that cleanses the contaminated environment. Therefore, in this context, to remove wastewater contaminants from the environment and restore healthy ecosystems, biochar is gaining importance as a promising agent for wastewater treatment. The carbon-rich solid product obtained from any biomass is called biochar, differentiated from charcoal, which possesses large numbers of pores and aromatic functional groups on its surface (Qambrani et al. 2017; Enaime et al. 2020). Biochar is becoming the best choice as it has the following advantages: low cost, eco-friendly, easy preparation methods, availability of raw materials, improved physicochemical properties, and, most importantly, an effective adsorbent in removing the pollutants from wastewater (Thompson et al. 2016; Xiang et al. 2020). The application of biochar for different wastewater treatment along with diverse approaches is discussed in the upcoming topics.

17.4 Biochar Production and Its Application in Wastewater Treatment

Biochar is an eco-friendly, low-cost substance produced from organic wastes (Enaime et al. 2020). Biochar is a carbon-rich solid material obtained by heating biomass with little or no oxygen (Wei et al. 2018). Based on the type of production process, application, and general conditions, biochar has many definitions. International Biochar Initiative (IBI) defines biochar as a solid material and the thermochemical conversion of biomass in an oxygen-limited environment called biochar

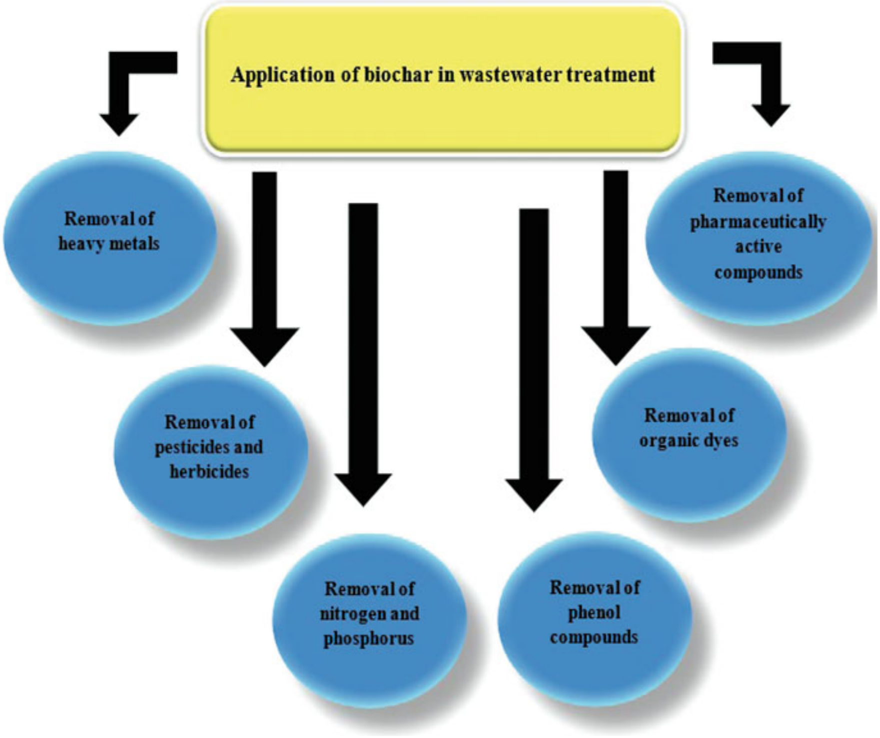

Fig. 17.1 Various potential applications of biochar

(Xiang et al. 2020). Biochar has several pores with oxygen functional groups and aromatic surfaces.

The feedstock used for the production of biochar includes canola straw, cattle manure, corn straw, hardwood, peanut straw, pine needles, pinewood, rice husk, rice straw, sewage sludge, soybean straw, *Spartina alterniflora*, sugar beet tailing, switchgrass, algal biomass, eucalyptus, kenaf fiber, maize straw, palm bark, peanut shells, rice hull, soybean stover, swine manure, wastewater sludges, bamboo wood, pomelo peel, paper mill sludge, green waste, banana peel, cauliflower leaves, maple wood, pecan nutshell, crab shell, reed, bagasse, sawdust, wheat straw, sugarcane harvest residue, hickory wood chips, wheat straw, hardwood, willow wood cottonwood, and sugar beet tailings. (Tan et al. 2015; Xiang et al. 2020). Different thermochemical processes, including slow pyrolysis, hydrothermal carbonization (HTC), fast pyrolysis, hydrothermal liquefaction (HTL), flash carbonization, torrefaction, and gasification, produce the biochar. The operating condition of these processes also varies. The features of biochar, such as large surface area, surface functional groups, and porous structure, play an essential role in removing contaminants from wastewater. Figure 17.1 shows the different contaminants removed by biochar.

17.4.1 Industrial Wastewater Treatment Using Biochar

The common industrial wastewater sources are mining, battery manufacturing, chemical industry, smelting, dyes, leather manufacturing, etc. The pollutants are heavy metals and organic pollutants. An effective adsorbent for heavy metals adsorption is the biochar mixed with chitosan after being cross-linked and cast into membranes, beads, and solutions. The adsorption of cadmium, copper, arsenic, lead, and other heavy metals depend on the proportion of biochar and chitosan.

Organic pollutants, heavy metals, nitrogen, and phosphorus, and other pollutants are mainly removed from the wastewater using biochar (Enaime et al. 2020; Xiang et al. 2020). For the removal of these pollutants, the biochar act as an excellent adsorbent. Heavy metals such as arsenic (As), copper (Cu), cadmium (Cd), nickel (Ni), chromium (Cr), and lead (Pb) are mainly present in the wastewater, and the long-term contact of these heavy metals in water bodies, even in low concentration, can lead to the serious health effects. Arsenic is a highly noxious heavy metal that is present in the wastewater. By the impregnation of biochar with $Zn(NO_3)_2$, the adsorption capacity of As^{3+} is increased from 5.7 to 7.0μg/g in the course of the surface modification.

In dye-based industries, for crystal violet elimination in an aqueous environment, *Gliricidia* biochar is efficient biochar. The sorption process depends on the pore volume, surface area, and pH value of biochar. Organic dyes are another major contaminant present in the textiles, rubber, paper, and dye industry wastewater. These contaminants have features like high chemical stability, high color, good solubility in water, and complex aromatic structure, making it complicated to decompose naturally. The presence of these organic dyes in water restricts light and oxygen to enter into the water, affecting the survival of aquatic organisms. Sewage sludge-derived biochar is used to eliminate the methylene blue dye from the wastewater, and it shows a maximum adsorption capacity of 29.85 mg/g at pH 7.

The biochar obtained from the algae, *Spirulina platensis* is used to remove Congo red (CR) and methylene blue dye. Some phenolic compounds, including phenol, bisphenol A (BPA), pentachlorophenol (PCP), and p-nitrophenol (PNP) produced from the paper, plastic synthesis, and also by agricultural activities, are in addition present in the wastewater as a contaminant. These phenol compounds are detached from the wastewater through ozonation by using the sludge-derived biochar (Huang et al. 2019).

In the battery manufacturing industry, effluent bagasse biochar is used to adsorb lead to a maximum of 12.7 mg/g. The adsorption depends on nominal pH value, dosage, and contact time. In dairy wastewater, the nutrients of ammonium and phosphate are recaptured by biochar. The biochar can adsorb 20–43% of ammonium and 19–65% of phosphate in the exit dairy manure within 24 h.

The biochar produced from the paper mill sludge as a feedstock is mainly used to remove the As^{5+} from the wastewater, and it gives maximum efficiency of 34.1 mg/g removal. For removing Cd^{2+}, Pb^{2+}, and Zn^{2+}, the biochar prepared using feedstocks such as sugarcane straw, sawdust, rice husk, and chicken manure mixed with sawdust are more effective. In this removal, the temperature increase

(350–650 °C) in pyrolysis leads to the enhancement in the removal capacity of biochar for removing Cd^{2+} from wastewater (Xiang et al. 2020). The rice straw biochar has shown the highest carbon and hydrogen contents, the most significant number of functional groups (i.e., H, C=C, and C=O), highest pH, physical stability, negative surface charge, and adsorption capacity for Pb^{2+} removal (Enaime et al. 2020). The removal efficiency of fresh and dehydrated banana peel biochar for removing Pb^{2+} is 359 and 193 mg/g, respectively (Wei et al. 2018).

17.4.2 Municipal Wastewater Treatment Using Biochar

For municipal wastewater treatment, biochar can be used directly or can be pooled with biofilter and other technologies to recover nitrogen and phosphorus. Biochar is a highly porous biofilter and the COD, TKN, TSS, and TP of wastewater lessen by 90, 89, 64, and 78%, respectively, after being passed through it. The biochar laden with aluminum oxyhydroxides (AlOOH) was useful to recycle and reuse phosphorus through adsorption by electrostatic attraction, and the phosphorus adsorbed from the secondary wastewater treatment on the biochar is used as a fertilizer for crop production (Hussain et al. 2017). To remove ammonium from municipal wastewater, biochar produced at 450 °C from the digested sludge is used as an adsorbent with higher surface area and functional group density. The process is controlled by chemisorption.

Biochar from waste sludge shows an elevated elimination rate of the total organic carbon used as catalysts to ozonate refinery wastewater. It contains functional carbon groups, Si/O structures, and metallic oxides. It can promote oxidation through the formation of hydroxyl radicals and mineralized petroleum contaminants. Wastewater from residential units can be treated with biochar in an on-site sewage treatment facility (OSSFs). The addition of biochar increases the removal rate of some polar and hydrophilic compounds and can be upgraded with low-cost biochar adsorbents.

17.4.3 Agricultural Wastewater Treatment Using Biochar

Due to the rapid development of agriculture, pesticides or toxic heavy metals are released into farmlands. Imidacloprid and atrazine are adsorbed using rice straw biochar and phosphoric acid tailored rice straw biochar. The pH and pore volume of soybean and corn straw biochar are important factors in the high adsorption of imidacloprid and atrazine. Sulfamethane is removed by steam-activated biochar, and the rate of removal is a function of pH (Zheng et al. 2019). The removal of pentachlorophenol can be done through zero-valent iron magnetic paper mill sludge biochar (ZVI-MBC). The biochar feedstock and the functional materials play a major role in biochar's adsorption capacity to pesticides.

Pesticides, herbicides, and antibiotics are also the major contaminants in agricultural wastewater, as shown in Fig. 17.1. For removing these contaminants, biochar is applied based on the interactions (hydrogen bonding, intermolecular, electrostatic, π–π and hydrophobic interaction, precipitation, and surface complexation ion exchange) between functional materials and agricultural contaminants. The most commonly found antibiotic in wastewater is tetracycline. The removal efficiency of tetracycline antibiotics from the wastewater with various biochar ranges from 18.53 to 455.33 mg/g. In the process of antibiotic removal from wastewater, there are two effects on functional materials on biochar were involved (Wei et al. 2018; Xiang et al. 2020). They are escalating the surface functional groups of biochar, which increases the surface area of biochar.

Other than antibiotics, pesticides also contaminate the water system. The most commonly seen pesticides in wastewater are atrazine and pentachlorophenol. With different biochar feedstocks, the adsorption capacity of biochar for the elimination of pesticides varies and ranges from 11.56 to 50.00 mg/g (Wei et al. 2018). Anti-inflammatory drugs, antibiotics, and analgesics are some pharmaceutically active compounds that cause serious environmental and health problems. Biochar with metal oxide/metal nanoparticles can efficiently remove the pharmaceutically active compounds (Huang et al. 2019). The modified biochar has the greatest adsorption capacity than the pristine biochar for removing nitrogen and phosphorus. The modified biochar has a more specific surface area (SSA), more reaction activity, and surface functional groups (SFG). Nitrogen present in the wastewater is removed around 73% by using digested sugar beet tailing biochar. Mg^{-} biochar is used to remove phosphate and ammonium from the wastewater. For industrial wastewater treatment, the biochar is combined with chitosan after cross-linking; it can be casted into membranes, beads, and solutions. The municipal wastewater is treated directly with biochar or combined biofilters.

17.4.4 Stormwater Treatment Using Biochar

Stormwater runoff causes deprivation of the natural water quality and needs to be treated before its discharge due to increased metals, biological pollutants, and organic matter. Biochar is used as a filter media in storm water treatment, economical and readily available, depending on aqueous chemistry, pollutant characteristics, and biochar properties. Zinc and copper in stormwater runoff are removed by a biochar-based filtration medium, and the removal rate is more than 85% and 95%, respectively. Bisphenol A (BPA) from stormwater is removed by biochar integrated with biofilters. Wood dust biochar adsorbs BPA and promotes *Phragmites australis* growth, increasing *Escherichia coli*, TOC, TSS, nitrogen, and phosphorus removal rates (Rajapaksha et al. 2015). Biochar-amended biofilters can show more than 99% TOC removal rate than the unamended ones and can raise the elimination of TOC, TN, and TP to greater than 60%.

The ammonium in stormwater can be adsorbed by poultry litter biochars (PLB), which are pyrolyzed at 500 °C, and the NH_4^- adsorption is subjugated by cation exchange. PO_4^{3-}-P and NO^{3-}-N from leachate are removed by Zn-activated sewage sludge-based activated carbon, and the rate of removal of PO_4^{3-}-P and NO^{3-}-N decreases with the increasing pH value. Biochar and zero-valent iron (ZVI) are amended in bio-retention systems to increase nitrate removal efficiency. The transport of *E. coli* depends on the morphology structures and hydrophobicity of the biochar. H_2SO_4-modified wood biochar improves *E. coli* retention and can be a bio-retention filter medium for *E. coli* removal from the stormwater. The surface modification of biochar increases the adsorption capacity of biochar. To effectively remove pollutants from the wastewater, a deep understanding of the surface modification of biochar is important, which will be discussed in further topics (Xiang et al. 2020).

17.5 Surface Modification of Biochar for Wastewater Treatment

Unlike normal biochar, modified biochar works efficiently by adsorbing the contaminants from wastewater. The modified biochar generally penetrates the sludge and easily neutralizes the charge on the sludge, thereby removing the toxic waste (Guo et al. 2020). Since biochar possesses hydrophobic properties, it hinders the adsorption efficiency of hydrophilic materials. In order to overcome this failure, an effective and targeted modification should be done on biochar (Shi et al. 2020). Scientists focus on modifying biochar for its excellent properties to improve the environmental benefits and easy remediation to pollution (Godwin et al. 2019). Chitosan is an important material used to modify biochar, since it contains many functional groups on its molecular chain, making the biochar hydrophilic and improving its adsorption sites. Four common methods can do modification: physical modification, chemical modification, impregnation process, and magnetic modification, as indicated in Fig. 17.2 (Shi et al. 2020).

In the physical modification, the surface area is made to increase in order to improve the pore structure of biochar. A study reported that pore volume increased by 6.4–48 times when the physical modification is carried out on biochar (Liu et al. 2019). In chemical modification/activation, the surface functional groups are increased in number and are activated to provide more binding sites for the removal of pollutants. The removal rate of pollutants from wastewater increased from 72 to 99.6% while using modified biochar (Zhang et al. 2020).

Surface modification methodologies include steam activation for introducing oxygen-containing functional groups, heat treatment for adsorbing hydrocarbon, an alkaline modification for producing positive surface charges, impregnation methods for facilitating physical or chemical attachment of metal ions on biochar structure, an acidic modification for increasing the acidic property, and hydrophilic nature of biochar. KOH- and H_3PO_4-modified biochar greatly help remove dyes from wastewaters, especially methylene blue (Ahmed et al. 2016). The phosphorus recovery ratio using unmodified biochar is 73 and 37%, which is very poor compared with modified biochar (Fang et al. 2014). The use of biochar for removal of phosphates and nitrates adsorbed only 2.5 and 1.5μmol/g. When the modification is done on produced biochar by Mg-Al, it showed three times of removal efficiency than normal biochar (Yin et al. 2018).

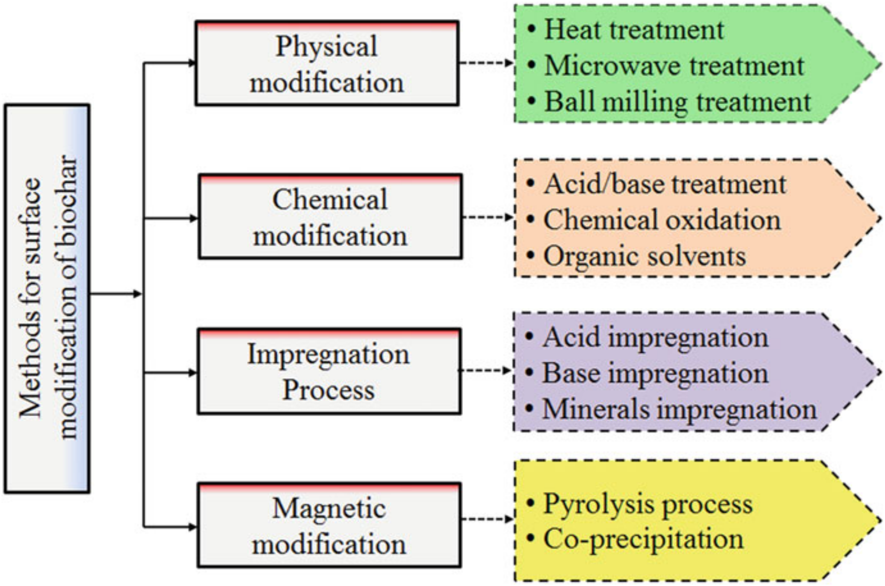

Fig. 17.2 General methods for surface modification of biochar

On reviewing all methods for modification, alkali-modified biochar and nanomaterial impregnated biochar shows good adsorption properties, which favors the removal of different contaminants from wastewater (Fang et al. 2014; Yin et al. 2018). The biochar has an immense ability for metal sorption from aqueous solutions and has received better attention during the past decade. However, studies are mostly at a lab scale, focusing on the sorption of single metal from spiked solution. In natural waters, different heavy metals may coexist with other pollutants; hence, there is a competition for sorption sites on biochar surfaces between metals and other ions or organic pollutants. Only a small number of studies have analyzed the competitive sorption of metals by biochar (Vickers 2017). The reported studies have utilized pristine biochar developed by conventional pyrolysis and not microwave-assisted pyrolyzed biochar (Luo et al. 2008). The sesame straw pristine biochar for the sorption of multi-metals from synthetic wastewater showed that sorption behaviors of multi-metals (Pb, Cr, Cd, Cu, and Zn) differed mono-metal sorption. In this competition, other metals reduced Cd sorption. Similarly, they compared the sorption of corn straw pristine biochar for aqueous Hg and/or atrazine and showed that Hg and atrazine inhibited each other's sorption (Tan et al. 2016). The direct competitive sorption on soybean stalk-based pristine biochar, each suppressing the other when phenanthrene and Hg coexisted in solution, are observed (Kong et al. 2011). In addition, humic acids coexisting with the contaminants in the aqueous environment influence the metal sorption by biochar. It was shown that the humic acids increased the sorption capacities of Pb^{2+} and Cr(VI) by sludge-derived pristine biochar from 197 to 233 mmol/g and 688 to738 mmol/g, respectively. Due to the adsorbed humic acids, their functional groups offer additional sites for Pb^{2+} ion and supply more reducing agents, facilitating Cr(VI) transformation to Cr(III). Further studies are required to accurately estimate the metal sorption capacity of biochar in natural environments. Currently, there is no report on the usage of biochar to eliminate heavy metals from polluted wastewater for field application (Zhou et al. 2015). Besides, future studies are needed on the pH, dosing and recovery approaches, and the regeneration, and disposal of metal-sorbed biochar for field application.

17.6 Future Prospects of Biochar for Wastewater Treatment

Supply and removal of water are the central components of settlement structures. Lack of sanitary facilities and water scarcity is the key issues because many people die or fall ill every day. To provide sustainable wastewater treatment, specific technologies are to be further developed. The researchers are working on these particular topics to improvise wastewater treatment in all possible methods. These methods may include using certain highly potential materials, which increase the efficiency of wastewater treatment. Biochar is a highly efficient material that can be used to remove pollutants from wastewater because they are low-cost, renewable, and sustainable material compared with activated carbon.

Biochar has become increasingly important in remediating contaminants in the industrial and agricultural sectors to improve environmental quality. It can be used with all kinds of wastewater such as industrial, municipal, agricultural wastewater, and stormwater. Some future needs should be focused on increasing the usage of biochar in wastewater treatment, which helps in the easy removal of pollutants. Some of them are feedstocks that need to be readily available and cheap sources. Nevertheless, the major constrain in the process of production is the high cost due to this modification procedure.

Hence, in the future, researchers should attempt to find a compromising solution sandwiched between the production processes and enhancing the applicability of biochar with more and suitable functional to minimize the cost. The stability of biochar in biochar-based products needs to be increased to improve industrial and municipal wastewater treatment efficiency. New methods can be optimized in the future to increase the adsorption capacity of biochar for the sorption of heavy metals, organic contaminants, nitrogen, and phosphorus. Certain solutions for recovery or desorption of biochar, like magnetization of biochar, may also be made, making it handy to separate the contaminant loaded with biochar from water by applying an external magnetic field.

17.7 Conclusion

This chapter gives a systemic outline of the importance of wastewater treatment in general and the specific function of biochar in wastewater treatment. Various biomass materials, including agricultural crop residues, forestry residues, sewage sludge, solid organic municipal wastes and manure, are most widely used for producing biochar, which is an efficient and low-cost adsorbent material. The alteration of biochar through physical and chemical activation methods is also discussed to regulate the functional groups on the surface of biochar to improve its surface area and porous structure. These modifications amplify its surface oxygen-containing groups, leading to increased efficiency of biochar to remove pollutants from the wastewater. Biochar, rather than activated carbon, can extract pollutants and has many benefits, including recovering nutrients from wastewater, enhancing activated sludge treatment to minimize energy use for aeration, and increasing sludge settling capacity and the energy recovery from sludge through anaerobic digestion. Hence, biochar plays an efficient role in wastewater management, which may need specific future improvements to make it more effective in future economic routes.

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Restoration of Contaminated Agricultural Soils

18

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Abstract

Industrialization, urbanization, and mining activities are the primary sources of soil contamination. Human-made and rare natural activities are disseminating potentially toxic elements and organic pollutants in the environment. Restoration of ecology also blends several related disciplines, including hydrology, geomorphology, and oceanography. The primary role of the restoration of ecology is to conserve or improve the soil ecosystem services and implement efficient environment-friendly techniques for the characterization of pollutants, risk assessment in problematic zones, and reclamation of polluted agricultural sites. Physical and chemical methods are widely in practice to restore the contaminated agricultural soil efficiently. There are also eco-friendly better techniques that comprehend the mobilization and immobilization of enzymes/microbes to reawaken the polluted soil. Restoration of agricultural soil is an important concept needed in the present and future to make the upcoming generation healthier and make the ecosystem stable.

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Keywords

Agricultural soils · Human-made pollutants · Contaminated soil restoration · Soil restoration techniques · Stable ecosystem

18.1 Introduction

Soil is one of the most primitive of all resources available in the environment that provides an essence to the terrestrial ecosystem and cultural heritage. Soil is found to be finite in extent and has a threat by various natural and man-made factors. The soil quality decides the health of the ecosystem, environment, and all life forms living in this universe. There are different means of components provided in the ecosystem. The soil environment is maintained through services provisioned throughout the soil like food, fiber, waste disposal, climate moderation through carbon cycling, elemental cycling, and water filtration. Soil quality or soil nutrient content needs to be confined or restored to augment these services. It has been becoming mandatory to have public awareness and elementary perceptive of basic biology, chemistry, physics, and ecology to improve long-term productivity (Lal 2015) and enhance the health of the environment.

Soil is an important key factor that helps regulate natural and socioeconomic processes for sustaining human and animal survival. Soil needs to be maintained appropriately in order to overcome the crises of food and water in the future. Agriculture is facing many challenges since the twenty-first century. Researchers are framing new technologies to protect the soil from various contamination types that threaten human and animal life. The expanded demanding and arbitrary use of agrochemicals unfavorably altered the biodiversity of soil and sustainability in agriculture and food safety, which in the long-term creates harmful effects on human, animal health, and nutrition. The activities of soil microbes and their biochemical processes are negatively affected by agrochemicals.

Soil holds diverse flora, fauna, and rich sources of microorganisms that can self-renew the soil contamination to a permissible limit. These soil microorganisms have an interrelation with the soil fertility on the basis of different soil properties:

1. **Chemical properties** include pH, cation exchange capacity (CEC), salinity, and nutrient content of the soil (micronutrient, macronutrient, and organic matter).
2. **Physical properties** such as stability of the soil, aeration in the soil, porosity, water retention, and also the contact between mineral and organic soil components.
3. **Biological properties** should have appropriate interaction between the micro- and macrobiota in the soil.

All these aspects are closely interrelated. Consequently, their stability is responsible for soil fertility. There are plenty of reasons for the contamination of soil (Tetteh 2015). A large number of highly noxious components were delivered into the surroundings because of numerous industrial and agricultural activities. Organic chemicals comprise fuels, alkanes, pesticides, solvents, phosphorus compounds, polycyclic aromatic hydrocarbons (PAHs), nitrogen, explosives, and dyes (Karthik et al. 2020), whereas the inorganic contaminants are toxic heavy metals.

In most countries, soil, groundwater, and surface water contamination are considered a global problem. Furthermore, composite pollution, which contains more than one contaminant and toxic metals, may mount up in the environment (Banu et al. 2020). Toxicological risk evaluation and the practicability of bioremediation technologies have been important points of concern in contaminated agricultural soil sites.

There are many methods for remediating the contaminated agricultural soil, like physical methods, chemical methods, and biological methods (Gianfreda et al. 2006). The majority of the chemical and physical techniques (such as stabilization, encapsulation, electrokinetics, solidification, vitrification, soil washing, vapor extraction, and flushing) are costlier than the biological processes. Such physical and chemical methods are incapable of making the soil suitable for plant growth. In comparison, the biological approach (bioremediation) promotes the establishment/reestablishment of plants on contaminated soils at low cost (Chibuike and Obiora 2014). Bioremediation is an environmentally friendly technique since it occurs through natural processes. It is also a cost-effective remediation method in contrast with other remediation techniques.

To renovate soil properties, soil contaminated with heavy metal and other contamination requires remediation. Soil washing, phytoremediation and immobilization techniques are recurrently used for the remediation of contaminated agricultural land. Soil washing is one of the stable management alternatives used to detach heavy metals from agricultural soils. It has a greater advantage of removing heavy metals at a maximum value at a considerable cost. Phytoremediation is a technique that reduces the toxic heavy metal content in the soil using plants and its related soil microorganisms. It comprises different sub-methods like phytostabilization, phytodegradation, phytoextraction, phytovolatilization, and phytofiltration (Mitra et al. 2020). The in situ technique of immobilization achieves the remediation of contaminated soil with the help of varied processes like adsorption, precipitation, and complexation reactions. Heavy metals are immobilized with immobilizing agents and amendments, making them less available for transportation to other sites in the soil and reducing their bioavailability. Broadly used amendments for immobilization are limestone, zeolites, clay, minerals, lime, phosphates, organic composts, etc. Immobilization has gained its advantage for remediation with negligible impact on agricultural production compared with soil washing and phytoremediation (Cagnetta et al. 2018). However, large-scale engineering is a major limitation in the reclamation of agricultural soils due to high operating expenses during the scale-up of the restoration process. At this juncture, phytoremediation is one of the best green solutions for restoring the agricultural soil contaminated with heavy metal. The soil environment will be healthy, mainly for agricultural purposes.

There is a vast diversity in the sources of the pollutants and also chemical complexity in organic contaminants corresponding to the pollutants and contaminants. There are extensive constituents of microbial biota to synthesize and remove the organic compounds. There are three main approaches to deal with the polluted agricultural site: (1) classification of the problem, (2) evaluation of the nature and degree of the hazard, and (3) the best choice of remedial action. To recreate the ecosystem, new technologies have been incessantly refabricated to reestablish and renovate the contaminated agricultural soil, further to detoxify the contaminated agricultural site. Remediation, whether by biological, chemical, or a combination of both means, is the only way to get rid of toxins in the soil without passing them to future generations (Ramakrishnan et al. 2011).

The selection of a suitable remediation method is based on the toxic limit of pollutants and the peril it poses to the surroundings. It must be prominent that the remediation does not intend for entire refinement. The central focus is to bring the pollution level well below the toxic regulatory limit (Kulkarni et al. 2008). This is done by clearing the poisonous pollutants and/or immobilizing the pollutant that restrict its movement through the subsurface geo environment. The remediation techniques are broadly classified as physical, electrical, chemical, biological, thermal, and blending methods (Asquith et al. 2012). In the forthcoming topics, various causes of agricultural soil pollution and different methods for remediating polluted agricultural soil are discussed in detail.

18.2 Sources of Agricultural Soil Contamination

The rapid development of industries and increased use of chemical amendments to the soil have drastically amplified soil contamination in recent decades. The contaminants are from different sources and of varied types. The sources of soil pollution are grouped by different means in various kinds of literature as agricultural, nonagricultural, and natural sources (Palansooriya et al. 2020). Figure 18.1 explains the classification of various sources of pollutants, which are the primary reasons for contaminating agricultural soil.

18.2.1 Agricultural Sources

18.2.1.1 Fertilizers

Fertilizers are chemical-based components infused with micronutrients and macronutrients in a particular ratio. Fertilizers are applied to the soil to improve the soil nutrients like nitrogen (N), potassium (K), and phosphorus (P) to get a high yield from the crops. Sometimes the fertilizers are prepared with the microorganisms that promote the particular nutrients to the soil. They are in different forms like solid, liquid, semisolid, and slow-release particles. However, these fertilizers improve the productivity of the crop, but it has many harmful impacts on the soil health and the microorganisms that reside in the soil. Soil health refers to the complete physical, biological, and chemical properties of the soil. The critical nutrients such as N, K, and P are supplemented in the soil to improve crop productivity (Velusamy et al. 2021). These inorganic fertilizers also hold many heavy metals like mercury, copper,

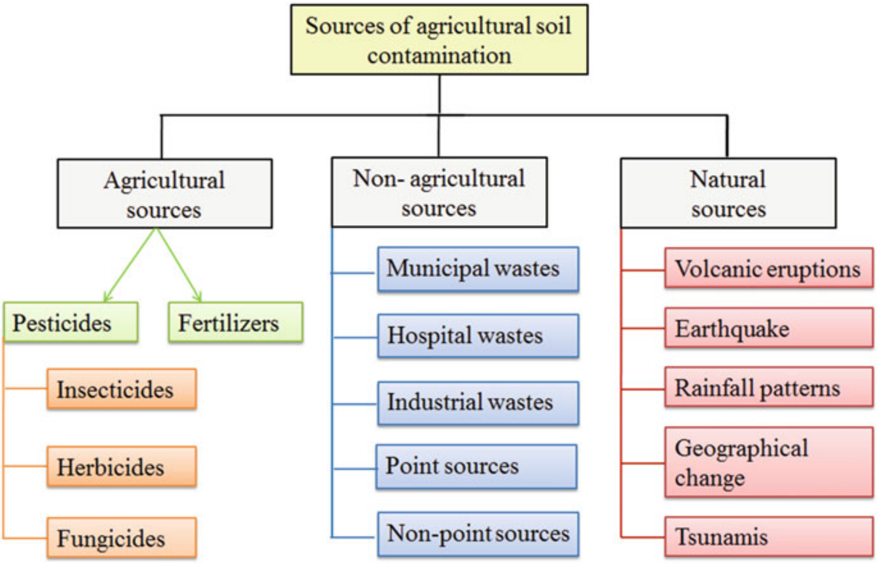

Fig. 18.1 Different sources of agricultural soil contaminants

cadmium, lead, and nickel, contributing to soil degradation and contamination (Iqbal et al. 2021).

Research studies explained that continuous use of chemical fertilizer on the soil would have many ill effects on the soil and on all life on the soil in due course of time. The vital component that is degraded due to these fertilizers is the soil structure. Fertilizers degrade the soil structure with the help of the chemical components present, and repeated use of acid-forming nitrogen fertilizer causes a decrease in the soil's pH. Research by Savci (2012) reported the ammonium sulfate fertilizer effect on the tea field in turkey. Application of nitrogen fertilizer in the tea field increased soils' acidity, and nearly 85% of the territory reached a pH below 4 (Savci 2012). This research also portrayed the effect of potassium fertilizer, which created an imbalance in the nutrient content of the agricultural soils. It made the plants deprive of necessary essential nutrients for the growth and yield of the plant.

18.2.1.2 Pesticides

In modern-day agriculture, pesticides contribute to be a vital factor for increasing the yield of the crop. However, it destroys the pest and insects in the crops, thereby increasing productivity. On the other hand, it has several negative consequences for the soil and humans. These pesticides reach the soil causing degradation, and some of the soil properties are lost. The pesticides also increase the toxicity of the soil, thereby killing the beneficial soil microorganisms, which are essential for plant growth (Tetteh 2015).

It was estimated that less than 10% of the applied pesticide alone reach the target pest in particular research. The remaining content will reach soil and water bodies contaminating the soil, air, and water. The levels of pesticides that become persistent in the soil are at diverse ranges, disrupting the soil's chemical composition. Pesticides also have been known to harm soil microbes. It can alter the nature of the soil microorganisms, which are accountable for soil health, plant growth, and the proper maintenance of the ecosystem. The interference of the chemical pesticides in the soil deteriorated soil fertility by spoiling the microflora and microfauna (Pimentel and Burgess 2012). Fungicide is harmful to the fungi present in the soil and to the actinomycetes by altering the structure of the microbial community. All kinds of pesticides have a serious influence on the microbes present in the soil. Some of the organochlorine pesticides are found to impact the nitrogen-fixing bacteria by reducing the crop yield (Terziev and Petkova-Georgieva 2020). Similarly, pentachlorophenol, dichlorodiphenyltrichloroethane (DDT), and methyl parathion are also identified to interfere in symbiotic soil bacteria.

18.2.2 Nonagricultural Sources

Nonagricultural sources include the solid waste obtained from all kinds of waste treatment plants, including garbage, constructional debris, sludge, and other redundant materials. The rapid increase in population has maximized the amount of solid waste delivered into society. These solid wastes are of different compositions, which cause adverse effects on human, animal, and agricultural soil health (Palansooriya et al. 2020). These solid wastes also vary based on the different localities and sources.

18.2.2.1 Municipal Solid Wastes

Municipal solid waste encompasses a list of items that are being used in routine and discarded daily, including domestic waste, kitchen waste, clothing, bottles, food scraps, newspapers, paint, and batteries (Pedrero et al. 2010). Municipal wastes are classified into five major types based on the kind of pollutants, as indicated in Table 18.1.

Municipal wastes are disposed by two major methods like dumps and landfills. Landfills are designed especially with the help of clay linings and synthetic sheets.

Table 18.1 General classification of solid wastes (Pedrero et al. 2010)

Type of pollutants	Materials
Recyclable materials	Plastics, metals, aluminium cans, and glass
Hazardous wastes	Batteries, bulbs, medicines, fertilizer, pesticide containers, paint, old computers, printers, and cell phones
Biodegradable wastes	Food wastes and kitchen wastes
Inert waste	Demolition wastes and construction wastes
Nonbiodegradable wastes	Organic materials and heavy metals

These sheets are used to separate the waste materials from the soil. These kinds of landfills are practiced since the olden days to avoid pollutants contaminating the agricultural soil (Tabasso et al. 2020). The total production of municipal solid waste (MSW) was 292.4 million tons in 2018, or 4.9 pounds per person per day. Of the MSW produced, roughly 69 million tons were recycled, and 25 million tons were composted. Almost 94 million tons of MSW were casted off and composted, equivalent to a 32.1% recycling and composting rate. An additional 17.7 million tons of food were handled by other methods (Angelovičová and Fazekašová 2014). Pollution of agricultural soil due to the improper disposal of municipal wastes in developing countries creates lots of environmental threats to the soil health and water environment (Selvakumar and Sivashanmugam 2018), which disrupts the balance of the ecosystem.

18.2.2.2 Hospital Wastes

Hospital wastes also constitute a major portion of a pollutant that causes several adverse impacts on the agricultural soil. Hospital wastes originate from the disposal, diagnosis, and treatment procedures done in the health sector. These comprise medical wastes like surgical instruments, blood, tissues, amputated body parts, and contaminated microbial cultures. Additional utilities are the following: dressings, bandages, gloves, cotton, noxious and corrosive chemicals, solvents, diagnostic kits, genotoxic waste and radioactive liquid wastes, etc. According to the World Health Organization (WHO) report in 2018, it was summarized that the hospital waste generated per bed in developed countries is found to be 0.5 kg. In developing countries, the hospital wastes generated per bed are analyzed as 0.2 kg. The risk is high in developed countries than the developing countries and causes numerous health hazards. Most commonly, these wastes are disposed of by the landfill method, in which some contaminants will penetrate into the soil and cause the surrounding soil to get contaminated due to water percolation.

Another important strategy that is employed in remediating the hospital wastes in developing countries is incineration. Incineration of waste releases many pollutants like polycyclic aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), and many carcinogenic compounds that foist many unpleasant effects on the environment. The ash predominantly released from these incineration processes causes many worse effects on the soil health and environment. The ash also constitutes some heavy metals like cadmium, lead, chromium, mercury, and zinc, contaminating agricultural soil (Gidarakos et al. 2009). To overcome these issues related to hospital wastes, novel strategies need to be employed to mitigate the environmental hazards.

18.2.2.3 Industrial Wastes

Industrial wastes are developed due to urbanization and industrialization, which discard various materials like concrete, gravel, scrap, metals, paints, oil, trash, gravel, and organic and inorganic chemicals (Wuana and Okieimen 2011). These materials are chemical compounds released into the environment without understanding the futuristic problems that will be a threat to human and animal life, which will completely modify the healthy ecosystem. Those pollutants are highly corrosive, toxic, and reactive materials that pose a severe threat to the environment

(Selvakumar and Sivashanmugam 2020). Developed countries have identified many strategies for these industrial wastes disposal, but the developing countries are still struggling a lot in these issues (Ahmed et al. 2019). The point sources are discrete and localized contaminations, whereas nonpoint sources are associated with a wide range of processes or human activities that cover huge areas.

18.2.3 Natural Sources

Natural sources that cause soil contamination consist of volcanic eruptions, earthquakes, geographical changes, and alterations in rainfall patterns. Accumulating these naturally occurring compounds or chemicals in the soil and environment will cause serious disturbance to the ecosystem and human beings. These chemicals are getting converted to toxic compounds, which are affecting all forms of life.

18.2.3.1 Volcanic Eruptions

Dust, lava, ash particles, and gases were exploded from the interior of the earth's crust in hot magma, referred to as volcanic eruption. According to the US Geological Survey, a huge amount of hazardous substances are produced by volcanic eruption and demolish the surrounding environment. The contents released from those eruptions are toxic to humans and other life on earth. Volcanic eruption releases aerosols and greenhouse gases like sulfur dioxide, carbon monoxide, carbon dioxide, hydrogen fluoride, and hydrogen sulfide, accumulating in the atmosphere termed as outgassing. Lava, which is realized from the volcano along with the ash particles, destroys the surrounding land area. The fertile portion of the soil is eroded by lava, a hot material released from the volcano.

18.2.3.2 Earthquakes

Earthquakes are caused due to the sudden movement of tectonic plates below the soil surface with the release of energy due to volcanic activities. Earthquake causes serious damage to the constructions, dams, bridges, roads, railway lines and pipelines, etc., thereby causing contamination to the groundwater, affecting the agricultural soil. Agricultural soil fertility is affected after the earthquake, which makes the soil to be unavailable for cultivations. There are enormous secondary impacts of earthquakes like breakage of pipelines of water, fuel, electrical, and oil.

During nuclear power generation, a large amount of radioactive and other wastes are released into the environment. These harmful pollutants continue to stay in the environment for long times, which are used up by the atmosphere to accumulate and biomagnify potential toxic contaminants for the organisms that live on the earth. Medical waste, sewage waste, and radioactive waste release toxic material, affecting the soil, water, and air. Earthquake leads to one of the most dangerous effects of soil liquefaction. The soil loses its stability, strength, and stiffness by converting soil to liquid or mud form. This effect has a severe impact on the residential area construction, which loosens the soil and makes it unfit for construction.

18.2.3.3 Rainfall Patterns

Soil constitutes many varied organic materials to balance the nutrient of the soil, oxygen content, and water holding capacity, which forms the basic framework of the soil. Variation in rainfall patterns considerably affects the composition of the soil organic materials sensitive to climatic aberrations. Moreover, the acidic content increase in the soil due to the excessive rainfall further leads to leaching. Alteration in rainfall patterns has a serious problem in the arid and subhumid areas. For instance, due to excessive rainfall, pyrite-rich materials are oxidized to acid sulfate soils, which are important for leaching.

18.2.3.4 Geographical Changes

A wide range of undesirable effects on soil health is observed due to the geographical changes in the surrounding. The soil erosion with these geographical changes can be observed with modern techniques like Geographic Information System (GIS) and Remote Sensing (RS). These modern advanced techniques are used to acquire details regarding the soil health and diverse characteristics of the soil surface in addition to examine the extent of land degradation.

18.2.3.5 Tsunamis

It is caused by the sudden displacement of water from the interior of the sea due to unexpected underwater explosions, earthquakes, landslides, and volcanic eruptions. These changes happen in the depth of the sea due to the instability occurring below or above the water level. Tsunami creates many problems by accumulating many pollutants in the water, soil, and air, thus making the soil, water, and land unfit for cultivation. The pollutants keep on increasing on the soil surface, causing land and water pollution.

18.3 Techniques Used for the Restoration of Contaminated Agricultural Soils

Various techniques were employed to treat the contaminated soil and to restore the fertility of the agricultural soil. To maintain soil health and to preserve the stability of the ecosystem, the polluted soil needs to be remediated and recycled (Bini 2009). There are different methods of soil remediation, such as physical, chemical, biological and concoction, or novel remediation, as represented in Fig. 18.2.

To better understand each process, the different soil remediation methods shown in the figure are examined in detail, along with their remediation effectiveness. The overall objective of any soil remediation approach is to generate an enhanced solution that protects human health and the environment. Physical and chemical treatments effectively remediate the soil, but there are some disadvantages causing soil disturbance (Karthik et al. 2020). The biological remediation, which degrades the soil contaminants in a natural process, produces positive results, but it is time-consuming. Bioremediation is also an environment-friendly and less expensive

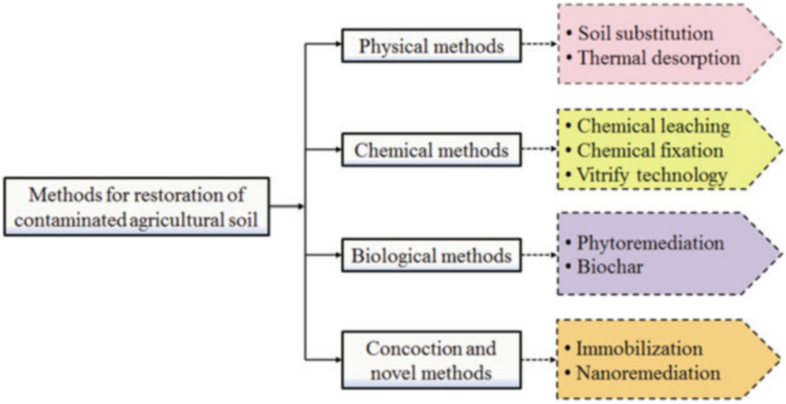

Fig. 18.2 Techniques for restoring contaminated agricultural soil

technique for maintaining soil health (Gong et al. 2018). In general, soil remediation techniques are classified into two types based on the way of application:

- In situ remediation
- Ex situ remediation

In Situ Remediation In situ treatment allows the soil fertility to be restored without excavating it. It also restricts land disposal limitations on the redeposition of treated soil. In situ remediation generally involves longer handling times due to the heterogeneity of the subsurface, which makes it laborious to assure uniformity of treatment. A significant concern regarding soil remediation in situ treatment is to avoid the spread of contamination resulting from inducing the contaminants to remove from the zone of contaminated soil (Wuana and Okieimen 2011).

Ex Situ Remediation Ex situ remediation is done by removing the soil from the area of the polluted site. Ex situ treatment of excavated soils includes the technological principles used to remove organic contaminants from the soil, namely, washing and volatilization. Ex situ treatment of excavated soil has a further concern in treatment and preparing the soil for processing. These include control of emissions, screening, homogenization, dewatering/drying, feed rate control, and measurement (Wuana and Okieimen 2011; Yao et al. 2012). These two methods will be applicable for all the methods that are given in the upcoming topics.

18.3.1 Physical Remediation

Remediation of soil by physical method comprises technologies that isolate the pollutants from the soil. The process involves reducing the volume of pollutants by transferring them to another medium (e.g., air or water). Based on amount and concentration, the new contaminated media may require additional treatment to either concentrate or devastate the waste for the reuse of soil. Hence, physical separation treatment requires a series of steps to complete the process (Yao et al. 2012). Physical remediation mainly includes (1) soil substitution strategy or soil replacement method and (2) thermal desorption or warm desorption.

18.3.1.1 Soil Substitution Strategy or Soil Replacement Method

The soil replacement method or soil substitution strategy is a method used to clean contaminated agricultural soil by replacing or moderately removing the contaminated soil to dilute the pollutant concentration, which increases the soil environmental capacity, thereby promoting soil fertility (Qayyum et al. 2020). The soil substitution strategy is also divided into three types: soil replacement, new soil importing, and soil spading.

1. **Soil replacement** is the removal of the contaminated soil and shifting it into the new soil. This method is suitable for contaminated soil with a small area. Furthermore, the replaced soil must be treated appropriately. Otherwise, the second contamination may occur.
2. **Soil spading** is to trench the contaminated soil, making the pollutant diffuse into the deep sites, thereby diluting and degrading naturally.
3. **New soil importing** is the process of adding up a large amount of clean soil into the contaminated soil on the surface or mixing the clean soil with contaminated soil, which will decrease the pollutant concentration.

The soil replacement can successfully isolate the contaminated soil and thus diminish its effect on the environment. Soil replacement helps in renewing the ecosystem by maintaining the proper natural healthy soil conditions. However, this technology is tough to handle, high in cost, and suitable only for small areas with profusely polluted soil (Yao et al. 2012).

18.3.1.2 Thermal Desorption or Warm Desorption

The thermal or warm desorption method is based on the contaminant's volatility. It is done by heating the contaminated soil using microwave, steam, and infrared radiation to make the pollutant (e.g., Hg and As) volatile. The volatile heavy metals are then made together using the negative vacuum pressure or carrier gas, removing the heavy metals. According to the temperatures, the traditional thermal desorption can be classified into:

- High-temperature desorption (~320–560 °C)
- Low-temperature desorption (~90–320 °C)

This technology is a simple process, with mobile devices, and the remediated soil can be reused (Qayyum et al. 2020). However, limiting factors, such as expensive devices and long desorption time, limit their application in soil remediation.

18.3.2 Chemical Remediation

18.3.2.1 Chemical Leaching

The chemical method of leaching implies washing the polluted soil with chemical reagents, gases of varied types, or other fluids, which help remove the heavy metals (Pd, Zn, Hg, etc.) from the polluted soils. The heavy metals present in the polluted soil are then recovered from the leachate (Asaithambi et al. 2020). Investigations were reported on wide concentrations of hydrogen chloride (HCl), sulfuric acid (H_2SO_4), hydrogen fluoride (HF), nitric acid (HNO_3), phosphoric acid (H_3PO_4), and for their effect of removal efficiency of arsenic (As) from yellowish-brown contaminated soil. One of the most promising chemicals for the extraction of arsenic is phosphoric acid, and potassium phosphate was found to be most efficacious for the removal of As from stream sediments around the abandoned mine areas in Goro, Korea (Pająk et al. 2020).

Tea saponin is reported to be an effective solution for the removal of heavy metals in addition to soluble acid, which will significantly minimize ecological hazards. Chemical leaching was a proven method to eliminate heavy metals like nickel (Ni) and vanadium (V). These impurities were there in the black carbon waste produced from the gasification of crude oil bottom in refineries. Acid leaching with two molar nitric acid (HNO_3) was analyzed to be a very advantageous method (more effective than alkali) for the removal of both Ni (95%) and V (98%). Further, the acid-treated carbon black waste was used as an absorbent for dye removal. It was suggested that chemical leaching be a potent method for extracting Plutonium (Pu) from radioactively contaminated soil. Although efficacy mainly relies on the type of soil and nature of heavy metal(s) present, chemical leaching is found to be one of the best methods for effective remediation of polluted soils (Yao et al. 2012).

18.3.2.2 Chemical Fixation

Chemical fixation is a type of remediation method in which chemicals or reagents are introduced into a polluted soil environment and combined with heavy metals to form insoluble, nontoxic content, minimizing the amount of heavy metals released into the soil and water environment, thus preventing pollution. Qayyum et al. (2020) analyzed the ability of bonemeal in the remediation process when added to the contaminated soil. The pollutants/contaminants are immobilized on the soil and reduced bioavailability with the formation of metal phosphates. Extraction of metals was done batchwise in the bonemeal amended soil using 0.01 M $CaCl_2$ and DTPA. Cadmium (Cd) contamination was assessed with the help of bentonite and diatomaceous earth. The experiment results showed a reduced concentration of cadmium 21.40, 27.63, 27.24, and 32.30% compared with the control when the chemical addition quantity was 20, 30, 50, and 40 g/kg, respectively (Qayyum et al. 2020; Prieto et al. 2018). Particular research reported the remediation of contaminated soil with attapulgite clay in which the particular amendment can reduce the concentration of cadmium pollutants by 46%. The soil quality will not be disturbed, thereby enhancing the productivity of the soil.

Various literature on chemical fixation analyzed the efficiency of phosphate rock, furfural, and weathered coal on the polluted soil. The outcome explained that the above materials could reduce the concentration of different metals (Cu, Zn, Pb, and Cd) to some extent. The chemical fixation could renew the soil with low concentration pollutants; however, the bioavailability of fixed heavy metals may be altered with the changing environmental condition. The use of conditioning agents could alter the soil organization to some degree and affect the microbes in the soil (He and Yang 2007).

18.3.2.3 Vitrify Technology

Vitrify technology is the process of raising the temperature of the soil in the range of ~1400–2000 °C, by which the organic matters volatilize or decompose. The steam is produced and an offgas treatment system collects the pyrolysis product. The melt formed after cooling forms rock shape vitreous, sieges the heavy metals and makes it lose migration. For ex situ remediation, the energy can be supplied by fossil fuel burning or electrode directly heating and then through an arc, plasma, and microwave. For in situ remediation, the heat can be through electrodes inserted into the contaminated soil (Wuana and Okieimen 2011). In summary, this technology can remove heavy metals, and the efficiency was also high. However, it is complicated and needs lots of energy to melt, making it to cost high that restricts its application.

18.3.3 Biological Remediation

Physical and chemical methods of remediation may negatively impact the soil up to a certain limit due to the usage of chemicals and reagents. This problem would be reduced with the help of biological remediation, which uses biological compounds or materials to remediate the soil. With the alteration in physical and chemical characterizations of microorganisms, the movement and transformation of heavy metals can be reduced. It cannot destroy or completely degrade the pollutant. However, biological remediation is affected by various conditions like pH, temperatures, moisture, and oxygen. It is also limited to certain applications, such as some microorganisms that can only degrade special contaminants and microbes that may incur secondary pollution (Wuana and Okieimen 2011). The biological remediation includes phytoremediation, bioremediation, and combined remediation methods.

18.3.3.1 Phytoremediation

Phytoremediation comprises a pool of agricultural techniques for reducing the concentration of pollutants and the risk associated with the occurrence of organic and inorganic contaminants by using plants or their components. Phytoremediation uses living green plants to fix and adsorb contaminants to remediate the environment and ecology (Fiorentino et al. 2018). Three main types of phytoremediation are phytostabilization, phytovolatilization, and phytoextraction.

18.3.3.1.1 Phytostabilization

Phytostabilization is the process in which the metals are immobilized in the soil with the help of plants, thus reducing their mobility to groundwater, which will protect the groundwater from contamination. Plants have the ability to immobilize the contaminants in the soil through adsorption, accumulation in roots, or precipitation in the area of the roots, which in turn prevents the migration of the pollutants, minimizing erosion, leaching, and dispersion in the soil (Liu et al. 2015).

18.3.3.1.2 Phytovolatilization

Phytovolatilization is the process by which the heavy metals are absorbed and converted into volatile compounds, i.e., into gaseous matter using special compounds secreted by root. The process works by taking up the contaminants or heavy metals and transpiration of pollutants by plants. It not only is primarily applied to groundwater but also can be applied to sludges, sediments, and soils. Chlorinated solvents can also be removed with the help of phytovolatilization, e.g., selenium, mercury, and arsenic. Mercury is the most studied heavy metal. When contaminants are adsorbed, the metabolic processes of the plant commence their functions to renovate into other compounds or volatilize into the atmosphere. However, phytovolatilization technology is only suitable for volatile contaminants, limiting the application (Wuana and Okieimen 2011).

18.3.3.1.3 Phytoextraction

Phytoextraction is a method of adsorbing heavy metals using the most tolerant and accumulating plants and then transferring them to overground parts. It is to employ the plants that can hold and concentrate metals from the soil on the roots. The roots of sunflowers have been used to treat wastewater containing lead, uranium, strontium, cesium, cobalt, and zinc; other plants with this perspective are popular and water hyacinth. Studying the adsorption characterization of different plants and screening high uptake plants is the key to this technology (Fagnano et al. 2020). Following the rules of US department of energy, the plants used for this phytoextraction should have the following characteristics (Prieto et al. 2018): (1) high metal accumulating efficiency even under low concentration of contaminants, (2) accumulation of high concentrations of the contaminants, (3) Accumulation of many different kinds of heavy metals, and (4) high resistance to pest and disease.

18.3.3.2 Biochar

Biochar is carbonaceous porous materials developed from the conversion of organic material through the thermochemical like pyrolysis and gasification and hydrothermal process. In recent years because of the benefits reported on biochar, it has been extensively used in the field of bioremediation. Researchers also acknowledge that biochar was proved to be a beneficial one for improving crop productivity by remediating the contaminated agricultural soil and making it available for reuse by the crops (Mohamed et al. 2015). Biochar is most widely used as a soil amendment for its important advantages like sequestration of carbon from the atmosphere into the soil, stabilizing soil properties and enrichment of soil nutrients. Despite a wide range of applications available for biochar, there are various issues related to public health. The addition of biochar to the soil causes severe respiratory problems to human health, and also the accumulation of heavy metals also causes the same. Having a considerable dose of biochar for remediation will be appropriate for the purpose without causing much damage. Improvement needs to be done to make biochar an eco-friendly and effective method for agricultural soil remediation (Yi et al. 2017; Zahed et al. 2021).

18.3.4 Concoction and Novel Methods of Remediation

18.3.4.1 Nanoremediation

Nanotechnology finds its use in all the fields and has contributed a great diversity of materials with the technology for varied applications. As common knowledge, nanotechnology is used to get the materials or product in the nanorange of 1–100 nm. Nanotechnology aims to improve the quality of the product with a longer lifespan. The arrival of nanotechnology has many environmental benefits. The emergence of nanotechnology presents several budding environmental benefits (Nehra et al. 2021). Nanotechnology keeps up an assuring ability for the preservation of the environment and agricultural soil restoration. A significant sustainable strategy has been employed to replenish soil nature by degrading the toxic pollutants, thereby enriching biodegradation. An efficient and eco-friendly choice to other remediation techniques can be made using this technology to extract varied organic (PAHs) and inorganic (heavy metals) contaminants. Nanoparticles have made specific physical and chemical properties as the particles of preference to restore the polluted environments. Immense importance for remediation of polluted soil is given to the nanoparticles that are attained from hyperaccumulator plants, bacteria, yeast, and fungi. Multitudes of research are now concentrated on the green synthesis of nanoparticles, i.e., nanoparticle production using biological materials like plants, algae, fungi, and bacteria.

Similarly, it is mandatory for the researchers to achieve the sustainability of nanoparticles and comprehend the meticulous mechanisms and their mode of action. In the years to come, additional improvements and transformations can be accomplished in the nanotechnological field that will certainly enhance the efficiency of nanobioremediation (Gong et al. 2018; Karthik et al. 2021). A furthermore thorough study heeding the effect of nanoparticles on soil flora ought to be suggested. It is critical to plan a powerful strategy that may affect soil microbes to maintain the soil biodiversity.

18.3.4.2 Immobilization

Several advanced technologies have been developing to remediate the soil; one among them is immobilization. Immobilization has become an important technology in almost all fields. It is used in the agricultural area to retain the total microbial count in the soil, which is not possible in using the microorganisms directly in the soil.

Microbial load in the soil is one of the major reasons for the maintenance of soil quality (Guo et al. 2018). Agricultural products are in the current situation are prepared and developed with this technology. Stella et al. (2019) selected four gram-negative bacteria strains used to improve N, P, and K concentration in the soil. All four beneficial strains are immobilized with alginate solution. Results showed that the bacterial count in compost fertilizer was 10^7 cfu/g, while organic fertilizer (5:5:5) was 10^6 cfu/g, after 1 year of shelf-life. Mineral fertilizer (15:15:15) and immobilized bacteria mixed in 1:50 ratio exhibited 10^5 cfu/g after 210 days. Pelleting the cells found to be effective for immobilizing with the organic fertilizer. The immobilized bacterial cells are mixed in a ratio of 1:50 with organic fertilizer and results observed that 10^6 cfu/g of bacteria retained for 348 days, showing the immobilized bacterial cell will be a useful alternative for the agricultural soil remediation (Stella et al. 2019; Nejad et al. 2018).

The efficiency of different restoration methods of various pollutants is represented in Table 18.2. These remediation methods for the restoration of agricultural soil have been discussed clearly in the above topics, which will provide a better solution for the contaminated agricultural soil. Even though the remediation methods are effective in its use, it has some limitations due to various factors. The general limitations are addressed in the following discussion for understanding the proper restoration conditions.

Table 18.2 Efficiency of different restoration methods of various pollutants

Methods	Focused pollutant	Removal efficiency (%)	Reference
Phytoremediation plant–*Celosia argentea*	Cadmium	84.5	Niu et al. (2021)
Electrokinetics process	Nickel	43.2	Kamal et al. (2021)
Soil washing with GLDA chelators	Lead	58.0	Gluhar et al. (2020)
Soil washing with GLDA chelators	Cadmium	76.0	Gluhar et al. (2020)
Soil washing with EDTA chelators	Lead	75.0	Gluhar et al. (2020)
Soil washing with EDTA chelators	Cadmium	71.0	Gluhar et al. (2020)
Biological remediation	Polychlorinated naphthalene	75.0	Gu et al. (2021)
Biochar	Cadmium	63.0	Qiao et al. (2020)

18.4 General Limitations of Contaminated Agricultural Soil Restoration

18.4.1 pH

The pH of soil plays a significant part in the mobility and bioavailability of heavy metal present in the soil and affects the cation exchange and metal-binding processes. An increase in the pH of acid paddy soils fallout in the creation of additional negatively charged sorption sites on the soil colloid and organic matter surfaces, decreasing the metal availability. As the pH of the soil increase, the concentration of OH^- also increases with the carbonate and hydroxide precipitate formation. The pH of the soil is one of the important factors for the proper survival of the microbial community and the production of essential nutrients from those microbes. pH of the soil alters the nutrient availability in the soil (Neina 2019). The optimum pH for the biodegradation of soil contaminants is at pH 7, which is neutral; it may range from pH 6 to 8.

18.4.2 Temperature

The temperature has a major role in the biodegradation rate in enzymatic reactions with microorganisms. The speed of the enzymatic reactions in the cell doubles for every 10 °C rise in temperature. There is a maximum temperature that microorganisms can sustain in the environment (Neina 2019). The mesophilic bacteria present in the soil are most predominantly capable of degrading the soil contaminants at the optimum temperature of 25–45 °C. A type of bacteria that can survive in extreme temperatures is thermophilic bacteria found in hot and cold soil areas. These bacteria can be activated to degrade the contaminants present in the soil by increasing the temperature of the soil to 60 °C. This approach is not always possible in all environmental conditions but can be applied to some extent in areas where the temperature is moderate to high. It has a disadvantage in the places, which have the temperature low to mild conditions (Yi et al. 2017).

18.4.3 Water Condition

Redox potential plays a vital role in the solubility and bioavailability of heavy metals in the soil. Water condition affects the redox potential in the agricultural soils. A field experiment was conducted to inspect the optimum pH and redox potential of soil with the decrease of arsenic and cadmium in the rice field. The above experiment results illustrated that alternating irrigation with flooding and drainage concurrently reduced the accrual of arsenic and cadmium in agricultural soil. These may also include an important limitation in restoring the contaminated agricultural soils by reducing the remediation effects. Flooding with water increases the pH of the soil with the decrease in redox potential, which will raise the negative charge on soil particles allowing the heavy metals to get accumulated, and there will be a reduction in mobility (Liu et al. 2015; Yi et al. 2017). The reduction in soil mobility will help restore the contaminated agricultural soils.

18.5 Future Prospects of Agricultural Soil Restoration

The success of the agricultural soil remediation strategy lies in the quality and quantity of the contaminant or pollutants present in the soil. The restoration is also based on the geographical location and type of contaminant accumulated in the soil (Kalsi et al. 2020). Single remediation would not be an effective one without having any deterioration effect in the soil. To restore the contaminated agricultural soil effectively, concoction (combining physical, chemical, and biological strategies) and novel remediation methods by integrating more than one remediation method can be used (Wang et al. 2021). Remediation methods explained in the above topics can be used to design an efficient restoration method to restore the lost agricultural soil health, which will make the ecosystem healthy. Thus, ideal soil restoration strategies guarantee environmental protection by using natural resources for proper soil remediation, cost-effectively, and environmentally advantageous for society (Mench et al. 2006; Ayub et al. 2020).

18.6 Conclusion

Agriculture health determines the wealth of the country, and it also helps in human development. Due to the expansion of industries, soil quality deterioration has become the major issue of the environment. Agricultural soil pollution is caused by several sources like agricultural, nonagricultural, and natural sources. The impact of these sources is in ascending order with natural sources, agricultural sources, and nonagricultural sources. The majority of the pollutants that affect agricultural soil health are by human activities and causing the shrinkage of the agricultural land, affecting food security. The vital contaminants of the soil are heavy metals like mercury, copper, cadmium, zinc, arsenic, and organic compounds (PAHs, PCBs, etc.). All these contaminants get accumulated on the soil and increase the toxicity. This toxicity of the soil needs to be removed from the soil to keep the environment stable. For these reasons, scientists and researchers have designed many remediation methods of diverse physical, chemical, and biological methods. Each technique has specific pros and cons, which can be applied appropriately for the varied types of pollutants. Besides, environmental policies concerning the administration of soil standards should center on implementing appropriate and integrated soil remediation strategies to improve soil quality.

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Application of Biochar for Soil Remediation

19

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Abstract

Bioremediation by biochar can occur by immobilizing, stabilizing, and reducing contaminants' bioavailability such as toxic metals, polycyclic aromatic hydrocarbons (PAHs), phthalic acid esters, polychlorinated biphenyls (PCBs), and pesticides. Biochar characteristics depend on the biomass used, on the pyrolysis conditions, changing material characteristics and influencing the contaminants' sorption capacity and affinity. In addition to immobilization, the degradation of organic contaminants in the soil can stimulate specific microbial groups. The aim is to synthesize the methods used in the production of biochar and the recent advances in the application of biochar in the remediation of different contaminants in the soil, summarizing the main methods used to improve the structural and physicochemical properties of biochar to increase its potential for remediation. Also, consideration was given to the biological and abiotic processes that can alter the physical and chemical properties of the biochar, and the main applications were presented as in soil amendment and composting, carbon sequestration, wastewater treatment, and bioenergy, relating the use of the biochar with the sustainable development goals.

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Toxic metals · Organic pollutants · Soil · Biochar · Fertilizer

19.1 Introduction

Biochar is a porous material, rich in carbon and essential functional groups, and produced from raw materials such as biomass from other processes or different types of waste. The use of biochar can significantly alter an environment's characteristics contaminated by organic and inorganic compounds (Li et al. 2017; Cheng et al. 2020).

The applicability depends on the chemical composition of the biochar, which is dependent on the production method. The biochar can have different functional groups of bonds with carbon and oxygen, oxygen, and hydrogen, in addition to ester groups that are responsible for increasing the adsorption capacity, increasing the cation exchange rates, reducing the loss of nutrients, and spreading the plumes of contamination in leaching processes (Majumder et al. 2019).

The production of biochar involves the pyrolytic conversion of organic biomass, in a process characterized by scarcity of oxygen. Depending on the variability of raw materials and production methods, some fundamental properties of the biochar may vary, such as pH, the composition of functional groups, porosity, cation exchange capacity, and surface area. These properties directly influence this agent's behavior in the remediation processes (Oni et al. 2019). The biochar has an alkaline pH, around 8–11, cation exchange capacity ranging from 27 to 485 cmol kg^{-1}, and a surface area of 140–336 m^2, assigning properties of high reactive potential to the material. It has a water-holding capacity of 75–257%, which can reduce leachate generation in contamination processes (Xie et al. 2015; Ghosh and Maiti 2020).

In soils, the applicability of biochar can bring numerous benefits, such as increased plant growth and the remediation of different contaminants, in addition to promoting changes in soil properties, such as correcting the pH of soils by updating acids and adding nutrients (Gascó et al. 2019; Ghosh and Maiti 2020). Among the contaminants that can be remedied by biochar are organic and inorganic compounds, such as PAHs, pesticides, dyes, polybrominated diphenyl ethers, and dichlorodiphenyltrichloroethane (Yu et al. 2019), and among the inorganic ones arsenic (As), chromium (Cr), lead (Pb), zinc (Zn), cadmium (Cd), copper (Cu), and mercury (Hg) (Nejad et al. 2017). Remediation can occur through mechanisms such as adsorption, absorption, immobilization, and microbial influence, in addition to the properties of the soil and biochar.

The aim of this chapter is to synthesize the methods used in the production of biochar and the recent advances in the application of biochar in the remediation of different contaminants in the soil, summarizing the main methods used to improve the structural and physicochemical properties of biochar to increase its potential for remediation. Besides, consideration should be given to the biological and abiotic processes that can alter the physical and chemical properties of the biochar and the main applications and were presented as in soil amendment and composting, carbon sequestration, wastewater treatment, and bioenergy relating the use of the biochar with the sustainable development goals.

19.2 Biochar Production Methods and Characteristics

Among the most cited raw materials for the production of biochar for soil application, there are rice husks (pyrolysis at 400 °C, with a residence time of 5 h, pH 10.19), wood husks, beet tailings (pyrolysis at 400 °C, with a residence time of 4 h, pH 11.9), residues of fruit clusters (pyrolysis at 600 °C, the residence time of 6 h, pH 9.2), organic residues (pyrolysis at 500 °C, with a time residence time of 5 h, pH 9.4), and sludge from domestic sewage treatment plants (pyrolysis at 500 °C, with a residence time of 4 h, pH 8.1). These raw materials were converted and showed yields of 22.1–37.4% biochar (Oni et al. 2019).

The main ways of producing biochar are through fast, intermediate, or slow pyrolysis, gasification, hydrothermal carbonization, roasting, and among others (Rangabhashiyam and Balasubramanian 2019).

Pyrolysis involves temperatures between 500 and 1000 °C, with a residence time of fewer than 2 s. The intermediate pyrolysis performs the conversion at average temperatures of 500 °C, with a retention time of 10–20 s. In slow pyrolysis, the process occurs at temperatures of 350–600 °C with a retention time of 1–24 h (Liu et al. 2015). Pyrolysis involves temperatures between 500 and 1000 °C, with a residence time of fewer than 2 s. The intermediate pyrolysis performs the conversion at average temperatures of 500 °C, with a retention time of 10–20 s. In slow pyrolysis, the process occurs at temperatures of 350–600 °C with a retention time of 1–24 h (Cheng et al. 2020). In gasification, the raw material comes into contact with a mixture of gases at high temperatures (750–900 °C), oxygen, nitrogen, and carbon dioxide.

The dry raw material is oxidized, but this process can present a disadvantage compared with the pyrolysis process, due to the possibility of formation of by-products derived from burning at high temperatures in the presence of different gases, with the formation of toxic substances, such as polyaromatic hydrocarbons and consequently a reduction in the yield of the biochar (Zhang et al. 2019). On the other hand, hydrothermal carbonization uses temperatures ranging from 180 to 300 °C and 2–6 Mpa pressures. The raw materials used do not require pre-drying treatment. Compared with other conversion technologies, this process has advantages in generating biochar with high purity, greater aromatization degrees, and more significant amounts of hydroxyl, carboxylic, and amino surface functional groups (Kambo and Dutta 2015).

As mentioned, the conversion technologies are classified according to the heating rates, with variations in temperature peaks, biomass exposure time, and reaction atmosphere variability. The yield of biochar production is directly linked to these processes. Combining strategies, raw materials, and biochar properties is required for a fair production process and efficiency in the degradation of compounds (Ghosh and Maiti 2020).

The pyrolysis of organic substances and their exposure to the environment lead to oxygenation of the biochar surfaces. Oxygenated surfaces produce oxygen that contains functional groups, including hydroxyl, carboxyl, phenol, and carbonyl groups with high CTC and that break down organic contaminants into their by-products. As the pyrolysis temperature increases, the COC of the biochar increases and subsequently reduces, breaking the contaminants into small compounds. Ion exchange is defined as the process that functional groups containing oxygen on the surface of the biochar, such as carboxyl, carbonyl, and hydroxyl groups, can ionize H^+ ions or surface ions, such as sodium (Na^+), potassium (K^+), magnesium (Mg^+) for exchange with heavy metal ions or cationic organic contaminants (Koul and Taak 2018). The biochar produced at high temperatures and longer retention times is characterized for having a higher amount of P and K and having higher levels of Ca, Mg, Si, Fe, Mn, and S, elements essential for plants' development.

At lower temperatures (150 °C), the groups most present are –OH, C=O, C=C, and –COOH; for temperatures of 250 °C, the groups C=O and C=C predominate; and when the temperature changes to 350 °C, the C=C bonds are strengthened, which remain present up to temperatures above 700 °C (Cheng et al. 2020). This abundance of functional groups promotes oxidation stability in the biochar, cation exchange capacity, which, in turn, can act to control the leaching of soil nutrients, managing the process of adsorption of contaminants from the soil matrix, an essential factor for remediation processes. The elementary composition and action of critical functional groups brings to biochar two essential elements directly linked to soil remediation processes and mechanisms. These elements are the cation exchange capacity (CTC) and the specific surface area (ASE), which vary according to the pyrolysis temperature and the raw material (Weber and Quicker 2018).

The higher the exposure temperature of the raw material during the conversion technique, the lower the CTC and ASE values. There is a reduction in functional groups in these cases, which consequently reduces the CTC and ASE values. On the other hand, at high temperatures (>600 °C), the biochar structures' predominant functional groups provide negative loads to the material. These negative charges directly influence the biochar's behavior and interaction with loads of the soil and different contaminants (Kavitha et al. 2018).

The pH of the biochar produced is also dependent on the temperature used during the conversion technology and the raw material used. Generally, the biochar's final pH is alkaline, which is why it is widely used in the correction of acidic soil pH. Alkalinity is linked to organic functional groups, which improve soil properties, changing pH, and cation exchange capacity. The biochar's alkalinity can also be connected to organic compounds, carbonates, and bicarbonates from the converted raw material. Other organic alkalis, such as oxides and hydroxyls, which are characteristic of being alkaline compounds and easily solubilized, may be present. These play an essential role in controlling soil acidification and different contaminants' degradation processes (Weber and Quicker 2018).

The elementary composition of the biochar varies between nitrogen, phosphorus, potassium, calcium, and magnesium. With the use of raw materials such as poultry manure, the C/N/P/K ratio is higher than that present in the biochar produced by woody raw materials (Xie et al. 2015; Ghosh and Maiti 2020). This factor is essential for applying biochar since when analyzing the application in soil remediation, the biochar produced with higher C/N/P/K ratios presents advantages, as it facilitates the development of plants, acting as an agent corrective (Ghosh and Maiti 2020). Therefore, the use of raw materials from manure or sludge is more suitable for the production of biochar when applied to soils since its conversion results in elementary compounds essential to developing plants or correction of soils. These factors can influence from beneficial way soil remediation (Xie et al. 2015; Qambrani et al. 2017).

The presence of negative charges from the elemental composition and functional groups raises the biochar's pH values, bringing with it the ability to interact with the elements of the environment where it will be applied. This interaction results in adsorption reactions and different complexations of the contaminants, which results in their degradation. Therefore, the temperature of pyrolysis and the choice of raw material are essential for the future uses of biochar since they determine and constitute the properties of the material, its elemental composition, pH, functional groups, CTC, and ASE. In turn, these properties influence the biochar's interaction mechanisms with the soil and contaminants.

19.3 Potential Contaminants to be Treated by Biochar

The presence of contaminants in the soil can come from numerous sources. According to the geochemical compositions of the soil and rocks, they can be natural by sedimentation or volcanic eruption. However, the main concern with the soil's health and the local ecosystem occurs due to contamination from an anthropogenic source through mining, agricultural and industrial activities, and gas and oil production. Conventional treatments cannot remove many compounds that can reach the soil through these activities, so the biochar presents favorable characteristics to promote soli treatment (Palansooriyaa et al. 2020). Contaminants come from various activities and sources and can be divided into organic or inorganic elements.

19.3.1 Organic Contaminants

Soil contamination can occur by numerous types of contaminants, such as PAHs (polycyclic aromatic hydrocarbons), pesticides, dyes, polybrominated diphenyl ethers, and dichlorodiphenyltrichloroethane (DDT). Biochars can be used to treat contaminated soils with organic compounds, hydrophilic or hydrophobic, due to the adsorption material of these compounds through electronic interactions. Carbonized fractions of coal act as adsorption sites and non-carbonized fractions as partitioning agents (Yu et al. 2019).

Organic pollutants such as aromatics and chlorines are highly toxic. They can cause damage to the biology of various plants, generating mutations and cancer cells, in addition to being recalcitrant and harmful to microbial communities present in the soil (Yu et al. 2019). Dichlorodiphenyltrichloroethane (DDT) is a hydrophobic compound that has a low rate of biodegradation. Its presence in soils represents significant risks to plant health since it can be bioaccumulative and have a high toxicity. Organic dyes can destroy plant DNA structures, are resistant to biodegradation, and are stable when exposed to sunlight (Yu et al. 2019; Kavitha et al. 2018).

Polycyclic aromatic hydrocarbons (PAHs) are a class of compounds within the hydrocarbon family and have multiple fused aromatic rings (Zama et al. 2018). The presence of high PAH concentrations in soils has increased over the last 30 years and continues to grow more each year. This contaminant is more present in industrialized regions and usually reaches the soil through atmospheric deposition after transport. They are relatively stable elements, recalcitrant, and difficult to degrade by conventional methods. The PAH group contains more than 100 hazardous compounds generated by incomplete combustion of organic materials, such as oil, coal, and wood (Yu et al. 2019).

The adsorption mechanisms of hydrophobic organic compounds, such as PAHs, usually occur in internal regions of the biochar, where it can happen through π–π interactions between electrons within the aromatic rings of hydrophobic organic compounds with the π electrons present in the biochar (such as C=O and C=C) and aromatic compounds of hydrophobic organic material. PAHs are nonpolar hydrophobic contaminants, as are organophosphates and organochlorine pesticides. For the remediation of more polar contaminants (nitrobenzene, pyridazine herbicides, pharmaceuticals, etc.), polar groups must be present on the biochar's surface (Gomez-Eyles et al. 2013).

The removal efficiency of these compounds by the biochar performance can vary according to coal production. Biochar produced by slow pyrolysis can be efficient in removing some organics contaminants due to the more significant number of pores and organic functional groups on its surface, interacting through hydrophobicity. Chemical treatment by NaOH and coal composite with microorganisms can present greater efficiency in the removal of PAHs. Besides, the microorganisms present in the soil can be stimulated in the biochar's presence, promoting the contaminant's microbial degradation (Zama et al. 2018; Ogbonnaya et al. 2016).

19.3.2 Inorganic Contaminants

The inorganic compounds most commonly found in contaminated soils are arsenic (As), chromium (Cr), lead (Pb), zinc (Zn), cadmium (Cd), copper (Cu), and mercury (Hg) (Nejad et al. 2017). These compounds are highly toxic to the health of plants and humans. They are absorbed by the roots and can accumulate within the plants that eventually enter the food chain. Thus, biochar's use decreases its bioavailability in the soil, preventing it from causing more significant damage to ecosystems (Cheng et al. 2020). Unlike organic compounds, removal of inorganic compounds can be performed only by immobilizing the contaminant by biochar, in which case there is no degradation by microbial action. Biochars can complex metal ions on their surface, reducing their bioavailability, but the immobilization of compounds and essential nutrients for plants can also occur (Beesley et al. 2011).

The element arsenic (As) is an oxy-anion that represents significant challenges for soil remediation, and it is commonly found in the soil due to geogenic and mainly anthropogenic action (Vithanage et al. 2017). Human activities that most impact the disposal of this element on the ground are those arising from the use of pesticides in agriculture, mining, and fly ash disposal. Arsenic is a carcinogenic trace element highly toxic to human health, fauna, and flora (Yu et al. 2019).

The soil pH directly affects the As mobility. High pH values allow arsenic to bind to local anions in the soil, such as iron (Fe), aluminum (Al), and manganese (Mn) oxides, and oxyhydroxides. Thus, the introduction of basic biochars in acidic soils reduces this contaminant's mobility (Beesley et al. 2011). Also, optimization processes, such as impregnation of the biochar with iron oxides, can increase the soil's retention capacity through the anion exchange between the elements (Kuppusamy et al. 2016). Many studies on the removal of As from aqueous medium and the removal of this soil element are still challenging. Some techniques for removing As from soil use phosphorus (which has chemical properties similar to As) as a critical treatment factor, since the presence of phosphorus (P) in the biochar can generate competition between soluble phosphate and As in the phase solid, increasing the availability of arsenic in the pore water (Cheng et al. 2020).

Like As, chromium (Cr) is an oxy-anion compound with a double valence in sedimentary systems and soils. It can be presented in trivalent (nontoxic) or hexavalent form (highly toxic). Biochar can reduce the contaminant's toxicity and bioavailability and reduce Cr (IV) to Cr (III). Furthermore, this contaminant is more easily immobilized by biochar in acidic conditions (Wang et al. 2018).

The Cr immobilization processes that can occur in its interaction with the biochar are adsorption, reduction, or precipitation mechanisms. The contaminant will interact with the functional groups present on the biochar's surface, mainly by those that have oxygen in their formation, such as CO, C=O, –OOH, and –OH (Cheng et al. 2020).

Lead (Pb), copper (Cu), cadmium (Cd), and zinc (Zn) are divalent compounds with similar behaviors, so it is suggested that their behaviors in the presence of biochar also have the same characteristics (Wang et al. 2018).

Lead is the second most toxic heavy metal, after As. Pb can cause damage to plant health in germination and yield, and its toxicity depends on time and concentration. This metal can inhibit the enzymatic, photosynthetic activity, and the permeability of the plant membrane, in addition to disturbing the water and nutritional relationships available in the soil (Zulfiqar et al. 2019). It is a challenging metal for soil remediation because it is highly insoluble in soil due to phosphates and carbonates' complexation (Yu et al. 2019). Due to this characteristic, it was identified that biochar with P could immobilize the contaminant through electron donor–acceptor interactions, ion exchange, precipitation, complex formation, and pore filling. Thus, when compared with other heavy metals, Pb is relatively more straightforward to immobilize due to the variety of mechanisms that can occur between biochar and contaminant (Zama et al. 2018).

Several biochars were tested in the Pb-contaminated soil. It was observed that the coal production with slow pyrolysis at a lower temperature (around 200 °C) showed promising results, probably due to the presence of P on its surface under these conditions. The biochar from the green waste compound also showed good efficiency promoting immobilization by the covalent bonding of functional groups containing N. Thus, the combination of these factors can have combined effects on retaining this contaminant (Beesley et al. 2011; Cheng et al. 2020).

For Cu removal, certain functional groups in the biochar, such as –OH, are essential. The negative zeta potential found in biochar from chicken manure promotes immobilization of the Cu by increasing the soil's pH. Basic biochar can promote the contaminant complexing with the elements present on the material surface. Coal produced by wood and bamboo shavings promoted copper adsorption by forming $CuCO_3$ and $Cu(OH)_2$. For cadmium, alkaline substances such as CO_3, PO_4, and OH^- in the biochar increase the sorption capacity. The presence of more than one contaminant, such as Cu and Zn, can affect their retention; immobilization of more than one element in the functional groups present in the biochar can occur (Cheng et al. 2020).

Mercury is one of the most dangerous contaminants with high toxicity, mobility, and long residence time in the environment. Due to its geochemical characteristics similar to the soil, including redox reactions, sorption and desorption, methylation, and biological processes, it is difficult to carry out its retention (Wang et al. 2018). The characteristics of the biochar also determine the efficiency of its removal. Functional groups on the surface containing oxygen have more significant interaction with Hg. Wood-derived biochars provide the formation of a $COOHg^+$ complex that reduces the mobility of Hg in the soil (Cheng et al. 2020).

19.4 Mechanisms of Interaction Between Biochar and Contaminated Soil

The use of biochar as a strategy for the remediation of contaminated soils has excellent advantages, such as an increase in the availability of nutrients present in the soil, an increase in microbial activity, and an increase in soil organic availability matter. Its application also reduces the use of fertilizers in soils, emission of greenhouse gases, leaching of nutrients, and soil erosion. The application of biochar in the remediation of contaminated soils has a simple technology to be applied and suitable for a wide range of soil types. However, its large-scale application still depends on economic viability and optimization of results (Ye et al. 2017). The application of biochar involves different devices, such as sorption, microbial influence, and its relationship with the properties of soils, such as the cation exchange capacity, which is defined by the total amount of cations retained on the surface of the soil (Brady 1989) and pH, having excellent potential for sorption and delaying the bioavailability of organic and inorganic contaminants (Koul and Taak 2018).

For inorganic contaminants present in soils, He et al. (2019) point out several reactions that can, directly and indirectly, influence the treatment of heavy metals in soils using biochar. As interactions directly involved between biochar and toxic metals in soils, electrostatic attractions, complexation reactions, precipitation, and ion exchange were mentioned. For the relationships indirectly involved, mention is made of the biochar's ability to change pH, CTC, mineral composition, and the percentage of organic matter in the soil as influencing the mobility and bioavailability of toxic metals.

Regarding organic contaminants, the application of biochar to remove them from the soil is essential, mainly to treat fungicides, pesticides, and herbicides, including atrazine, carbofuran's, and polycyclic aromatic hydrocarbons (PAHs) and volatile organic compounds (VOCs), such as benzene. The treatment of these compounds in the soil involves several characteristics of biochar and chemical and physical reactions of sorption, such as chemical transformation, attraction, electrostatic repulsion between electrons, and diffusion. Besides, most of the bound contaminants are mineralized through biodegradation carried out by microorganisms present on the surface and in the biochar's microcores. The pH, pyrolysis, and proportion ratio between the contaminant and the biochar also affect the interactions between organic pollutants and the biochar (Oni et al. 2019). The main mechanisms of interaction between contaminants and biochar are highlighted below.

19.4.1 Sorption and Adsorption

Physical adsorption indicates that the biochar uses its surface characteristics, called porosity and specific surface area, so contaminants, such as heavy metals and organic substances, can be absorbed on its surface and micropores. The diameter of the contaminant ions, such as heavy metals, is generally smaller than the biochar's average pore diameter. Thus, the smaller the contaminant's diameter, the more its pores penetrate the pores of the biochar, increasing its adsorption capacity. The intensity of physical adsorption is strongly correlated with the biochar properties (as a specific surface area) and the properties and concentration of contaminants. Temperature is also taken into account during the adsorption process (Yang et al. 2019).

The biochar has a high specific surface area. It is rich in porous regions that can develop double surface properties, both negative and positive, indicating that the biochar can adsorb negative and positive charges. Also, the valence of contaminants can vary in the presence of biochar, producing different adsorption behaviors. This phenomenon's main reason can be attributed to the microbiological process because biochar can stimulate microbial activities in soils and sediments (Wang et al. 2018). The efficiency of the physical adsorption of the biochar is generally correlated with the adsorption kinetics, adjusted by first- and second-order models, and the adsorption process can occur in a single layer or in multilayer adsorption, where the model of adsorption kinetics of Langmuir and Freundlich (Yang et al. 2019).

The adsorption of hydrophobic organic pollutants by biochar can, with high efficiency, decrease the contaminant's concentration in the aqueous phase. The use of biochar reduces the availability of organic pollutants in the soil, sediments, and flooded soils. In this property, the minerals that make up the biochar are carbonates ($CO_3{}^{-2}$), phosphates ($PO_4{}^{-3}$), sulfates ($SO_4{}^{-2}$), combined with heavy metal ions to form water-insoluble substances, such as metal oxides, metal-phosphates, and metallic carbonates, promoting the adsorption and immobilization of heavy metals (Yang et al. 2019).

Sorption is considered a physicochemical process in which contaminants are divided between the absorbent and aqueous phases. Some sorbent properties include surface area, pore volume, size, CTC, pH, functional surface groups, molecular structure, hydrophobicity, solubility, polarity, and critical factors in transferring soil contaminant to the sorbent material (Zama et al. 2018).

The biochar's structure and chemical composition are generally very well correlated with its function as a sorbent. Large pore sizes and pore volumes with high surface areas (greater than 100 $m^2\ g^{-1}$) mean that biochar has high sorption properties. The pyrolysis temperature also influences the factor that determines the pores' distribution (including pore size and volume) and the property of specific surface area. These properties make biochar a sorbent with qualities similar to activated carbon but with its application focused on nonpolar substances (Koul and Taak 2018).

The potential use of biochar as a sorbent material is advantageous since the material has the mentioned properties, also having resistance to decomposition and mineralization. Too important are the high availability and low cost of raw materials, especially when using sources of agricultural by-products (bark, sawdust, and bagasse) (Zama et al. 2018).

19.4.2 Interaction with Autochthonous Native Microorganisms

Changes in the properties of soils and sediments induced by the biochar can alter the abiotic (nutrients, pH, and oxygen) and biotic systems (different habitats that can lead to changes in the microbial community's composition and structure). Wang et al. (2018) indicate that studies involving the relationship between biochar and its interaction with microorganisms are abundant, suggesting that microbial biomass and microbial activity in soils and sediments are treated with biochar increase.

In general, the porous structure of the biochar can promote habitat for microbial communities. The soluble organic carbon and other nutrients absorbed by the biochar can provide substrates for developing microorganisms. Furthermore, the addition of different biochar compositions leads to varying distributions of the microbial communities associated with the nutrients adsorbed on the biochar's surface, which may increase or suppress the microbial community present on the site (Wang et al. 2018).

The soil microbiota can be an indicator of soil quality and the extent of soil contamination, that is, if the contamination has advanced and stabilized or if the contaminant has been effectively treated. The porous formation of the biochar and its ability to absorb organic carbons provides a medium in which microorganisms can synthesize nutrients from the sorbed organic substrates. This can be considered why it is reported that there is a correlation between the increase in microbial biomass and activity in soils treated by biochar (Beesley et al. 2011). With soil contamination, the biodiversity of microorganisms present on the site is usually compromised, mainly due to the high concentrations of contaminants present in the soil. Thus, the application of biochar in contaminated soils can help to preserve the biodiversity of contaminated soils.

The use of biochar affects microbial activity, and the increase in biomass alters the rate of fungi and bacteria present in the soil and the soil's enzymatic activity. According to Zhu et al. (2017), the biochar can influence microbial activity positively or negatively as follows: the biochar provides shelter for microorganisms through pore structures and soil surfaces or nutrients and ions essential for microbial growth, which are adsorbed in the biochar particles; the biochar can present a potential for toxicity with volatile organic compounds (VOCs) and free radicals persistent in the environment.

Also, biochar can modify the natural habitat of microorganisms, improving soil properties essential for microbial development, such as aeration conditions, water quality, and pH; it can induce changes in enzymatic activity that affect the soil cycle that is related to microorganisms; the biochar can interrupt microbial inter- and intraspecific communication between microbial cells through the combination of sorption and the hydrolysis of signaling molecules; the biochar can increase the sorption and degradation of soil contaminants, reducing the bioavailability and toxicity for the microorganisms present.

19.4.3 Other Interaction Mechanisms

Other mechanisms of interaction between the biochar and the contaminant present in soils can be identified, such as oxidation and reduction phenomena, exchange of nutrients, and carbon sequestration.

Oxidation and reduction reactions in the soil are essential, as they regulate the solubility of many elements, creating compounds and altering the soil's biochemistry. The addition of the biochar causes these reactions to intensify and can remedy contaminants in the soil. The application of biochar increases soil porosity while reducing soil density. Soil pores contain aqueous and gaseous fractions and are essential for the occurrence of toxic and anoxic reactions (Koul and Taak 2018).

Arsenic, for example, is one of the metals that has less toxicity in its reduced form (As(III)) under anoxic conditions when compared with As(V) formed under oxic conditions. Reduction conditions can develop in the soil pores due to increased soil aeration, resulting in reduced arsenic valence. Oxides have a high affinity for heavy metals, forming covalent bonds or ionic bonds (Koul and Taak 2018).

Iron oxide is well known for its interaction with heavy metals. It can be used in soil remediation and metals such as arsenic, mercury, chromium, lead, and selenium.

The organic carbon present in the biochar has been reported to have the ability to oxidize and reduce arsenic and cadmium in their less toxic forms, such as As(III) and Cd(VI). The effects of different forms of iron oxides, such as iron salts, red mud, or by-products, containing iron in contaminated soils were evaluated, observing that iron oxides increase the immobilization of trace elements present in the soil (Koul and Taak 2018).

The exchange of nutrients is a chemical process where cations and anions are stabilized in the soil instead of undergoing a leaching process. The cation exchange capacity (CTC) is the primary indicator of the soil's ability to absorb cations. Soils with high CTC are generally considered fertile soils because they can absorb nutrients. Anion exchange commonly occurs in positively charged locations due to the dissociation of hydroxyl ions from iron hydroxide ions, minerals present in the clay, and amino groups present in the soil's organic matter (Singh et al. 2017).

19.5 Removal of Contaminants from Soil by Adding Biochar

Many studies have been developed to remove various contaminants from the soil by biochar and have good removal efficiency, both for organic contaminants and for inorganic contaminants (Gai et al. 2014; Oni et al. 2019; Mukherjee et al. 2011).

In removing organic contaminants, several contaminants were analyzed. Soils contaminated with carbofuran had removal rates of 65 and 80% with biochar produced from beet waste and fruit bagasse (Mukherjee et al. 2011; Zimmerman et al. 2011). Atrazine and trifluralin had removal rates of 61.54–65.06% and 62.50–72.35% in soils treated with wheat straw biochar (Nag et al. 2011). Insecticides such as cypermethrin had 82.18% of their content removed when the biochar was associated with a consortium of bacteria, showing how there can be a biodegradation of these contaminants by the action of microorganisms both present in the soil and together with coal (Liu et al. 2018).

Table 19.1 shows some other studies carried out in removing inorganic contaminants and the main mechanisms of interaction between the contaminant and the biochar during remediation.

Through Table 19.1, it can be seen that several raw materials and pyrolysis temperatures are used in the manufacture of biochar, resulting in a variety of materials with different characteristics for the treatment of contaminated soils. Some biochar optimization processes are also used, thus generating better efficiency in specific contaminants (Gonzaga et al. 2020; Yu et al. 2017; Gao et al. 2019). In this way, biochar is a new prospective material with the potential to increase soil quality and minimize the harmful effects of organic and inorganic contaminants on soil quality (Oni et al. 2019).

Table 19.1 Removal efficiency and mechanisms involved in removing contaminants from the soil

Raw material	Conversion technology	Contaminant	Application dose	Duration	Efficiency	Mechanism	Reference
Orange bagasse	Slow pyrolysis (500 °C)	Cu	60 t ha^{-1}	24 months	28.0% Cu reduction in soil	Increasing soil pH raises the number of active sites that can bind with Cu	Gonzaga et al. (2020)
Chicken manure	Slow pyrolysis (550 °C)	Cu	5%	14 days	88.4% Cu reduction in soil	An increase in pH may favor the precipitation of Cu as $Cu(OH)_2$, in addition to adsorption being selected by the coordination of Cu with groups containing electronegative O and N or π electrons of aromatic functional groups	Park et al. (2011)
Corn straw	Slow pyrolysis (600 °C) for 2 h Mn oxides impregnation	As	0.5–2%	100 days	As(V): Biochar without impregnation: 11.7% reduction Biochar with impregnation: 28.5% reduction As (III): Biochar without impregnation: 54.0% reduction Biochar with impregnation: 81.6% reduction	Complexation of As(III) and As(V) with Mn oxides occurred on the surface of the biochar	Yu et al. (2017)
Cornstalk	Slow pyrolysis (550 °C) for 2 h Magnesium ferrite impregnation	Cd	1.5%	4 days	98.0% Cd reduction in soil	An increase in soil pH promoted the precipitation of Cd hydroxides and carbonates, leading to the deprotonation of the soil surface, generating a more negative charge and increasing the affinity with Cd	Gao et al. (2019)

(continued)

Table 19.1 (continued)

Raw material	Conversion technology	Contaminant	Application dose	Duration	Efficiency	Mechanism	Reference
Soybean straw	Pyrolysis (700 °C) for 3 h	Pb	10%	90 days	95.0% Pb reduction in soil	Biochar had a greater oxygen presence on the surface and could form complexes between Pb (cationic metal) and functional groups containing oxygen, such as –COOH The electrostatic attraction may also occur between the biochar (negatively charged) and Pb (positively charged)	Ahmad et al. (2016)
Chicken manure	Slow pyrolysis (550 °C)	Pb	5%	14 days	93.5% Pb reduction in soil	An increase in pH favored the precipitation of Pb in Pb5 (PO_4) 3Cl	Park et al. (2011)
Rice husk	Slow pyrolysis (480–600 °C)	Hg	24 t ha^{-1}	118 days	44.0% Hg reduction in soil pores	S contents in the biochar decrease Hg mobility by reducing sulfate to sulfide and precipitation with Hg to form Hg sulfides	Xing et al. (2019)
Wheat straw	Slow pyrolysis (600 °C) Fe sulfide impregnation	Cr	2.5 mg g^{-1}	180 days	95.6% Cr reduction in soil (only biochar decreased by 65.5% and only FeS reduced by 91.6%)	Immobilization can occur by complexing Cr with functional groups on the biochar surface such as –COOH, C–O, and –OH. There is also a reduction of Cr(IV) by FeS, and the carbon surface	Lyu et al. (2018)

19.6 An Overview of Other Environmental Applications of Biochar

In addition to the possibility of using biochar in remediation processes of soils contaminated by organic and inorganic compounds, there are several other environmental applications of biochar, such as carbon sequestration, reduction of greenhouse gas emissions, waste management, wastewater treatment, renewable energy, and soil amendment (Kuppusamy et al. 2016; Oni et al. 2019; Qambrani et al. 2017). This variety of potential uses is due to the biochar's physicochemical properties (Nanda et al. 2016). In this sense, biochar is considered as an alternative technology with the potential to mitigate environmental and food problems in contemporary society (Tang et al. 2013). In the following items, different environmental applications of biochar will be synthesized to provide an overview of its potential uses.

19.6.1 Soil Amendment and Composting

One of the primary uses of biochar is soil improvement since they increase carbon storage, fertility, and soil quality. Simultaneously, it can immobilize and transform contaminants present in this environmental compartment, which increases the yield of crops (Kalus et al. 2019; Nanda et al. 2016; Zhu et al. 2017). This potential is fundamental nowadays since, with population growth, there is a greater demand for food, directly dependent on agriculture (Kavitha et al. 2018).

The use of biochar for agricultural purposes is due to its composition, containing carbon, nitrogen, hydrogen, potassium, phosphorus, and magnesium, which can result in an increase in the amount of organic matter and nutrients that are favorable to plant growth (Kavitha et al. 2018; Nanda et al. 2016; Yang et al. 2019; Yuan et al. 2019). Besides, the biochar increases soil aggregates' stability and the water holding capacity, improving the soil's physical properties (Kavitha et al. 2018). Yuan et al. (2019) also report that biochar can improve the physical, chemical, and biological properties of salt-affected soils.

High resistance to microbial decomposition and high retention capacity of essential nutrients for plants are some aspects that make the use of biochar for agricultural purposes viable (Nanda et al. 2016). However, this effect can vary according to some factors, such as pyrolysis temperature, feedstock, soil type, and biotic interactions (Kavitha et al. 2018). Zhu et al. (2017) reported that biochars produced at high pyrolysis temperatures tend to have better positive effects from the point of view of fertility, since biochars that have a higher ash content may result in better cation exchange capacity of the soil, facilitating the maintenance of nutrients to the biotic community of this environment.

Regarding biotic interactions, Kavitha et al. (2018) emphasize that biochar's application creates a favorable environment for the development of soil microbiota, which consequently favors plants' growth. These authors also report that biochars influence the soil's enzymatic composition and mitigate plant stress, beneficial in the agronomic context.

Soils that receive biochar application can reduce nitrogen (N) leaching, preventing high concentrations of this element from reaching water bodies and causing eutrophication (Tang et al. 2013; Yuan et al. 2019). According to Yuan et al. (2019), the reduction of N leaching does not reduce its bioavailability for plants since biochar can improve this nutrient's efficiency, favoring the development of crops.

However, it is necessary to consider the appropriate amount of biochar to be used in the soil since an excessive application of biochar can inhibit the nutrient content and, thus, not favor the growth of crops (Kuppusamy et al. 2016; Yang et al. 2019). Kuppusamy et al. (2016) list some negative points that can occur from the use of biochar for soil amendment that must be considered: (1) binding and deactivation of herbicides and nutrients in the soil, (2) excessive supply of nutrients, (3) increase in pH and electrical conductivity of the soil, (4) adverse effects on germination and soil biological processes, and (5) release of heavy metals and polycyclic aromatic hydrocarbons present in the biochar.

Biochar has some benefits concerning economic aspects since payments for sequestration of carbon dioxide combined with higher productivity of crops make this technology economically attractive to rural producers (Oni et al. 2019). Besides, water and nutrient retention caused by adding biochar to the soil can result in minors with irrigation and fertilizers (Oni et al. 2019; Tang et al. 2013; Yuan et al. 2019).

Biochar has another important environmental application in the context of soil amendment and waste management, as it can be produced from agricultural wastes and used in composting processes, one of the leading technologies used for the treatment of organic solid wastes (Gopinath et al. 2020; Kalus et al. 2019; Tang et al. 2013; Wang and Wang 2019). The addition of biochar in composting is a viable approach since the decomposition of waste is faster and, at the end of the process, an organic compound rich in nutrients is obtained, which can be used as a biofertilizer for different crops (Gopinath et al. 2020; Wang and Wang 2019).

19.6.2 Carbon Sequestration

The concern about climate change is rising, especially concerning reducing carbon dioxide emissions, as this is one of the leading gases that contribute to climate change (Oni et al. 2019; Nanda et al. 2016; Wang and Wang 2019). Biochars are considered a potential alternative to performing carbon sequestration to the soil (Oni et al. 2019; Wang and Wang 2019; Zhu et al. 2017). In addition to soil amendment applications, biochar can reduce the emission of greenhouse gases (GHG) and remove oxides of nitrogen (NOx) and oxides of sulfur (SOx) in air purification uses (Kavitha et al. 2018; Nanda et al. 2016; Oni et al. 2019).

The performance of biochar as a carbon sequestering agent, mainly CO_2 from the atmosphere, is due to its ability to retain larger amounts of stable carbon in the soil when compared with other uncharred organic matter (Nanda et al. 2016). The maintenance or increase of carbon in the soil is advantageous for improving the quality of agricultural soils. The reduction of GHG emissions decreases the agro-industrial sector's contribution to global warming (Kuppusamy et al. 2016; Nanda et al. 2016).

According to Wang and Wang (2019), biochar's performance as a carbon sequester varies according to feedstocks and pyrolysis conditions. Biochars produced at high pyrolysis temperatures are the most suitable for carrying out carbon sequestration. They have a more stable carbon structure and a higher C/N ratio, making them recalcitrant to microbial decomposition (Zhu et al. 2017).

However, the effect of using and applying biochar for carbon sequestration purposes is not entirely elucidated (Wang and Wang 2019). Kuppusamy et al. (2016) consider that, although biochar is regarded as a potential carbon sequester, studies show adverse effects of biochar, especially on ecological needs.

Nanda et al. (2016) list some factors that must be considered to elucidate the real effectiveness of different biochars in carbon sequestration and, consequently, in the reduction of GHG emissions: (a) GHG emissions associated with the production of biomass; (b) release of CO_2 and energy consumption during logistics operations (production, harvesting, and transportation of biomass); and (c) energy consumption during pretreatment, conversion of biomass, and final product processing. Therefore, it is essential to apply methodologies, such as life cycle assessments, that provide accurate information about biochar's real impact in reducing GHG through carbon sequestration.

19.6.3 Water and Wastewater Treatment

Providing clean and safe water is a current concern because this resource is fundamental to human activities. However, with the advancement of detection techniques, numerous contaminants are present in aquatic environments in concentrations around the planet. Therefore, it is urgent and necessary to develop treatment technologies to provide suitable quality water for various uses.

Biochar is an emerging and alternative technology for the treatment of water and effluents since it can adsorb organic and inorganic contaminants in aqueous matrices due to functional groups and charges on the surface of the biochar (Qambrani et al. 2017; Xiang et al. 2020). Biochar is commonly used to remove heavy metals, organic pollutants, and nutrients from wastewater (Xiang et al. 2020). According to Qambrani et al. (2017), biochar's performance as an adsorbent for different contaminants is similar to that of activated carbon, differing in terms of raw materials, production method, and physicochemical properties of the material.

Some factors directly influence the adsorption capacity of contaminants by biochar, such as temperature and pyrolysis time, as these affect the biochar's physicochemical properties (Gopinath et al. 2020; Wang and Wang 2019). The effectiveness of biochar in removing contaminants from aqueous media depends on its surface area, pore size, functional surface groups, and the molecules' size to be removed (Enaime et al. 2020). Wang and Wang (2019) emphasize that the recycling and reuse capacity of biochars must be considered when applied to the treatment of aqueous matrices. These factors increase the economic and environmental viability of their use for this purpose.

19.6.4 Bioenergy

Energy is fundamental to human activities and economic development, and its demand increases with the increase in the world population (Nanda et al. 2016; Oni et al. 2019). Among the energy sources, fossil fuels are one of the most used, but they can cause several adverse environmental impacts (Nanda et al. 2016; Nazari et al. 2020). Fuels from biomass are considered an alternative and sustainable source of energy and are based on converting carbohydrates present in the biomass of plants, residues, or microorganisms into biofuels (Nanda et al. 2016; Oni et al. 2019). These biomasses can be converted into biochar, bio-oil, and syngas (Oni et al. 2019).

During pyrolysis, part of the biomass carbon is stable in the biochar. Still, there is also the production of liquids and gases with high energy density with the potential for generating heat and energy (Nanda et al. 2016). According to Nanda et al. (2016), the amount of energy released from biomass during pyrolysis may be more significant than combustion. Oni et al. (2019) report that the two main products (syngas and oil) obtained from the biomass pyrolysis process can be used as an energy source since the syngas presents the possibility of being used as an input during pyrolysis, while the oil can later be transformed into biodiesel.

Syngas from thermochemical conversion of biomass contains CO, H_2, CO_2, and volatile hydrocarbons, which can be turned into fuels (Nanda et al. 2016; Xiong et al. 2017). Xiong et al. (2017) reported that biochar increases hydrogen production during pyrolysis/gasification of biomasses. Biochar can also be used as a catalyst to produce biodiesel (Xiong et al. 2017; Wang and Wang 2019) and as a substrate for the anaerobic digestion (Gopinath et al. 2020).

19.6.5 Relationship Between Biochar and Sustainable Development Goals

The 2030 Agenda, adopted by all United Nations countries, contains 17 sustainable development objectives (SDGs) created to protect the environment and guarantee health, education, and income so that all people can live with prosperity (United Nations 2015).

As presented throughout this chapter, biochar has several applications, such as soil amendment and remediation, carbon sequestration, bioenergy, water and effluent treatment, and air purification. Therefore, this emerging technology can have a positive impact on several SDGs. The biochar production stage can impact SDG 9 (industry, innovation, and infrastructure), SDG 11 (sustainable cities and communities), and SDG 12 (responsible consumption and production) since obtaining the biochar requires aspects of innovation to make its use more viable.

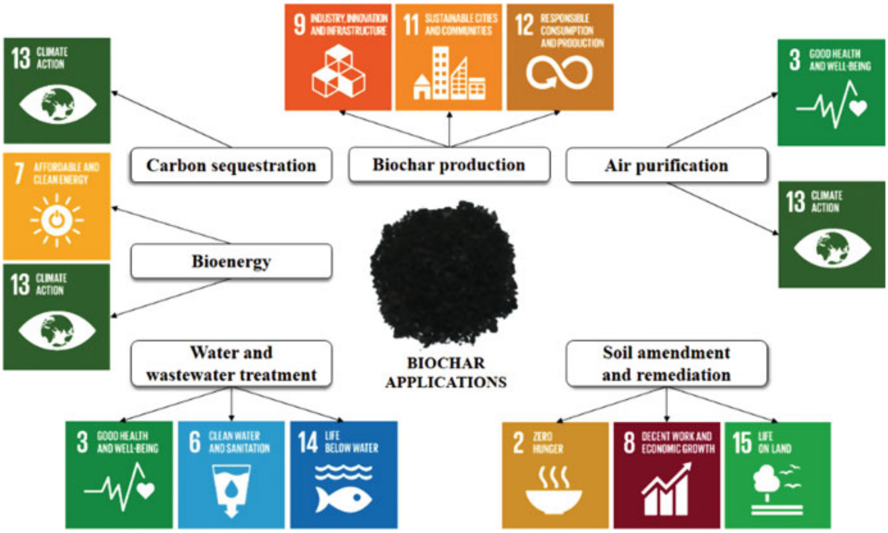

Fig. 19.1 SDGs impacted by production and different uses of biochar

In contrast, biochar can be produced from solid organic waste, making it a more sustainable approach to waste management in cities and industries.

When used in the correction and remediation of agricultural soils, biochar can increase crop productivity and, thus, favor food security and sustainable agriculture (SDG 2—zero hunger), increase the income of agricultural producers (SDG 8—decent work and economic growth), and make the soil healthier for the terrestrial ecosystem (SDG 15—life on land). Regarding the application in the treatment of water and effluents, biochars favor SDG 6 (clean water and sanitation), SDG 3 (good health and well-being), and SDG 14 (life below water) since they remove contaminants that can affect public health and the aquatic ecosystem.

The production of bioenergy from biochar favors the achievement of SDG 7 (clean and affordable energy) and SDG 13 (climate action) by reducing the demand for fossil fuels and, thus, reducing GHG emissions and provide renewable energy. The use of biochar for gas purification can positively impact SDG 3 and SDG 13 since it removes nitrogen and sulfur oxides, preventing them from being emitted into the atmosphere. Finally, biochars' ability to perform carbon sequestration can directly impact SDG 13 by reducing GHG emissions. Still, it can also indirectly favor SDGs 2, 8, and 15. Maintaining more significant amounts of stable carbon in the soil can increase crops' yields, improve the local economy, and make the soil healthier for terrestrial ecosystems. Figure 19.1 summarizes all the SDGs that can be positively impacted by the biochar's production and environmental applications.

19.7 Conclusions

Because of the presented, it is concluded that biochar production from residual raw materials is a current theme. It still needs studies to arrive at greater generalizations and use about its use; because of the abundance of materials that can be used and the factors that can lead to biochar production, as the temperature during pyrolysis and the heating rate as the main factors, characterization studies of these materials are required. Likewise, a wide range of compounds can be removed or immobilized from liquid or solid media using biochar. Still, the relationships that are established in the liquid and solid phases, chemically and physically, are not yet well elucidated, being a challenge for the consolidation of this technique, and to study the life cycle involving these process and the recycling of these materials, when used for remediation in liquid media. Biochar studies, therefore, consist of opportunities and the need for current science.

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Active Control of Environmental Enteric Viruses and Bacteria Using Biochar

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Abstract

Applying organic materials such as biochar has been aimed at removing water contaminants due to the overall low production cost, easy handling, and generation of renewable wastes after the application. Biochar materials have been proposed to remove metal contaminants and pharmaceutical compounds. Furthermore, such application ranges can extend to microorganism control, especially enteric viruses that require specific detection and control procedures. Water

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pathogens present a constant but increasing worry in agriculture systems, threatening to contaminate an entire production chain and the adjunct population through a single contaminated source. In this approach, studies have presented promising results in the retention of bacteria and viruses through biochar, combined or not with additional materials filters, further increasing the relevance of such compounds in water and wastewater sanitation.

Keywords

Microorganisms control · Sanitation · Health

20.1 Control of Environmental Enteric Viruses and Bacteria by Biochar-Based Materials

Biochar is a flexible, cheap, and highly accessible material, managing to cover a wide range of contaminant retention capabilities using only quickly produced materials and low-cost enhancements. Such products have an increasing demand as a renewable utensil in treating different waste sources, especially in low-income communities or industries that produce many wastes and require further use for the byproduct of organic matter. Still, most studies only cover biochar that used to treat bacterial pathogens and inorganic contaminants, such as pharmaceuticals and metals, with few pieces of literature covering viral pathogens responsible for a wide range of diseases. Several experiments managed to archive expressive amounts of containment of viral indicators using biochar-based materials, whether using enhancements like common sanitation materials and treatments or not, highlighting that this material may be used as a viable alternative in viral contaminations.

20.1.1 Enteric Viruses Need Control

The global need for clean water is a constant challenge as the world population grows exponentially. Enteric pathogens are often found in the water, easily spread via fecal–oral transmission in low sanitation areas. Furthermore, gastrointestinal illness can lead to death if left untreated. Viral diseases are also problematic for crops and not just for humans, acting as many rural populations income. Some types of cultivations, such as cowpea grain or rice, provide low-cost and nutritious food for low-income communities. A wide diversity of viruses affects the agriculture industry, causing an annual loss of millions of dollars. Viruses are the second leading cause of plant diseases after fungi. Some examples are the tomato spotted wilt virus (TSWV), cowpea mottle virus (CMeV), and tomato leaf curl virus (TLCV); in general, diseases caused by a viral agent are far more complex to manage (Aliyu et al. 2011; Florey and David 2012; Zeshan et al. 2018; Bonanomi et al. 2020).

The wastewater reuse for irrigation purposes is applied mainly for plants' services, such as retrieving nutrients. Unfortunately, the spread of pathogens can often occur when untreated or improperly treated wastewater is used. Different strategies have been studied; organic amendments are a material that improves its properties when added to the soil. Many agricultural wastes can be used in this sense; some can even control plant infections (Aliyu et al. 2011; Perez-Mercado et al. 2019).

On the other hand, one of the biggest threats to public health concerns is the human enteric viruses (HuEV). These viruses are fecal–oral and are responsible for several diseases (gastroenteritis, enteric hepatitis, conjunctivitis, meningitis, and others). Some of them, especially rotavirus, are important causes of diarrhea in children in developing countries. According to the World Health Organization (WHO), annually worldwide, 600 million people get ill after ingesting contaminated food, resulting in 420,000 deaths, 125,000 of these covering children under five. Diarrheal disorders are the main burden caused by a large sort of pathogens, being driven primarily by rotavirus, *Campylobacter spp.*, and *Shigella spp.* at 1-year-old children and Shigella *spp.*, *Campylobacter spp.*, and pathogenic *Escherichia coli* at 2-year-old children. Other common diarrheal pathogens include norovirus, *Yersinia spp.*, and non-typhoidal *Salmonella* (Donowitz et al. 2021; WHO 2015).

Environmental contamination of viruses is a severe threat to human and animal health. Viral pathogens need a relatively low dose to start an infection, and because they are very resistant in the environment, they are responsible for several outbreak diseases. Discharges of rural and urban runoff have a vital role in the contamination of these environments. Furthermore, many enteric virus species remain infectious after passing through wastewater station treatments. They may contaminate water supplies and crops. Bacterial monitoring is generally the only microbiological parameter required for attesting water potability and bathing worldwide. However, there is no correlation between bacteria and enteric virus presence (Bosch et al. 2005).

There are over 100 types of HuEV that are present in sewage-contaminated waters, that are capable of causing different types of diseases in humans, that includes hepatitis A and E; gastroenteritis, e.g., norovirus, rotavirus, astrovirus, and adenovirus; respiratory illness, e.g., coronavirus and meningitis; poliovirus; and coxsackie (Bosch et al. 2005).

Bacteriophages are also found continuously in treated and untreated sewage. Since they are not pathogenic to humans, bacteriophages are primarily used in tests as an enteric viral indicator. Bacteriophages MS2 and ϕX174 are the most used for this purpose; ϕX174 has an icosahedral shape and is classified as a coliphage since it attaches itself to the host cell wall. In contrast, MS2 has the same condition but it is called an f-specific bacteriophage to infect the bacterial cell by its sex pili. Different from MS2, ϕX174 has been showing a high rate of adsorption to filter media. Although MS2 studies showed low adsorption levels, it is still considered a suitable model organism for HuEV (Bosch et al. 2005; Molaei 2014).

One of the essential enteric viruses capable of causing health problems in humans is the Mastadenovirus (early called adenovirus), belonging to the family *Adenoviridae*, in which the genera *Mastadenovirus* comprehend the viruses that infect mammals (ICTV 2019), being these eliminated in feces, urine, or respiratory excretions. The early infection occurs in the pharynx mucosa, conjunctiva, and even in the intestinal mucosa, causing different clinical features in the respiratory, gastrointestinal tract, and other organs (Knipe and Howley 2013).

Rotaviruses, another type of enteric viruses, are members of the family *Reoviridae*. Rotavirus A is the main species involved in outbreaks by rotaviruses and is responsible for most diarrhea cases in children under 5 years old. This virus is zoonotic, and it is very stable in manure and animal waste (Knipe and Howley 2013).

Picornaviridae family has three genera (*Enterovirus*, *Kobuvirus,* and *Hepatovirus*) that have species associated with water/foodborne diseases. Enterovirus genus multiplication occurs primarily in the gastrointestinal tract; however, this genus has species that cause infections in other tissues. They may cause gastroenteritis, respiratory diseases, encephalitis, and others, depending on the specific tissues' viral tropism. Among the species that cause human diseases, this genus comprises enterovirus species A–D and rhinovirus species A–C. Rhinovirus causes respiratory diseases (Elrick et al. 2021). The most studied enterovirus (an enterovirus C) is poliovirus, which was the cause of poliomyelitis pandemic worldwide. Aichi virus is a *Kobuvirus* that causes diarrhea, abdominal pain, vomiting, and fever. Several Aichi virus infections have already been reported in various continents, South America, Asia, Africa, and Europe (Rivadulla and Romalde 2020). Hepatitis A virus (HAV) is also a picornavirus, *Hepatovirus* genus, but causes enteric hepatitis. After Norovirus, it is the most frequent foodborne virus associated with shellfish-contaminated consumption (Romalde et al. 2017). Genotypes AI, BI, AII, BII, AIII, and BIII infect humans. The viruses infect small intestine cells and hepatocytes but replicated predominantly within the liver, and disease may run more severely, with fulminant hepatitis, in adults (references). Hepatitis A accounts for half of the global hepatitis infection (Bosch et al. 2005).

The *Norovirus* genus, the *Caliciviridae* family, is responsible for the majority of foodborne gastroenteritis. Several outbreak diseases were reported associated with bivalve mollusks contamination. Because these animals are filter feeders, they retain viruses present in seawater inside their organs. Especially *Norovirus* can persist for a long time in these animals (Guyader et al. 2012). The risk is increased because some species of mollusks are eaten raw or lightly cooked.

Hepatitis E virus (HEV) is another cause of enteric hepatitis. It belongs to the *Hepeviridae* family and causes epidemic hepatitis in low- and middle-income countries. In these places, waterborne transmission is mainly, but in industrialized countries, it infects humans through consumption of meat from viremic animals (Purdy et al. 2017). HEV is a zoonotic virus and can contaminate crops through contaminated manure, mainly with swine waste (feces and carcasses).

Astrovirus is the common name from the viruses that represent the family *Astroviridae*. They are the third most frequent causative agent of human gastroenteritis, especially in young children (Bosch et al. 2005; Fongaro et al. 2015).

These viruses are diverse in terms of their properties since they do not belong to the same family but somewhat different ones. Genome type (single- or double-stranded RNA and single-stranded or double-stranded DNA), capsid

Table 20.1 Summary of the main characteristics of the most relevant enteric viruses with environmental rote

Common name	Family	Genome	Most common disease
Adenovirus	*Adenoviridae*	*dsDNA*	*Gastroenteritis, respiratory disease, and others*
Rotavirus	*Reoviridae*	*dsRNA*	*Gastroenteritis*
Parvovirus	*Parvoviridae*	*ssDNA*	*Gastroenteritis*
Poliovirus	*Picornaviridae*	*ssRNA+*	*Paralysis, meningitis*
Coxsackie A	*Picornaviridae*	*ssRNA+*	*Hand, foot, and mouth disease*
Aichi virus	*Picornaviridae*	*ssRNA+*	*Gastroenteritis*
Hepatitis A	*Picornaviridae*	*ssRNA+*	*Enteric hepatitis*
Hepatitis E	*Hepeviridae*	*ssRNA+*	*Enteric hepatitis*
Norovirus	*Caliciviridae*	*ssRNA+*	*Gastroenteritis*
Astrovirus	*Astroviridae*	*ssRNA+*	*Gastroenteritis*

structure, etc. tend to be quite diverse as there is a wide variety of enteric viruses (Table 20.1).

Rotavirus tends to cause a high mortality and hospitalization per infection in countries undergoing development, while hepatitis A accounts for half of the global hepatitis infection. Such diseases have a fecal–oral route of transmission. This means that insufficient quality water and low sanitized food have an essential role in maintaining these infections (Bosch et al. 2005).

Viral contaminants are generally more persistent to disinfection, and their capacity to adsorb to solid particles protects the virions from inactivating factors (Florey and David 2012; Fongaro et al. 2015). HAV and HEV have persisted for many weeks in the soil (Parashar et al. 2011) since their unique viral features make these particles more resistant to typical techniques of pathogens removal, such as their capacity to adsorb to solid particles, protecting the virions from inactivating factors (Florey and David 2012; Fongaro et al. 2015).

Enteric viruses also can be a bioindicator of sanitary security, being essential tools to guarantee quality water for drinking or even agricultural use. Because of this, some of them were included in the Drinking Water Contaminant Candidate List by the United States Environmental Protection Agency (USEPA) (USEPA 2016). Therefore, developing new methods and tools for pathogen removal, especially on farms and crops, is needed. Manure is a precious source of nutrients, which could lower farm costs. However, viral pathogens' presence in the waste makes its use inviable (Fongaro et al. 2015; Perez-Mercado et al. 2019).

20.1.2 Biochar Uses for Virus Control

Organic amendments improve the soil's physical, chemical, and biological parameters and act as a suppressor against a large microbial diversity, like oomycetes, fungi, and bacteria, which are already known. Still, little information about its activity in viruses is available, especially on an on-farm scale. Also, in biofilters, the addition of organic amendments such as biochar has already been determined a potential enhancer in pathogen removal (Florey and David 2012; Afrooz et al. 2018; Kranner et al. 2019; Bonanomi et al. 2018, 2020).

Some studies suggest that microbiome diversity is one of the primary mechanisms modulating viral removal. Bonanomi et al. (2020), comparing classic soil management (mineral fertilizers and fumigation) with the use of organic amendments (especially biochar) in soil, found that organic amendments were responsible for the change of bacterial and fungal microbiome and also reduced the TSWV infection symptoms in plants. A couple of pieces of evidence suggest that beneficial bacteria can mitigate viral diseases in plants, from *Pseudomonas fluorescens* control TSWV in tomato plants to *Paenibacillus lentimorbus* controlling cucumber mosaic virus in *Nicotiana tabacum* (Bonanomi et al. 2020).

Wang et al. (2013) demonstrated a significant alteration in the denitrifying bacteria population due to N_2O-producing bacteria diminished as the N_2O consumption enhanced, such phenomenon occurred after an amendment with biochar on a composting experiment using pig manure, wood chips, and sawdust. This happened by shifting the microbiome and changing soil features, such as quality in terms of nutrients available to plants, improving the organism growth, strengthening biochemical mechanisms, and increasing the plant resistance to fight off the viral infections (Zeshan et al. 2018). Cui et al. (2016) described a considerable reduction of antibiotic-resistant genes after the application of different kinds of biochar. The authors suggest that the results may correlate with the differential diversity status proportionate by applying the organic amendment, with a decrease in specific taxa of bacteria that can carry antibiotic-resistant genes.

Ye et al. (2018) associated biochar with bacteriophages in the treatment of soil–plant systems. The researchers performed biochar treatment coupled with a polyvalent bacteriophage. They were applied in a soil–lettuce system due to the high amount of antibiotic-resistant pathogenic bacteria and antibiotic resistance genes in agricultural soil–plant systems. They observed that after 63 days of incubation, the amount of *E. coli* K-12 (tet^R), *Pseudomonas aeruginosa* PAO1 ($\text{amp}^R + \text{fos}^R$), and their antibiotic resistance genes decreased significantly ($p < 0.05$), showing very similar results to the ones obtained in lettuce tissues after treatment.

Afrooz et al. (2018) investigated the potential of biofilters amended with biochar to remove human pathogens (such as *Salmonella enterica* serovar Typhimurium and *Staphylococcus aureus*) and the indicators microorganisms *E. coli* and MS2 coliphage. The group concluded that biochar-amended biofilters had achieved better outcomes than sand ones in tests aiming to remove microorganisms from stormwater. The authors also suggest that electrostatic interactions were the mechanisms that proportionate viral removal, with interactions between MS2 negative surface charges and biochar. Unlike the essay mentioned earlier, Sasidharan et al. (2016) found negligible effects on bacteria and virus removal from biochar amended sand. Afrooz et al. (2018) argue that the solution's chemistry can explain this difference. While Sasidharan et al. (2016) used NaCl electrolyte solution, Afrooz and his lab team used synthetic stormwater with natural organic matter. The coliphages' surface charges differ between both studies, and biochar properties are also deviant factors. In other words, physical entrapment in small pore spaces is a factor that can be disregarded for viruses when it comes to biochar since viral particles are relatively smaller than biochar pores (Afrooz et al. 2018; Perez-Mercado et al. 2019; Sasidharan et al. 2016). These conflicting results showed that there is still a need to conduct further research to elucidate the limitations and possibilities of using biochar in pathogen control.

Kranner et al. (2019) noted that biochar amendment of sand biofilters was responsible for improving the removal of fecal contamination indicators; the group compared with sand and biochar-amended sand biofilters during 61 weeks. In this study, F+ coliphage MS2 removal was enhanced by the biochar amendment. The authors discussed that these results agree with another previous analysis, even suggesting that the increase in removal efficiency compared with sand occurs because of biochars' surface area, which is larger than sand, providing additional sites to pathogens attachment. This argument is by the findings of Florey with David (2012). Florey and David found that biochar activated with KOH, which has the most significant surface area, exhibited the most efficacy in pathogen removal. The authors also detected no effect from biochar derived from corn stove pyrolysis in removing MS2 coliphage from PBS when no activation process was done. It was stated that the sorption efficiency could not be attributed only to the measure of the surface area since other variations of activated biochar did not show this pattern; e.g., $ZnCl_2$-activated biochar (surface area 611.15 m^2/g) exhibited more excellent removal than H_3PO_4-activated biochar (surface area 703.78 m^2/g).

Gerba et al. (1975) affirmed that enteroviruses are adsorb in media surfaces with high organic matter presence and low pH. Also, the author observed that poliovirus is removed from wastewater by adsorption on activated carbon, especially at low pH. Soluble organics in the sewage compete with viral particles for adsorption in the activated carbon sites. These experiments used sewage with low organic matter concentration, treated with lime coagulation, or reduced the pH, archiving optimal viral adsorption. The amount of virus adsorbed was 25 times greater in sewage with low pH values than at the level usually found in secondary effluent.

Perez-Mercado et al. (2019) evaluated the effect of biochar filtration as an on-farm treatment for irrigation with wastewaters, measuring the viral, bacterial, and oocystis indicators removal at high hydraulic loading rate and electric conductivity. They found that the removal efficiency was reduced with the increase of the hydraulic loading rate, except for the oocysts. They saw no effect by the electric conductivity, but the results indicate that the effective biochar particle diameter was the principal factor for pathogen removal. The biofilter with biochar was efficient in removing *Saccharomyces cerevisiae* but inefficient in bacterial and viral indicators. The authors suggested that the hydraulic loading rate can be optimized to provide a more efficient microbe removal.

A study conducted by Molaei (2014), which aimed to compare the efficiency of four different types of filters (biochar, bark, activated carbon, and a mixture of bark and activated carbon) to remove viral and bacterial indicator organisms from graywater, found a lower reduction of the viral indicators in comparison with bacteria. This happened because of the size of viral particles, which are smaller than the bacteria. Due to that, bacteriophages have competed for the adsorption sites with bacteria and organic particles, decreasing the chances of viruses being adsorbed. Electrostatic interactions, the isoelectric point of the viruses, and the biochar's specific surface area were also important variables that affect viral removal. Size particles interfere in the number of electrostatic charges. This number is lower when particles are small, ultimately reducing the particle's affinity to the filter media.

Bacteriophage ϕX174 isoelectric point is higher than MS2. This characteristic gives MS2 a more significant amount of harmful charge sites than all filters tested since the isoelectric point dictates the attachment of small-sized organisms (especially those smaller than <60 nm) to the surface of solid particles. Biochar and activated carbon filters showed a relatively high reduction (4 and 6 $\log_{10}$) in the first week of the experiment. After that, a decrease in the retention efficiency of the viral indicators was observed. Activated carbon filters have the most significant surface area, more positively charged particles, and more adsorption-free sites. These characteristics promote better efficiency by this filter than the compared ones. Generally, MS2 had a lower reduction than ϕX174, but the filter followed the same pattern for both bacteriophages. A worrying data is the release of viruses from filters after several days, but not bacteria, implying a risk of releasing viruses in the environment. Complementary studies should be performed to avoid the problem (Molaei 2014).

In some viruses, such as TLCV, biochar was proposed as an alternative to pesticides. In this assay, the group of Zeshan et al. (2018) treated tomato plants with different quantities of biochar, and as a result, they found that biochar significantly diminishes disease severity. Mechanisms proposed for this effect range from improved nutrients to benefits in the change of the soil's physical properties responsible for enhanced resistance in plants due to plant growth and benefits in biochemical mechanisms accountable for plant defenses (Zeshan et al. 2018).

Among the already documented benefits of biochar performance in the crop, there is the ability to increase the pH of soil due to the alkaline characteristics, detoxify allelopathic and xenobiotic substances, improve the soil water holding capacity, and stimulate the growth and development of beneficial microbes, and there are still some studies that report the ability to suppress diseases that affect plants (Jeffery et al. 2011). The biochar can provide porous soil structures that physically protect the microbial colonies from pastors or predators, such as mites, protozoa, collemboli, and nematodes (Bonanomi et al. 2020).

The effect of biochar amendment on the extent of bacterial retention has been observed to depend on the type of biochar and soil. For instance, Abit et al. (2014) examined the effect of biochar addition on the transport of bacteria in sand and soil columns. They observed that soil texture chronically affected bacteria recovery percentages, with lower bacterial retrieval in sandy soil than in fine sand. For the uncorrected treatments, the recovery percentages of both bacteria (*E. coli* and *S. typhimurium*) in the sandy soil columns was 3.3 orders of magnitude lower than in the fine sand columns (Abit et al. 2014). This can be explained due to the presence of exposed positively charged groups at the edges of the clay crystals, causing the negatively charged bacteria to be attracted (Fletcher and Loeb 1979).

During a study carried out by Aliyu et al. (2011), it was possible to state that a rice husk, grounded into powder, can control diseases that affect cowpea, a food crop essential to the subsistence of the communities through West Africa. The cowpea plants, infected with the cowpea mottle virus, had increased growth and yield when the soil was previously treated with rice husk powder. This result is an excellent indicator that the rice husk powder can be used as a soil corrective to improve growth, productivity, and suppression of viral diseases in infected cowpea plants. This effect is possibly due to a competitive advantage of plants that grow in corrected soils characterized by increased photosynthetic activity.

Besides all the benefits as mentioned above and positive effects for plants in agriculture based on the use of biochar and biochar-amended biofilters to provide drinkable clean water, besides other uses, data is still limited to lab scale. Evidence of on-farm viral removal is still insufficient to say that the outcomes collect in lab-scale studies could be translated to a large scale situation, especially when considering some data that found a significant amount of microorganisms remaining, which can lead to unintentional contamination of the environment and population (Kranner et al. 2019; Perez-Mercado et al. 2019).

20.1.3 Enterobacteria and Environmental Control

With the advance of the human population, the food production process needs to expand to meet demand. The growing need for more food results in the accelerated conversion of natural landscapes into cultivated fields and pasture areas. Accompanying the growth of areas aimed at raising cattle, swine, and poultry, there was also an expansion in the volume of waste generated, with thousands of liters of waste containing remnants of antibiotics, hormones, and enteric microorganisms being produced daily. Without planning for the correct waste destination and treatment, these contaminants are discarded in the soil. The contact with the water used to irrigate the fields or wash the farm will direct them to the surrounding springs and water bodies, contaminating the whole water system. As they are infiltrated through water into the region’s soils and water sources, contamination by pathogens becomes challenging to be treated, as the source of contamination will not be at a specific point, occurring in all places of contact with water bodies (Abu-Ashour 1994).

Enteric bacteria that compose these animals’ intestinal microbiota usually have resistance to the environment’s unfavorable conditions, remaining stable for an extended period outside the animal tract. Thus, when incorrectly disposed of in soils, the bacteria present in these wastes will contaminate groundwater and other sources, causing risks to all organisms that depend on this water source. According to the data from the WHO, approximately 500 thousand children under five die each year from diarrheal diseases, such as gastroenteritis caused by enteric bacteria, being the second causer that kills the most children of this age group (WHO 2017).

The *Enterobacteriaceae* family is the most common gram-negative bacteria that affect the intestinal microbiota of humans and animals. Although some species are found harmlessly inhabiting the human intestinal tract, such as *E. coli*, in an immunocompromised person, physical integrity can increase the bacteria number, generating infection even by nonpathogenic strains. When colonizing the intestinal tract, the most at-risk species are classified as enteropathogenic and are represented by the genera *Salmonella*, *Shigella,* and *Yersinia* (Santamaría and Toranzos 2003).

Salmonella is a genus of enteric bacteria with worldwide distribution. It comprehends a large number of serotypes with different specificities capable of infecting a wide variety of hosts. In addition to being one of the leading causes of intestinal diseases worldwide, it is an enterobacter that is capable of generating more compromising conditions, such as typhoid and paratyphoid fever. Like other enteric bacteria, *Salmonella spp*. is disseminated through the fecal–oral route by ingesting contaminated water and food, demonstrating the importance of ensuring that the water sources used to supply residences and agricultural demand are following the bacteriological quality standard. This microorganism is frequently found in the environment, reaching water sources directly, through the contact of contaminated human or animal feces, or indirectly, through the incorrect disposal of urban sewage. Salmonella's presence has already been detected in different water sources, such as rivers, lakes, beaches, aquifers, and even in waters that have already undergone the treatment process. Due to its frequent presence in environmental samples, the consequences of infections in humans, and its high capacity to survive outside the host and to form biofilms, bacteria of the genus *Salmonella* are a significant health concern (Levantesi et al. 2012).

As well as *E. coli*, bacteria of the genus *Enterococcus* are also usually present in human and other animals' intestinal tract and are excreted at high rates in the feces. Due to its high excretion rate, a frequent presence in the environment, and relation with human health issues, its presence in water sources is a reliable indicator that contamination by wastes is occurring and, consequently, by other enteric organisms that may be pathogenic (Boehm and Sassoubre 2014). Bacteria of the genus *Shigella* are genetically related to *E. coli* and *Salmonella* and can cause similar pathologies. Enterobacteria is also transmitted through the fecal–oral route, and the development of the condition known as Shigellosis starts from a low infectious dose. It can generate severe cases of inflammatory diarrhea (Lampel and Maurelli 2003). These are just a few examples of enteric pathogens present in contaminated water and food, representing a risk to the population's health. This data demonstrates the necessity to prevent these enteric pathogens from reaching water sources or soils destined for food cultivation.

The transport of these microorganisms across the soil surface to underground layers will depend on several factors, such as the soil's physical and chemical properties and the interaction with the presence of other microorganisms. One of the main properties that influence the infiltration of bacteria by the soil is related to its texture. Depending on the size of the particles that make up the soil, it will have a more compact or lighter structure, generating differences in the transport flow of these pathogens through their layers (Abu-Ashour 1994). In the same way that the soil characteristics influence the transport of bacteria, it can facilitate the contamination of water sources. Management techniques that alter the soil qualities will affect this transport and dissemination, preventing these pathogens' displacement.

With the transformation of natural landscapes into urban areas full of buildings and facilities, the advance of waterproofed soils over the spaces remains with vegetation. The compaction and waterproofing generated by the construction of roads have adverse effects on rainfall. By preventing water from infiltrating and spreading through the soil, it causes the rainfall to be carried to water bodies taking all the roads' pollutants. The retention systems perform as a solution to improve urban areas' flow and overcome problems such as floods and water source contamination. These systems are made up of mixtures of sand, soil, husks, and other compounds that promote rapid water infiltration into the soil. They also act as biofilters, retaining microorganisms contained in soils or infiltrated waters. However, there is a need for further development in biofilters, as they have limited efficiency in removing enteric bacteria, such as fecal coliforms. Still, some filters carry out the mobilization of bacteria, but that do not succeed in retaining and releasing these pathogens back to the soil when there is a flow of infiltrated water (Mohanty and Boehm 2014).

20.1.4 Biochar Uses for Enterobacteria Control

One of the most used bioremediation techniques of contaminated soil and water is activated carbon, whose adsorbent properties remove the contaminants present in the environment. A more profitable management alternative is the use of biochar as a removing agent because although it is also a porous structure composed essentially of carbon, the raw material used in its production is abundant and has a low cost, with alternatives such as crop residues, animal waste, forest residues, remnants of paper mills, food production, and sewage sludge (Cantrell et al. 2012). Other advantages of using biochar are the need for lower temperatures for organic matter degradation compared with activated carbon and not needing to undergo activation processes. However, despite having a more accessible production than activated carbon, the biochar's physical and chemical properties will influence its operation in removing contaminants.

An alternative to improve these systems' retention capacity is the inclusion of biochar in biofilters, as they can remove, in addition to fecal coliforms, heavy metals, and organic contaminants from contaminated soil water. Mohanty et al.'s (2014) study of the *E. coli* removal capabilities of standard filters and filters implemented with biochar demonstrated how the water decontamination rate could be improved with biochar's addition to the filters. Inoculating water containing *E. coli* in different filtration systems, Mohanty et al. obtained 95 ± 1% removal of the pathogen using sand filters implemented with 30% biochar. By inoculating the same contaminated solution in filters composed only of sand, the removal of *E. coli* dropped to 35 ± 6%. Therefore, this study demonstrates the improvement in pathogen removal generated by the inclusion of biochar in the filters that compose the bioretention systems.

However, as already elucidated, the properties of the biochar and the characteristics of the matrix where it will be applied interfere with its efficiency, requiring previous studies to establish which method best relates to the desired application and thus obtain better results in removal of contaminants (Mohanty and Boehm 2014).

Biochar acts as a filter through its porous structure, retaining microorganisms that came into contact with the material. The efficiency of the system will depend mainly on the adsorption capacity of the material composing the biochar. Still, its functioning will also be influenced by organic origin issues, such as biofilms' formation and structural origins, such as the surface area and the pores' size and distribution. The presence of biofilms in the biochar composition can simultaneously generate advantages and disadvantages. Simultaneously, they change the standard pore diameter, increasing the variety of bacteria and viruses that the biochar will retain, thus improving its role in removing contaminants. It can also create an ideal environment for the growth of enteric bacteria, whose replication can increase the environment's contamination rates. In addition to including heterogeneity in the pore diameters, biofilm formation also changes the patterns that influence the water flow's hydrodynamics infiltrated into the biochar. One of the main components that characterize biofilms is extracellular polymers, substances that can change the texture, hydrophobicity, and electrokinetic properties of biochar surfaces. These biochar structure changes will affect the relationship between the contaminating organisms and the adsorbent pore, thus changing the efficiency in removing pathogens. The biofilms in the biochar are only advantageous when the biofilm's growth is contained, as the accelerated colonization will reduce the adsorption process until the biochar loses its bioremediation property (Afrooz and Boehm 2016; Perez-Mercado et al. 2019).

Despite the increasing demand for biochar used as bioremediation of contaminated areas, most studies still focus on evaluating the properties and effectiveness of this system in soils, with few studies related to its application in water sources, sewers, and treatment plants. When it comes to disinfecting water sources, the main techniques used still are chlorination and ozonation, which are methods that generate chemical residues such as trihalomethanes (THMs), haloacetic acids (HAAs), formaldehyde, and acetaldehyde, products known to be carcinogenic to human and toxic to the aquatic environment and the species involved (Park et al. 2016). The use of biochar is an alternative that presents less risk to the environment, being a sustainable method of removing enteric pathogens and other contaminants from water sources. One way to use the wastewater produced daily is to apply it to irrigation, providing water and nutrients for cultivated plants. However, wastewater often contains pathogens that can remain viable for a long time outside a host and represent a risk of contamination by consuming food irrigated with this water.

Depending on the purpose for which the biochar application is intended, the association with other compounds can increase the system's efficiency in removing various contaminants, both organic and inorganic. The antibacterial copper capacity has already been elucidated through several studies. Still, its direct application as a treatment agent for contaminated environments presents impasses mainly in its subsequent removal from the treated environment (Dankovich and Smith 2014).

The application of metal derivatives for decontamination generally occurs by handling particulate material, making it difficult to remove after treatment and can cause health problems for the population that consumes these waters. The frequent aggregation of copper particles in a liquid medium is also responsible for reducing the removal process' efficiency that impairs water quality recovery. In addition to its antimicrobial action, copper oxide, like iron oxide, also attracts attention due to its ability to remove arsenic from groundwater, a highly toxic compound in its inorganic form (Goswami et al. 2012; Hao et al. 2018). Metal oxide nanoparticles are produced at a low cost due to their availability in the environment. Their physical and chemical properties, such as the presence of a large adsorbent surface area and functional groups for the binding of toxic ions, make these compounds essential allies in the bioremediation of soils and waters contaminated by chemical enteropathogenic bacteria. Studies that explore the effects of biofilters with metal oxides show promising results in the production and application of this filtration system. Because it is a stable material and insoluble in water, biochar is the right candidate for accommodating metal particles. Its easy separation of residues from the treatment process solves the issue of removing nanoparticles from the environment and presenting reasonable rates of reduction of the two classes of contaminants (Priyadarshni et al. 2020).

The Nivedita Priyadarshni experiment was conducted using biochar derived from rice husk, posteriorly treated with solutions of iron chloride ($FeCl_3$) and copper chloride ($CuCl_2$). During the biochar incubation with its respective solutions, the content was slowly agitated to produce iron and copper oxide nanoparticles using the coprecipitation method. To evaluate the improved biochar's efficiency in removing contaminants, a mixture of the biochar under both treatments was brought into contact with solutions using natural groundwater containing coliforms and over different concentrations of arsenite and arsenate. The adsorption of pollutants by treated biochar occurred quickly, reaching 95.3% removal of substances composed of arsenic in 60 min. To evaluate the effect of the biochar in removing bacteria, water samples were inoculated on agar plates before and after treatment. While the plaque referring to the contaminated samples showed the growth of 13 bacterial colonies, the plaque with treated water inoculum indicated only one colony present, which means an insignificant bacterial contamination rate in the water. The colonies of both plates were tested to determine the bacteria's nature through a traditional gas production test in Durham's tube containing lactose broth. The bubble production indicated that they were coliform bacteria. The recovery of the biochar implemented with metal oxides was tested by washing the residues from the treatment process containing the retained arsenic with alkaline water and sodium chloride solution, obtaining a significant recovery of the biochar five washing cycles. The possibility of recovering the biofilter and the metal oxide nanoparticles guarantees the decontamination of the medium, including the remains of the products used in the treatment process, in addition to reducing implementation costs. Through images performed by field emission scanning electron microscopy technique, it was possible to conclude that the improvement in the adsorption of contaminants generated by the association with the nanoparticles of metals was due to a greater volume of pores and the greater surface area acquired after the treatment (Priyadarshni et al. 2020).

From studies such as Priyadarshni's, it is possible to show how the development of filters that associate materials with limited decontaminating capacity can increase the rate of pollutant removal in general, being more efficient than when applied individually. The removal of 92% of bacteria and 95.3% of arsenic compounds from a natural water sample demonstrates how two different filtration systems' adsorption properties can be combined to improve their productivity and achieve better results in retaining compounds frequently associated with environmental pollution. In addition to presenting consistent results in eliminating undesirable substances and organisms, the association of biochar with metal oxides solves the recovery of the material after treatment. When nanoparticles are attached to the structure of the biochar, the metal oxides are quickly recovered. The possibility of reusing the filter on other occasions can also positively affect treatment cost, generating applications in other contaminated areas. Just as other studies have already evidenced the antibacterial action of copper, there are antimicrobial compounds that in association with stable materials such as biochar can generate an increase in the efficiency of the system, thus developing appropriate methods for bioremediation of environments with different contamination profiles (Priyadarshni et al. 2020).

The advantages of applying biochar as a tool for bioremediation of contaminated environments include economic factors, through the low cost of raw materials used in its production; environmental factors, as it is a biodegradable resource that sequests atmospheric carbon; and practical issues, such as diversity of applications that can be benefited through management using biochar. The residues containing enterobacteria that jeopardize the quality of water and soils and the surrounding ecosystem's integrity come from waste related to agricultural activities and homes, industries, and businesses. The use of biochar is a viable application in various treatment systems and is a cost-effective option that reduces decontamination costs. Therefore, the possibilities of using biochar surpass its use as bioremediation in contaminated environments and can also be applied in treatment systems, guaranteeing water quality as to the presence of enteric pathogens, and in drainage systems as a solution to soil waterproofing in urban centers.

20.2 Environmental Challenges and Use of Biochar: Case Studies

Many countries still rely on the road system as the primary means of transporting people and cargo, which implies a gradual increase in the need for paved roads and the extension of the territory to meet the growing demand for fast and reliable transportation. Despite significant importance in the national economy, road construction also creates disadvantages, especially for the environment. The land needs to be compacted for the construction of roads, which results in the removal of local vegetation and the consequent interference in the regional environment diversity. After being opened and compacted, the roads are produced with waterproofing substances, which, together with the lack of vegetation and soil settlement, will generate impacts on the region's rainfall. The number of vehicles related to individuals who use the road system daily implies an increase in the amount of waste and pollutants discarded on the highways. When coming into contact with rainwater, these wastes will end up being washed to water bodies due to the waterproofing of roads and compaction of the surrounding soils. In addition to increasing the volume of organic matter and waste in these water sources, these pollutants may contain residues of feces, carcasses, and other wastes, containing pathogens such as viruses and bacteria, representing a risk of contamination (Cambi et al. 2015).

Aiming to reduce the impact of soil sealing by roadway constructions, road border filtration systems are being developed to improve rainwater drainage and filter the pollutants carried by the infiltrated water. These structures are biofilters, composed mainly of a mixture of soil, sand, and carbon-rich compounds in proportions that will depend on the desired application. One of the main challenges of implementing these biofilters for rainwater drainage from roads is soil compaction, related to the prevention of landslides and traffic accidents, but negatively influences water infiltration. When added together with the biofilter, certain materials can reduce soil compaction on water infiltration and increase the efficiency in removing contaminants, as is the case with biochar. To evaluate the differences in the efficiency of *E. coli* removal in sand filters and sand filters implemented with biochar and the impact of compaction on the filters, the researcher, Maryam Ghavanloughajar, carried out an experiment testing the removal of the infiltrated contaminant in the two systems of biofilters (Ghavanloughajar et al. 2020).

In the Ghavanloughajar experiment, biofilters were kept in containers with a column shape and hollow bottom, where mixtures of biochar, sand, and garden compost were kept. Periodically, a solution of artificial rainwater inoculated with *E. coli* was added to the top of the columns, and a sample of the residue that dripped down was collected. In addition to analyzing the functionality of retaining contaminants from biofilters with and without biochar, soil compaction was also analyzed about the effects on the degradation of biochar particles. The results showed that removing *E. coli* was increased in the biofilters that contained a consortium of biochar and sand and pointed out a greater efficiency of the biochar in compacted biofilters. This factor can be attributed to a greater surface area for microbial adsorption created by breaking and simplifying the biochar particles, as shown in Fig. 20.1. The functionality of the biofilter was, once again, maximized in columns that contained the mixture of biochar, sand, and compost because, in addition to generating a more efficient removal of pathogens, the compost increased the flow rate and water infiltration. Thus, the experiment proved how the association between different materials and biochar could improve the efficiency in removing pathogens and generate the possibility to customize this tool's use to best suit the remediation situation (Ghavanloughajar et al. 2020).

The use of biochar amended filters for water treatment on a full scale implies the inclusion of several factors that must be considered. Stormwater produced in laboratories for use in experiments does not contain the same properties as natural

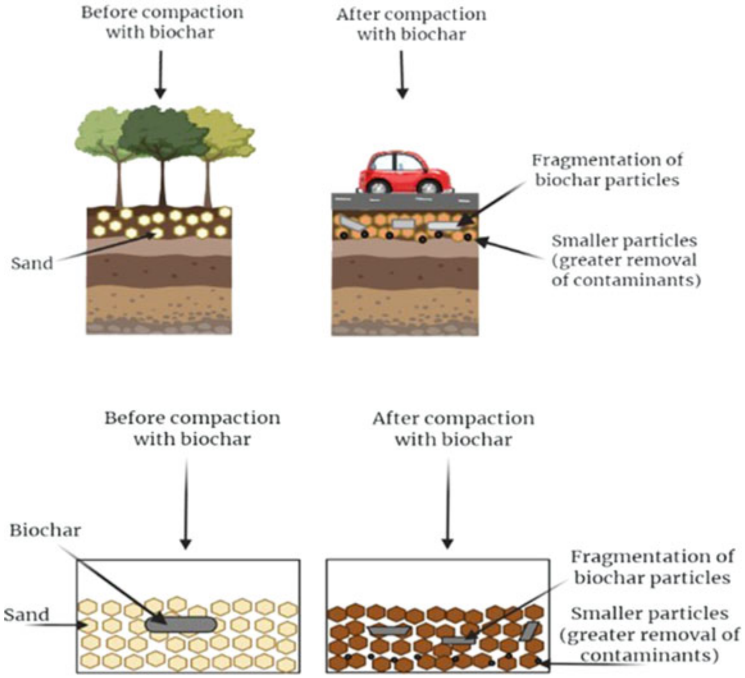

Fig. 20.1 Effect of compaction on the efficiency of removing contaminants in associated filters

stormwater and has chemical pollutants and microorganisms in its composition. At the same time, rain still transports contaminants present in the soil. Therefore, what will be filtered by the bioretention systems is water with a considerable content of organic matter capable of competing with the enteric pathogens present in the adsorption sites of the filters (Mohanty and Boehm 2015; Kranner et al. 2019).

Conventional biofilters are usually based on either compost or sand sources and are widely used due to the relatively low price, easy manufacturing, and overall great disponibility. However, such filters alone do not provide a reliable removal of bacteria and viruses on a scale that allows safe use of the wastewater after filtration. More importantly is that even if such utensils can filter most of the high size pathogens, such as bacteria and amebas, a small contend of living bacteria can be enough for the wastewater to be considered as the untreated source by federal health organizations that manly analyze the bacterial content of the liquid medium. This is even without considering the low retention that these filters can offer in treating viruses' particles usually accounted for in sanitation regulations (Afrooz et al. 2018).

Standard sand filters amended with biochar powder were used in the treatment of typical, not as highly organic mass dense, water sources like stormwater, as was observed in the study realized by Afrooz et al. (2018), which previously measured for *E. coli*, *S. typhimurium, Staphylococcus aureus*, and MS2 coliphage. Compared with standard sand filters, biochar powder's addition achieved retention over nine times higher than that of the target bacteria and three times higher than that of the MS2 bacteriophages. This method not only is a cheap and straightforward method to enhance the filtration capability using highly accessible biochar materials that allowed a dramatic immobilization of bacterial pathogens but also exhibited significant retention of smaller structures such as viruses, possibly implying a useful and accessible way to amplify the retention of different viral families, which usually escape most filtration methods.

The characteristic of hydrophobic nature of the biochar appeared to be responsible for a significant part of the attraction between the material and the bacteria, for the rate of removal matches the hydrophobic nature of each bacteria, being *Staphylococcus aureus* the most hydrophobic, and therefore, the one that showed more significant adsorption in this study, followed by *S. enterica* and then *E. coli*. Such characteristics may also explain the increased adsorptive rate of viruses after biochar application. Such organic material's hydrophobic and electrostatic properties may enhance the entrapment of even small viruses like MS2. Fine particles of the biochar for the amendment in sand filters also appeared to have allowed a hydrophobic attachment and straining, facilitating pathogens' removal. However, one must beware that finer particles can clog the filtering mechanism. Therefore, such conjunct technology may still require further observations and improvements (Afrooz et al. 2018).

The experiment by Perez-Mercado et al. (2019), aiming to recreate a model of farming wastes treatment, used hardwood biochar-based filters to achieve a significant difference in the reduction of bacterial and viral pathogens (such as *E. coli, Enterococci* spp., *Bacteriophage MS2, Bacteriophage ϕX174,* and *Saccharomyces cerevisiae*). Such a decrease was mainly attributed to the particle diameter of the powdered biochar, with the smallest diameter of 1.4 mm, compared with the highest of 5.0 mm, which achieved an overall more significant reduction of bacteria and viruses. In this study, the *ϕX174* bacteriophage significantly reduced the treatment compared with the MS2 virus. Such a difference in the removal rate can be again attributed to the different isoelectric points and hydrophobicity. Another issue that may heavily influence the filtration potential in these systems is the hydraulic loading rate (HLR), which was the most determinant factor in the retention potential than the biochar diameter when the first one was present at higher levels ($\geq$200 L m^2/d), reducing the adsorptive potential when compared with lower levels (34 L m−2 d−1). This influence is implied due to the high flow of matter, impairing the contact time between biochar and pathogen, for the flux of medium is too intense for the electrostatic interactions to form between the pathogen and subtract. Therefore, a low HLR would allow a more significant surface contact opportunity between particles, resulting in an increased adsorptive rate. Similar to how the lower diameter of biochar particles grow the surface area and pores, causing an increase of adsorptive sites for planktonic pathogens, lower HLR levels increased the absorptive surface by allowing biofilms to form, allowing the retainment of pathogens, and increasing the probability that such pathogens may interact with the adsorptive sites. In this way, viral and bacterial removal may be impaired in systems with high HLR, requiring thin powdered biochar to compensate for the lost adsorptive potential if aimed at high demanding treatment systems (Perez-Mercado et al. 2019).

Another factor disregarded in laboratory experiments is the probable formation of biofilm in the filtration systems, considering that microorganisms' deposition is facilitated through the water flow. The appearance of biofilms in filters modified with biochar can increase or diminish its efficiency in removing pathogens, and its consideration in a large-scale application is fundamental (Mohanty and Boehm 2015; Kranner et al. 2019). In addition to the rate of organic matter in rainwater and the probability of biofilm formation and issues often overlooked in filtration tests, biochar's behavior when in alternate irrigation and drought regimes should also be included in the analyses approaching a natural rain cycle. The intermittent flow of water will reflect on the retention of microorganisms, as pathogens trapped in the biochar pores during the drought period can be detached during the next flow of water. Despite the significant effect of the interspersed flow cycle, most experiments still base their results on tests with a continuous flow of water, thus moving away from the actual application conditions. When considering these three factors, the content of organic matter, formation of biofilms, and regime interleaved between rains and droughts, it is possible to verify the authentic effectiveness of these bioretention systems in removing pathogens on a full scale (Mohanty and Boehm 2015; Kranner et al. 2019).

Considering these factors related to the large-scale application of bioretention systems, better results of removing enteric pathogens in filters amended with biochar are still obtained compared with standard filters composed of sand. To simulate the use of this filtering and decontamination model in the environment for which it was developed, with good long-term performance, simple sand filters and sand filters in conjunction with biochar in a 2:1 ratio went through about 60 weeks of tests under an intermittent water flow regime. The water used, unlike most experiments, was not artificial water produced in the laboratory but natural stormwater implemented with wastewater. The indicator of fecal contamination used was *E. coli*. Even competing with the high rate of organic matter present in the stormwater used, the biochar's porous surface still obtained better results in removing the bacteria than ordinary sand filters. After the testing period, the filters were deconstructed to make it possible to seek a formation of biofilms and determine whether their presence influenced the filtration system's efficiency (Kranner et al. 2019).

Similarly to this study, another experiment further analyzed biofilms' influence in retaining bacteria in an artificial porous structure filled with glass beads. The retention of *E. coli* was higher when the porous material was covered in the naturally formed drinking water biofilm. The biofilm also expressed significant retardation in adrift bacteria's movement, as these have the activity slowed down by covering organic matrix. The cells immobilized or retarded by the structure remained in the filter system longer. Therefore, the cells were more likely to be immobilized by the pores and other reactive surfaces of the material (Bauman et al. 2009). In that case, the presence of biofilm in a biochar filtration system may not always be considered a liability and treated as a typical "dirt" clogging the mechanism, primarily if the present biofilm consists of a nonpathogenic organism like a free water bacteria. Such organic structures may, in numerous cases, indeed help the immobilization and assist in biochar retention mechanisms, being a viable asset in pathogenic control.

Biofilm influence in the retention of microorganisms is not restricted to bacteria. Biofilm-covered spheres, for example, achieved noticeable retention of 28B *Salmonella* bacteriophage together with *Legionella pneumophila* bacteria in pretreated drinking water by Långmark et al. (2005). Granting a persistence for over 38 days of the contaminants in the organic matrix, allowing for the contaminated biofilm to be discarded and, by doing so, removing an expressive amount of a target virus. Also, an insight that a biofilm's colonization in a determined surface is based on the biofilm characteristics and surface structure. One must know the particular features of both factors for the functional biochar surface to maintain strong interaction with the polysaccharide biofilm matrix's specific traits. For example, in this study, it was noticed that the subtract's physicochemical properties showed a more significant influence in the adsorption of pathogens than the biofilm density, having hydrophilic spheres demonstrated more excellent retention than hydrophobic ones.

However, biofilm-enriched biochar filters have also been shown to decrease the overall adsorptive potential in some studies. In an experiment by Afrooz and Boehm (2016), biochar amended sand filters, as was previously expected, allowed more retention of *E.coli* compared with regular sand filters; however with the presence of *Pseudomonas aeruginosa* biofilm matrix, the effect of these two types of filters was the opposite, with sand filters exhibiting a significant increase in the retention of *E. coli* when enhanced with a biofilm, while the biofilm–biochar presented a decrease in the absorptive capability. Due to the large surface area, rough, porous structure, and higher hydrophobicity compared with sand, the biochar material's unique characteristics were also attributed to the higher retention and biofilm density in biochar amended sand filters compared with regular sand ones.

Biofilm presence may act as a surface enhancer by increasing the reactive sites for anchoring planktonic bacteria, especially in sand substrates, which have an overall lower area than biochar. However, this mechanism can be negligible in biochar systems. The material's extensive surface is not significantly increased by adding a few reactive sites to be considered a noticeable percentage. In fact, due to no small part of the reactive surface is based on the porous structure, that potential can be diminished by the incorporation of a biofilm, for the matrix impregnation in the porous may decrease the attractive sites to planktonic bacteria and the porous offer a considerable amount of adsorptive sites (Afrooz and Boehm 2016).

In an insight of the interactions that rule over the particles and the biochar surface, the biofilm matrix may also reduce the hydrophobicity of the material, reducing the *E. coli* retention. The hydrophobicity of *P. aeruginosa* biofilms appears to be lower than the hydrophobicity of the biochar surface, possibly explaining why biofilm improved the retention potential in sand filters but decreased in biochar-sand ones. Also, Afrooz and Boehm (2016) highlighted the interference of organic matter in stormwater filter systems. In this study, biochar's presence showed a different performance with "natural organic matter" (NOM), added in the filter medium to simulate high organic loaded stormwater. Without the presence of NOM, the sand filter had a more excellent retention performance than with the NOM addition.

However, in biochar–biofilm filters, the NOM presence indicated no alternation in the bacterial immobilization, being underperformed by the regular sand filters in both cases.

In virtue that the biochar material can be created using different substrates, pyrolysis and additional treatments are essential to remind that these factors can result in other properties. By that, they offer a contrasting behavior against the same contaminant. An experiment by Dalahmeh et al. (2018) resulted in distinguished grades of adsorption of certain pharmaceuticals, comparing the use of biochar amended sand filters and regular sand filters with and without the presence of biofilms, similar to the method used by Afrooz and Boehm (2016). In this study, carbamazepine was efficiently filtrated by biochar and biochar–biofilm treatments, with a slight increase in non–biofilm treated filters, possibly due to the compound's nature. It does not allow it to be easily biodegraded, as observed for the low retention of the non-biofilm sand filter (31–46%). Also, the high adsorptive area of the biochar was efficient in the retention of metoprolol regardless of the presence of biofilm (roughly 95–99% reduction), while sand filters struggled to obtain similar results (36–73%), demonstrating that the biochar's high adsorptive potential is not disrupted by the presence of biofilm in the retention of certain substances. For proper use of this technology, the characteristics of both material, contaminant, and biofilm (if present) must be previously selected based on the reactive attraction among these factors. Such regards should also be applied in viruses' adsorption since little literature covers the most efficient viral retention strategy based on the biochar characteristics, even without biofilm.

In an insight of these characteristics, it is essential to presume the biofilm's duality as a biochar enhancer. For one, such material may act by improving the efficiency by removing microorganisms. Simultaneously, its presence adds variety in the pores' diameter present in the biochar, increasing the size range of the organisms that will be retained. However, the biofilm's excessive development can alter the biochar properties, such as texture and hydrophobicity, thus reducing the removal effectiveness (Afrooz and Boehm 2016; Kranner et al. 2019).

Considering the influence of factors related to the large-scale application of filtering systems implemented with biochar, it is still possible to obtain greater efficiency in removing pathogens than standard filters. Biochar is an accessible and environmentally friendly material, and its association with standard filters can improve the retention of pathogens even when considering issues such as the rate of organic matter present in stormwater that seeps through the roads, the effectiveness of these systems in the long term, and the effect of biofilm formation on filtration systems. As more experiments are developed focusing on this system's practical application, it will be possible to get closer and closer to the real inclusion of this material in water treatment and other possible uses (Afrooz and Boehm 2016; Kranner et al. 2019).

20.2.1 Biochar Enhancement

Porous adsorbent materials, such as the termically treated organic materials denominated as biochars, hold a capacity of high microorganism immobilization due to surface adsorption and entrapment of particles in the interior of their porous. Such interactions are ruled by physical phenomena like electrostatic attraction and van der Waals forces, which can retain a distinguishable spectrum of particles based on the nature of the interaction and the contaminant's physical and chemical properties as any physical and chemical phenomenal; such range of interactions can have their intensity amplified or diminish based on the chemical conditions of the material in question and the present medium, being the attractive potential directly influenced by the pH of the material or medium, ionic force, temperature, and the presence of ionized metals (Sasidharan et al. 2016).

Furthermore, due to biochar being a primarily low-cost and green material, additional adsorption capability modifications can be highly valued or even necessary to replace standard water purification substances on an industrial scale. Such adsorptive properties can be further modified and dramatically amplified by controlling the conditions that rule the attractive process and the addition of external modulatory materials that can interact with the biochar compound and increase the overall adsorptive potential, like the addition of standard sand filters mixed in the biochar substrate. The process aiming to increase the relevance of biochar further subtracts in high demanding purification systems by the use of external materials, or substances can be defined as an enhancement, for it "enhances" dramatically the adsorption capability of the biochar by achieving a higher particle immobilization potential (Sasidharan et al. 2016).

The enhancement of the biochar structure can dramatically change its properties, and more importantly, change the overall function to a specific target contaminant or particular use, for the primary appeal of the material is based on the general cost of production and surface properties, which can extend or constrict one's application. Such additional variations allow a better all-around performance against a specific range of subtracts or compounds, either metals, pathogens, or even interactions, aiming to increase crop production and improve the soil, as previously mentioned. The enhancement factors are based on chemical and physical alterations or addition of reactive materials, such as ionized metals, influence the fundamental properties that give the biochar its adsorptive nature, such as their reactive surface area, porosity, pH, and presence of interfering substances that can change the material interaction with specific functional groups. The amendment addition of importance, or even environmental conditions, that results in, for example, an increase of cations or anions in the adsorptive surface can result in a higher affiliation to metal ions, allowing a greater use in the removal of heavy metals. These treatments can occur before, during, or after the pyrolysis step that results in the final commercial biochar, and overall, they are as affordable as the biochar itself. One of the main advantages of using these reactive materials and biochar remains the lower cost compared with other industrial sanitation products (Premarathna et al. 2019).

Biochar characteristics such as surface area, surface activity, porosity, and physicochemical stability can vary mainly depending on the feedstock used in the char production (different organic materials like crop residues, wood, municipal waste, sewage sludge, and manure; the majority of which are considered waste), a pyrolytic temperature which usually occurs at a range of 400–700 °C, heating rate, reaction media, and residence time (Premarathna et al. 2019). These variations can affect the efficiency of the pathogen removal and take pyrolysis temperature; for instance, higher temperatures tend to produce biochars with greater surface area, elevated pH levels, higher ash contents, and lower total surface charge; all of those characteristics could reduce or even enhance the removal efficiency (Bolster and Abit 2012; Sasidharan et al. 2016).

Bolster and Abit (2012) tested if biochar produced from two different temperatures would react in distinct ways to reduce the amount of *E. coli* transported in sand and soil columns. When added a high-temperature poultry litter biochar to the fine sand, they observed that the result was a large increase in the *E. coli* retention, showing that the biochar pyrolysis temperature is one of the various characteristics of the biochar that can influence the pathogen uptake. When these soils were corrected with biochar, it was possible to observe that when adding high-temperature poultry litter (HTPL) to the fine sand, there was a reduction in the *E. coli* recovery percentages by 1.8 orders of magnitude. Besides, low-temperature pine chip (LTPC) and high-temperature pine chip (HTPC) biochars decreased by approximately 2.0 and 2.5 orders of importance in the recovery of *E. coli*, respectively. For *S. typhimurium*, the addition of HTPC reduced the recovery percentages by 2.2 orders of magnitude. The results on the effect of adding biochar on bacterial transport in the sandy clay were visibly different. The low-temperature poultry litter (LTPL) biochar to the sandy clay increased recovery percentages by more than three orders of magnitude for both microorganisms. The mixture of HTPL biochar with sandy clay caused a sharp increase (almost three orders of magnitude) in the *S. typhimurium* recovery percentages (Abit et al. 2014). These results indicate that retention of microorganisms may occur differently due to changes in pores, water chemistry, or soil surface properties after biochars' addition (Bolster and Abit 2012).

Being one of the main biochar qualities, the overall low cost and sustainable nature of the material, such organic compound, has an increasing demand and interest in strategies of cheap and "green" removal and treatment of contaminated sources, whether those are with toxic levels of metals and pharmaceuticals compounds, or by rapid spreading pathogens. Compared with most of the active carbon materials, however, the smaller surface area, lower porosity, and negative influence of biotic and abiotic processes in the proper function of the biochar make the material less than ideal in removing pathogens and other contaminants. Further, amplifying the relevance and search for additional enhancements methods, aiming to improve biochar capabilities in the retention and inactivation of these contaminants. Being the temperament or soaked with different metals and acidic or alkaline compounds, one of the most common strategies to increase the overall adsorptive area, and by that, increase the availability of interactive parts of the material with the target particle (Premarathna et al. 2019).

With metals or ionized metallic compounds, the treatment usually results in impregnation of the biochar surface, providing a more reactive adsorptive area, generally archiving such structure by soaking the biochar base with solutions of metal nitrates or chlorides. Temperature is also a simple and effective way to increase the overall adsorptive properties of the organic compounds and other wastes, having one of the most significant decreases in the medium's carbon content and being easily achieved and measured by alterations in the max temperature of pyrolysis. Also, temperature further increases the pores volume and size by thermal destruction of hydrogen- and oxygen-based compounds like aliphatic alkyl, ester, and phenolic groups (Premarathna et al. 2019).

Other ways of improving the biochar's adsorptive potential lie in different physical treatments, such as microwaving, gas or steam activation, ball milling, magnetic inductions, and gas or steam activation. Physical enhancements have the advantage of not creating by-product impurities than chemical methods, being a safe, easily controlled, and reliable type of treatment without the need to worry about the influence of potential by-products interfering with the particle-retaining capabilities. Besides nearly doubling the particle retention potential, steam activation can also expel remaining impurities and incomplete combustion products of the biochar mass. This method needs to be followed with caution because useful functional groups can be removed as well; for that, a second treatment may be advised to retain certain available compounds. Magnetic improvements also have their drawbacks because this method can result in small density and size particles, which can be challenging to remove or collect after the use in water remediation, giving the risk that such particles can decompose and by that release the adsorbed contaminants, requiring additional treatments to magnetize the structure for been further collect by a magnetic source (Panahi et al. 2020).

Chemical treatments can promote undesirable alterations, like by-products that interfere with the functional groups, resulting in reduced adsorption of an aimed target; such methods are still highly studied and used for biochar activation through the use of chemical compounds and inert gases. Acid or essential components are commonly added to promote the material's oxidation, improving the overall surface area, cation exchange capability, availability of micropores, and specific functional groups. Certain treatments produce distinguishable functional characteristics; acidic and alkaline modifications increase the surface area by particular dimerizing compounds in the biochar structure. However, alkalic-treated materials appear to result in an even larger surface area (Panahi et al. 2020). Based on the comportment of distinguishable alterations, it is necessary to choose a treatment, or even a conjunct of treatments wisely, to produce a material that can be both efficient in removing the target contaminant and economically desirable.

Such improvements in the retention of large and microscopic particles are highly desirable in retaining pathogens in wastewater treatment plants, which usually hold an exponential bacteria and virus concentration per liquid or solid waste. For efficient removal of microorganisms and to ensure that the final material can be reused in human and animal activities, it is necessary that no active pathogen can be found in the final product since contamination is based on a living organism that can easily repropagate to even higher concentrations before treatment and thus contaminate different sources with little more than a few particles of infectious material. Even traditional old methods like composting still require additional treatments to increase the degree of safety before proper use for the average temperature, and toxin build-up in such systems is usually not enough for full pathogen removal. Besides also producing undesirable toxins after biological degradation, which can be potentially harmful if aimed to be reused in agriculture and livestock systems. For that, additional materials such as biochar continue to be highly desirable. Those are cheap yet efficient, pathogens removers and toxin compounds regulators, enhancing these products based on various low-cost waste products, such as the addition of sawdust and other wood shavings. (Ravindran et al. 2019).

In an experiment organized by Ravindran et al. (2019), the addition of biochar with sawdust in composting systems not only significantly decreased the pathogenic bacterial load of *E.coli* and *Salmonella sp.* but also reduced the bulk density, increased the aeration and porosity of the bulk compared with biochar without such addition or the presence of any biochar compound. More remarkable is that the conjunct treatment allowed a more significant decrease of carbon, nitrogen, and total moisture in the compost, probably due to the enhanced activity of decomposing microorganisms influenced by the biochar's presence, which may have protective properties to certain types of microbiota, as previously mentioned. Such variation of the nutrient composition and decrease of moisture can further reduce the necessary conditions for proliferation and survival of different kinds of potential pathogens present before treatment or even lower the odds of future colonization. Alterations of pH and temperature during the decomposition phase could also be attributed to many microorganisms' increasingly hostile situations.

Even without many studies focusing on the interaction of enhanced biochars combined with macrobiotic bacterial populations in the viral population, it is not precipitous to imply that the extreme variations of physical and chemical conditions of one waste influenced by the enhanced biological activities of the local bacterial population can decrease the viability of virion particles present in the waste container. For these organic structures, even though they can sustain themselves in an extensive period without a host, they are susceptible to degradation by sudden environmental variations (Ravindran et al. 2019).

20.3 Final Considerations

There is evidence that studies on an experimental and real scale to explore new technological configurations using biochar are promising trends in the control of environmental pathogens and chemical contaminants, reducing negative impacts on human, animal, and environmental health based on sustainable and low-cost technology.

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21 Application of Biochar for Soil Remediation

Shubhangi Parmar, Sagar Daki, and Anupama Shrivastav

Abstract

Biochar refers to black solid carbonaceous material produced majorly by the process of pyrolysis or sometimes produced by application of chemicals under oxygen-limited environmental conditions. The term biochar is specifically associated with a substrate that is used as soil ameliorant, and the surge in research interests toward biochar is due to its varied applications. One of the critical reasons to promote biochar as an excellent long-term soil conditioner is its stability. The characteristic properties of biochar when added to the soil are an increase in pH, nutrient retention capacity leading to elevated soil quality in agriculture, crop biomass, the fertility of the soil, cation exchange capacity, and carbon sequestration so its application in bioremediation of contaminated soils would be a substantial way to initiate many green processes in the environment. With large surface areas, accelerated sorption of organic and inorganic substances is possible, which helps reducing contaminant mobility during amendments of polluted soil. Biochar is quite promising for the removal of heavy metals, persistent organic matter, improvement of soil quality, and stabilization of soil for revegetation. This chapter summarizes biochar preparation methods and parameters, the role of biochar in bioremediation, different approaches used for soil restoration with potential drawbacks, and further scope of research with biochar in soil amendments.

Keywords

Biochar · Pyrolysis · Bioremediation · Soil amendment

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21.1 Introduction

Soil pollution refers to the entry of any primary or secondary toxic pollutant in the environment that poses toxic effects to biota and humans in the surrounding. Soil can be contaminated with organic and inorganic contaminants, which occurs universally and naturally; accepted techniques have been developed for their disposal. Modern remediation techniques are focused on cost-effectiveness with in situ amendments of contaminated soil with substances that would remediate the soil and lead to plant growth stimulation and overall ecological restoration. Soil quality assessment systems have now adopted the risk-based approaches, which are concerned more with the hazardous effects of the contaminants rather than assessing only the total concentration of pollutants in the soil. Organic matter is preferentially used more compared with other substances as it is obtained from biological sources and very few preprocessing steps are required before it is added to the soil (Beesley et al. 2011). Biochar refers to black solid carbonaceous material produced majorly by the process of pyrolysis or sometimes produced by the application of chemicals under oxygen-limited environmental conditions. The term biochar is specifically associated with a substrate that is used as soil ameliorant, and the surge in research interests toward biochar is due to its varied applications. The main objective of land remediation is the reduction of hazardous effects caused by land pollutants to biota. The process of remediation can be simplified with familiarity with terms like source and receptor. Source refers to any physical location from where contaminants have been generated. A receptor could be defined as any location like water bodies and tissues of biota that could have harmful effects due to the source. The main idea of remediation is to reduce the source pathway receptor linkage to shrink the harm on receptors. The most common approaches used to date include removal of source or removal of the receptor; however, application of such method on large scale seems to be an impractical and expensive process. Numerous properties of biochar make it an efficient tool for remediation of contaminants in the soil as it has a large adsorption area, negative charge, and is highly resistant to degradation. The surface area of biochar is said to be increased along with the higher pyrolysis temperature up to an extent. Further, the property of negative charge helps in attracting the metals and organic in the internal surface of biochar from the polluted soil, and due to this potential risk of their uptake by organisms can be reduced greatly. Biochar can efficiently help in breaking the source and receptor pathways by adsorbing contaminants on the surface that act as pollutants for soil (Gomez-Eyles et al. 2013; Bardos et al. 2002).

Sustainable soil remediation techniques for contaminated soil are generally focused on maintaining or enhancing the quality of soil, which can occur by carbon sequestration, reducing soil erosion, and providing suitable environmental conditions for increasing soil biodiversity. The porous nature of biochar makes it possible to provide such a suitable environment with carbon sequestration properties. Biochar has clearly demonstrated the potential for the reduction of a variety of organic and inorganic contaminants present in the soil, in their mobile forms. The characteristic properties of biochar when added to the soil are an increase

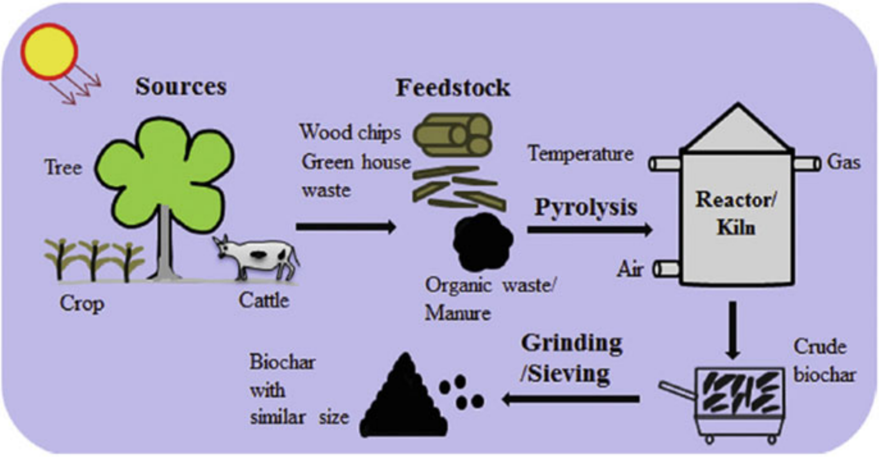

Fig. 21.1 Schematic representation of biochar source and production process

in pH, nutrient retention capacity leading to elevated soil quality in agriculture, crop biomass, the fertility of the soil, cation exchange capacity, and carbon sequestration so its application in bioremediation of contaminated soils would be a substantial way to initiate many green processes in the environment. With large surface areas, accelerated sorption of organic and inorganic substances is possible, which helps reducing contaminant mobility during amendments of polluted soil. Biochar is quite promising for the removal of heavy metals, persistent organic matter, improvement of soil quality, and stabilization of soil for revegetation. The basic introductory schematic representation of biochar source and its production is shown in Fig. 21.1 (Kumar et al. 2016).

21.2 Biochar Preparation Methods

Biochar can be prepared from organic waste, which has a high potential for the generation of biochar. Waste materials that could be used as the source of biochar preparation include agricultural waste like crop residues, food waste, animal manure, and municipality waste (El-Naggar et al. 2019) (Varjani et al. 2019). Biochar is generally prepared using different thermochemical methods. Common thermochemical techniques employed for biochar preparation are pyrolysis, hydrothermal carbonization, gasification, torrefaction, and flash carbonization (Bridgwater 2012). There are many different factors that affect the pyrolysis process of biochar production, and one of the major factors to be considered while production is a type of biomass used for the process. Biochar can be produced from residues like rice straw, wheat straw, waste wood, corn cob, and many other agricultural waste substances that are rich in cellulose, hemicellulose, and lignin compounds. The process conditions in which biochar is prepared will play a crucial role in determining the morphological characteristics of biochar. Different methods used for the preparation of biochar preparation are explained in details below.

21.2.1 Pyrolysis

Pyrolysis is the process of decomposition of organic matter at temperatures ranging from 250–900 °C along with the maintenance of an oxygen-free environment. Pyrolysis is used for the production of commercially valuable products from organic material like biochar, bio-oil, and syngas. In pyrolysis, the cellulose, hemicellulose, and lignin present in the source material go through series of reaction like depolymerization, fragmentation, and cross-linking at varied temperatures that ultimately leads to the production of products in three different solid, liquid, and gaseous states. At the end of the pyrolysis process, solid products obtained are bio-oil and biochar, while the gaseous state products include hydrogen, syngas, and carbon dioxide gas. In this method, temperature is a crucial deciding factor that controls the production efficiency of biochar, but at very high temperatures, there is a reduction in the overall yield of biochar (Wei et al. 2019). The pyrolysis process carried out can be classified into two different types, which are fast pyrolysis and slow pyrolysis. Fast pyrolysis causes liquefaction of solid biomass materials into bio-oil. The process is carried out in steps like the warming of biomass particles at a temperature of about 100 °C per minute with reduced duration of production of pyrolysis fumes and biomass particles, and finally, moderate pyrolysis treatment that occurs in the temperature range of 400–600 °C. In slow pyrolysis, the better yield of biochar is obtained where the temperature of the system is kept about 5–7 °C per minute less compared with fast pyrolysis and the residence time is more than 1 h (Al Arni 2018).

21.2.2 Hydrothermal Carbonization

The hydrothermal carbonization method for biochar preparation is a cost-effective technique where the process is performed at a temperature range of 180–250 °C. The biochar prepared from the hydrothermal method is also commonly named hydrochar as it uses wet biomass. The biomass is first blended with water in a closed reactor, and then the temperature is increased eventually to maintain biochar stability. In this process, different products are obtained at different temperature ranges. Biochar is produced at temperatures below 250 °C, production of bio-oil occurs in between 250 and 400 °C, which is known as hydrothermal liquefaction, and gaseous syngas is produced as carbon monoxide, hydrogen, and methane around 400° and above by the process of hydrothermal gasification. Hydrochar is produced through series of reactions like condensation, polymerization, repolymerization, cross-linking and dehydration (Jain et al. 2016).

21.2.3 Gasification

Gasification is the decomposition of organic material into gases by the use of thermochemical techniques. The gas produced after gasification is called syngas, which is abundant in carbon monoxide, carbon dioxide, methane, hydrogen, and micro-quantities of hydrocarbons. Gasification agents employed include steam, air, high temperature, and oxygen. On fluctuation of temperature, the concentration of different gases obtained also changes. When gasification is done, biochar is obtained as a by-product after the production of syngas, and thus, the yield is low as compared with other methods. Steps involved in the gasification process include drying, pyrolysis, and oxidation or combustion (Prabakar et al. 2018). The comparison between different pyrolysis techniques and gasification is explained in Table 21.1 (Tisserant and Cherubini 2019).

21.2.4 Torrefaction

Torrefaction emerged as a method for biochar production, which is also known as mild pyrolysis as it requires low heating. Inert atmospheric air is used for the removal of oxygen and moisture present in biomass under anaerobic conditions at 300 °C. The main objective of the torrefaction process is a modification of particle size, surface area, heating rate, and moisture content of biochar. Torrefaction can be classified into three different types as steam torrefaction, wet torrefaction, and oxidative torrefaction. In steam torrefaction, treatment of biomass occurs with steam at temperatures not exceeding 260° with 10 min of residence time. In wet torrefaction, the water is added, and treatment is done at 180–200 °C temperature, while residence time is increased up to 5–240 min. It is also termed hydrothermal carbonization at times. In oxidative torrefaction, the treatment of biomass is done with oxidizing agents usually gases that are used in combustion, where energy is generated after the end of the process. The initial methods of torrefaction achieve incomplete pyrolysis, and after that, processes like drying, pre-drying, and post-drying are carried out. The temperature range for the torrefaction process is

Table 21.1 Comparison of operative conditions for slow pyrolysis, fast pyrolysis and gasification

	Slow pyrolysis	Fast pyrolysis	Gasification
Pyrolysis temperature	270–750	550–1000	≥500
Heating rate	0.1–1	10–200	5–100
Feedstock particle size	5–50	≤1	0.2–10
Solid residence time	450–550 up to days	0.5–10 s	≥1 h
Vapor residence time	5–30 min	~1 s	10–20 s
Biochar yield	45–20	5–30	~5
Bio-oil yield	40–50	50–75	~10
Syngas yield	10–25	5–35	~85

200–300 °C, while residence time is 30 min, with a heating rate less than 50° per minute with the presence of oxygen in the surrounding environment (Yu et al. 2017).

21.3 Parameters Influencing Biochar Quality

The type of reaction conditions is very crucial for the production of biochar. Different factors have a cumulative effect on the production of biochar. The factors like temperature of the reaction, size of the particle, heating rates, and type of source material directly affect the quality of biochar. The in-depth knowledge of how these factors affect biochar property is very important before the application of biochar to any process. The most common materials used for production are agricultural residues, solid waste, wood, etc. for biochar preparation (Shaheen et al. 2019). Solid wastes produce more biochar as compared with other biological materials. The different parameters affecting biochar quality are discussed below.

21.3.1 Source Material for Biochar Production

Biomass is the source material used for the production of biochar, which is defined as complex material that is composed of biological, organic, and inorganic matter which is derived from living plants and living organisms. The biomass used for production can be categorized into two different categories like woody biomass and non-woody biomass (Tripathi et al. 2016). The woody biomass includes tree residues, barks, twigs, and forestry parts with characteristics like low debris, high density, less void-age, and low dampness with calorific value. On the contradictory, the non-woody biomass includes industrial and agricultural solid wastes and animal wastes showing features like high dampness, increased void-age, and high debris with low calorific value and low density. Important parameters of source material are its moisture content as it affects the biomass formation directly. The moisture can be retained in the source material in many different ways in the form of water, vapors, or present in the pores of the biomass. High moisture content hinders the formation of biochar and increases the energy required to achieve suitable pyrolytic temperature for that source material. The source material with lower moisture content is selected for the formation of biochar as it requires significantly lower heat energy and pyrolysis time when compared with the one with high moisture content. Overall materials with low moisture make the process economically efficient and easy (Jafri et al. 2018).

21.3.2 Pyrolysis Temperature

Pyrolysis to date remains the most common method for conversion of biomass into biochar by thermochemical decomposition process in the absence of oxygen and elevated temperature. With regard to pyrolysis conditions, the process can be divided into three classifications like slow pyrolysis, moderate pyrolysis, and quick pyrolysis. The best pyrolysis method for the production of good biochar can be moderate pyrolysis. The difference between all three types is that they are operational at different temperatures. The slow pyrolysis process occurs at temperatures below 300 °C, while moderate pyrolysis occurs at a temperature range of 300–500 °C, while quick pyrolysis carried out at temperatures exceeding 500 °C. The temperature at which pyrolysis of biomass is carried out affects the physiological and chemical parameters of biomass like its surface area, pore structure, functional groups, and physical features (Dhyani and Bhaskar 2018).

21.3.3 Residence Time

Residence time is the total duration for which all the components react in the reactor also defined as the time required by all reactants to displace the total volume of the reactor. The low pyrolysis process is significantly affected by changes in residence time, as an increase in residence time during this method decreases the yield of biochar. The increasing residence time in high pyrolysis does not affect the process of biochar formation or pH alteration and so the same amount of biochar is obtained in case of variation. The residence time is also known to affect the iodine adsorption number of biochar, which was observed to be reduced with an increase in residence time for low pyrolysis; however, it increased on increased residence time in case of the quick pyrolysis method (Liang et al. 2016).

21.3.4 Pretreatment of the Source Material

The biochar characteristics are governed by the pretreatment applied to the source material before it undergoes the process of pyrolysis. The most widely applied pretreatment methods include immersion of source material into different solutions and reduction in particle size of the source material. It is observed that reduced particle-sized raw materials are capable of producing high biochar yields. Other pretreatment methods like nitrogen or metal doping also influence the biochar characteristics, while the elemental composition of biochar can be modified by soaking the source material or steaming the source material in a chemical solution. Baking is another common pretreatment method that increases the carbon content present in biochar and also helps in the reduction of moisture in the biochar production. The properties of biochar can vary depending on the source material as it has different concentrations of different mineral elements in it. Elements like nitrogen, hydrogen, and sulfur are volatile in nature during pyrolysis, but minerals like phosphorus, magnesium, silicon, and calcium remain present even after biochar is formed as they are not volatile in nature (You et al. 2018).

After the production of biochar, characterization of biochar can be done using various parameters, which include the physical, chemical, surface, and molecular characteristics of biochar. Parameters like pH and electrical conductivity are checked under physical characteristics, while chemical characterization includes checking the surface area, particle size distribution, bulk density, and pore size. Surface parameters can be checked using different spectroscopic methods and scanning electron microscopy. The molecular parameters include thermal analysis, structural arrangements, and aromatic characterization using transmission electron microscopy, nuclear magnetic resonance spectroscopy, etc. (Brewer et al. 2014).

21.4 Impacts of Biochar on Soil and Its Biota

Different articles on biochar provide sufficient evidence that biochar improves the physical, chemical, and biological characteristics of soil, which leads to an increase in crop yield in agriculture and remediation of toxic pollutants present in the soil in an efficient manner. Soil sensitivity is defined as the sensitivity level of soil toward natural or man-made disturbances caused to it, while the flexibility of soil is defined as the ability of soil to restore its original properties and qualities after being affected by natural or induced interference. The quality of soil can be checked by assessing the sensitive indicators of soil by certain parameters. Numerous properties of soil including biological properties like microbial biomass, respiration, soil enzymes, and earthworm activity are considered to be the indicators of soil quality.

Application of biochar to the soil causes an elevation in pH-dependent charge in the soil, which causes further increased cation exchange capacity of the soil. Increased pH in the soil leads to an increase in lime and calcium levels in soil, which can decrease the aluminum toxicity seen in red iron soils. The addition of biochar not only helps in the treatment of acidic soil but also helps in increasing the pH of alkaline soil to an extent. The properties of biochar, which depend on the source material, environmental conditions, and type of soil it is applied to, may change over time. Some of the beneficial effects of biochar include a reduction in soil bulk weight, improvement in phosphorus, soil pH, organic matter, and water content of the soil, which can overall increase the cultivation performance of such soils in agriculture. Characteristics like soil bulk density, porosity, water retention capacity, and redox conditions play a crucial role in microbial growth and plant growth in the soil. The soil with high volume density has very low absorption capacity for water, which affects the penetration of roots and plant growth, but with the application of biochar decrease in bulk density, increase in soil porosity and soil aeration can be achieved. Soil aggregation rates are higher in soils modified by the addition of biochar as compared with controls. With the addition of biochar to soil, there is an increase in water and nutrient content of soil over time, and the hydrophobic nature of biochar causes elevated water absorption and retention capacities. Along with all these benefits of biochar, it also enhances the soil redox conditions and behavior of microbes.

The source of nutrients in the soil is the organic matter that is present in it. The absorption of nitrogen by organic matter and microbes present in the soil can promote plant growth. The soil organic matter is determined by soil texture, moisture content, temperature, and many other factors. When biochar is added to the soil, it improves the organic content in the soil and soil humus, which increases the proportion of carbon to nitrogen ration in the soil that is further absorbed by the plants. Biochar significantly reduces the leaching of organic matter from the soil and supports the development of soil organic matter–mineral complexes and microbial organic mineral complexes.

Biochar is useful in the reduction of carbon dioxide emissions occurring from the soil, while increases the total nitrogen by promoting mineralization and nitrification reactions in the soil. The usage of biochar with ash as a biofertilizer in the soil is very economic and an efficient approach that improves environmental sustainability with beneficial effects in the long term. Biochar also has pieces of evidence of nutrient acquisition, and so, it acts as a source of nutrients for plant roots.

The physical and chemical properties of biochar can modify the soil microbes and their enzymatic activities. Biochar voids provide suitable habitat for microbes and consequently; it also improves the density, pH, aeration, water, and nutrients in the environment. Biochar obtained from different sources have fulvic and humus content similar to organic carbon present in the soil, which is thermally stable. Soil enzymes are secreted from soil microbes or plant roots or from decomposition reactions taking place in soil, and they play important role in all biochemical reactions in the soil. The activity of biochar influences microbial growth providing increased surface area for nutrient absorption and accumulation properties of soil that contributes to the health of plants and provides nutrients that are essential for higher yield. In most cases, the application of biochar can significantly improve enzymatic activity and the number of microorganisms in the soil. Studies indicate that there are many other important factors that influence the microbial activity and secretion of enzymes on the application of biochar (Mandal et al. 2021).

The microbial reproduction rate is also increased in biochar amended soils and wastewater. The colonization rate of beneficial symbiotic mycorrhiza with plant roots is increased positively on the treatment of soil with biochar. After the application of biochar, there is seen an increase in microbial abundance of nonsymbiotic microbes specifically. The pH of biochar produced may range from values below 4 to above 12 depending on the material used for preparation and temperature of pyrolysis. With the increase in pH of hydrochars, stimulation of microbial reproduction, that too particularly bacteria, is observed, while some fungi got inhibited drastically due to unfavorable pH conditions in the soil. The bacteria get sorbed on the surface of biochar, which makes them unavailable for leaching out in the soil. Adsorption on the surface of biochar can occur by different processes like hydrophobic interaction and electrostatic forces. The bacteria and fungi are protected by competitors by residing in pore habitats of biochar. Drying of soil causes stress on microbes that lead to dormancy or death of microorganisms, but large surface areas and greater water holding capacities of biochar with enough pores continue to provide hydration to microbes that would otherwise die in the drying soil (Pathy et al. 2020). The different applications of biochar with particular focus on applications in soil quality can be represented in Fig. 21.2 (Kumar et al. 2016).

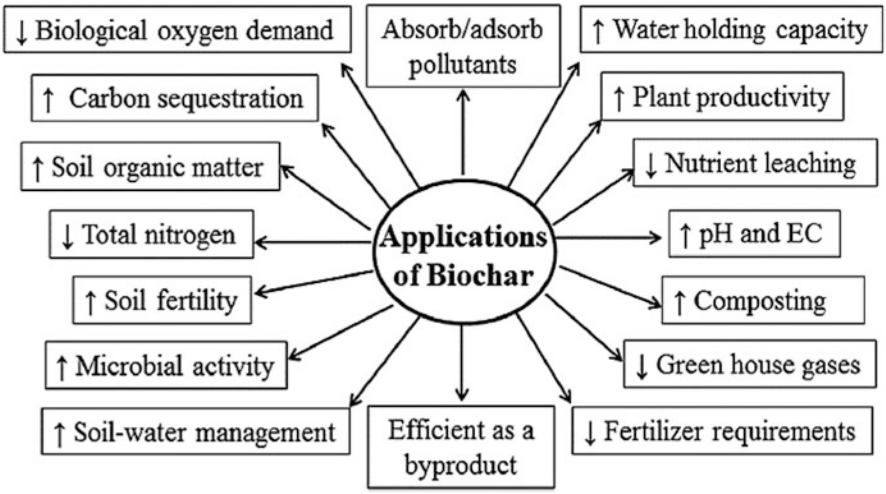

Fig. 21.2 Different applications of biochar and its effects on soil quality

21.5 Biochar and Environmental Pollution

The interest in biochar research has increased over time due to its eco-friendliness, inexpensive, and easy thermochemical techniques for preparation characters. Biochar can address many different environmental problems as it plays a major role in the removal of contaminants from soil and water. The carbonaceous biochar produced at high temperatures shows more efficiency for the removal of organic pollutants as compared with inorganic ones due to its properties like porosity, pH, less dissolved carbon, and hydrophobicity. The biochar that is produced at low pyrolysis temperature are more suitable for the elimination of inorganic contaminants. Biochar has a variety of applications in pollution control and different fields like wastewater treatment, composting, carbon sequestration, and amendment of soil, which are discussed here (Yaashikaa et al. 2020).

21.5.1 Biochar for Removal of Organic Pollutants

Biochar is widely applied for the removal of organic pollutants persistent in soil and water. When biochar is applied to the soil, the adsorption of organic pollutants present in the soil occurs. On increasing the biochar concentration in soil, the degradation rate and adsorption rate of contaminants increase as they have a direct proportional relationship. The organic contaminants that can be adsorbed on the surface of biochar include agricultural chemicals, insecticides, herbicides, pesticides, aromatic hydrocarbons, antibiotics, dyes like methylene blue, and volatile organic compounds. Pesticides like carbofuran can be adsorbed easily on the biochar surface due to the presence of functional groups like aromatic phenolic groups or carboxylic groups. Biochar can remove organic pollutants from the soil by using many different mechanisms like electrostatic attraction, pore diffusion, biodegradation, transformation, hydrophobic interactions, or electrophilic interactions, which mainly depends on the quality of interaction between pollutant and biochar. The major factors that would affect the elimination of organic pollutants by biochar include the type of source material, temperature, pH, pollutant concentration, applied biochar type, and the kind of biochar-pollutant interaction. Biochar adsorbs the soil organic pollutants and decreases its bioavailability and uptake rates by plant roots and animals. Biochar removes the soil conditions, and experiments show better soil properties of soil amended with biochar as compared with one without biochar application. Along with biochar properties and application methods, the type of soil to which it is applied and its original conditions also contribute to its efficiency. The principal mechanism by which the removal of organic matter occurs by biochar is adsorption (Mondal et al. 2016).

21.5.2 Biochar for Removal of Inorganic Pollutants

The nonbiodegradable compounds and metals are counted under inorganic pollutants that affect the health of humans and pose a serious risk on environments when present in high concentrations. The important inorganic pollutants include carcinogenic compounds and heavy metals like zinc, nickel, mercury, copper, and calcium as they are attributed to the environment from sources like industrial effluents and municipal waters. The biochar, which is produced at low temperature by the process of slow pyrolysis, is used for the sorption of inorganic compounds on its surface. It is possible to remediate inorganic pollutants with biochar produced at low temperatures as it possesses many different functional groups with porosity in nature and high content of carbon. The main principle by which remediation of inorganic pollutants like heavy metals occurs is ion exchange.

The characteristic immobilization property of biochar can cause alteration in heavy metal properties like surface functional groups, pH, and cation exchange capacities. Studies indicate that zeta potential and cation exchange capacities of biochar are reduced with increasing the pH of the soil. The biochar amended soils show efficient immobilization of heavy metals and their remediation as compared with other techniques. The source material used for the preparation of biochar, which is to be applied for remediation of inorganic pollutants, includes sugar beet, corn cub, straw, soybeans, and animal sewage. Another factor that affects the removal capacities of biochar is pH and also the type of metal that that is needed to be eliminated. At pH ranging from 6 to 7, the main mechanism for elimination is ion exchange, while at pH 7 or higher, the main mechanism for elimination of pollutants seems to be surface complexation and electrostatic attractions. The dosage of biochar applied for remediation is also important as increasing the dosage provides more surface area and increased pH, which enhances the rate of removal. In-depth studies are still required in the field of the removal of pollutants for efficient operation. The competition between metal binding and adsorption increases as the metals may possess chemically the same functional group, and so many mechanisms are still left unexplored (Karami et al. 2011).

21.5.3 Biochar in Air Pollution

Biochar is used as low-temperature selective reduction catalysts in many experiments. The source material like sewage sludge or rice straw can be used for the preparation of biochar that is used in air pollution control. The biochar obtained from these materials is further physically or chemically modified and applied for the removal of air pollutants after checking its removal efficiency. Before biochar becomes functional for the elimination of pollutants, its activation by various physical and chemical agents is done. Experiments suggested that chemical activation has produced better results as compared with physical methods. The type of functional group present and absorption sites plays important role in the elimination of air contaminants (Yu et al. 2009).

21.5.4 Biochar in Wastewater Treatment

Biochar is a very promising candidate when considered for treatment of wastewater because it has higher porosity and high surface area. It can be used as media for capturing elements that can be used as fertilizers in soil later. Due to its adsorption capacities, the toxins from wastewater can accumulate on the surface of biochar, and ultimately clean effluent can be obtained. Researchers studied and compared the role of biochar and activated carbon for the removal of toxic contaminants from the wastewater and the execution of the biochar-based method on the basis of financial view, and biochar seemed to be much economical than activated carbon. Biochar is good option for the removal of contaminants from wastewaters when compared with production cost and greenhouse gas emissions from activated carbons (Yaashikaa et al. 2020).

21.6 Techniques for Soil Restoration with Biochar

When biochar is applied to soil for increasing the fertility of soil, it should be applied to soil surface present in proximity with root zone because nutrient cycling and uptake of nutrients in bulk amount takes place in that area; when biochar is applied with an aim of carbon sequestration or moisture management, then it should be applied in the deeper layer of the soil as no destruction by microbial activity takes place at deeper soil levels. The biochar can be protected from losses due to wind and water erosion.

If they are applied thoroughly to the soil, the type of plants or crops growing in the soil also decides the method by which biochar can be applied to that particular soil; in conventional crop management systems, biochar is directly applied to the soil with the help of farm machinery used in traditional farming, which would reduce the cost associated with biochar application in conventional fields, biochar is, mixed with lime for application as solid lime incorporates well with layers of soil.

Biochar can also be applied to the field with the help of lime or solid manure spreaders, which is called broadcasting. After broadcasting that biochar is incorporated into the soil using different plowing methods used in field, which includes animal draft plow, disc harrows, and chisels, one of the limitations of broadcasting and incorporating method is losses that occur due to wind erosion and precautions needed to be taken while applications. Banding is a common method used for the application of seeds and fertilizers in fields where material or seeds are applied in a narrow band in the soil by using equipment that forms bands on the soil surface without disturbing the entire surface of the soil; with banding technique, biochar can be applied in the soil even after crop establishment with the minimal disturbance caused to the soil. Another method of application is mixing of biochar with other soil amendment agents like manure, compost, or lime instead of direct application; as such method can protects against leaching and improves the efficiency of applied amendments.

Biochar can be applied to soil as slurry when mixed with liquid fertilizers. The particle size of biochar to be applied with liquid should be fine in nature. The reduction of nitrogen losses in holding ponds can be achieved by the application of biochar mixed with liquid manure. When sufficient data on soil characteristics and quality is available, it is possible to apply biochar specifically to certain areas of field where the fertility of soil is low. Uniform mixing of biochar can be done with sand, topsoil, compost, or turfgrass substrate prior to application in the landscape environment. It can also be applied specifically in layers below the rooting zone of grass, which helps in the protection of leached nutrients and pesticides from the soil. Biochar can also be applied in localized areas around the root by excavation soil around tree roots, which is later covered after application the biochar can be applied over the planting area by creating planting holes in the soil. Biochar can also be applied in trenches that radiate out from the base of established trees or holes that are created at some distance from the base trees (Major 2010).

21.7 Limitations of Biochar

Biochar has inhibitory effects on the aging of soil and the addition of biomass into the soil intermittently, which is essential for the recycling of nutrients. It can affect the growth of fungi and earthworms in the soil. The positive effects of biochar amendments done to the soil are soil-specific, which depends on the type of soil to which it is applied and cannot be always beneficial for all soil types. Findings suggest that the problem of weed growth increases with the addition of biochar in soil. Biochar can further cause a delay in the flowering of different plants. The ability of biochar to adsorb pollutants on its surface is also very selective. The biochar that is produced using quick pyrolysis method contains higher amount of ash into it, which might cause harmful effects on plant grown soils. Biochar at times can also react with plant nutrients as a competitor instead of acting as a substance that provides plant nutrients. The decomposition process of organic matter, which continuously takes place in the soil, interferes with the addition of biochar to the soil, which can have negative effects on fungi. The contamination of biochar source in another problem can deteriorate the plant growth process. The cost of biochar production depends on the type of biomass used, and sometimes the costs are very high. The yield can also decrease at times due to the sorption of water and nutrients by biochar. Biochar has also affected the germination process and showed an inhibitory effect on it. The presence of fine ash in biochar is the source of dust, which can cause respiratory ailments in organisms. The long-term effects of the skin of microorganisms that come in contact with biochar are still needed to be explored. Application of large quantities of biochar in the soil for the long term may cause negative effects in the soil due to nitrogen limitation. Emissions of black carbon from the soil after the application of biochar can contribute to climate change and toxicity when the environmental assessment of soil is conducted. Biochar after application in soil may remain up to years as it cannot be removed from the soil all at once, and so, long-term aging effects on soils are uncertain. Analysis of all important parameters is a must before applying biochar to any kind of soil (Kavitha et al. 2018).

21.8 Future Perspective

Biochar is a promising renewable resource that can help in many environmental problems and remediation of pollutants present in soil, water, and gas. Future research in biochar scopes for studying adsorption and desorption mechanisms of contaminants on biochar surface. The interaction of microbial population with biochar and the diversity of microbes can also be explored. The alteration in growth pattern and physiology of microbes on the application of biochar has to be explored yet. More knowledge in the field of binding mechanisms of biochar with soil is needed. Future research will also focus on studying the life cycle of biochar produced from the specific source material. The area of biochar characterization has been progressive, but optimization of biochar properties and activation methods are yet to be improved to enhance the activity. The effects of biochar on plants have been studied, but less literature is available on the effects of biochar on fauna present in the soil. For practical applications of biochar on a large scale, a better understanding of long-term toxicity must be evaluated to provide safe environmental applications. Future research can also focus on techniques for the development of biochar composites and evaluation of their efficiency. Necessary research should be conducted on reducing the production and equipment costs of biochar. A standardized management system is needed to be developed for tracing the after application (Lehmann et al. 2011). Further, all the areas having scope in biochar research in the field are explained as shown in Table 21.2 (Kuppusamy et al. 2016).

Table 21.2 List of areas with scope in biochar research for future

Research area
Develop production guidelines
Develop biochar quality standards
Screen suitable feedstock for high grade biochar production
Explore the enzymatic activity of biochar in different soil types, particularly, hypersaline and sodic soils
Study the long-term impact of biochar on soil fertility and crop productivity
Study the adverse effect of biochar on soil flora and fauna
Explore the mechanism of nutrient release of biochar with respect to aging effect
Investigate the long-term greenhouse gas abatement potential dynamics of heterogeneous biochar in different soil types
Investigate the phyto/ecological risk of biochar in long run

21.9 Conclusion

The depletion of quality agricultural land has created a need for the development of sustainable crop production methods as population is increasing day by day. To make the contaminated soil renewable and retain it's original properties, biochar is a promising means for remediation of contaminated soils and improvement of soil fertility, by reducing its acidity and also increasing the nutrient availability in the soil. The addition of biochar to soil is sustainable and eco-friendly method for reduction of biotic stress created on solid. Biochar can increase the productivity of soil by positive interactions between the soil plant and water, which would later improve the photosynthetic efficiency nitrogen fixation and water activity in agriculture. The physiochemical properties of biochar play key role in enhancing the quality of soil. Properties of biochar like porous structure, high carbon content, and ion exchange characters are very important for its application in removal of organic and inorganic pollutants from soil, immobilization of heavy metal, and carbon sequestration. The effect of biochar on the microbial communities present in the soil is significant as it increases the microbial abundance in the soil. It simultaneously provides soil with good nutritional status and proper microbial structure. Biochar is one of the highly recommended substances in agricultural practices due to its easy application methods and its cost-effectiveness. There are many trending areas that can be explored in biochar research, and one of the interesting topics is application of biochar combined with other substances with focus on achievement of particular objective.

Biochar has not been used commercially on a large scale as most of the people have based opinion fact that it is just a waste. Biochar is emerging as a tool for remediation due to array of other benefits it provides to the soil along with elimination of compounds; it is important to sufficiently study the environmental safety of compounds before it is applied to the soil.

Conflict of Interest Shubhangi Parmar, Sagar Daki, and Anupama Shrivastav declare that they have no conflict of interest.

Ethical Approval This chapter does not contain any studies with human participants or animals performed by any of the author.

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Correction to: Conversion of Agricultural Wastes into Biochar and Its Characteristics

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The **Chapter** was inadvertently published without references, missing references are as follows:

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