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Biomass Derived Activated Biochar for Wastewater Treatment

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11 Biomass Derived Activated Biochar for Wastewater Treatment

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11.1 OVERVIEW

Green energy is becoming a basic need for all nations and societies due to the rapid growth in human population. Given the increasing demand for energy and the wide use of fossil fuels in the region, many countries are looking for a secure energy supply and are increasingly concerned about finding alternative sources. Many countries, including India, have identified biomass as an abundant, easily available energy resource that could play a significant role in reducing their

energy deficit. India is an agriculture-presiding country that produces a total biomass about 600 Mt annually, among which 150–200 Mt is considered as additional biomass waste (UNDP 2011). This surplus residue could be used as a feedstock for animals and as an energy source for domestic as well industrial thermal application. About 85 Mt of unutilized biomass, especially agro residues, includes straw and stubbles burnt in open fields by some peasants (Pawar and Panwar, 2020). Therefore, appropriate waste recycling facilitates the production of energy-rich and efficient green fuel, whether solid, liquid, or gas, and has become an important issue throughout the world. There are different biomass-conversion technologies, and out of them, pyrolysis is one of the economically feasible thermochemical conversion routes; it produces mainly three end products, biochar, bio-oil, and syngases, respectively. Biochar is carbonaceous material mostly produced from a carbonization process in absence of air as per its end application (Panwar et al., 2019). Further, the produced biochar is further modified by adopting two activation methods (physical and chemical) for the preparation of activated biochar. The feedstock material, production conditions, and activation mode significantly effect the physical and chemical characteristics of activated biochar. The activated biochar possesses a larger surface area, surface functionality, porous structure, and the availability of oxygenated functional groups, which pose improvement in adsorption performance for different contaminants in wastewater. The adsorption process mainly depends on the type of activated biochar and the properties of targeted pollutants. The heavy metals, organic, and inorganic pollutants, and phenols, etc., are present in the water and enter the human body via the food chain, which may expose humans to many dangerous diseases. In addition, the organic contaminates (mostly phenol) present in the water can change the test and odour of drinking water. Activated biochar have huge prospects for the adsorption of contaminates from wastewater due to its strong adsorbing affinity and capacity. Initially, coal or grain were mostly utilized as precursors for making granular-activated carbon; however, they were not economically sustainable, requiring more money to the manufacturers for procurement. Activated biochar prepared from the synthesis of biochar shows remarkable properties, mainly high internal surface area and porosity. Due to its microporous structure, it acts as an adsorbent for the elimination of different contaminants. In addition, activated biochar becomes a reliable renewable material because of its successful phase application, such as deodorization, color removal, separation, purification, storage, and catalysis. Activated biochar derived from biomass as a precursor acts as a pollutant removal and has many applications in industrial sectors, such as for treating wastewater, chemical processing, controlling the air pollution, petroleum refining, and adsorption of volatile organic compounds. The literature reports that different kinds of agro wastes, such as groundnut shell, rice husk, corn cob, straw, wheat, and cotton residues, have been utilized appropriately as a precursor from many years to obtain a low-cost activated biochar, which acts as an adsorbent. Therefore, conversion of waste into energy-rich activated biochar, which is a sustainable and cost-effective adsorbent material, plays an important role in different environmental applications.

The present book chapter focuses on the synthesis of activated biochar from different feed stocks, its operating condition, physical and chemical characteristics of activated biochar, and its applications in wastewater treatment. An attempt has been made to divide the current chapter into two parts: the first part shows the preparation of activated biochar using different precursors and the influence of different experimental processes, and the second part comprises the classification, properties, and applications in wastewater treatments.

11.2 BIOMASS RESOURCES

Biomass is simply an organic material that is available on Earth's surface. The plant absorbs the solar energy and stores it in chemical form through the photosynthesis process. The plant species or animal waste is considered as organic biomass material, which is renewable in nature (Fahmy et al., 2020). The biomass sources are mainly classified into two categories: the first is natural, and the other is derived materials. Generally, raw materials like woody waste, forest waste, agriculture residues, and by-products, MSW, waste generated from agricultural-processing industries, animal waste, and aquatic waste, etc., are considered as main resources of biomass (Pawar and Panwar 2022).

- Agriculture wastes: wheat straw, rice straw, rice husk, groundnut shells, cobs, sugarcane waste, herbaceous crops, etc.
- Forest residues: woody biomass, sawdust, logging residues, shrubs, trees, bark etc.
- Food-processing industrial waste: dairy waste, industrial waste, oil residue, brewery waste, fruit waste, marine waste, bakery waste etc.
- Animal waste: animal dung, poultry waste, animal carcasses, animal excreta etc.
- Municipal solid waste: kitchen waste, vegetable waste, garden waste, waste from office, homes etc.
- Aquatic waste: Algae waste, marine waste etc.

Figure 11.1 shows the different biomass resources available for energy generation.

11.3 BIOMASS POTENTIAL FOR ENERGY GENERATION IN INDIA

The total available land in India is about 328 Mha (million hectares). Among this total, nearly 39 Mha is covered by marginal land, which is 12% of the whole area. Marginal land is simply defined as the agricultural land initially used for sowing and cultivation purposes, but presently, is not in use due to reduced productivity. Generally, marginal land is not recognized for agricultural practices because of the high risk of lower production, which simultaneously affects the agricultural economy. Therefore, reforming marginal land for good agricultural production requires large amounts of chemical fertilizer dosages, raising the economics and affecting the environment. However, many researchers reveal that marginal land can produce 230–720 MT of energy crops annually. These energy crops have a

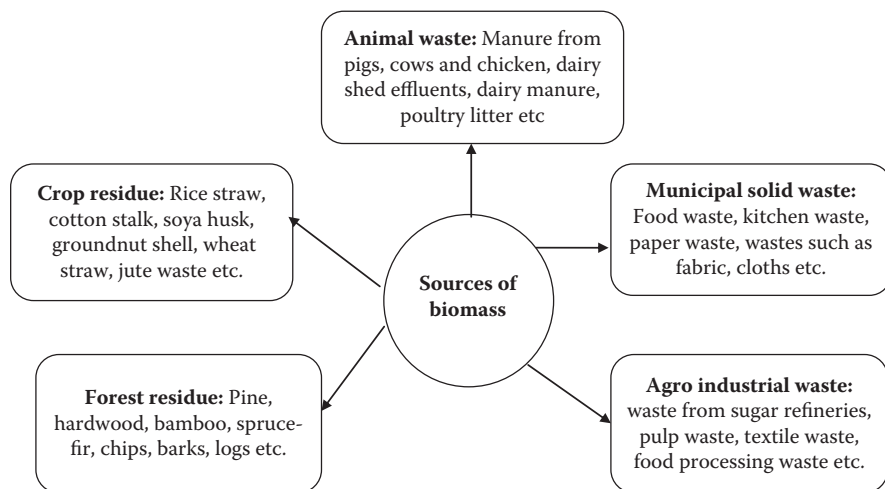


FIGURE 11.1 Resources of biomass.

potential between 1–13 EJ annually, which covers approximately 11% to 160% of the energy demand of the transport sector. The energy crops have a total bio-fuel potential between 3–103 GGE/y, which covers about 5% to 160% of the gasoline demand in the transport sector. The total availability of the agriculture and forest residues in India is about 439 and 19 MT, respectively, which has the potential to generate 1.8–7.2 EJ of energy annually, which fulfills the 21%–84% energy demand in the transport sector. In terms of biofuel, energy crops have the potential to produce 6–37 GGE annually, which covers 10%–56% of the gasoline demand.

11.4 BIOMASS CONVERSION ROUTES

Various biomass conversion routes are available, including: thermochemical, biochemical, direct combustion, and chemical conversion, as shown in Figure.11.2. However, the most commonly used biomass routes for sustainable biofuel production are thermochemical conversion and biochemical conversion. The thermal-conversion process consists of biomass gasification via pyrolysis, while the biochemical-conversion process includes anaerobic decomposition of organic waste for biogas production. The trans-esterification method is also a chemical conversion, but of vegetable oil into biodiesel, with the direct combustion of forest waste or woody biomass used to generates heat for thermal applications.

11.4.1 THERMOCHEMICAL CONVERSION

Multiple thermo-chemical conversion routes are available, including combustion, liquefaction, pyrolysis, gasification, etc. However, the pyrolysis process has gained significant attention due to its direct biomass conversion into solid, liquid, and

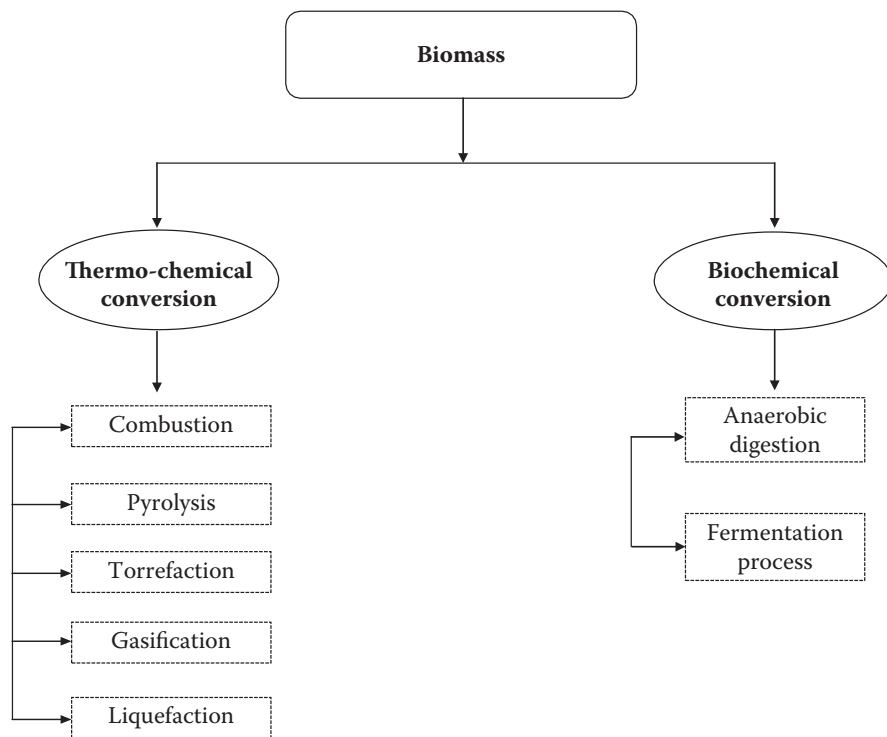


FIGURE 11.2 Schematic representation of classification of biomass conversion processes.

gaseous fuel via thermal decomposition in anaerobic conditions. These can occur at low or high temperatures.

Biomass Combustion: This is the direct burning of biomass in aerobic conditions, readily converting chemical energy into thermal, electrical, or mechanical energy. Such combustion processes face several disadvantages, such as requiring pre-treatment and causing environmental pollution.

Gasification: This is the thermochemical conversion of biomass at a very high temperature (800°C–1000°C) in a controlled air supply, resulting in partial oxidation of organic waste into a producer gas, which is combustible in nature, and which has a calorific value ranging from 900–1100 kcal/m³. The producer gas is mainly composed of some combustible gas components, such as CH₄, H₂, and CO, as well as other inert gases like N₂, and CO₂.

Liquefaction: The thermochemical conversion of biomass takes place under high pressure, at a minimum temperature, in the presence of hydrogen, and with the use of a catalyst.

Pyrolysis: Pyrolysis is one of the more economically feasible thermochemical conversion processes in which waste material is indirectly heated in the range of 400°C to 700°C in absence of air, yielding primary end products like bio-oil, biochar, and syngases. Pyrolysis processes are broadly categorised into three classes: slow, fast, and flash pyrolysis.

11.4.2 BIOCHEMICAL CONVERSION

Biological or biochemical conversion includes both anaerobic digestion and the fermentation process. In the case of the anaerobic digestion process, organic waste material can be transformed into gaseous fuel by breaking the larger molecules into smaller molecules in the presence of bacteria, offering economically viable applications worldwide. While, in the case of the fermentation process, sugar feedstock is converted into ethanol in the presence of yeast. However, produced diluted alcohol can't be used directly without distillation; it also suffers a high cost with lower performance of the plant. This process takes longer to complete as compared to the thermo-chemical conversion process, although it needs considerable external energy.

11.5 WHAT IS ACTIVATED BIOCHAR

In India, 686 Mt gross residues are available from agriculture crops, in which 23.5 Mt signifies the surplus residues reported by Hiloidhari et al. (2014). The surplus residues can be converted into biochar through the thermochemical conversion process. In a carbonization process, biomass is thermally decomposed at higher temperature in the absence of air/oxygen for a specific duration, resulting in the production of biochar. The produced biochar can be further activated using physical and chemical activation methods to obtain an activated biochar. Biomass is thermally decomposed at a higher temperature in the absence of air for a specific duration, resulting in the production of biochar. Activated biochar have an ability to minimize the environmental problems like accretion of agricultural residues or waste, air pollution, as well as water pollution. Activated biochar is also known as activated carbon or charcoal (Hiremath et al., 2012) and sporadically known as a solid sponge (Vaghela et al., 2022). A lignocellulosic biomass is mainly composed of cellulose, hemicelluloses, and lignin. However, lignin content in biomass feedstock is found a very useful component for the preparation of activated biochar (Carrott and Carrott, 2007).

Crop residues or biomass obtained from agriculture waste have become a promising type of precursor because of their minimal cost and abundant availability for making the activated biochar. Any agriculture waste with a greater percentage of carbon and lesser availability of inorganic components may be preferred for making activated biochar (Tsai et al., 1997). In addition, rather than fossil resources like coal and other petroleum by-products, activated biochar obtained from lignocellulosic biomass or crop residues helps reduce the greenhouse effect. Therefore, distribution of carbon and adsorption process occurs simultaneously, referred to as a carbon neutral cycle (Nor et al., 2013). (Figure 11.3).

11.6 PREPARATION OF ACTIVATED BIOCHAR

The first stage in the preparation of activated biochar is the indirect heating of biomass at higher temperatures in anaerobic condition. This is simply a carbonization or pyrolysis process (Suhas et al., 2007). During the biomass carbonization, due to higher process temperatures, all moisture and volatile components present in

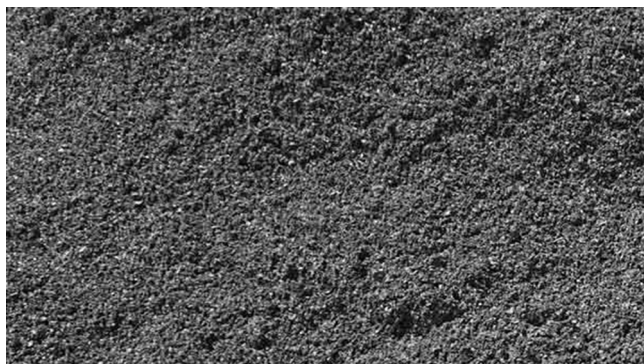


FIGURE 11.3 Activated biochar.

biomass are released. The produced biochar at higher pyrolysis temperatures can be further activated using physical and chemical activation. In most cases, chemical activation is more widely preferred over a physical activation. The chemical activation increases the yield of activated biochar, showing a larger surface area without any need of higher temperatures and auxiliary energy (Gratuito et al., 2008). Therefore, at the moment, the production of activated biochar is popular because of its environmental friendly characteristics (Hernández-montoya et al., 2012; Zhang et al., 2013).

11.6.1 CARBONIZATION

A good quality biochar is essentially required to produce activated biochar. For the purpose of quality biochar, biomass is heated or thermo chemically decomposed at a temperature ranging from 400°C–850°C in inert atmosphere for a specific residence time to enrich the percentage of carbon. The type of biomass feedstock, particle size, pyrolysis temperature, and heating rate, etc., significantly affect the physico-chemical composition of biochar. At moderate temperatures, the lignocellulosic composition of biomass is thermally degraded, and kinetic reactions take place, such as fragmentation, depolymerisation, and crosslinkings, resulting in a yield of biochar followed by bio-oil and syngases. The solid carbon-rich endproduct and a brown liquid endproduct are mainly referred to as “biochar” and “bio-oil,” whereas the condensable and noncondensable composition of gases are known as syngases, respectively. The syngas is mainly composed of some combustible gas components, i.e. the mixture of hydrogen, methane, and carbon monoxide. Biochar produced at higher carbonization temperatures (600°C–700°C) showed a positive relationship relative to its aromatic nature and a well-improved carbon layer on its surface. The higher carbonization temperature showed a negative relationship with hydrogen and oxygenated functional groups. Therefore, it possesses low ion-exchange capacity, which might be due to the dehydration and deoxygenation reactions taking place during biomass carbonization at a high temperature. On the other hand, the produced biochar at moderate carbonization temperatures from 300°C to 400°C

possess large availability of aliphatic, C=O, C functional groups, and celluloses on biochar surface. Therefore, from above discussion, it was concluded that the produced biochar up to 700°C have some limited properties, mainly the initial porosity and surface area, and it restricts its direct application in waste-water treatment. During the carbonization process, the pores inside the biochar are filled with some tars and other volatile components, so it showed minimum surface area; to overcome this barrier, there is a need of the secondary process for the preparation of well-developed porous-structured biochar. In addition, it is necessary to produce biochar at higher carbonization temperatures above 700°C because the biochar at a mentioned temperature possesses higher surface area, electrical conductivity, porosity, pH, microscopic structure, and the availability of micro and macro nutrients. Therefore, it could be used for further activation to prepare a good quality activated biochar.

11.7 BIOCHAR ACTIVATION

The biochar activation using the physical and chemical modification methods could increase the surface area, porosity, pore volume, and diameter of pore (Al-Swaidan and Ahmad, 2011). These treatments are responsible for or influence the physical characteristics of biochar, mainly increasing the size and shape. In case of physical activation, biomass is pyrolyzed or carbonized (up to 800°C), followed by modification using steam or CO₂ (Ioannidou and Zabaniotou, 2007). Therefore, physical activation mainly involves carbonization. And it means that physical activation has two main steps: a carbonization and a modification step. On the other hand, in chemical activation (also called as wet oxidation), the raw biomass is impregnated by using some chemicals (reported later), followed by pyrolysis in inert atmospheric conditions (Giraldo and Moreno-Piraján, 2012).

11.7.1 PHYSICAL ACTIVATION

The activated biochar was prepared from precursors using mild oxidizing gases. Carbonization of raw feedstock and then modification of biochar has been done using steam, and CO₂, among others. The use of carbon dioxide as an activation agent is mostly preferred due to its significant properties and the fact that it may provide control in the activation process. Compared to carbon dioxide, steam is effective in forming greater surface area in the resulting biochar. In addition, the conversion process, activated using steam, was found two to three times faster than using carbon dioxide (Nowicki et al., 2010). Many researchers have studied and reported that various raw materials like corn cob, hulls, and stover, oak, peanut hull, and rice hull, are also suitable for creating activated biochar through the physical activation process (Ahmedna et al., 2000). Carbonization temperature usually ranges from 400°C to 850°C, and up to 1000°C, while modification temperature varies from 700°C to 900°C (Ioannidou and Zabaniotou, 2007). The end product of carbonization is charcoal with high carbon content but less surface area, so it is inactive material. McDougall (1991) has studied that due to biomass pyrolysis, all noncarbon elements, as well as volatile matter (including tar, moisture content and

volatile matter), were eliminated and resulted in charcoal having a maximum percentage of fixed carbon. So, it becomes more suitable for activation purposes. In the first stage of physical activation, the initial porosity appeared on charcoal (Daud et al., 2000), in addition to further activation by the presence of oxidizing gases on charcoal that will help to prepare activated carbon with high porosity (Baseri et al., 2012). The category and degree of modification in physical treatment take priority in determining the physio-chemical properties of activated biochar. Zhang et al. (2004) obtained activated biochar from different agricultural residues including corn hulls, corn stover, and oak wood waste by using the physical activation process with carbon dioxide as an activating agent and observed that resultant product had larger surface area (400–1000 m²/g) and micropore volume (0.38–0.66) at a higher activation temperature (700°C and 800°C). Authors also reported that activated biochar prepared from oak wood waste required more time for activation, and activated biochar prepared from oak wood waste shows high adsorption capacity as compared to other materials. Apparently, the biomass with lower ash content and high fixed carbon content should be preferred in the gasification process for the production of activated biochar Haykiri-Acma et al. (2006).

Ahmedna et al. (2000) used a physical activation process for granular-activated biochar from different agro waste, such as rice hulls, rice straw, and sugarcane bagasse, etc. The granular-activated biochar prepared from sugarcane bagasse found more desirable in sugar decolorizing than rice straw and hulls. Hernandez et al. (2007) used cotton gin trash as a agro waste for making activated biochar at different pyrolysis temperatures 600°C, 700°C, and 800°C for 30, 45, and 60 min, and then activated using steam for a temperature range from 250°C–600°C for 60 min. During the experiment, the authors observed that as pyrolysis temperature and time were increased, then the yield of char significantly reduced. The iodine number increased value from 200–427, when pyrolysis temperature was 700°C for 45 min.

11.7.2 CHEMICAL ACTIVATION

Impregnation of a catalyst or chemical agent into a biomass, followed by pyrolysis, produces an end product such as an activated biochar. Compared to physical activation, chemical activation provides two salient advantages: one is that it requires lower temperature, and another is that this process produces a global yield of activated biochar (Chen et al., 2011). According to Molina-Sabio and Rodriguez-Reinoso (2004), the temperature required for wet or chemical activation varies from 400°C to 600°C. Many studies report that chemical activation needed a lower temperatures in comparison with physical activation, varying from 300°C–700°C (Giraldo and Moreno-Piraján, 2012), 400°C–700°C (Girgis et al., 2002), or 400°C to 800°C (Alhamed, 2006), and 500°C to 800°C (Hu and Srinivasan, 2001). The variation in temperature range during activation is due to impregnation of inorganic additives and their action for degradation or dehydration of cellulosic materials present in the precursor. Activating or chemical agents involved in chemical activation act as oxidants or dehydrating agents, assisting with pyrolytic decomposition. The maximum carbon percentage is recorded in activated biochar obtained from chemical activation and may be due to the used chemical oxidants inhibit the formation of tar and ash. The

following chemical or oxidizing agents act as a catalyst and take part in activation: zinc chloride ($ZnCl_2$), phosphoric acid (H_3PO_4) (Cruz, et al., 2012) sulphuric acid (H_2SO_4), potassium sulphide (K_2S), potassium thiocyanate (KSCN) (Demiral et al., 2008), nitric acid (HNO_3), hydrogen peroxide (H_2O_2), potassium permanganate ($KMnO_4$) (Al-Qodah and Shawabkah, 2009), sodium hydroxide ($NaOH$), potassium hydroxide (KOH) (Zhengrong and Xiaomin, 2013), and potassium carbonate (K_2CO_3) (Adinata, et al., 2007). Zinc chloride is the most preferred chemical for the degradation of lignocellulosic material. However, zinc chloride does have some environmental drawbacks (Teng et al., 1998). In addition, phosphoric acid is being used for activation because it does not have any environmental effect compared to zinc chloride, but it does have an inefficient chemical recovery and minimizes the problems regarding corrosion. Many reviewers report that any precursors used in chemical activation should be of cellulosic or lignocellulosic origin, such as coconut, peach stone, coal, hard wood, or peach stone. These materials are used for making modified or activated biochar by impregnating the chemical agents into precursors. Among all the oxidizing chemical agents, zinc chloride and phosphoric acid are the most preferred for the modification of lignocellulosic biomass, while potassium hydroxide is mostly used on char as a virgin material to make activated biochar. According to Srinivasakannan and Bakar (2004), activated biochar prepared by impregnation of zinc chloride into a precursor produces a high surface area compared to that produced by phosphoric acid.

The final, and one of the most important stages in activated biochar preparation using chemical treatment, is washing. It helps to determine the porosity of the resulting sample. Generally, some acids or alkali are used to wash activated biochar, followed by washing it with water. Basically, the process of washing removes chemical contaminants from the surface of biochar. Kalderis et al. (2008) have made activated biochar in a single-stage chemical-activation process by using raw material bagasse and rice husk. The authors examined the surface area of activated biochar by using three different chemicals ($ZnCl_2$, $NaOH$, H_3PO_4) at three different temperatures ($600^\circ C$, $700^\circ C$, $800^\circ C$) and reported that activated biochar prepared from rice husk showed greater surface area up to $750\text{ m}^2/g$ with an equal concentration of zinc chloride and rice husk (1:1). It was also observed that zinc chloride was more effective oxidizing agent than $NaOH$ or H_3PO_4 . Sharath et al. (2017) used rice husk for the preparation of activated biochar by using sodium hydroxide ($NaOH$) as a chemical. The modification was carried out at three different temperatures $650^\circ C$, $700^\circ C$ and $800^\circ C$ and noted a higher yield of about 48.2% at $650^\circ C$ and corresponding yields at 47.65% and 45.95%, respectively. Mahamad et al. (2015) produced biochar activated from pineapple waste (including leaves, crown, and stem) for the application of dye removal from wastewater. The activated biochar was prepared by using impregnation of $ZnCl_2$ into biomass, and activation was conducted at $500^\circ C$ for duration of 1 h. The resulting product showed a greater surface area ($914.6\text{ m}^2/g$) and indicated the highest dye removal ability due to its adsorption capacity (288.34 mg/g). The impregnation ratio and process temperature could effect the porosity, as well as the surface chemistry of the resulting sample investigated by Prahaz et al. (2008). Further, the authors prepared activated biochar from jack fruit peel waste using H_3PO_4 ; chemical activation took place in the

temperature range of 450°C–550°C and found that the resulting end product had a maximum surface area (907–1260 m²/g) and pore volume in between 0.525 and 0.733 cm³/g, respectively.

11.8 CHARACTERISTIC OF MODIFIED BIOCHAR

The physical and chemical characterization of activated biochar is significantly influenced by kind of biomass, pyrolysis temperature, residence time, heating rate, and activating agents, etc. The properties of modified biochar-like mineral contents, molar ratio, pH, surface area, porosity, surface charge, and elemental composition significantly varied according to activation condition (Panwar and Pawar, 2020). Many pyrolysis technologies, such as fluidized bed reactor, vacuum pyrolyzers, etc., play a significant role while determining the morphology and structural composition of activated biochar. In addition, the activated biochar obtained via physical activation of biomass showed larger surface area and microporous structure, while chemically (H₃PO₄) modified biochar showed surface area up to 600 m²/g, respectively. The spouted bed reactor was found most promising for activated biochar preparation instead of fixed and fluidised bed reactor. Spouted bed reactor promotes uniform distribution of heat inside the pyrolysis chamber and mixing of raw material. Owing to this Niksiar and Nasernejad (2017) found that the physically modified biochar using pistachio shell activated biochar showed larger surface area 2596 m²/g at a activation of 850°C. This might have happened due to significantly less heat loss and resistance between the biomass and heat inside the reactor.

Activated biochar prepared using steam activation exhibit the enriched textural properties of activated biochar. Steam modification build up the better properties of activated biochar, mainly larger surface area, pore volume, and higher porosity, etc. (Pallarés et al., 2018). Besides, this physical activation using carbon dioxide creates greater microporous structure as compared to steam activation. The activated biochar obtained through the steam-activation process contains less percentage of hydrogen to carbon, oxygen to carbon, and nitrogen to carbon molar ratios than chemically activated biochar. This might be due to steam modification containing less oxygen, carbon, and hydrogen (Rajapaksha et al., 2015).

In cases of acid activation, the presence of oxygenated functional groups on activated biochar with a larger surface area is greater. The phosphoric acid-based pine sawdust modified biochar showed larger surface area up to 950 m²/g, respectively (Iriarte-Velasco et al., 2016). In addition, the cucumber waste biochar, which was treated using sulphuric and oxalic acid, also showed larger surface area and pore volume. In some cases, however, acid-activated biochar showed lower surface area. This could be due to breakage of the pore structure inside the biochar. In addition, Vaughn et al. (2017) found that oxalic and sulphuric acid-activated biochar possess minimum surface area, pH, electrical conductivity, surface area, and cation exchange capacity compared to pristine biochar. The acid-activated biochar has low pH and therefore has a potential application in alkaline soil. In some cases, acid-activated biochar possesses an average value of hydrogen to carbon, oxygen to carbon, and nitrogen to carbon molar ratio, which might be caused due to the produced acid-activated biochar containing a lower percentage of

carbon. Recently, Zhang et al. (2019) made modified biochar from organic waste using acid agents HCL, H_2O_2 , NaOH for the adsorption of nitrobenzene from the wastewater. Among the three different chemicals, the hydrochloric acid-modified biochar was observed to be more efficient for effective remediation of NB. This might be possible because of larger surface area, higher electron transfer rate, and the availability of acidic functional groups as compared to other activated biochar.

Alkali-activated biochar showed good physico-chemical properties for wastewater treatment. Potassium hydroxide biochar possesses a larger surface area, almost 50 times greater than raw biochar. The alkali-activated biochar can enhance the cation exchange capacity, porosity, thermal stability, surface area, and also improve surface functional groups, therefore resulting in modified biochar showing many environmental applications. Sodium hydroxide-treated modified biochar produced using *Hickey* biomass showed good mineral composition on the surface of biochar (Ding et al., 2016). (Table 11.1).

11.9 APPLICATION IN WATER AND WASTEWATER TREATMENT

Open water sources, such as ponds, lake, rivers, contains many toxic pollutants, heavy metals, and other organic and inorganic pollutants that causes water pollution. These harmful pollutants primarily originate with certain industries, such as mining, leather and battery industries, as they discharge pollutants into the water (Clemens and Ma, 2016). Heavy metals are recognized as the most toxic and dangerous pollutants, and the potential for bioaccumulation and carcinogenicity is extremely harmful for living organisms in the environment. Therefore, these toxic pollutants that threaten the environment also create health issues for humans (Zou et al., 2016). There are various traditional and modern wastewater treatment technologies, such as membrane removal, flotation, ion exchange, and chelation (Fu and Wang, 2011; Huang et al., 2016; Kaya, 2016). These techniques, however, are not economically feasible or effective, and they produced toxic secondary waste material like volatile organic and inorganic compounds and persistent pollutants, etc. Therefore, there is an urgent need to optimise environmentally friendly treatments that effectively remove heavy metals. The availability of functional groups like carboxyl, hydroxyl, and carbonyl shows a remarkable potential for the adsorption of contaminants for wastewater. Among the different adsorbent materials is modified biochar, which is prepared with a different activation technique that has attracted widespread attention (Li et al., 2010). The adsorption of heavy metals and pollutants from wastewater is significantly attributed to targeted pollutants and activated biochar. For example, the Mg-activated biochar showed enhanced adsorption capacity (ranging from 6.4% to 98.9%) to eliminate Pb^{2+} from wastewater (Wang et al., 2015). Magnesium-modified biochar showed good adsorption performance due to the availability hydroxyl groups on the biochar surface. Similarly, MgO and citric acid activated biochar also reported Pb(II) removal ability of 121.8 mg/g and 159.9 mg/g, respectively (Cerino-Córdova et al., 2013). In addition, zinc nano-composites based magnetic biochar showed good sorption performance for a targeted Pb(II) heavy metal of 367.6 mg/g. This might be due to the availability of zinc nano particles on the activated biochar surface (Yan et al., 2015). The biochar-produced rice husk and MSW were further modified using ferrous oxide

TABLE 11.1
Activation Conditions and Its Affect on Characteristics of Activated or Modified Biochar

Precursor/ Particle Size	Carbonization Condition	Activation Agent	Activation Condition	C (%)	H (%)	O (%)	N (%)	Molar H/C	Molar O/C	Molar (O+N/C)	Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \cdot \text{g}^{-1}$)	Pore diameter (nm)	References
Burcucumber plants (< 1.0 mm)	700°C/2h, 7°C/min	Steam	700°C, 5 mL/ min, 45 min	50.55	1.66	44.88	2.54	0.39	0.67	0.71	7.10	0.038	8.393	(Rajapaksha et al., 2015)
Giant <i>miscanthus</i> (4 cm)	N ₂ , 500°C/1h, 10°C/min	Steam	800°C	82.1	2.67	11.0	0.31	0.0325	0.138	0.138	322	n.a.	n.a.	(Shim et al., 2015)
Barley malt bagasse (< 4 mm)	N ₂ , 800°C/1h, 10°C/min, 0.25 mL/min	CO ₂	900°C/1h, 10°C/min, 0.15 L/min	68.32	1.46	28.38	1.74	0.21			80.5	0.0468		(Franciski et al., 2018)
Corn straw	500°C/1.5h	KOH	800°C/0.5h, 2 g: 500 mL (Biochar: KOH)	67.20	0.80	6.8	0.537	0.144	0.076	0.082	466.37	0.081	4.40	(Tan et al., 2016)
sesame straw	600°C/2h, 5°C/min	ZnCl ₂	600°C	74.1	1.8	21.1	2.7	0.29			319.4	0.2270		(Park et al., 2015)
Sugarcane residue	n.a.	MgO	N ₂ , 550°C/1h,	27.17	2.37		1.47				40.6	0.372	22.38	(Li et al., 2017)

and calcium oxide for the removal of Cr^{6+} and As^{5+} . Due to electrostatic interaction between the targeted pollutants and activated biochar, it reported a 95% removal capacity (Agrafioti et al., 2014). Similarly, the haematite-activated biochar also showed good adsorption capacity for the sorption of arsenic for potable water. The impregnation of Fe^{3+} on the biochar surface significantly affected the (O+N)/C and oxygen-to-carbon ratio, which results in enriched adsorption capacity of activated biochar for targeted As^{5+} sorption. Thus, the impregnation of haematite, magnate, calcium, and manganese oxide on biochar surface assists in creating the magnetism, adsorption sites, and its widespread distribution.

Several organic contaminants create a serious result when they enter the animal body via water and the food chain. Mostly, the organic pollutant like phenol mainly affect the taste and odour of the drinking water. The activated biochar prepared from different activating agents possess good affinity and adsorption capacity for the adsorption of such types of contaminates. The alkali- and acid-modified biochar also showed higher furfural removal. Langmuir sorption capacity varies between 93.5 to 109 mg/g, respectively. The properties like basicity and hydrophilicity for alkali- and acid-derived biochar showed a good adsorption performance. However, the bamboo waste-modified biochar reported the highest furfural removal capacity of 253.20 mg/g, due to the hydrophobicity property of activated biochar (Li et al., 2014). Saw dust biochar activated using citric acid showed the higher adsorption ability of 158.6 mg/g for removal of methylene blue from wastewater, which could be achieved because of the presence of carboxyl groups on the modified biochar surface. The hydrogen peroxide, acidic, and potassium permanganate-activated biochar prepared at higher activation temperature of 550°C showed moderate phenol removal capacity of about 93.5 mg/g, respectively. Sometimes, alkaline groups like OH^- ions and $-\text{NH}_2$ reacted with functional groups that present on the modified biochar surface, which results in improved removal of negatively charged organic contaminants from wastewater. The Cr (VI) adsorption was recorded in the range of 46.9 to 94.4 mg/g using sugarcane bagasse-derived activated biochar using zinc oxide. It was observed that alkali-activated biochar showed the highest adsorption capacity 435.7 mg/g for Cr (VI) from wastewater. The plentiful availability of amino groups was present on alkali-activated biochar surface, which became one of the favorable conditions for the removal of heavy metals.

11.10 CONCLUSION

The production of biochar from crop residues via the thermochemical conversion process and further preparation of activated biochar provide a new platform for sustainable solid-waste management. Different activation methods could be used to prepare a good quality activated biochar. Chemical activation substantially improves the surface physicochemical properties of biochar. The acid and alkali agents help modify the physical characteristics and improve the availability of functional groups on activated biochar surfaces. However, the alkali-modified biochar possesses higher surface morphology, aromaticity, and N/C molar ratio. Heavy metals are toxic and dangerous, and they have extremely harmful effects on living organisms and the environment due to their bioaccumulation and carcinogenicity. The

activated biochar is considered a promising material for the adsorption of heavy metals and toxic contaminants from wastewater.

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