

# Chapter 8

## Environmental Benign Biochar Technologies: Strategic Utilization for CO<sub>2</sub> Capture and Wastewater Treatment



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### 8.1 Introduction

For a sustainable world, the implementation and execution of sustainable technologies are essential. Therefore, valorization of wastes originating from domestic, industrial, and agriculture can play a critical role in accomplishing sustainable goals (Khan et al. 2020). Agricultural, forest or any flora related organic wastes can be considered as biomass. For instance, the waste related to crop, forest, algae, organic municipal solid waste, sewage sludge, and manures can be included in biomass waste (Demirbas 2001). Globally, an estimated 12 billion tonnes of dried biomass waste are generated annually which highlights the presence of enormous amount of biomass waste (Pandey et al. 2015). Common applications of this waste biomass include animal feeding, as fuel, and production of biochar.

Biomass mainly contains hemicellulose, cellulose, and lignin in different proportions depending on the biomass type (Hao et al. 2014). The carbonaceous biochar can be obtained by applying thermal treatment on biomass waste in restricted or no oxygen. The yield of biochar greatly depends on the lignin concentration in respective biomass waste as lignin is the main source of carbon (Pandey et al. 2015). Major thermal treatments for the conversion of biomass into biochar include pyrolysis, microwave heating, hydrothermal carbonization, dry torrefaction, and gasification (Kambo and Dutta 2015; Liu et al. 2015). Each method differs in terms of temperature, oxygen content, duration, and therefore quality of produced biochar. The produced biochar offers two main advantages, i.e., the production process

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prevents the carbon dioxide emission by its conversion into stable form (carbon), restricting the greenhouse gas emission during biomass degradation (Creamer and Gao 2016). Secondly, biochar is an asset as adsorbent, providing environment friendly, low cost, and extraordinary performance in wastewater treatment (Inyang et al. 2015). The enhanced adsorption characteristics are the synergistic effect of large surface area and availability of ample functional groups. However, these physicochemical properties significantly depend on thermochemical decomposition technique, duration, production temperature, and feedstock pre/post treatments (Zhang et al. 2017a). These parameters are regulated depending on the type of feedstock and required applications. The pretreatment process includes physical (grinding, sieving, washing, drying), chemical (acid, alkali, or functional materials), and biological (treatment with bacteria) techniques (Son et al. 2018; Zhang et al. 2017a; Yao et al. 2015). Whereas the posttreatment includes physical (milling, carbon dioxide treatment, magnetization, etc.) and chemical (acid/alkali treatment) techniques (Cha et al. 2016; Tan et al. 2016; Dai et al. 2017). The biochar can be effectively used for the adsorption of heavy metals, anions, and organic pollutants in a wide range of concentration. Other applications include alternative of fuel particularly coal, catalyst/catalyst support, enhancing soil fertility, and adsorbent of air pollutant. Therefore, biochar can be considered as a potential solution for major global issues such as air/water pollution, climate change, and soil degradation (Creamer and Gao 2016).

Combustible natural resources, fuels, cement, and other chemical products are the major sources of environmental concern particularly global warming. Among all gases, CO<sub>2</sub> has been considered critical and required urgent mitigation as suggested by United Nations Framework Convention on Climate change and Intergovernmental Panel on Climate Change (IPCC). The major mitigation options provided by IPCC include renewable energy, nuclear power, CO<sub>2</sub> capture, sequestration, and mineralization. However, due to intensive cost involved, a renewable, efficient, and economic CO<sub>2</sub> sorptive materials are desired (Ello et al. 2013). Researchers globally are focussing on biochar performance against CO<sub>2</sub> sorption (Coromina et al. 2016; Deng et al. 2014). The carbon-rich biochar can probably last millennia and therefore can provide a strategic option for CO<sub>2</sub> sequestration. Numerous studies are evident of CO<sub>2</sub> sorption on biochar surface and therefore biochar amendment in soil can also be a promising option.

Continuous anthropogenic activities resulted in surface and underground water pollution causing severe environmental issues such as eutrophication, agitated pH, and metallic poisoning making water unfit for aquatic ecosystem (Khan et al. 2020; Wang et al. 2015c). Major point sources of water pollution include domestic, industrial, and agricultural sectors which leads to the introduction of heavy metals, organic, and anionic contaminants into surface waters. It has been estimated that on an annual basis, > 10 million tons of chemicals are discharged in water environments with the detection of almost >700 chemical compounds (Ali and Gupta 2006). Heavy metal ions such as Pb<sup>2+</sup>, As<sup>3+</sup>, As<sup>5+</sup>, Cd<sup>2+</sup>, and Cu<sup>2+</sup> are toxic and responsible for severe health and environmental issues owing to their high solubility in aqueous medium (Dong et al. 2017; Wang et al. 2015c; Zhou et al. 2017).

Secondly, anions are required for aquatic life sustenance; however, beyond threshold limit they can cause severe damage to aquatic ecosystem and humans. Even a low concentration of anionic contaminants such as NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, PO<sub>4</sub><sup>3-</sup>, and ClO<sup>-</sup> can illustrate adverse impacts, whereas contaminants such as CN<sup>-</sup> and AsO<sub>3</sub><sup>3-</sup>/AsO<sub>4</sub><sup>3-</sup> are toxic and hold the potential to trigger catastrophe (Bhatnagar et al. 2008; Hamadi et al. 2001; Wang et al. 2015c). Conventional removal techniques are generally expensive, possess high operation cost, generate secondary pollutant and toxic sludge, and often resulted in limited performance against lower, yet hazardous heavy metal and anionic contaminant concentrations in wastewater. Biochar derived from waste biomass can reduce the associated cost and environmental issues compared to conventional methods. While adsorption in aqueous medium, a highly porous biochar with excessive surface to mass/volume ratio and binding functional groups greatly enhance its performance (Wang et al. 2015d; Yao et al. 2014; Zhu et al. 2018). However, biochar has few drawbacks in terms of recycling, required cost intensive reagents, and sophisticated instruments.

In presented chapter, an overview of various biomass feedstocks, pre- and post-treatment methods, biochar production techniques, and performance against adsorption of metallic and anionic contaminants are presented. The adsorption mechanism of contaminants on biochar surface has been discussed. This critical chapter also focusses on the future research directions and perspectives of the biochar in the application of wastewater treatment.

## 8.2 Biomass Feedstocks

Among the three main component of biomass, lignocellulosic biomass (lignin and cellulose dominant) are preferred precursors for thermochemical conversion to biochar, with forestry and agricultural sectors being its primary sources (Collard and Blin 2014). The biomass feedstock accommodates various plant polymers, particularly hemicellulose, cellulose, and lignin. The highly complex characteristics of these plant macromolecules are responsible for the quality of biochar and other chemical products post thermochemical conversion (Channiwala and Parikh 2002; Parikh et al. 2005). In present study, the focus has been made on forestry (woody) and agricultural (herbaceous) biomass due to its wide availability and lignocellulosic content in biomass. The proximate and ultimate analysis of forestry and agricultural biomass feedstocks are depicted in Table 8.1.

The major point sources of waste woody biomass are forestry and pulp and paper industries. These biomass are dominant in lignin content which is a complex 3-D structure responsible for binding plant materials into compact fibers, transferring high strength to woody biomass structure (Hao et al. 2014). The thermochemical conversions not only provide biochar with enhanced physicochemical characteristics but also produce valuable bio-oil (depending on the type of thermochemical technique used) (Kambo and Dutta 2015; Liu et al. 2015). Another advantage of woody biomass is that it contains higher organic content which on thermal treatment

**Table 8.1** The proximate and ultimate analysis of forestry and agricultural biomass feedstocks

Biomass	Proximate Analysis (Dry wt. %)			Ultimate Analysis (Dry wt. %)			References
	VM <sup>a</sup>	FC <sup>b</sup>	Ash	C	H	O	
<i>Forestry and hardwood biomass</i>							
Spruce wood	29.25	69.33	1.41	51.88	6.12	40.89	Demirbas (1997)
Beech wood	24.59	74.04	1.36	49.55	6.15	41.22	Demirbas (1997)
Bamboo wood	11.26	86.78	1.96	48.74	6.35	42.75	Channiwala and Parikh (2002)
Chaparral wood	18.57	75.20	6.22	46.94	5.11	40.09	Channiwala and Parikh (2002)
Wood chips	23.48	76.38	0.13	48.09	6.01	45.76	Parikh et al. (2005)
Neem wood	12.21	85.90	1.88	48.29	6.25	43.45	Channiwala and Parikh (2002)
Wood bark	31.78	66.57	1.64	53.08	6.09	40.63	Demirbas (1997)
Red wood	19.95	79.69	0.35	50.58	6.02	42.90	Parikh et al. (2005)
Ailanthus wood	24.77	73.52	1.71	49.53	6.17	40.98	Demirbas (1997)
Mulberry stick	22.72	75.05	2.22	44.19	6.63	46.27	Parikh et al. (2005)
Subabul wood	18.49	80.99	0.51	48.14	5.90	44.73	Channiwala and Parikh (2002)
<i>Agricultural biomass</i>							
Olive husk	26.04	70.24	3.71	49.94	6.24	42.22	Demirbas (1997)
Groundnut shell	21.57	72.66	5.76	48.61	5.61	39.51	Parikh et al. (2007)
Peanut hull	21.10	72.98	5.92	45.76	5.45	39.58	Parikh et al. (2007)
Rice husk	17.01	61.78	21.20	38.49	5.18	34.64	Channiwala and Parikh (2002)
Coconut shell	22.07	77.21	0.72	50.18	5.67	43.40	Channiwala and Parikh (2002)
Pistachio shell	16.90	81.97	1.12	48.83	5.89	43.40	Parikh et al. (2005)
Sal seed husk	27.99	62.61	9.40	48.10	6.51	35.95	Parikh et al. (2005)
Hazelnut shell	28.26	69.25	2.49	52.87	5.59	42.74	Demirbas (1997)
Walnut Shell	18.80	80.00	1.20	49.84	5.62	42.96	Channiwala and Parikh (2002)
Brazil nut shell	22.16	76.09	1.75	49.17	5.69	42.79	Parikh et al. (2007)

<sup>a</sup>Volatile Matter<sup>b</sup>Fixed Carbon

like pyrolysis (as it valorize the organic content at ~500 °C) resulted in a development of complex pore network (Aller 2016). A recent study also reported that the resulting biochar pH is strongly dependent on pyrolysis temperature, i.e., higher the temperature, higher will be the biochar pH. It was suggested that the resulting pH rise is associated with the loss of acidic groups particularly alcohol and carboxyl functional groups along with enhancement of alkaline minerals (Zhang et al. 2017b).

### 8.3 Pretreatment Processes

Biomass feedstocks comprise varying physicochemical properties and thereby required appropriate pretreatment process prior to biochar production. Generally, pretreatment processes can be characterized into three major categories, i.e., physical, chemical, and biological pretreatment processes (Son et al. 2018; Zhang et al. 2017a; Yao et al. 2015).

The physical pretreatment methods broadly consist of crushing, washing, drying, and sieving of biomass feedstock. Generally, biomass feedstock with higher lignocellulosic content is dried at 105 °C until the weight reaches constancy followed by crushing into finer particles (Wang et al. 2016; Zhang et al. 2017a). In special cases particularly with plant feedstock possessing larger range of moisture content, step-wise drying is required. For instance, physical pretreatment of organic sludge includes initial dewatering with subsequent overnight drying in an oven, crushing, sieving, and finally storage in sealed containers (Agrafioti et al. 2013). Moreover, biomass feedstock based on their physicochemical properties sometimes required additional modifications. For instance, waste cardboards and newspapers are shredded, and feedstock is prepared after mixing with pulp (Randolph et al. 2017). The paper mill sludge generally has high content of minerals and therefore required acid-washing followed by rinsing with deionized water (Cho et al. 2017).

Chemical pretreatment methods include chemical reactions to modify and enhance the characteristics of biomass feedstock. The main reason behind chemical pretreatment is to induce functional agents and chemical precursors into biochar which may assist specific type of application. The treatment follows immersion of biomass feedstock into colloidal suspensions or specific chemical solutions, washing, and drying prior to biochar production (Tan et al. 2016). For instance, numerous biochar-based metal oxyhydroxide (i.e., MgO, Fe<sub>3</sub>O<sub>4</sub>, and AlOOH) rich nanocomposites can be synthesized through treatment of biomass with metal ion (MgCl<sub>2</sub>, FeCl<sub>3</sub>, and AlCl<sub>3</sub>) solutions (Zhang et al. 2013; Son et al. 2018). Moreover, biomass can also be modified by induced engineered designed nanoparticles such as nanotubes, clay, and graphene which also resulted in production of nanocomposites (Inyang et al. 2015). To provide biomass/biochar with larger surface area and micro-pore volume, biomass often get treated with corrosive chemicals such as alkali, acids, and oxidants (Zhao et al. 2018).

Biological pretreatment is currently at emerging stage in the field of engineered biochar production, depending on biological processes such as bacterial treatment, biofuel processes, and anaerobic digestion. This treatment is relatively slow but has been proven to compel an efficient biologically activated biochar (Yao et al. 2015). It is evident from the literature that numerous biomass such as bagasse, sludge, and sugar beet were pretreated with anaerobic digestion prior to biochar production and resulted in improved physicochemical characteristics (Yao et al. 2011; Tang et al. 2019). It has been reported that anaerobic digestion enhances the adsorption performance and also improves surface area of resulted biochar (Yao et al. 2011). Other benefits of biological pretreatment include reduction in solid waste, economic

disposal, and eco-friendly bioenergy (Yao et al. 2015). Another example of biological pretreatment includes the conversion of biomass enriched with high content of heavy metals to biochar through bioaccumulation (Wang et al. 2017b). A recent study concluded that the conversion of heavy metal hyperaccumulating biomass into respective biochar through bioaccumulation can simultaneously provide two benefits, i.e., eco-friendly hyperaccumulator disposal and valorized biochar nanocomposites (Wang et al. 2017b).

## 8.4 Biochar Production Processes

Biochar production can be carried out through thermochemical processes such as pyrolysis, hydrothermal carbonization, dry torrefaction, and gasification. However, proper thermochemical process and appropriate operating conditions (i.e., pressure, temperature, moisture, reaction medium, residence time, and heating rate) are essential for obtaining a good quality biochar (Kambo and Dutta 2015; Liu et al. 2015). Table 8.2 provides the ranges of operating conditions and possible yields of biochar for different thermochemical processes.

Among aforementioned thermochemical processes, gasification and dry torrefaction processes are not appropriate for biochar production. A gasification process mainly includes a partial and rapid (10–20 s of residence time) combustion of biomass at relatively higher temperature range of 600–1200 °C. The main objective of gasification is to produce gaseous products from biomass feedstock such producer gas, syngas, H<sub>2</sub>, and CO<sub>2</sub>. Thus, gasification is not an ideal process to produce biochar; however biochar with very low yield (~ 10 wt.%) is produced (Brewer et al. 2009). The biomass contains inorganics and thus converted to oxide forms on high temperature combustion, also polycyclic aromatic hydrocarbons (PAHs) are produced as by-product from gasification process. Hence, metal oxides and PAHs in biochar are considered toxic and problematic for environmental remediation. Also, IBI firmly recommended a minimum accumulation of toxicants and air-pollutants in the produced biochar (IBI 2013).

**Table 8.2** Ranges of operating conditions and possible yields of biochar for different thermochemical processes (Kambo and Dutta 2015; Liu et al. 2015)

Thermochemical process	Residence time	Heating rate (°C min <sup>-1</sup> )	Temperature (°C)	Pressure (Atm)	Yield (%)
Hydrothermal carbonization	10 min–12 h	5–15	180–260	12–25	40–70
Pyrolysis (flash)	<5 s	>800	400–1000	1	10–25
Pyrolysis (fast)	1–10 s	400–800	400–600	1	15–40
Pyrolysis (slow)	1–4 h	5–10	300–800	1	35–50
Gasification	10–60 s	50–100	600–1200	1	<10
Dry torrefaction	0.5–4 h	10–15	200–300	1	50–80

Dry torrefaction on the other hand is a thermochemical process that operates at moderate temperature (200–300 °C) and atmospheric pressure with a residence time ranges between 30 min and few hours (Bach and Tran 2015). Dry torrefaction generally increases the energy density by small portion (~10%) with the release of small fraction of volatile matter and considerable portion still resides in torrefied biochar. Therefore, this process is preferred as a pretreatment of biomass and mostly used in combustion related applications. Also, the physicochemical characteristics of torrefied biochar are in midst of biomass and biochar. Thus, technically torrefied biochar is not generally considered as biochar; however numerous literature argue over the physicochemical characteristics of biochar and torrefied biochar. Hence, the present work mainly focusses on pyrolysis and hydrothermal carbonization processes. Table 8.3 presents typical biochar yields and physicochemical characteristics of thermochemical processes.

### 8.4.1 Pyrolysis

Pyrolysis can be considered as a principal process for the production of biochar. This process mainly involves thermal decomposition of organic matter in biomass at exalted temperatures with constant heating rate and controlled inert medium such as constraint or no oxygen, nitrogen, and carbon dioxide. During pyrolysis, the volatile component of biomass decomposes and released in the form of gases leaving behind carbon dominating biochar as a residual solid. A fraction of volatile matter containing polar and higher molecular weight compounds liquefies (bio-oil) on cooling, whereas non-condensable gases with low molecular weight such as H<sub>2</sub> and CO<sub>2</sub> continue to be in gaseous phase.

On the basis of exalted temperature and heating rate, a pyrolysis process can be broadly categorized as slow, fast, and flash pyrolysis. Slow pyrolysis is usually carried out within a temperature range of 300–800 °C (>1 h) and a constant heating rate of 5–10 °C min<sup>-1</sup>, providing comparatively higher yield of ~50% (Mohan et al. 2006). Fast pyrolysis is conducted within a temperature range of 400–600 °C (2–10 s) at a constant but rapid heating rate of 300–800 °C min<sup>-1</sup>. Fast pyrolysis process generally provides high bio-oil yield and a small biochar yield of ~35% (Onay and Kockar 2003). Lastly, flash pyrolysis also dominates bio-oil yield, conducted at a higher temperatures ~1000–1200 °C (1–2 s) with a tremendous heating rate of ~1000 °C, providing very low biochar yield of ~15% (Onay and Kockar 2003).

In general, the pyrolysis products are strongly influenced by operating parameters, reactor conditions, and physicochemical characteristics of biomass feedstock. For instance, in slow pyrolysis with both low operating temperatures and heating rates, yield of solid product (biochar) dominates. In contrast, high operating temperatures, residence time, and heating rates have positive impact on high heating value and fixed carbon content of biochar. Volatile matters, such as C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>, C<sub>x</sub>H<sub>y</sub>, NH<sub>3</sub>, CO<sub>2</sub>, and CO, are released from biomass on pyrolysis at lower temperatures and the carbon content in biochar is gradually reduced (Becidan et al. 2007).

**Table 8.3** Physicochemical characteristics of biochar synthesized from different thermochemical conversion processes

Biomass	Conversion Technique and operating conditions	SSA <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Yield (%)	Ash (%)	pH	Ultimate analysis			Reference
						C	H	N	
Chicken manure	Pyrolysis, 2 h (550 °C)	7.11	77	87.1	9.9	7.50	0.42	0.77	Zhao et al. (2020)
Rice straw	Pyrolysis, 2 h (550 °C)	4.14	33.5	43.0	10.3	45.69	2.11	1.18	Zhao et al. (2020)
Acacia	Pyrolysis, 2 h (~ 400 °C)	1.30	–	3.5	7.6	69.80	4.40	0.62	Arán et al. (2016)
Coconut fiber	Pyrolysis, 3 h (600 °C)	4.51	–	3.70	7.4	–	–	–	Wu et al. (2017a)
Almond shells	Pyrolysis (650 °C)	145	–	–	–	–	–	–	Kilic et al. (2013)
Sewage sludge	Pyrolysis, 2 h (550 °C)	8.17	78.9	68.9	7.6	19.00	1.69	2.91	Zhou et al. (2017)
Wheat straw	Pyrolysis, 5 h (600 °C)	26.2	–	41.0	9.8	51.00	2.41	1.00	Bogusz et al. (2017)
Rice husk	Pyrolysis, 1 h (650 °C)	21.8	34.0	36.1	–	60.28	0.11	0.40	Jian et al. (2018)
Citrus	Pyrolysis (300 °C)	~ 1.0	41.7	8.45	7.8	60.40	4.42	1.40	Wang et al. (2015a)
Anaerobic sludge	Pyrolysis, 2 h (600 °C)	163.0	52.8	–	–	28.10	1.29	9.71	Ni et al. (2019)
Rice husk	HTC, 1 h (260 °C)	3.5	28.0	2.7	–	73.4	5.0	2.8	Jian et al. (2018)
Rice husk	HTC, 20 min (300 °C)	358	80.6	60.0	–	–	–	–	Lju and Zhang (2011)
Sawdust	HTC, 12 h (190 °C)	7.88	–	–	–	60.88	6.01	0.96	Deng et al. (2019)
Banana peel	HTC, 2 h (230 °C)	31.7	15.7	0.55	–	71.40	6.31	0.61	Zhou et al. (2017)
Pinewood sawdust	HTC, 1 h (300 °C)	425	53.9	2.8	–	–	–	–	Lju and Zhang (2011)
Wood chips	Gasification, 1 h (1000 °C)	258	–	0.27	–	–	–	–	Runtti et al. (2014)

<sup>a</sup>Specific Surface Area



However, with higher temperature, the discharge of carbon-dominating compounds such as C<sub>x</sub>H<sub>y</sub>O<sub>z</sub> and C<sub>x</sub>H<sub>y</sub> starts decreasing without affecting the random discharge of NH<sub>3</sub>, CO<sub>2</sub>, and CO, resulting in higher carbon content in the residual biochar. Also, higher the discharge of volatile matter, higher will be the pore volume and surface area in resulting biochar.

Apart from operating parameters discussed earlier, moisture content in biomass feedstock is also found to aid the biochar yield; however, it leads to energy intensive process. The lignocellulosic content of biomass also greatly modulates the biochar production. Numerous reports evident that biomass with higher lignin ratio such as pine wood begets or spruce wood resulted in biochar with both higher biochar yield and fixed carbon content (Antal and Grønli 2003). Another important parameter includes the proportion of inorganic compounds particularly containing alkaline earth metals in feedstock. It has been reported that these alkaline earth metals can play a catalytic role during thermochemical decomposition of biomass (Yaman 2004). Pretreatment of biomass feedstock with dilute acid or hot water has also been found to reduce the biochar yield and can be explained as hot water and dilute acid can considerably dissolve the alkaline earth metals from the biochar. Under hydrogen environment, pyrolysis of various biomass feedstocks such as woody, herbaceous, microalgae, and poultry litter showed a reduction in biochar yield and increment in polycyclic aromatic hydrocarbons PAHs with rise in temperature (Mcbeath et al. 2015). Biochar with higher carbon content such as derived from woody biomass possesses low ratio of PAHs and total organic carbon (TOC), whereas biochar derived from low carbon content biomass such as herbaceous biomass possesses high ratio of PAHs and TOC. Additionally, pH and surface area of the produced biochar are mainly influenced by pyrolysis temperature, while ash content, TOC, inorganic content, carbon content are predominantly affected by the group of biomass feedstock (Zhao et al. 2013). Experimental and modelling results in available literature are evident that with proper selection of biomass feedstock and pyrolysis operating conditions, the physicochemical characteristics of produced biochar can be altered suitable for specific applications.

Apart from biochar, pyrolytic products such as syngas (gas) and bio-oil (liquid) are other two important pyrolysis products, contributing to a distribution of almost 25–30% of overall pyrolysis products. All three products of pyrolysis are considered as renewable energies and can be used as fuel or fuel supplements. Therefore, the overall pyrolysis process can be considered as cost-effective and environmentally benign process (Zhang et al. 2010). A recent research examined the modelling and empirical relationship between biochar and bio-oil yield and economic trade-off. Through quadratic polynomial functions, optimum values of pyrolysis temperature for biochar/bio-oil price ratio under different economic conditions were estimated. The biochar or bio-oil yield and related characteristics are decidedly associated with type of biomass feedstock and pyrolysis operating conditions.

### 8.4.2 *Hydrothermal Carbonization (HTC)*

Hydrothermal carbonization (HTC) is an emerging thermochemical process where biochar is a dominating product. The chemistry involved in biochar formation and the reaction rates are still at infant stages due to limited research. Hydrothermal carbonization, hydrothermal gasification, and hydrothermal liquefaction are the three sub-classification of HTC process. Each process has different dominating final product and therefore used based on the required applications. The major advantages (other than high conversion efficiency) of HTC is that no pre-drying of biomass is required and operates at moderate temperatures (180–260 °C) with autogenous pressure controlled within a reactor for specific residence time (Hoekman et al. 2013).

The HTC process generally operates under subcritical condition where water properties and vapor pressure considerably vary with reaction temperature. The merit of water in subcritical state is that even at temperatures higher than 150 °C, water exist in liquid phase and resembles the characteristics of nonpolar solvent; for instance, at ~200 °C, it behave like methanol, whereas at ~300 °C, it behaves like acetone. With >374 °C, the dielectric constant of water decreases, thereby making the hydrogen bonds of water fragile which leads to higher ionization constant. This turns the water to act like an acid as the alienation of water increases and H<sub>2</sub>O molecules start to break, forming H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> ions (Marcus 1999). Unlike normal water, the subcritical water encourages a competently higher H<sup>+</sup> concentrate which can be considered extremely suitable for organic compound degradation through acid catalyzed reaction, though no acid was added, and therefore possessing a strong tendency to dissolve organic fraction of biomass in subcritical water. The polymeric portion of lignocellulosic biomass comprises low molecular weight compounds, and thereby during subcritical condition, the breakdown tendency of organic compounds particularly with COOH and OH bonds increases drastically and eventually dissolves in water. Additionally, there are reports emphasizing that the polychlorinated biphenyls and polychlorinated dibenzofurans, being a hazardous waste, can be destroyed under sub- and super-critical water (Weber et al. 2002).

HTC is the only thermochemical process suitable for wet biomass or biomass with high moisture content as water is a solvent used in this process. This leads to the elimination of biomass pre-drying step, thereby reducing the overall cost of the process as the pre-drying step is considered time consuming and energy intensive step. HTC process provides 3-phase products, i.e., biochar, bio-oil, and a mixture of gases dominated by CO<sub>2</sub>. The distribution of these phases is dependent on operating conditions particularly temperature (Kambo and Dutta 2014). The biochar yield (wt.%) obtained from HTC process generally varies from 40% to 70%. The produced biochar is generally obtained in the form of slurry and thus required dewatering steps which include filtering, mechanical compressing, and drying prior its usage. The mechanical compressing reduces the moisture content to <50% because in the reactions involved in the dehydratization and decarboxylation, a considerable fraction of oxygen is removed (Kambo and Dutta 2014). This significantly

suppresses the time and energy required for thermal/ solar drying for achieving further reduction in biochar moisture content making the process economical.

In the biochar producing process through thermochemical process, the rigid polymeric lignin content is reduced to low molecular weight chemical compounds. However, in HTC process, subcritical water initiates the hydrolysis of biomass which is the first step of biomass decomposition. The hydrolysis of biomass resulted in a rapid depolymerization forming water-soluble monomers and oligomers. Lignocellulosic biomass feedstocks generally contain various inorganics such as Na, Ca, Mg, P, S, and Fe which after thermochemical combustion process get converted to their respective oxide forms, i.e., Na<sub>2</sub>O, CaO, MgO, P<sub>2</sub>O<sub>5</sub>, SO<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub> and reside in ash (Tortosa Masia et al. 2007). These inorganic metal oxides are responsible for fouling, corrosion, clinker formation, and slagging. However, in the case of HTC process, acetic acid is formed as a by-product stream and due to acid solvation metals are leached out, thereby curtailing the distribution of ash in produced biochar (Liu and Balasubramanian 2014). Moreover, with chlorine-rich biomass feedstock, HTC process converts chlorine from organic to inorganic form and thus restrains the formation of corrosive and dioxins that are hazardous for the aquatic environment (Zhao et al. 2014).

The HTC process is a water intensive process and a continuous supply of massive amount of water for industrial HTC is a major challenge for a full-scale operation and also is economically nonviable. A recent study found that for the HTC conversion (at 260 °C) of miscanthus into 1 ton of biochar with ~50 wt. % yield, 12 tons of water is required. Therefore, for industrial HTC process, water recirculation and heat recovery is critical which will indirectly reduce both the amount and cost involved in wastewater treatment and lowers the expenditure for external heat (Stemann et al. 2013).

## 8.5 Posttreatment Processes

For the enhancement of physicochemical characteristics of produced biochar suited for diverse applications, required posttreatments are often carried out. Posttreatments generally modify the surface chemistry, pore volume, surface area, composited nanoparticles, and functional groups on produced biochar (Tan et al. 2016; Dai et al. 2017). Presented chapter briefly overviews the commonly applied posttreatments such as chemical, magnetization, and mechanical treatment.

Chemical or corrosive posttreatments of biochar generally include alkali, acid, and advanced oxidation for the alteration and modification in surface chemistry. The most commonly used chemicals are KOH, KMnO<sub>4</sub>, NaOH, HNO<sub>3</sub>, HCl, and H<sub>2</sub>O<sub>2</sub> (Cha et al. 2016; Wang et al. 2017a). The main objectives of chemical treatment are to induce higher specific surface area, micropore volume, functional groups, and composites to improve the sorption capacity. Also, an integrated chemical treatment is also evident of providing superior physicochemical properties. For instance, an integrated NaOH(alkali)-HNO<sub>3</sub>(acid) posttreatment on municipal sewage sludge

biochar resulted in induction of considerable oxygen-rich functional groups, generates porosity and thereby enhances the specific surface area of biochar, which significantly raises the adsorption capacity of tetracycline over  $286 \text{ mg g}^{-1}$  (Tang et al. 2018). KOH and  $\text{KMnO}_4$  treatment on peanut-derived biochar increase the surface area and active sites and thereby significantly enhance the adsorption of  $\text{Ni}^{2+}$  in aqueous medium (An et al. 2019). An example of potential oxidant is  $\text{H}_2\text{O}_2$ , a recent study provided evidence of generated oxygen and carboxyl groups on  $\text{H}_2\text{O}_2$ -treated manure-based biochar surface, illustrating exceptional heavy metal adsorption capacity (Wang and Liu 2018).

Magnetization is a posttreatment process mainly employed to induce magnetic characteristics in treated biochar. The iron oxides such as  $\text{CoFe}_2\text{O}_4$ ,  $\gamma\text{-Fe}_2\text{O}_3$ , and  $\text{Fe}_2\text{O}_3$  are generally used to load Fe content into biochar (Tan et al. 2016). An important advantage of magnetic modified biochar is that a magnetic separator can be used to isolate biochar from the aqueous solution (Son et al. 2018). A peanut hull-derived biochar has developed considerable adsorption rate for  $\text{Cr}^{6+}$  post treating with magnetic zero-valent iron (at  $800^\circ\text{C}$ ), manifesting with higher surface area and loaded reductive iron (Liu et al. 2019a). The magnetic characteristics in biochar can also be introduced through Fe-based composites synthesized by direct coprecipitation of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  on the surface of the biochar. For instance, the switchgrass-derived Fe-based biochar composite prepared by treating with an aqueous solution of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  recorded the highest metribuzin adsorption capacity of  $205 \text{ mg g}^{-1}$  (Essandoh et al. 2017).

Mechanical posttreatment processes are often used to obtain a required particle size suitable for the adsorption-related applications. Mechanical posttreatment generally includes crushing or grinding followed by sieving. Ball milling is a most common mechanical posttreatment process owing to its simple operation and efficient performance. It utilizes the kinetic energy obtained from heavy metallic balls to crush/grind biochar, thereby breaking the chemical bonds and can reduce the particle size even up to nanoscales (Lyu et al. 2017). The physicochemical characteristics of biochar such as negative zeta potential, pore volume, surface area, and oxygen-rich functional groups greatly modify post ball milling (Wang et al. 2017a; Lyu et al. 2018). For instance, when compared with pristine bagasse biochar, ball milled biochar illustrates much higher adsorption capacities for both  $\text{Ni}^{2+}$  and aqueous methylene (Lyu et al. 2018). The superior performance can be the resultant effect of higher surface area due to induced cracks, uncover graphitic structure, and oxygen-rich functional groups. A recent study successfully developed nitrogen-doped biochar by simultaneous ball milling of ammonium hydroxide and pristine biochar. The nitrogen-doped biochar resulted in providing enhanced adsorption capacities against anionic reactive red and acidic carbon dioxide (Xu et al. 2019). Mechanical posttreatment therefore not only reduces the size of the particle but is also capable of elemental doping.

Although posttreatments feature numerous advantages, a wider range of research to extract maximum benefits still needs to be explored. For instance, recent research provides the possibilities for posttreatment of biochar by organic solvents. A biochar derived from municipal solid waste through methanol provides an esterification

between biochar and carbonyl groups, culminated with considerable enhancement in adsorption performance of tetracycline (Jing et al. 2014). Despite its significant performance, organic solvents are still not commercially used because of its volatile nature and high cost.

## 8.6 Biochar as an Adsorbent

### 8.6.1 CO<sub>2</sub> Capture

The conventional physical activation of thermochemically synthesized biochar not only exhibits improved structural properties but can also significantly adsorb CO<sub>2</sub>. For instance, a study reported that biochar synthesized via pyrolysis of biomass (vine shoots) at 600 °C followed by physical activation in CO<sub>2</sub> medium for 3 h at 800 °C exhibited an improved surface area of 765 m<sup>2</sup> g<sup>-1</sup> where the surface area of unmodified biochar was 1.91 m<sup>2</sup> g<sup>-1</sup> (Manya et al. 2018). The more economic procedure can be the employment of single-step pyrolysis followed by physical activation as it will make the process less time consuming and hence consumes less energy. Another study performed an optimized work and reported the effect of activation time, temperature, and O<sub>2</sub>:N<sub>2</sub> ratio on biochar synthesized from almond shells and olive stones under CO<sub>2</sub> environment (Gonzalez et al. 2013). It was observed that a cumulative CO<sub>2</sub> intake during both processes was 3.1 mmol g<sup>-1</sup>. Chemical activation however shows greater tendency of CO<sub>2</sub> adsorption than physical activation. A study reported the synthesis of biochar derived from Africa palm shells via pyrolysis for 1 h at 600 °C in N<sub>2</sub> medium having a surface area of 365 m<sup>2</sup> g<sup>-1</sup>. The synthesized biochar was then chemically activated by KOH with a ratio of 3:1 (dry biomass wt. %) heated for 1 h at 860 °C providing a surface area of 1250 m<sup>2</sup> g<sup>-1</sup>. The improved surface area was the resultant effect of increased pore generation and nano- and micropore volume (Ello et al. 2013). In addition, the maximum CO<sub>2</sub> adsorption capacity increased from 1.9 mmol g<sup>-1</sup> (biochar) to 4.4 mmol<sup>-1</sup> (chemically activated biochar) at 25 °C and atmospheric pressure. Similar trend were observed with other biochar such as wheat flour, rice husk, vine shoots, camellia japonica, and pine nut shells with CO<sub>2</sub> adsorption capacities of 3.48, 3.71, 2.46, 5.0, and 5.0 mmol g<sup>-1</sup>, respectively (Li et al. 2015; Hong et al. 2016; Coromina et al. 2016; Deng et al. 2014). This range of CO<sub>2</sub> adsorption falls in the range provide by other porous CO<sub>2</sub> adsorbent such as metal organic frameworks at ambient conditions (Oschatz and Antonietti 2018). Structural characteristics and CO<sub>2</sub> adsorption performance of thermochemically derived biochar is depicted in Table 8.4.

Considering the kinetic diameters of gaseous molecules post combustion (CH<sub>4</sub>: 0.380, O<sub>2</sub>: 0.346 nm, CO<sub>2</sub>: 0.330 nm, N<sub>2</sub>: 0.364 nm), selective CO<sub>2</sub> adsorption can be a serious challenge. Besides, elevated temperature is another factor which can reduce the CO<sub>2</sub> adsorption capacity due to high kinetic energy of gaseous molecules (Lahijani et al. 2018). Therefore, the interactions of CO<sub>2</sub> with biochar surface should

Table 8.4 Structural characteristics and CO<sub>2</sub> adsorption performance of thermochemically derived biochar

Biochar synthesis		Structural characteristics of biochar			Adsorption capacity (mmol g <sup>-1</sup> ) at 25 °C			Reference
Biomass	Thermochemical conversion	Modification	SSA <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	0.15 (bar)	1.0	20	
Mesquite wood	Hydrochar, 450 °C, 2 h	KOH exposure (5:1); heating (N <sub>2</sub> ), 800 °C, 45 min	3162	1.63	–	6.5	–	Li et al. (2016)
Jujun grass	Hydrochar, 250 °C, 2 h	KOH exposure (4:1); heating (N <sub>2</sub> ), 700 °C, 1 h	3140	1.51	0.9	3.9	12.5	Coromina et al. (2016)
Coconut shells	Pyrolysis (N <sub>2</sub> ), 500 °C, 2 h	KOH exposure (3:1); heating (N <sub>2</sub> ), 800 °C, 45 min	1169	0.45	1.43	4.21	–	Yang et al. (2017)
Camellia Japonica	Hydrochar, 250 °C, 2 h	KOH exposure (2:1); heating (N <sub>2</sub> ), 700 °C, 1 h	1350	0.56	1.43	5.1	14.0	Coromina et al. (2016)
Pine nut shell	Pyrolysis, 500 °C, 1.5 h	KOH exposure (2:1); heating (N <sub>2</sub> ), 700 °C, 1.5 h	1490	0.65	2.1	4.9	–	Deng et al. (2014)
Jujun grass	Hydrochar, 250 °C, 2 h	KOH exposure (2:1); heating (N <sub>2</sub> ), 700 °C, 1 h	1510	0.75	1.5	4.9	12.8	Coromina et al. (2016)
Camellia japonica	Hydrochar, 250 °C, 2 h	KOH exposure (4:1); heating (N <sub>2</sub> ), 800 °C, 1 h	3536	1.83	0.67	2.8	25.8	Coromina et al. (2016)
					Adsorption capacity (mmol g <sup>-1</sup> ) at 0 °C			
Vine shoots	Pyrolysis (N <sub>2</sub> ), 600 °C, 1 h	KOH exposure (5:1); heating (N <sub>2</sub> ), 700 °C, 1 h	1440	0.68	2.28	6.1	–	Manya et al. (2018)
Arundo donax	Pyrolysis (single step)	KOH exposure (2:1); heating (N <sub>2</sub> ), 600 °C, 2 h	1120	0.60	–	6.2	–	Singh et al. (2017)
Vine shoots	Pyrolysis (N <sub>2</sub> ), 600 °C, 1 h	KOH exposure (2:1); heating (N <sub>2</sub> ), 600 °C, 1 h	1302	0.55	2.2	6.0	–	Manya et al. (2018)
Pine nut shell	Pyrolysis, 500 °C, 1.5 h	KOH exposure (2:1); heating (N <sub>2</sub> ), 700 °C, 1.5 h	1489	0.65	3.2	7.6	–	Deng et al. (2014)

Vine shoots	Pyrolysis (N <sub>2</sub> ), 600 °C, 1 h	Activation (CO <sub>2</sub> ), 800 °C, 3 h	766	0.4	1.9	4.1	–	Manya et al. (2018)
				0 °C	25 °C	100 °C		
Almond shells	Pyrolysis (single step)	Activation (CO <sub>2</sub> ), 750 °C, 4 h	860	0.35	–	2.6	0.9	Gonzalez et al. (2013)
Rice husk	Pyrolysis (N <sub>2</sub> ), 520 °C, 20 min	KOH exposure (3:1); heating (N <sub>2</sub> ), 780 °C, 1 h	2698	1.12	6.25	3.7	–	Li et al. (2015)
Africa palm shell	Pyrolysis (N <sub>2</sub> ), 600 °C, 1 h	KOH exposure (3:1); heating (N <sub>2</sub> ), 850 °C, 1 h	1249	0.6	6.1	4.3	–	Ello et al. (2013)
Wheat flour	Pyrolysis (N <sub>2</sub> ), 900 °C, 2 h	KOH exposure (3:1); heating (N <sub>2</sub> ), 700 °C, 1 h	1440	0.66	5.67	3.5	1.1	Hong et al. (2016)
Olive stones	Pyrolysis (single step)	Activation (CO <sub>2</sub> ), 800 °C, 6 h	1211	0.50	–	3.0	0.8	Gonzalez et al. (2013)

<sup>a</sup>Specific surface area

be selective and strong enough to adsorb  $\text{CO}_2$  molecules. As a nonpolar Lewis acid,  $\text{CO}_2$  adsorption has been widely studied through surface functionalization which is found to improve alkalinity and hydrophobicity of biochar surface (Oschatz and Antonietti 2018; Rashidi and Yusup 2016; Choi et al. 2009). For the enhancement of  $\text{CO}_2$  adsorption on biochar surface, surface functionalization generally includes heteroatom doping, metal and metal oxide impregnation, and  $\text{N}_2$ -based thermal treatment. For instance, a study reported an amine functional group doping on black locust-derived biochar surface (Zhang et al. 2016). Biochar was synthesized via pyrolysis followed by KOH-based chemical activation providing large surface area and micropore volume. The activated biochar was then thermally treated under  $\text{N}_2$  and  $\text{NH}_3$  environment for the induction of amine functional groups on biochar surface. Compared to pristine biochar and activated biochar, the  $\text{CO}_2$  adsorption capacity after amine functionalization increased 2.7 times ( $5.05 \text{ mmol g}^{-1}$ ) and 35% higher, respectively, at ambient condition (Zhang et al. 2016). The elevated temperature ( $50^\circ\text{C}$ ) resulted in reduction of  $\text{CO}_2$  adsorption ( $3.37 \text{ mmol g}^{-1}$ ), still competitive with other activated biochar. However, surface functionalization without chemical activation showed ordinary  $\text{CO}_2$  adsorption capacity. The biochar derived from rice husk and cotton stalk with amine surface functionalization (without chemical activation) did not show much improved  $\text{CO}_2$  adsorption capacity (Zhang et al. 2014; Zhang et al. 2015). Other sources of nitrogen-based functional groups doping include urea, chitosan, melamine, and aminopropyl triethoxysilane (Singh et al. 2017; Bamdad et al. 2018). A recent study reported the  $\text{CO}_2$  adsorption capacity of walnut-derived biochar which was KOH activated followed by amine functionalization via urea (Rouzitalab et al. 2018). Remarkable  $\text{CO}_2$  adsorption capacity of  $7.42 \text{ mmol g}^{-1}$  was recorded with  $\text{CO}_2/\text{N}_2$  selectivity of 12.7 at ambient condition (Rouzitalab et al. 2018).

Metal/metal oxide doping has also been found to enhance  $\text{CO}_2$  adsorption capacity with considerable selectivity. The saw dust-derived biochar (activated by  $\text{MgCl}_2$ ) doped with MgO showed remarkable  $\text{CO}_2$  adsorption capacity of  $5.45 \text{ mmol g}^{-1}$  at  $80^\circ\text{C}$  and atmospheric pressure. Generally,  $\text{CO}_2$  adsorption capacity decreases with increase in adsorption; however in this reported study the  $\text{CO}_2$  adsorption capacities increased from  $50^\circ\text{C}$  to  $80^\circ\text{C}$  by 2.7 and  $5.45 \text{ mmol g}^{-1}$ , respectively, whereas decreased at  $400^\circ\text{C}$  with  $1.3 \text{ mmol g}^{-1}$  (Liu et al. 2013). Provided explanation suggested the strong hydrogen bond between OH and  $\text{CO}_2$  and formation of  $\text{MgCO}_3$  were responsible for stronger interaction at  $80^\circ\text{C}$  (Liu et al. 2013). Another study reported  $\text{CO}_2$  adsorption on Persian wood-derived biochar doped with copper oxide (Nowrouzi et al. 2018). The  $\text{CO}_2$  adsorption capacities of activated and metal oxide impregnated biochar were found to be  $3.02$  and  $6.78 \text{ mmol g}^{-1}$ , respectively, at  $30^\circ\text{C}$  and 1 bar. Similar  $\text{CO}_2$  adsorption capacities were observed with Persian wood-derived biochar doped with other metal oxides such as MgO ( $5.98 \text{ mmol g}^{-1}$ ), Cu/Ni oxides ( $6.27 \text{ mmol g}^{-1}$ ), Al oxide ( $5.82 \text{ mmol g}^{-1}$ ), and Ni oxide ( $6.48 \text{ mmol g}^{-1}$ ).



## 8.6.2 Heavy Metals

Numerous biomass feedstocks derived biochar have been thoroughly investigated for the removal of heavy metal ions from natural and wastewater. Researchers have identified various factors such as solution pH, attached functional groups, specific surface area, synthesis dosage, and biochar modification that can influence the heavy metal selectivity and removal performance of biochar (Hong et al. 2019; Senthilkumar et al. 2020; Wang et al. 2013).

### 8.6.2.1 pH and Electric Charge

The electric charge and pH associated with biochar can be significant in deciding the adsorption capacity of particular heavy metal. These parameters mainly depend on the type of biomass and synthesis method (Hong et al. 2019). For instance, in the case of pyrolysis, as the temperature rises, biochar surface starts losing the attached acidic functional groups and results in rise of biochar pH, consequently enriching the alkaline characteristics (Kwak et al. 2019). The loss of acidic functional groups affecting the pH also indirectly regulates the adsorbent protonation, and thereby can modify biochar surface charge (Vijayaraghavan and Yun 2008). In general, low pH resembles presence of high concentration of H<sup>+</sup> ions which can compete with cationic metal ions and therefore can reduce the adsorption capacity and vice versa (Vijayaraghavan and Yun 2008). It was observed that with biochar derived from corn stalk, the adsorption capacity of Pb(II) surged with increase in solution pH from 4 to 6. It was also concluded that the adsorption of Pb(II) ions were suppressed in acidic medium due to competition with H<sup>+</sup> ions (Liu et al. 2019b). However, this is not the case with every metal ion as it was also found that the adsorption capacity of As(V) via biochar synthesized from *Ulva reticulata* increased by ~40% when the pH of the solution was raised from 2 to 4, and decreased thereafter. It was suggested that the form of arsenic within the pH range 4–6 is H<sub>2</sub>AsO<sub>4</sub><sup>-</sup> and HAsO<sub>4</sub><sup>2-</sup>, and the lack of high protonated active sites at higher pH weaken the electrostatic attraction (Senthilkumar et al. 2020).

### 8.6.2.2 Surface Functional Groups

Surface functional groups are considered as one of the most significant factor heavy metal ions removal because of their adsorption and chelate formation characteristics (Carrier et al. 2017). The organic functional groups present in lignocellulosic biomass particularly hardwood feedstocks can be transferred to biochar during thermochemical conversion, resulting in chelation with metal ions, electrostatic interaction, adsorption, and ion exchange (Xie et al. 2017). It was identified that the biochar chemical structure is enriched with functional groups such as carbonyl (-C=O), aliphatic carbon (-C-H), hydroxyl (-O-H), amine (-N-H), and numerous other aromatic

groups (Wang et al. 2013). The authors also investigated a temperature-dependent transformation of functional groups, i.e., when a pyrolysis temperature was raised from 500 to 700 °C, a considerable loss in amine and carbonyl groups were observed whereas aliphatic and hydroxyl groups were completely vanished (Wang et al. 2013). It has been noticed that the  $\text{Cd}^{2+}$  ions prefer to interact with deprotonated carboxyl groups on biochar surface, and being a weak Lewis acid,  $\text{Cd}^{2+}$  ions give preference to interactions with  $\pi$  electrons of carboxyl group (Harvey et al. 2011). Another study proposed that the metal ions such as  $\text{Zn}^{2+}$ ,  $\text{Cu}^{2+}$ , and  $\text{Ni}^{2+}$  are removed due to carboxylate chelation, whereas  $\text{Pb}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ni}^{2+}$  are removed by conversion to their oxide forms due to hydrolyses (Carrier et al. 2017).

### 8.6.2.3 Biochar Modification

Biochar modifications can further enhance the adsorption capacity by improving the physicochemical characteristics of biochar. Among all available biochar modification methods, metal or mineral impregnation, acid/base, and functional group modifications are most common (Rosales et al. 2017; Wan et al. 2018; Wang et al. 2015e; Liu et al. 2012).

Metal, metal oxide, and mineral impregnation are preferred to enhance the adsorption performance by improving pore porosity and functional groups development particularly enriched with oxygen. Electrostatic attraction,  $\pi$ —metal ions bonding, surface complexes, and ion exchange can be the possible interactions between biochar and metal cations (Rosales et al. 2017). A study reported a pyrolysis of a mixture of hickory chips, bagasse, and bamboo with clay for 1 h at 600 °C and found a surge of five times in adsorption potential when compared with only biochar (Yao et al. 2014). The impregnation of ferric chloride into biomass resulted in biochar with high surface area due to evaporation of ferric chloride during pyrolysis leaving behind highly porous structure (Yap et al. 2017). Another study revealed the generation of electrostatic adsorption sites, doubling the As adsorption capacity ( $429 \text{ mg kg}^{-1}$ ) post impregnation with iron oxide particles (Wang et al. 2015e). A nanocomposite fabricated from biochar and hydroxyapatite resulted in improved surface area ( $> 15$  times) and doubling the Pb(II) adsorption capacity to  $1000 \text{ mg g}^{-1}$  against virgin biochar (Wang and Wang 2018). Impregnation of hydrated manganese oxide particles were carried out into biochar derived from peanut shells, sequestering Cd(II) and Pb(II) via manganese oxide induced -COO- and -CO- generated surface complexation (Wan et al. 2018). The improvement in terms of removal performance of Cd(II) and Pb(II) was found to be 4–6 times more than virgin biochar. Table 8.5 demonstrates various biochar modification techniques, adsorption characteristics, and the pattern involved in the removal of metal cations from wastewater.

The introduction of various functional groups on biochar surface has been proved to greatly enhance the adsorption performance. The functional groups can be incorporated through acid/base treatment by altering the porous structure and surface acidities. Chemicals such as HCl,  $\text{H}_3\text{PO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ , NaOH, and KOH are

**Table 8.5** Modification, adsorption characteristics, and behaviors involved in the removal metal cations from wastewater

Type	Biomass	Modification and pyrolysis temperature	Target metal ions	Adsorption capacity (mg g <sup>-1</sup> )	Behaviors	Reference
Metallic nano-particles	Sugarcane leaf	MgO nanoflakes (550 °C)	Pb <sup>2+</sup>	103	Nano sized carbon sponge enriched with -OH and Mg-OH groups	Li et al. (2018)
	Bamboo	H <sub>2</sub> O <sub>2</sub> + nZVI HNO <sub>3</sub> + nZVI (600 °C)	As <sup>5+</sup> Ag <sup>+</sup>	109.1 1218	Modifies surface free energy and atom structure, lowers nZVI's chemical reactivity	Wang et al. (2017a)
	Cornstalk	nZVI + HCl (500 °C)	Cr <sup>6+</sup>	–	Modification resulted in improved efficiency of ~35%	Dong et al. (2017)
	Cottonwood	Fe <sub>2</sub> O <sub>3</sub> nanoparticles (600 °C)	As <sup>5+</sup>	3147	Increases ferromagnetic property and surface area	Zhang and Gao (2013)
	Herbal residue	nZVI + sulfide	Cr <sup>6+</sup>	130	Providing a precise core shell structure	Zhu et al. (2018)
Mineral loadings	Pinewood	MnCl <sub>2</sub> ·4H <sub>2</sub> O (600 °C)	As <sup>5+</sup>	4.91	Adsorption enhanced by 72.3 times	Wang et al. (2015c)
	Oak bark	Fe <sup>2+</sup> / Fe <sup>3+</sup>	Pb <sup>2+</sup>	–	Provide porosity, O-containing group, and negative sites	Yao et al. (2014)
	Pinewood	Hematite (600 °C)	As <sup>5+</sup>	0.43	Enhanced surface area and induce magnetic properties	Wang et al. 2015d
	Hickory chips	Fe impregnation (600 °C)	As <sup>5+</sup>	2	Enhanced O-containing group through crystalline Fe(OH) <sub>2</sub>	Hu et al. (2015)
	Marine macroalgae	Magnetite	Cd <sup>2+</sup>	55.86	Easy separation	Wang et al. (2019)

(continued)

**Table 8.5** (continued)

Type	Biomass	Modification and pyrolysis temperature	Target metal ions	Adsorption capacity (mg g <sup>-1</sup> )	Behaviors	Reference
Surface oxidation/reduction	Rape straw	KMnO <sub>4</sub> exposure (600 °C)	Cd <sup>2+</sup>	80.9	Enhanced O-containing group and micropore creation	Li et al. (2017)
	Banana peels	20 wt. % H <sub>3</sub> PO <sub>4</sub> (230 °C)	Pb <sup>2+</sup>	359	Enhances O/C ratio and surface area	Zhou et al. (2017)
	Municipal solid waste	KOH exposure (500 °C)	As <sup>5+</sup>	31	Modifies functional group, texture, and surface area	Jin et al. (2014)
	Bamboo charcoal	10 wt. % HNO <sub>3</sub>	Hg <sup>0</sup>	92.1	Enhances COOH and C=O groups	Tan et al. (2012)
	Broiler litter	Activated by steam	Cu <sup>2+</sup> , Cd <sup>2+</sup> , Ni <sup>2+</sup>	–		

employed for desired modifications (El-Hendawy 2003; Liu et al. 2012). For example, it has been reported that a controlled exposure of HNO<sub>3</sub> to biochar resulted in the development of oxygen groups on biochar surface providing improved hydrated Pb<sup>2+</sup> adsorption (El-Hendawy 2003). A recent study conducted an experiment on adsorption of tetracycline by H<sub>2</sub>SO<sub>4</sub> and KOH-modified biochar (Liu et al. 2012). The results highlighted that KOH treatment provided better physicochemical characteristics to biochar such as porosity, carbon and oxygen-rich functional groups, and large surface area, in comparison to H<sub>2</sub>SO<sub>4</sub>-treated and unmodified biochar (Liu et al. 2012). In addition, hydrogen peroxide-exposed biochar synthesized from peanut hull showed oxygen enrichment in terms of carboxyl groups resulting in Pb(II) adsorption increment of 20 times compared to unmodified biochar (Yao et al. 2014).

### 8.6.3 Anions

The presence of anionic contaminants in water particularly derived from nitrogen, phosphorus, arsenic, and chromium even in trace amount can be catastrophic for all living organisms. For instance, nitrogen and phosphorus are among the vital nutrients for living organisms; however, exceeding threshold limits can cause eutrophication in surface waters such as lakes, rivers, and even oceans. Conventional processes for the removal of nitrogen and phosphorus include biological process as these processes are environmentally benign and cost effective. Although biological processes have advantages, they are generally slow particularly with high nitrogen

and phosphorus concentration in wastewater. Other common treatment methods include membrane filtration, electrochemical, adsorption, and ion exchange (Khan et al. 2020). Also, the most frequently observed heavy metals that exist in anionic form in wastewater are arsenic and chromium. Therefore, the removal processes and corresponding mechanisms for these heavy metal anions from wastewater differ from that of other heavy metal cations. Recently, the biomass-derived biochar and biochar composites have been widely studied and showed superior performances against adsorption of aforementioned anionic contaminants. Following subsections provide brief details of anionic adsorption performances through biochar. Table 8.6 summarizes the anionic adsorption characteristics of biochar.

### 8.6.3.1 Phosphorus

Phosphorus is mostly present in the form of phosphates ( $\text{PO}_4^{3-}$ ) with high solubility in natural and wastewater. A recent study conducted on macroalgae revealed that the pyrolyzed biochar (~ 400–600 °C) showed considerable P removal performance with an adsorption capacity of 12.5–19.1 mg g<sup>-1</sup>, whereas raw macroalgae roots and derived biochar (200 °C) showed no observable adsorption of phosphorus (Jung et al. 2016). The biochar derived from orange peel through pyrolysis within a temperature range of 250–400 °C showed insignificant phosphorus adsorption. Same biochar when modified with Fe demonstrated much enhanced phosphorus adsorption capacity (Chen et al. 2011). Likewise, biochar when treated with AlCl<sub>3</sub> producing Al-based biochar nanocomposite exhibited improved phosphorus adsorption performance with an astonishing adsorption capacity ~135 mg g<sup>-1</sup>, estimated through Langmuir modelling (Zhang and Gao 2013). In addition, a study reported an extraordinary phosphorus adsorption capacity of ~887 mg g<sup>-1</sup> when treated with Mg-Al-biochar nanocomposite synthesized through electro-assisted modification method with MgCl<sub>2</sub> as electrolyte and Al-electrode (Jung et al. 2015).

### 8.6.3.2 Nitrogen

Nitrogen is mostly present in the form of nitrates ( $\text{NO}_3^-$ ) with high solubility in natural and wastewater. Numerous biomass feedstocks derived biochar have been used for the adsorption of nitrates from aqueous solution and real wastewater samples. For instance, a comparative study demonstrates that a biochar derived from waste bamboo provides better nitrate adsorption capacity (~1.25 mg g<sup>-1</sup>) than commercial activated carbon (~1.09 mg g<sup>-1</sup>), an enhanced performance by almost 15% (Mizuta et al. 2004). Similar comparative study was performed by Mishra and Patel (2009), reporting the nitrate adsorption capacities of biochar synthesized from mustard straw, wheat straw, and commercial activated carbon as 1.30, 1.10, and 1.22 mg g<sup>-1</sup>, respectively. Here also the nitrate adsorption capacity of mustard straw is superior than commercial activated carbon (Mishra and Patel 2009). A study conducted on untreated biochar produced via fast pyrolysis showed a low nitrate

**Table 8.6** Anionic adsorption characteristics of biochar

Biochar source/ modification	Target anion	Temperature (°C)	Initial concentration (mg L <sup>-1</sup> )	Adsorption performance	Reference
Bamboo powder	NO <sub>3</sub> <sup>-</sup>	900	10	1.25 mg g <sup>-1</sup>	Mizuta et al. (2004)
Cotton wood/ AlCl <sub>3</sub> impregnation	PO <sub>4</sub> <sup>3-</sup>	600	1–1600	135 mg g <sup>-1</sup>	Zhang and Gao (2013)
Mustard straw	NO <sub>3</sub> <sup>-</sup>	300	25	–	Mishra and Patel (2009)
Peanut shell/ MgCl <sub>2</sub> impregnation	NO <sub>3</sub> <sup>-</sup>	600	20	11.7%	Zhang et al. (2012)
Orange peel/ FeCl <sub>2</sub> and FeCl <sub>3</sub> modification	PO <sub>4</sub> <sup>3-</sup>	400, 700	2.4	11.0% (400 °C) 99.4% (700 °C)	Chen et al. (2011)
Oak sawdust/ LaCl <sub>3</sub> impregnation	NO <sub>3</sub> <sup>-</sup>	600	20	1.96 mg g <sup>-1</sup>	Wang et al. (2015c)
Rice straw	Cr(VI)	300	50	100% (pH = 1) 98.4% (pH = 3) 34.7% (pH = 5)	Hsu et al. (2009)
Ramie residue	Cr(VI)	300, 600	20–800	82.23 mg g <sup>-1</sup> (300 °C) 61.18 mg g <sup>-1</sup> (600 °C)	Zhou et al. (2016)
Oak sawdust/LaCl <sub>3</sub> impregnation	PO <sub>4</sub> <sup>3-</sup>	500	61.3	7.75 mg g <sup>-1</sup>	Wang et al. (2015c)
Coconut granular/ ZnCl <sub>2</sub> treatment	NO <sub>3</sub> <sup>-</sup>	500	5–200	10.2 mg g <sup>-1</sup>	Bhatnagar et al. (2008)
Sugar beet tailings	Cr(VI)	300	50–800	123 mg g <sup>-1</sup>	Dong et al. (2011)
Waste tires/CO <sub>2</sub> activation	Cr(VI)	900	60	29.93 mg g <sup>-1</sup> (pH = 2)	Hamadi et al. (2001)
Pine wood/MnCl <sub>2</sub> modification	As(V)	600	10	0.59 mg g <sup>-1</sup>	Wang et al. (2015b)
Chestnut shell/ magnetic gelation	As(V)	450	0.2–50	45.8 mg g <sup>-1</sup>	Zhou et al. (2016)
Corn straw/FeCl <sub>3</sub> impregnation	As(V)	600	0.25–100	6.80 mg g <sup>-1</sup>	He et al. (2018)
Wheat straw/ bismuth impregnation	As(III)	500	5–200	16.21 mg g <sup>-1</sup>	Zhu et al. (2016)

(continued)

**Table 8.6** (continued)

Biochar source/ modification	Target anion	Temperature (°C)	Initial concentration (mg L <sup>-1</sup> )	Adsorption performance	Reference
Perilla leaf	As(III)	700	0.05–7.0	11.01 mg g <sup>-1</sup>	Niazi et al. (2018b)
Rice straw/red mud treated	As(III)	600	1–50	0.52 mg g <sup>-1</sup>	Wu et al. (2017b)
Corn stover/FeCl <sub>2</sub> and FeCl <sub>3</sub> modification	Fluoride	500	1–100	4.11 mg g <sup>-1</sup>	Mohan et al. (2014)
Wood chips	Perchlorate	700	–	5.0 mg g <sup>-1</sup>	Fang et al. (2014)
Vermicompost	Red Congo	700	5–200	31.28 mg g <sup>-1</sup>	Yang et al. (2016)

adsorption capacity  $\sim 0.01$  mg g<sup>-1</sup>, and inversely proportional to pH of solution. Also, the adsorption capacity considerably decreased with co-existing ions such as sulfate and phosphate (Chintala et al. 2013). With untreated biochar, adsorbed nitrates were undetectable; however, post acid and hot water wash the nitrate adsorption capacity significantly enhanced with a value  $\sim 0.25$  and  $\sim 0.048$  mg g<sup>-1</sup>, respectively (Gai et al. 2014). Literature are evident of biochar-based nanocomposites illustrating improved nitrate adsorption. For instance, a modified lanthanum-biochar nanocomposite was able to provide a nitrate adsorption capacity of  $\sim 100$  mg g<sup>-1</sup> which is very high when compared with unmodified biochar  $\sim 8.94$  mg g<sup>-1</sup> (Wang et al. 2015c).

### 8.6.3.3 Arsenic

The observable forms of arsenic anions in natural and wastewater are arsenite [As(III)] and arsenate [As(V)]. Numerous studies have reported positive adsorption performances by biochar against both forms of arsenic in wastewater. A biochar produced from raw pine cone showed As(III) adsorption efficiency of 66%, whereas same biochar when modified with Zn provided an adsorption efficiency of 88% (Vinh et al. 2015). Paper mill sludge recovered from wastewater treatment was used to produce biochar for the removal As(V) from aqueous solution. The biochar was indirectly doped with Fe, as FeSO<sub>4</sub> was used as coagulant during wastewater treatment, showed a As(V) adsorption capacity of 22.7 mg g<sup>-1</sup> and was easily recovered from wastewater due to developed magnetic properties (Yoon et al. 2017). Another study also reported an improved efficiency  $\sim 89\%$ , when As(V) was treated from wastewater with biochar synthesized from sewage sludge (Agrafioti et al. 2014). Fe-doped biochar produced from corn straw exhibited better As(V) adsorption capacity  $\sim 6.8$  mg g<sup>-1</sup> whereas only 0.017 mg g<sup>-1</sup> was observed with unmodified corn straw biochar (He et al. 2018). A simultaneous removal of As(III) and As(V) from

water was examined by Niazi et al. (2018a, b), where biochar were synthesized from perilla leaf and Japanese oak wood. The measured adsorption capacities of As(III) and As(V) by perilla leaf-derived biochar were 11.0 and 7.2 mg g<sup>-1</sup>, respectively, while with Japanese oak wood they were found to be 3.1 and 3.9 mg g<sup>-1</sup>, respectively. It was observed that biochar produced from rice straw demonstrated a reasonable adsorption capacity for As(III) and As(V) as 0.45 and 0.55 mg g<sup>-1</sup>, respectively. For the enhancement of metal oxide content, when the rice straw feedstock was mixed with red mud prior pyrolysis, the produced biochar showed improved performance with adsorption capacities for As(III) and As(V) as 0.52 and 5.92 mg g<sup>-1</sup>, respectively (Wu et al. 2017b).

#### 8.6.3.4 Chromium

The most common form of chromium anion present in wastewater is hexavalent dichromate [Cr(VI)]. Numerous studies explaining the adsorption of Cr(VI) on biochar have been reported. For instance, the adsorption capacity ~44.05 mg g<sup>-1</sup> was observed with a biochar produced from rubber wood sawdust at 30 °C. It was also identified that the adsorption capacity further enhances as the production temperature increases, i.e., biochar synthesized at 40 and 50 °C revealed an adsorption capacity of ~59.2 and 65.80 mg g<sup>-1</sup>, respectively (Karthikeyan et al. 2005). The maximum adsorption capacities of Cr(VI) on biochar synthesized from sugar beet tailing and ramie residue were measured ~123 and ~82 mg g<sup>-1</sup>, respectively (Dong et al. 2011; Zhou et al. 2016). A nanocomposite based on Zn-biochar with excess COO- functional group was produced from sugarcane bagasse, and the observed Cr(VI) maximum removal efficiency was almost twice to that of biochar without Zn impregnation (Gan et al. 2015). When compared the Cr(VI) removal performance with commercial activated carbon, biochar synthesized from coconut shell was found less effective; however, the one synthesized from waste tire had similar adsorption capacities, i.e., 44–53 mg g<sup>-1</sup> with biochar from waste tire and 48–58 mg g<sup>-1</sup> with commercialized activated carbon, respectively (Mohan et al. 2005). Another study reported successful catalytic reduction of Cr(VI) with biochar embedded with Ag nanoparticle, fixing the environmental issue of waste biomass contaminated with Ag (Liu et al. 2016).

#### 8.6.3.5 Other Metallic Anions

Other than aforementioned anionic contaminants there are anions which can also adversely affect the aquatic ecosystem and humans when consumed beyond threshold limits. For instance, perchlorate (ClO<sub>4</sub><sup>-</sup>), fluoride (F<sup>-</sup>), anionic dye, etc.

Perchlorate (ClO<sub>4</sub><sup>-</sup>) is a rather new contaminant and therefore not much study has been conducted till date. It mainly disturbs the functioning of thyroid gland which regulates iodine controlling hormones in human body. A study conducted on biochar derived from wood via pyrolysis at 700 °C found a considerable



adsorption capacity of perchlorate of  $\sim 10.5 \text{ mg g}^{-1}$ . The suggested driving force for perchlorate adsorptions were hydrogen bonding and electrostatic attraction (Fang et al. 2014).

Anthropogenic activities are the major source of fluoride induction into natural waters and can be hazardous even in very low concentration ( $> 1 \text{ mg l}^{-1}$ ). Biochar synthesized from pine wood via fast pyrolysis at  $450 \text{ }^\circ\text{C}$  was found effective when treated at 2 pH and follows inverse relation with temperature (Mohan et al. 2011). Another study measured a fluoride removal efficiency of 83% when treated with biochar produced from *Cocos nucifera* shell with  $10 \text{ mg l}^{-1}$  of fluoride in aqueous solution; however this efficiency slightly reduced to 79% when a real water sample with  $7 \text{ mg l}^{-1}$  of fluoride was treated (Halder et al. 2016).

The rise in textile industries also boost the synthesis of various dyes that are posing severe environmental consequences. These dyes can be both cationic (methylene blue) and anionic (Congo red), where cationic dyes show good adsorption behavior on biochar, the anionic dyes show ordinary adsorption performance (Park et al. 2019). Congo red also consist of azo compounds making it even harder to adsorb. A rise in Congo red adsorption capacity of biochar with increasing synthesis temperature was reported, where biochar was produced via vermicompost and adsorption capacities were recorded in the range of  $\sim 11.5\text{--}31.3 \text{ mg g}^{-1}$  (Yang et al. 2016). Fe<sub>3</sub>O<sub>4</sub>-assisted biochar produced from cellulose also exhibited superior Congo red removal performance with maximum adsorption capacity of  $\sim 66 \text{ mg g}^{-1}$  (Zhu et al. 2011).

## 8.7 Summary and Future Perspectives

Biochar, a biomass derived thermochemically transformed product is a cost effective and potent adsorbent. It can be considered as renewable as biomass such as forestry residues, agricultural wastes, municipal wastes, sewage wastes, etc. are the sustainable source of biochar synthesis. The present chapter provides an overview of current biochar production techniques with focus on biomass pretreatment, thermochemical transformation, and posttreatment processes. It also provides a brief report summarizing the performance of biochar as an adsorbent in wastewater treatment particularly adsorption of heavy metal ions and cationic contaminants.

The denouement of this chapter can be construed as: (a) the characteristics of biochar are associated with biomass type, pre- and posttreatment techniques, and most importantly on the type of thermochemical conversion process. The biochar modifications in terms of induction of functional groups, gains much attention recently as the engineered biochar can divulge new possibilities in the field of wastewater treatment. (b) The modified biochar can be an efficient adsorbent of CO<sub>2</sub>, heavy metal ion, and anionic contaminants with precise selectivity. The adsorption can be controlled by regulating mechanisms such as electrostatic attraction, ion exchange, chelation, complex formation, surface precipitation, and

hydrogen bonding. The engineered biochar shows a great potential as an alternative of commercial activated carbon; however, onsite applications need detailed investigation.

Although a lot of research has already been done on biochar production and application in wastewater, convergence of research gaps is still required. There is an utmost need to develop biochar modification processes with high efficacy at low cost. Pilot and semi-pilot plant level research is required to examine the proper functioning of engineered biochar. Regarding CO<sub>2</sub> capture, adsorption at high temperature still requires further research. Adsorption capacity of biochar is relatively better for heavy metal ions; however more research is required to further improve the adsorption efficacy of anionic contaminants. In addition, biochar itself contains PO<sub>4</sub><sup>3-</sup> and NO<sub>3</sub><sup>-</sup> developed through thermochemical conversion as phosphorus and nitrogen reside as nutrients in plants. The possibility of dissolution and influence of these anions on performance of wastewater treatment need to be explored.

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