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Engineered Biochar

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As a product of the thermochemical decomposition of biomass, biochar is produced under the condition of a limited-oxygen or oxygen-deprived environment. Many organic raw materials can be employed for biochar production, including urban organic solid wastes, manures, algae, sewage sludge, agricultural and forestry byproducts, and wood chips. The techniques for the thermochemical decomposition of the organic materials are various, including gasification, torrefaction, microwave heating, hydrothermal carbonization, and pyrolysis, which differ in production duration and thermal condition. The reasons that biochar has drawn much attention are twofold. First, biochar production can mitigate climate change by storing carbon in a relatively stable form, thereby reducing the emission of greenhouse gases into the Earth's atmosphere. Second, due to its porous texture, biochar has plentiful surface functional groups (SFG) and a large surface area, which makes it an environmentally friendly, low-cost, and effective adsorbent/catalyst. Many studies have reported that the production temperature and duration, decomposition techniques, and feedstock type could considerably affect the final product's physical and chemical properties. In addition, pre-treatment of the feedstock and post-treatments can also influence biochar's properties.

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1.1 Overview of Biochar Production

Both living and recently living organic materials can be used to produce biochar. They include lignocellulosic materials, such as forestry agricultural byproducts, plants, and wood. Nonlignocellulosic materials are also suitable, including organic municipal solid waste (MSW) and livestock's manure. On the other hand, due to the benefits of quick reaction time and high conversion ratio, thermochemical methods are the most preferred amongst a variety of biomass treatment techniques.

The International Biochar Initiative (IBI) states that "Biochar is a solid material obtained from the thermochemical conversion of biomass in an oxygen-limited environment" [1]. In other words, biomass is processed using the dry carbonization method (e.g., pyrolysis), yielding several products including biochar. Although the term *hydrochar* is analogous to *biochar*, it cannot be considered as biochar. Hydrochar is made employing hydrothermal carbonization, through which the organic raw material is heated with water at a temperature range of 200–300 °C. The material undergoes solid and liquid phases (i.e., slurry). Because biochar and hydrochar are essentially distinct, the hydrochar produced using hydrothermal carbonization is not equivalent to biochar.

Among the various thermochemical methods, gasification and dry torrefaction are unsuitable for making biochar. During dry torrefaction, biomass is heated to 200–300 °C and within an inert gas from half an hour to several hours. After the process, the organic raw materials loses energy in gaseous forms, accounting for merely 10% of the total energy, hence the final product's energy density is increased. Because of this, dry torrefaction has been used to pretreat the biomass before combustion. By contrast, gasification is essentially a process of partially combusting biomass at a higher temperature range (600–1200 °C) than pyrolysis, and with a duration of 10–20 seconds. The main reason for using gasification is to transform carbon-based material into gas mixtures (CO_2, CO, and H_2), such as producer gas and synthesis gas (syngas). However, IBI stresses that the production of biochar must avoid accumulation of toxicants in the final product and emission of unsafe air-pollutant.

Before processing for biochar, the wet organic material must be dried. However, the drying process is usually energy intensive, reducing the production's economic efficiency. That's why some forestry and agricultural wastes that possess low water content (less than 30%) after harvest are preferred sources of biochar. In addition, organic waste, such as livestock manure, sewage sludge, agroforestry waste, food waste, and organic fraction of MSW, are also commonly used as feedstock. Utilizing a variety of organic wastes to produce biochar is undoubtedly cost-efficient because the organic raw materials used in the production do not require arable land that could have been better used for growing energy and food

crops. The consensus is that utilizing organic wastes for biochar production is eco-friendly and an ideal way to treat numerous wastes efficiently.

The main technology used to produce biochar is biomass pyrolysis. During the process, biomass is decomposed at a relatively high temperature and in an inert gas atmosphere (i.e., the inert gas N_2 with limited O_2). The organic constituents in the feedstock undergo thermochemical decomposition, releasing the gas phase and leaving solid phase residual (i.e., biochar). Next, the high-molecular-weight and polar compounds of the gas phase are cooled, producing a liquid phase (i.e., bio-oil), whereas the compounds that have lower molecular weight and primarily consist of noncondensable gases, such as H_2, CH_4, C_2H_2, CO, and CO_2, are left in the gas phase [2]. Slow pyrolysis can offer the highest yield of solid product (35 to 50 wt.%) and is most commonly adopted for producing biochar. The production takes place at temperatures ranging from 300 °C to 800 °C with heating rates of 5–10 °C min^{-1}, and the gas residence time varies from several minutes to a few hours.

During the pyrolysis process, cellulose starts to decompose between 240 °C and 350 °C, while the decomposition of hemicellulose starts between 200 °C and 260 °C, and lignin decomposes between 280 °C and 500 °C. In cellulose pyrolysis, cellulose first depolymerizes into oligosaccharides. The process of the cleavage of glycosidic bonds to form D-glucopyranose is as follows. It starts from the D-glucopyranose undergoing an intramolecular reorganization, producing levoglucosan. Levoglucosenone is then formed with dehydration of levoglucosan and subsequently proceeds through intermolecular condensation, dehydration, decarboxylation, and aromatization to create a complex solid porous structure (i.e., biochar). The pyrolyzing process of hemicellulose starts with the depolymerizing of hemicellulose into oligosaccharides, succeeded by the reorganization of oligosaccharides and cleavage of glycosidic linkages in xylan chains, forming 1, 4-anhydro-D-xylopyranose. This intermediate step is required for the formation of biochar, which undergoes intramolecular condensation, dehydration, decarboxylation, and aromatization. It is comparable to the pyrolyzing process of cellulose. In the pyrolyzing process of lignin, free radical reaction, among others, is the most crucial pathway. The β–O–4 bonds are cleaved in lignin to generate free radicals, which is the first stage of the free radical reaction. The generated free radicals capture protons of substances with weak O–H or C–H bonds (such as phenyl groups), yielding decomposition products, including vanillin and cresol [2]. They are passed on to other substances, causing chain propagation [2]. When the reaction progresses further and the two radicals collide, stable compounds are formed, ending the chain reactions of free radicals [2]. However, it is difficult to observe the free radicals being generated during pyrolysis [2]. The exact mechanism of lignin pyrolysis is still unclear, and fully understanding it remains a daunting task [2].

During the first stage (200–300 °C), the organic raw material starts to decompose, and during the second stage (300–600 °C), a large number of aliphatic

functional groups originating from hemicellulose and cellulose start to form [3]. It is worth noting that, at 350 °C, hemicellulose and cellulose begin to degrade and create O–H bonding of phenol (1375 cm^{-1}), OH bending of alcohol (3300–3400 cm^{-1}), C–O stretching of conjugated ketones (1600 cm^{-1}), CH_3 and CH_2 alkanes bend (1375 and 1465 cm^{-1}), C–H stretching (855 cm^{-1}), aromatic C–C stretching (1475–1600 cm^{-1}), and symmetric C–O stretching (1110 cm^{-1}) [3].

During the final stage (600–900 °C), polycyclic structures and benzene derivatives (700 cm^{-1}) start to form by transformation [3]. As the pyrolysis temperature increases, the oxygen-containing functional groups gradually decrease. However, vast majority of the prominent spectral features that could be observed at a lower temperature disappear when the temperature reaches above 600–800 °C, and the FTIR spectrum is analogous to an ordered graphitic structure. Aliphatic structures, including carboxyl, C–O, ester, and ketone, are completely degraded at such a high temperature. As a result, biochar produced at a low temperature is predominantly hydrophilic because of a broad variety of oxygen-containing functional groups [3]. In contrast, biochars produced at a higher temperature were more likely to contain aromatic structures and skeletons. The aromatic rings of biochar lead to hydrophobic functional groups [3]. Therefore, higher temperatures mainly generate aromatic structures, while lower temperatures prominently generate oxygen-containing functional groups.

1.2 Biochar Properties and Characterization

Surface properties, such as elemental distribution, porous structure, charge density, and surface area, are crucial features because of their ability to affect the fundamental functions of microbial activity, nutrients, and water retention. Operating parameters, such as reaction vessel pressure, reaction residence time, pressure (catalyst, size, stirring method, and direction, etc.), maximum processing temperature (HTT), the heating rate of the process, pretreatment (chemical activation, crushing, and drying, etc.), and flow rate of the auxiliary input all affects biochar's final physical properties, regardless of the types of organic material used.

A higher fixed carbon content usually leads to a higher biochar yield. The biochar production decreased exponentially with increasing pyrolysis temperature for each of the studied organic material groups. The exponential decay curves fit the experimental data well for the wooden raw material group ($R^2 = 0.936$), livestock manure ($R^2 = 0.814$), and herbaceous raw material ($R^2 = 0.867$), but not for the biosolids group ($R^2 = 0.508$) and all raw materials group ($R^2 = 0.677$). Compared with the other three groups of raw materials, the physicochemical properties of biosolids usually vary greatly, depending on the sludge treatment method, wastewater treatment process, and wastewater source.

The N, H, and C contents in biochar can be determined with an elemental analysis, where the content of O is recorded as 100%, excluding the percentage of N, H, C, and ash (O (%) = 100% – N (%) – H (%) – C (%) – ash). In addition, the ratios of O/C and H/C, as well as N-related ratios, can be calculated. Biochars made from livestock manure are likely to have lower H, O, and C contents content because the higher volatile OC compounds in the feedstock are lost during the drying and carbonizing stages of pyrolysis. By contrast, lignocellulose biochar has higher O and H contents because the plant-based feedstock possesses the –OH groups connected with the lignin, hemicellulose, and cellulose components of the plant structure [4]. Biochars made with lignocellulosic material are likely to have a higher fixed carbon content that is not easily mineralized, representing the carbon materials that are not easily lost during pyrolysis.

The ratios of O/C and H/C indicate the aromaticity and polarity of biochars [3]. The carbonization of the biosorbents is assessed using the molar ratio of H/C. When the molar ratio of H/C decreases, it indicates the carbonization is at a higher degree, and a lower amount of plant residues is left (e.g., hemicellulose and cellulose) [3]. In addition, the hydrophilic quality of biochar is determined using the O/C molar ratio. As the pyrolysis temperature increases, the molar ratios of O/C and H/C increase because of the higher carbonization degree [3]. When the pyrolysis temperature of woody and herbaceous raw materials was higher than 600 °C and that of livestock manure and biosolids were higher than 700 °C, the ratio of O/C became less than 0.2, indicating a good carbon sequestration potential [3]. In general, the C/N ratios of the plant-based and herbaceous biochar were relatively higher, while those made from livestock wastes or biosolids generally had lower C/N ratios. In each group of feedstocks, the ratio of C/N increased with rising pyrolysis temperature.

In general, biochar made from livestock manure has more inorganic components than plant-based biochar, which is made from grass and wood chips. Compared to the biochar made from livestock manure, biochar produced from lignocellulosic materials contains fewer nutrients and has lower $CaCO_{3\text{-eq}}$ due to the lower content of ash. Mixing feedstock before the pyrolysis process provides flexibility in designing biochar to increase the concentration of specific nutrients in the soil or to decrease the concentration of certain compounds to balance plant nutrient requirements. As the temperature of pyrolysis increases, so does the inorganic elements' relative weight % (except those volatile elements such as N) because of the decreased hydrogen and oxygen content in the biomass and evaporation, yet their weight content remained almost constant.

The pH value of biochar is generally around 5–12, but it differs with the pyrolysis temperature and raw materials. Although some biochars made from herbaceous feedstocks, biosolids, and wooden materials exhibit neutral to slightly acidic pHs, especially when the pyrolysis temperature is below 400 °C, several studies

suggest that most biochars tend to have an alkaline pH. Biochars made from livestock manure have higher pH and more ash contents. When different feedstocks were used, the pH of biochars all increased linearly with the pyrolysis temperature. The change in pH may be caused by the decline of acidic functional groups (–COOH) as the temperature climbs. In addition, the increased biochar content of carbonate and total base alkali cations also play a part in increasing biochar pH with a rising temperature. It is not difficult to notice that the sensitivity of the different feedstock groups to the pyrolysis temperature varies. The estimated rate of increase in pH was 0.6/100 °C ($R^2 = 0.657$) for the woody group, 0.5/100 °C ($R^2 = 0.504$) for the animal waste group, 1.4/100 °C ($R^2 = 0.785$) for the biosolid group, and 1.0/100°C ($R^2 = 0.803$) for the herbaceous group [5].

Some studies reported that, as temperature increases, biochar pH, carbon content, ash content, stability, and surface area rise, while O/C and H/C decline with rising pyrolysis temperature [3]. Evidence also showed that moderate positive correlations exist between temperature and the surface area of hardwood-, softwood-, and grass-, but not manure-derived biochar [3]. Comparably, biochars made with other materials usually have mild negative correlations with HTT, while MBC shows little correlation with O/C and HTT.

The surface charge of a particle is related to the point of zero charge (pH_{pzc}) and zeta potential, which can be used as indicators. If the solution pH is lower than the pH_{pzc} of biochar, the biochar surface will be positively charged. If the pH of the solution is higher than pH_{pzc} of biochar, then the biochar's surface will be negatively charged [6]. The charge difference on the surface of biochar is essential in deciding which of electrostatic attraction or surface complexation is the prominent adsorption mechanism.

The ability of certain materials to absorb and store positively charged ions, such as clays, soils, and biochars, can be commonly assessed using cation exchange capacity (CEC). The measure can indicate the negative charge on the biochar surface and thus reveals the biochar's ability to retain cations [7]. The biochars' CEC value increases with the degree of oxidation of carbon in the aromatic structure and the creation of carboxyl groups [7]. Biochars produced with biosolids exhibited the highest CECs, followed by biochars made with plant-based raw materials. Earlier research stated that the higher CEC values of biochars were a result of the facilitated formation of O-associated surface functional groups due to abundant minerals in the raw materials (e.g., K, Na, Ca, Mg, and P).

In order to understand the biochar's surface morphology, biochar samples were observed by reflected light optical microscopy, and scanning electron microscopy (SEM) was used to identify the microstructure. A backscattered electron image was observed from the Au-coated sample surface, representing average atomic abundance in a black and white image [8]. SEM and energy dispersive spectroscopy (EDS) with an acceleration voltage of 15 kV and beam current of 180 Pa was

used to identify the mineral phases of the sample with an Au coating in a vacuum of 25 Pa [8]. SEM images collected at a scale of 200 μm revealed that the residues of structural material inside the wood-based biochar appeared to be fibers. A much closer image shows that the surface edge of the wood-based biochar has large (200 μm) and small porous structures and is covered with small particles. SEM images of biochar made with the manure of swine and poultry showed that the surface contained void spaces and pores, and was extensively covered with particles of irregular shapes. These particles might be salt accumulated during manure production and excreted by animals. Theoretically, particle accumulation is caused by electrostatic interactions happening in the electron-dense regions and led by ions in dissolved salts involved in redox reactions, in which they are attracted to sites. Transmission electron microscope (TEM) images (×800 K) reveal surface morphology of sugarcane bagasse biochar in greater detail [3]. In general, the raw organic materials' TEM image usually shows an amorphous structure. Conversely, the amorphous carbon starts to recombine at low pyrolysis temperatures (250–350 °C), which is caused by the hemicellulose and cellulose structures breakdown. At a higher pyrolyzing temperature (600 °C), the surface of biochar organizes into a regular crystal-like structure, most likely graphite [3].

N_2 sorption isotherms analysis can be used to investigate the surface area and pore characteristics. Biochars produced with agricultural wastes usually have larger surface areas than biochars made from animal manure or sludge. Pyrolysis processing of organic materials can enlarge the crystallites and make them well organized, which increases with HTT [8]. Increasing the temperature of pyrolysis from 250 °C to 500 °C can expand the BET surface area because of the increasing evolution of volatiles in the organic materials, leading to enhanced pore development in the biochars. The biochars' surface area usually increases with elevating HTT until reaching a temperature at which deformation occurs, causing a subsequent reduction in surface area to happen [8]. The pore sizes distributed within the micropores contribute the most to the total surface area. Micropores develop with higher temperatures and longer reaction residence times [8]. The elevated temperatures offer activation energy, and the longer retention time allows time for the reaction to complete, resulting in a higher order degree of the structure.

The Boehm titration method is based on the observing the reaction features of various bases and acids with distinct surface functional groups containing oxygen and quantitatively analyzing the functional groups on the substances' surface.

Semi-quantitative analysis of biochar functional groups was carried out using CPMAS ^{13}C NMR (solid-state ^{13}C cross-polarization magic-angle nuclear magnetic resonance). During NMR analysis, the biochar sample is exposed to radio frequency pulses and a strong magnetic field for a period of time. The ^{13}C nuclear active isotope among the ^{14}C atoms absorbs radio frequency in a narrow band and resonates at a frequency because of the shielding of nearby electrons, which offers

a measurable magnetic spectrum, and differences in signal intensity are plotted along an *X*-axis [4]. These are chemical shifts in parts per million (ppm) [4]. Chemical shift regions are therefore assigned in the spectrum to core structural features, such as aromatic C (109–145 ppm), and in particular organic structures, such as C in unsubstituted aliphatic compounds (0–50 ppm), to perform the interpretation of ^{13}C NMR spectra [4]. Under each chemical shift region, the area is determined and reported as a distribution percentage of C [4]. The spectra showed that a higher proportion of aromatic C was found in the biochar with high pyrolyzed temperature (≥ 400 ˚C) [8]. The NMR spectral assignments of ^{13}C and C distribution percentage in the biochar are listed in Table 1.1 [4].

Fourier-transform infrared spectroscopy (FTIR) is another tool that is commonly used to analyze biochars because the method is nondestructive, the spectra can be quickly obtained, and the spectroscopic technique is easier to understand compared to NMR. As a vibrational spectroscopy method, FTIR offers a way to characterize the composition of organic and mineral samples. In FTIR spectroscopy, a number of ways can be used to present the samples to the instrument:

- *Transmission*, through which the IR beam penetrates the sample.
- *DRIFT or diffuse reflectance*, by which the sample absorbs the incident IR beam. The beam is then reflected re-diffusely and collected by the instrument.
- *Attenuated Total Reflection (ATR)*, where an optically dense crystal (such as diamond) is placed in contact with the sample. An infrared beam passes through the sample, and the absorbance information is reflected into the crystal and then transmitted by the detector [4].

Biochar samples are exposed to infrared radiation, and the bonds in the matrix absorb energy at the wavelengths of mid-infrared (4000 to 400 wavenumbers),

Table 1.1 The ^{13}C NMR spectral assignments to different C structures in biochar.

ppm	Chemical structures	Examples
0–50	Unsubstituted aliphatic	Alkanes, fatty acids
50–61	N-alkyl compounds	Amino acids, proteins
61–96	Carbohydrates	Cellulose
96–109	AnomericC	Monosaccharides
109–145	AromaticC	Benzene-like compounds
145–163	Phenolic C	Phenol, nitrophenol
163–190	Carboxylic C	Acetic acid
190–220	Ketonic C=O	Esters and amides

causing molecules to vibrate [4]. The molecules are excited to a higher state of energy, and the bonds will vibrate in one of several modes, depending on the mass of the bonded atoms and bond types [4]. The spectral wavelengths between 4000 and 550 wavenumbers (cm^{-1}) are usually used to scan the biochar samples [4]. Light absorption wavelengths are assigned to specific functional groups and core structures in mineral/impurities and biochar. In order to carry out FTIR analysis on carbonaceous solids, the pellet technique was utilized to prepare the samples, by which the dry biochars were uniformly mixed with the base substrate KBr powder. Biochars made at such low pyrolysis temperatures displayed a more diverse organic structural composition due to fewer volatile compounds loss. In real settings, as the pyrolysis temperature increases (400–600 °C), the number of aliphatic structure decrease manifested as stretching of the aliphatic C–H [7]. In the meantime, more aromatic structures are created with the enhancement or emergence of characteristic peaks in the C=O (1580–1700 cm^{-1}), C=C (1380–1450 cm^{-1}), C–C stretch, and C–H stretch (750–900 cm^{-1}) [7]. As the temperature of pyrolysis continues to climb (700–800 °C), the aromatic (3050–3000 cm^{-1}, 1600–1580 cm^{-1}) and hydroxyl groups (3200–3400 cm^{-1}) decrease slightly [7]. Also, the condensation and dehydration during biomass pyrolysis (400–600 °C) lead to the increase of aromatic structure and decrease of aliphatic structure [7].

In principle, aromatic C is deemed to have a stronger hydrophobic property than alkyl–C/O–alkyl–C, which means that pyrolyzing for biochar at a higher temperature (≥ 400 °C) would lead to a more hydrophobic product [8]. However, regardless of the biochar type, the hydrophilicity (contact angle ≥ 90°) of biochar pyrolyzed above 400 °C would increase. We hypothesize that HTT increases the structured regular spacing between planar results [8]. Interplanar distances also reduce with increased molecular order and organization, all of which lead to greater surface area per unit volume [8]. In addition, higher pyrolysis temperatures leading to a higher specific surface area and a bigger quantity of micropores might be the key factors for water retention capacity in biochar.

1.3 Pre- and Post-Modification of Biochar

The ability of raw biochar to remove pollutants is usually limited, especially at high concentrations. The main reasons for such limitation are threefold:

1) The functionality of the precursors after pyrolysis is low.
2) Biochars created at low temperatures have a small surface area and limited pore volume.
3) The size of the powdered biochar is so small that it is difficult to separate.

Biochar can be modified prior to, during, and/or after the process of pyrolysis. Currently, there are well-tested surface modification methods for carbon-based

materials, such as impregnation methods, chemical modification, and physical modification. Among them, physical modifications, such as ball-milling, microwave-assisted pyrolysis, gas activation, and steam activation, could drastically affect the physiochemical properties of biochar. On the one hand, physical modification is environmentally friendly, low-cost, and simple because no toxic chemicals are used in the modification process. On the other hand, several studies have suggested that physical modification might be less effective than chemical modification in most scenarios. Therefore, chemical modification is more commonly used than physical modification, primarily including oxidants modification, alkali modification, and acid modification. Typical biochar composites include (1) microorganism–biochar composites, (2) carbonaceous engineering nanocomposites, (3) nonmetal heteroatom dopped biochar composites, (4) layered double hydroxide–biochar composites, (5) mineral–biochar composites, and (6) metal–biochar composites.

1.3.1 Physical Modification

Steam Activation

In the steam activation process, biochar obtained after pyrolysis of biomass in a limited-oxygen or oxygen-deprived atmosphere and at moderate temperatures (400–800 °C) was partially gasified with steam at 800–900 °C [9]. The steam triggers a series of reactions ($C + H_2O \rightarrow C(O) + H_2$; $2C + H_2 \rightarrow 2C(H)$; $CO + H_2O \rightarrow CO_2 + H_2$) [9], in which surface carbon first reacts with oxygen from the water to form surface oxide C(O) and H_2 [10]. Furthermore, the generated C(O) reacts with steam to form CO_2 and H_2 alleviating the surface activation and affecting the inhibition of biochar gasification [10]. Moreover, the generated H_2 reacts with surface site C to form C(H) complexes [10]. Therefore, partial devolatilization occurs, and crystalline carbon forms on the biochar surface.

The cleavage of C=C bonds in the biochar during steam activation is comparable to the polymerization reactions to form C=C bonds in the biochar. The degree of self-aggregation increases significantly [11]. The activated biochar is composed of oxygenated functional groups such as ether, phenolic, carboxyl, and carbonyl, resulting in increased hydrophilicity. However, some studies suggested that steam activation has little or even negative effects on the properties of surface functional groups. The trapped products that are generated from incomplete pyrolysis are eliminated during steam activation and, in most cases, the carbon surface is oxidized because of the formation of syngas H_2 [12]. Thus, new pores are formed, and the diameter of the minor pores expands [12], leading to an increase in surface area. Thereafter, under the influence of process parameters – such as the activation time, water vapor flow, and activation temperature – reduced polarity, higher

aromaticity (decreased value of H/C) and strength of delocalized π bonds, and increased specific surface area and pore volume are key properties of steam-activated biochar [13].

Compared with other approaches intended to increase the surface area, for example, increasing the pyrolysis temperature, the method that uses steam to assist pyrolysis has the advantages of simple operation and moderate energy-saving. Many studies have theorized that using steam to assist pyrolyzing process in biochar production could successfully halt organic aromatic pollutants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs), because the cutback of oxygen-containing functional groups might lead to the above-described enhanced π-π interactions.

Gas Activation

Similar to steam activation, gas purging modification also consists of two procedures. The first is the pyrolysis of organic materials. The second is to modify biochar by removing carbon dioxide or ammonia. Compared with the standard reaction atmosphere, the presence of an active atmosphere drastically affects the functional groups, volatiles, and biochar yield [14]. The surface aromatic properties of sewage sludge biochar can be improved by using CO_2 as an atmosphere during pyrolysis [14]. When CO_2 is used as the reaction medium, the prepared biochar made from paper-mill sludge will result in a complex aggregate structure containing solid minerals (FeO, Fe_3O_4, and $CaCO_3$) and graphite carbon [14].

CO_2 has two crucial parts in the pyrolysis process: (1) it accelerates the thermal cracking of volatile organic compounds (VOCs) during pyrolysis and reacts with VOCs to increase the production of CO [14]; (2) it immediately leads to a substantial reduction (~40–60%) of condensable hydrocarbons (tars). The CO_2 medium helps the creation of both micropores and meso/macropores due to the intense carbon reformation at ≥ 710 °C through the Boudouard reaction ($C + CO_2 \rightarrow 2CO$). CO_2 may also react with pore-clogging condensable hydrocarbons, for example, volatile organic compounds and tars, which can be converted to gaseous products to free the clogged pores and/or produce new ones. CO_2 medium induced more structural edge defects and fused aromatic rings in the biochar matrix during pyrolysis. This could be the result of enhanced dehydrogenation of organic matter with CO_2 purging at high temperatures (*viz.* Boudouard reaction: $C + CO_2 \rightarrow 2CO$; biomass → biochar + tar + C_nH_m), which may create more vacancy and zigzag edges as structural dimensionality defects.

The basic nitrogen functional groups are introduced into the carbon matrix of biochar by ammonia gas purging [11]. During pyrolysis in an ammonia (NH_3) atmosphere, NH_3 may react with oxygen-containing species in the organic materials (such as furans, esters, aldehydes, and ketones) to create nitrogen (N)-containing heterocyclic compounds (such as indole, piperidine, pyridine, and pyrrole). At

higher temperatures, ammonia decomposes to generate free radicals such as H, NH, and NH_2 [15], which react with the active sites allocated on the edge of the graphene layer in biochar to introduce nitrogen-containing functional groups [11].

Pyrolysis in a low-oxygen atmosphere is also a possible way to yield carbon with moderate porosity [14]. The oxygen content during the pyrolysis process could increase ash content and enlarge the specific surface area.

Microwave-Assisted Pyrolysis

Microwaves have a wavelength in the range of 0.001 to 1 m and are a form of electromagnetic radiation that can be used as a dielectric heating method at specific frequencies (typically 2.45 GHz) [16]. By converting electromagnetic energy into heat, microwave radiation can heat objects without direct physical contact, thus providing comparatively high heating rates during the process of pyrolysis. Its heating rates range from 0.1 °C/s to higher than 1000 °C/s [11]. With the merits of selective heating conditions, higher homogeneity, and low temperature, using microwaves in pyrolysis processes can produce higher-quality biochars. Using microwave as the heat source also has the benefits of reducing energy consumption and accelerating the rate of the chemical reaction and internal volume heating.

The microwave heating mechanism involves interfacial polarization, dipolar depolarization, and ionic conduction. In the pyrolysis process with microwave heating, it is central that the organic materials can efficiently absorb microwaves to induce polarization effects. It is believed that a high water content helps the absorption of microwaves because the water can rotate and align in dipoles, causing friction and collisions [17]. Microwave receptors, such as metal-based microwave receptors or activated carbon, are added during the pyrolyzing process to ensure an efficient absorption of microwaves and assist the reaction to attain the pyrolysis temperature and targeted heating rate.

Microwave radiation can change the morphology and chemical properties of the biochar being produced [14]. Compared with traditional pyrolysis methods, a higher degree of carbonization of biochar at a lower pyrolysis temperature can be realized by microwave-assisted pyrolysis. Utilizing microwave-assisted pyrolysis to produce biochar has been reported to offer a higher surface area and larger pore volume [11]. Deep and narrow pores are created with the help of microwaves. During the microwave-assisted pyrolysis process, tiny microplasma spots spread throughout the reaction medium. Microwave-assisted pyrolysis also helps generate gas, increase the local temperature, and in turn promote the formation of pores in the biochar. Using microwaves as the heating source, the hollowed carbon nanofibers are created during the pyrolyzing process of the palm kernel shells because the self-extrusion of volatile substances from the interior of the organic material and the resolidification of the resulting biochar surface are augmented

by the formation of arc. Moreover, microwave irradiation can reduce the number of oxygen-containing functional groups [16].

Ball Milling

The mechanochemical technique seeks to find the right balance between producing defects through ball grinding and adjusting the size of a solid grain to nanoparticles (< 1000 nm). During the process, specific powder charges and a grinding medium are placed in a high-energy mill. The mechanisms of the ball-grinding process include ionic defects, electronic, structure, strain generation, and diffusion improvement, as well as interactions among the substrates [18]. The substrates and movement of grinding media create kinetic energy that can stretch or break chemical bonds of large molecules, resulting in the charge transfer, cleavage of glycosidic bonds, generation of electrochemical elements, and fragmentation of solid materials [18]. As the process has multiple phases and consists of several reactions, the mechanochemical technique improves the contact at the interfaces, thereby facilitating the reactions and removing products. Mechanochemical processes can lead to the sublimation and melting of reagents because thermal decomposition happens at the melting point of a particular compound [18]. The ball-grinding process also facilitates the creation of new surface structures, particle size reduction, and reagent contact. Therefore, the surface functional groups of biochars could be notably improved by ball grinding for broad implementation. The newly formed functional groups might be originated from broken chemical bonds of the materials because the energy generated during ball milling is associated with elevated temperature, higher defect density, and crystal deformation [18].

A variety of operational factors can change the properties of biochar during a ball grinding process. As a result, the optimization of ball-milling parameters is exceedingly crucial for tailoring the function and performance of ball-milled biochar [18]. The parameters include grinding temperature, reaction time, ball-size distribution, grinding speed, dry or wet grinding, and powder used to drive the grinding chamber [18]. The mass ratio of media to biochar and the solvent properties during a ball-grinding process is directly proportional to the surface area of the resulting biochar [18, 19].

Wet grinding and dry grinding are two distinct approaches to biochar modification techniques. The choice of grinding approach depends on the technical and economic analysis as well as the convenience of operation [18]. For materials that are difficult to filter, dry ball grinding usually work better [18]. In contrast, wet ball grinding is a labor-saving and green process that can be carried out at room temperature.

Wet ball milling of biochar using organic solvents such as heptane, hexane, and ethanol has been demonstrated to successfully expand the Brunauer-Emmett-Teller (BET) surface area of the resulting biochar [18]. The mass ratio of grinding media to

biochar during a wet grinding process has proved to be the most critical parameter, through which the best result is obtained at 100:1 [18]. Although relatively ineffective, adding salt in dry ball grinding is proved to be a cost-effective manner that can expand the total surface area and micropore ratio of biochar [18]. As the biochar is ground in the spherical grinding media, the salt crystals are continuously broken down into finer grains, which provide friction and impact force to augment the biochar's surface properties and pore structure [18]. The size of biochar grains is also influenced by the ball mill's rotational speed and processing time [18].

1.3.2 Chemical Modification

Chemical modification processes include two-step modification and one-step modification processes. In the presence of activation chemicals, the activation and carbonization steps are achieved at the same time in a one-step chemical activation process. The two-step chemical activation entails the carbonization of the original raw material, succeeded by the activation of the carbonized product [9], in which chemical reagents are added, or pretreatment of the precursor is performed prior to the carbonization process. Chemical modification treatments are usually conducted by adding acids, bases, or inorganic salts (potassium carbonate, zinc chloride). Activation by acid/alkaline can be a fairly straightforward step of modification as it merely requires washing and mixing procedures in moderate conditions. Therefore, the step is a useful and applicable modifying technique in ecological remedying applications. Nevertheless, since a variety of chemical reagents are required, the impact to environment and cost efficiency need to be thoroughly assessed on each case individually. In addition, a relatively large amount of water is required to neutralize the pH after acid or alkali activation [2], otherwise excess acidity/alkalinity may be harmful to the environment when biochar is applied [17]. Furthermore, intentional oxidation employing ozone (O_3), ammonium persulfate [$(NH_4)_2S_2O_8$], potassium permanganate ($KMnO_4$), and hydrogen peroxide (H_2O_2) has been utilized to modify surface functional groups. The process of chemical activation is cost-efficient and is usually performed at relatively low temperatures and in a shorter time duration [11]. The chemical activation proves superior efficiency in the development of biochar microporosity, reduction of mineral matters, activation of carbonaceous materials, and increase of the surface functional groups [11].

Acid Activation

Washing with strong acids, such as hydrochloric–HCl acid, nitric–HNO_3, sulfuric–H_2SO_4, and phosphoric–H_3PO_4, has been investigated for aqueous oxidation, which can enhance surface acidity and change the porous structure of biochars [9]. Typically, acid activation of biochars is conducted by moving the biochars to an

acid solution at a ratio of 1:10 and a temperature ranging from room temperature to 120 °C. The durations of reaction are generally varied from hours to days [11].

Phosphoric acid is one of the widely applied chemical modification activators and is more eco-friendly than other hazardous and corrosive reagents [9]. Phosphoric acid can break down aromatic, aliphatic, and lignocellulosic materials while forming phosphate and polyphosphate cross-bridges to prevent contraction or shrinkage during pore formation [9]. Because of its erosive character, oxidation treatment using HNO_3 has been proven to cause degradation of the micropore walls, causing a reduction in the total surface area to happen [9]. Likewise, H_2SO_4 treatment contributes to a reduction in the porosity of biochar from 10% to 40% and increased the size distribution of heterogeneous micropores [9]. Increasing the concentration of sulfuric acid used for activation from 5% to 30% has generally had a positive effect on increasing surface area [11]. Nevertheless, surface area reduction has been observed when the sulfuric acid concentration is excessively high. The dehydration of H_2SO_4 during pyrolysis might be detrimental to the surface area development because excess water vapor moves toward the surface structure [9]. Modification with citric acid and oxalic acid marginally reduced the surface area of the biochars. On the other hand, the combined modification of 30% oxalic acid and sulfuric acid drastically enlarged biochar surface area.

Generally, it is recognized that acidic functional groups such as amine and carboxyl groups can be introduced into carbonized surfaces by treatment with strong acids [20]. In light of the inherent oxidizing properties, H_3PO_4 or H_2SO_4 would also, to some extent, partially oxidize the C surface and augment carboxyl groups [9]. Surface carboxylation is mainly achieved by single-stage oxidation [9]. Citric acid and oxalic acid are weak acids that could similarly introduce the carboxyl group on the surface of biochar through esterification.

Acid activation, which in its essence is to introduce acid groups to the surface of the biochar, can lower the pH of the biochar and make alkaline materials less stable and more soluble [7]. However, acid activation might not be a feasible modifying option, if the organic materials to be modified contain heavy metals, as the heavy metals in the organic material could become more bioavailable. Heavy metals could be flushed out during acid activation and leaching tests are required to assess the possible changes in metal availability [17].

Alkaline Activation

Alkali activation of biochar employing sodium hydroxide (NaOH) and potassium hydroxide (KOH) can increase the surface basicity and oxygen content, at the same time, dissolving ash and concentrating organics such as lignin and cellulose to accelerate later activation. Sodium hydroxide treatment can lead to depolymerization. Potassium species (K_2O, K_2CO_3) may be formed during activation due to K^+ intercalation in the microcrystalline layer forming the condensed C

structure [9]. The potassium species might disperse into the internal structure of the biochar matrix, widening existing pores, and creating new pores for the product [9]. Nevertheless, it is worth noting that NaOH modification at lower temperatures (60–100 °C) is observed to cause a reduced surface area with only a few micropores [9]. The proportion of functional groups on the surface of the biochar changed slightly due to the dominance of C content in graphite [16]. The KOH activation process increases the silicon content available to plants due to the better solubility of silicon in alkaline environments, increasing the bioavailability of phytolith silicon. NaOH is considered more cost-efficient and less corrosive for carbon activation than KOH. On top of different types of alkali, the ratio between alkali and biochar could also considerably affect the properties of biochar. Nevertheless, KOH activation has both advantages and disadvantages. High concentrations (i.e., 5 M) would disrupt the rice husks' cellular structure under alkaline activation.

Oxidation

Conventionally, oxidation is carried out under reflux conditions in the presence of single or mixed inorganic acids, such as H_2SO_4 and HNO_3, and oxidizing agents, such as NaOCl, $KMnO_4$, and H_2O_2 [21]. The refluxing acids could occasionally be too detrimental or harsh to the physical aspects of carbons [21]. The modification with oxidizing agents could increase the content of oxygen-containing functional groups on the biochar. Hydrogen peroxide modification could reduce the pH and ash content of the resulting biochar and increase the oxygen-containing functional groups, especially carboxyl groups. It is analogous to hydrogen peroxide in that potassium permanganate modification would also increase the oxygen-containing functional groups. Moreover, the surface area of biochar can be increased with the modification of potassium permanganate.

1.3.3 Biochar Composites

Metal–Biochar Composites

Three synthesis methods are commonly used are applied to prepare metal–biochar composites:

1) Pretreatment of biomass/biochar with metal salts before pyrolysis
2) Chemical precipitation of metal-oxide particles onto biochar after pyrolysis
3) Pyrolyzing the organic materials rich in target metal element.

For pretreatment of feedstock/biochar with metal salts prior to pyrolysis, organic materials are initially impregnated with metal salts ($ZnCl_2$, $CaCl_2$, $MnCl_2$, $MgCl_2$, $AlCl_3$, $Fe(NO_3)_3$, and $FeCl_3$, etc.). Among them, organic based metal salt solutions

and sulfur based metal salts are treated either under electric field or no electric field conditions. Metal ions in solution deposit on the surface or inside the raw material. Second, the pretreated feedstock/biochar is pyrolyzed at fairly low temperatures of 400 °C to 800 °C in a limited-oxygen or oxygen-deprived atmosphere after drying. During the process, the metal ions are converted into zero-valent metals or metal oxide nanoparticles (ZnO, CaO, MgO, Al_2O_3, MnO_2, and Fe_2O_3, etc.) on the biochar's surface. But, direct pyrolysis techniques have drawbacks such as intensive consumption of energy and unsuitable for raw materials with high water content. By thermally reducing granules of Fe-pretreated biochar powder in a reducing gas, thermal reduction can be used to produce magnetic metal powder [22]. Fe_3O_4 is produced at a thermal reduction temperature of 300–500 °C and Fe^0 is created at a thermal reduction temperature of 500–800 °C [22]. Because of its cost-efficiency, the thermal reduction of impregnating biochar in the gas phase at moderate temperatures is prefered, in so doing, resulting in preservation and minimal changes of the support material and high dispersion of Fe [22]. As a result, 600 °C is deemed as a suitable temperature for thermal reduction of Fe [22].

The second synthesis method of metal–biochar composites is to load metal oxide particles onto biochar. First, the organic materials are converted to boichar through the pyrolysis. Next, the biochar is immersed in the metal salts solutions, adsorbing metal ions to the biochar's pores and surface. In the end, the metal oxide particles are deposited on the biochar's surface to create a composite material using reduction method, pyrolysis method, and adjusting the pH the metal salt solution.

The third production method that is commonly used to prepare metal–biochar composites is to directly pyrolysis the organic materials rich in the target metal element. The metal elements in the organic materials are converted to metal-oxide particles through thermal pyrolysis.

The three approaches for preparing metal–biochar composites all have their own merits and downsides. Pretreatment of biomass with metal salts prior to pyrolysis is simple and inexpensive. The disadvantage is that, although this method can be used for production on a large scale, the type, composition, shape, and size of metal particles are difficult to control. Loading metal particles onto biochar can improve control over the type, composition, shape, and size of the particles, and multilayer, double-layer, and single-layer metal particles supported on biochar could be created. But this method is fairly complex and expensive. In contrast, directly pyrolyzing the organic materials rich in the target metal element is straightforward and cost-friendly; unfortunately, the sources of the organic raw materials rich in the target metal element are rare.

This novel approach can maximize the advantages of biochar and metal particles. First, the inherent shortcomings of biochar and metal particles can be overcome using the synthesis of metal–biochar composites. The loaded metal particles

can be distributed and stabilized with metal–biochar composites, resulting in surface passivation, leaching, and reducing aggregation of metal particles. Biochar acts as a scaffold for anchoring and dispersing metal particles with minimum aggregation. Second, metal–biochar composites can also increase the active sites and oxygen-containing functional groups and change the properties of both, making metal–biochar composites display excellent functionality [18]. Third, metal–biochar composites can promote the reaction rate of pollutants by enhancing the catalytic/redox performance of the metal–biochar interface. Furthermore, metal–biochar composites could enhance biochar production and improve thermal stability. Therefore, these novel composite materials could be exceptionally useful in remedying environmental problems.

Mineral–Biochar Composites

Clay/mineral–biochar composites are made by combining a small amount of clays/clay minerals with biochar [23]. As a type of hydrous aluminosilicate mineral, clays consist of mixtures of fine-grained clay minerals and clay-sized crystals of other minerals, such as metal oxides, carbonates, and quartz. Clay minerals are a group of phyllosilicates with diameters less than 2 μm. They have a higher cation exchange capacity (CEC) due to the permanent negative charge brought about by isostructural substitution [23]. Phyllosilicate clay minerals also have variable charges at fracture edges due to unsatisfied bonding [23]. These variable charges are primarily responsible for the adsorption of anions by the clay minerals [23]. Clays and their minerals represent an indispensable, abundant, and low-cost group of geological materials and are popular adsorbents for pollutant adsorption studies [23]. Clay minerals are easy to mine and are nontoxic [23]. They have the advantages of intercalation, low cost, layered structure, and fairly high surface area.

In recent years, extensive research has been conducted on clay-biochar composites. Impregnation of biochar with clay minerals, such as kaolinite, bentonite, or montmorillonite, could change the composition and physical properties of biochar [23], thereby enhancing the adsorption capacity for polyatomic cations (e.g., NH_4^+) and oxyanions (e.g., PO_4^{3-}). In particular, clay–biochar composites combine the salient features of biochar and clay materials, exhibiting unique properties [24], such as compatibility, porous structure, and high carbon content, making them also suitable for reuse and regeneration.

There are essentially two preparation methods for making clay–biochar composites. The first one is to mix and pyrolyze raw materials with clay minerals, and the second one is to mix pyrolyzed biochar with clay minerals [25]. Specifically, the raw material is immersed in a stable clay suspension made by adding the powdered material to deionized water or other suitable solvent and heated in a muffle furnace at an appropriate temperature in a limited-oxygen atmosphere. On the other hand, biochar can also be straightforwardly steeped in a slurry made from

acetic acid, deionized water, and clay minerals, stirred overnight, and then dried in an oven at 60 °C for 24 h. The most widely used weight ratios of clay for both procedures are as follows: biomass/biochar = 1:5, 1:4, 1:2, and 1:1.

The association of Al and Si could act as binders to facilitate the interactions between biochar and clay minerals [23]. Clay minerals attached to the biochar surface are introduced to the internal pores to form organomineral complexes [23]. Biochar would also react with multivalent cations existing in clay minerals to form organomineral complexes through various mechanisms such as ligand exchange and acid-base reaction [23]. These interactions depend on the functional groups of the biochar and clay mineral and the type of clay mineral and are similar to the interactions occurred between clay minerals and organic matter in the soil [23].

Layered Double Hydroxide–Biochar Composites

Layered double hydroxides (LDHs) exhibit unique physical and chemical properties that are similar to those of clay minerals. Among these properties, the valuable ion exchange capability, high mechanical and chemical stability, and the high specific surface area stand out, resulting in excellent adsorption properties.

The term *layered double hydroxides* refers to the two dimensionally organized structure with two metal cations in the lamella that can incorporate negative species into the interlamellar region, thereby, neutralizing the lamellae's positive charges. The general formula of LDHs is

$$\left[M^{2+}_{1-X}M^{3+}_{X}\left(OH\right)_2\right]^{X+} A^{m-}_{X/m}\cdot nH_2O \tag{1}$$

where M^{2+} represents a divalent metallic cation, M^{3+} a trivalent metallic cation, A^{m-}, an anion interspersed with load m, x is the di- and tri-valent cations ratio, and n is the number of water moles. There are quite a few combinations of di- and trivalent cations for LDHs' synthesis. The divalent cations generally utilized are: Ca^{2+}, Zn^{2+}, Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+}, Mn^{2+}, and Mg^{2+}; whereas the trivalent cations are: Ni^{3+}, Co^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, and Al^{3+}. To compensate for the positive charge of LDH lamella, several anionic species, either organic or inorganic anions, can be utilized, including halides (F^-, Cl^-, Br^-, and I^-); oxyanions (CO_3^{2-}, NO_3^-, SO_4^{2-}, and CrO_4^{2-}); complex anions ($[Fe(CN)_6]^{-4}$, $[NiCl_4]^{-2}$); polyoxometalates ($V_{10}O_{28}^{-6}$, $Mo_7O_{24}^{-6}$); and organic anions (such as alkylsulfates, carboxylates eporphyrins).

In most of the cases, biochar/LDH composites are prepared by the methodology based on a liquid phase deposition process and consists of preparing biochar starting from any method, then putting it in contact with the metal precursors in proportions for LDH formation, and finally applying a vigorous mixing process under basic pH. In this process, fine LDH particles will be deposited by

precipitation over biochar surface. Then, the material should be subjected to the pH neutralization step through several washes with deionized water, and then the composite must be dried and sieved. In addition to the conventional methods just described, another form of composite preparation is the hydrothermal carbonization. The metallic salts are mixed in aqueous solution with the biochar under a constant agitation for 1 h. After that, the solution pH is adjusted using Na_2CO_3 and NaOH solution, assuring 2 h of contact. Then, the system is transferred to an autoclave at 100 °C for 1 h. The sludge obtained is dried at 80 °C for 12 h [26], bathed with deionized water and dried, again, at 70 °C for 12 h. In addition to post-precipitation, LDH/biochar can be synthesized by a process based on the co-precipitation followed by another heat treatment to improve the crystallinity. An alternative process developed was composite synthesis methodology called *electric field-assisted pyrolysis*. It consists of generating a type of electrochemical cell using the reagents by mixing the raw biochar and metal hydroxides under acid pH and constant agitation, passing a defined current density for 5 min. This process provided a material with a higher porous surface and a more homogeneous distribution of LDHs.

Nonmetal Heteroatom Dopped Biochar Composites

In recent years, the idea of metal-free heteroatom doping has become predominant in the carbonaceous filed. Earth-rich elements, including sulfur (S), boron (B), and nitrogen (N), were comprehensively applied to manufactured nanocarbons using doping techniques. The application of heteroatom doping technology, especially nitrogen doping (N-doping), has the best efficacy to enhance the dispersion of nanomaterials, improve the detection limit of sensors, and promote the catalysis of nanocarbons. Low-temperature processing (< 700 °C) of biochar produced with a low degree of graphitization is deemed unfitting for doping technique. Graphitized biochars with ordered crystalline domains produced at high temperatures allow heteroatom doping techniques to modify engineered biochars.

N-doping technologies can be divided into two categories according to distinctive nitrogen sources, namely internal nitrogen sources of organic materials and external nitrogen sources with purified ammonia or additives. According to the doping procedure in the certain preparation, the doping method could be broken into post-doping after carbonization and *in-situ* doping. The difference between them lies in the introduction time of the nitrogen source [27]. In particular, post-doping and *in-situ* doping refer to combining the nitrogen source with the organic materials and biochars individually, followed by heat treatments.

The critical point of N self-doping into biochar depends on the choice of the organic material. This designated organic material must contain a substantial proportion of the raw nitrogen content in its inherent macromolecular structure or the overall chemical composition [28]. Organic materials such as animal tissue,

microbes, algae, and other nitrogen-rich biowaste could more plausibly ensure an overall high nitrogen level in the resulting biochars [28]. For the N-doping from exogenous nitrogen sources, the generally used nitrogen additives include organic substances (such as aniline, melamine, and urea) and inorganic substances (such as nitric acid, ammonium salts, and ammonia) [28, 27].

Contrary to endogenous N doping, adding or impregnating external N-rich materials is used to construct an artificial nitrogen-containing environment. Therefore, operating conditions may need to meet stricter and more detailed prerequisites. After activation using a variety of nitrogen sources with different chemical compositions and macromolecular structures, the configurations of nitrogen bonds introduced in the resulting biochars also varied according to operating settings. It is important to note that the profusion of oxygen functional groups in the organic materials is positively correlated with the N-doping level in the resulting biochars because the oxygen functional groups could immediately bind with N precursors or go through thermal decomposition to react with nitrogen precursors [27].

During thermal reforming of the organic material, ammonia purging could provide NH_3 molecules to react with the carbon skeleton, however, a higher temperature is required, and the reaction intensity is low. Ammonia activation usually occurs at the solid-gas interface and cause partial N-doping (i.e., aminated contents) [27]. The abundant –OH groups in agar powder played a key part by reacting with NH_3 molecules at high temperature to form amino groups ($R–NH_2$). The introduced amino groups further reacted with –OH to generate –C=N. NH_3 is also thought to react with carbonyl groups on biochar through a Maillard reaction with concomitant H_2 production. The carboxyl groups are also thought to create hydrogen bonds with NH_3 to facilitate N-doping, followed by conversion to graphitic nitrogen and pyridinic nitrogen. Therefore, ammonia purging favors the formation of microporous structures due to the consumption of oxygen functional groups.

Ammonium salt is another low-cost nitrogen source, which, compared with ammonia gas purging, could mitigate nitrogen waste caused by inefficient collisions of solid-gas molecules at the raw material interface and gas purging. During the thermal decomposition, the ammonium salt used appears to act as both a pore-creating structure modifier and a reducing N-doping agent, as it releases N_2O, N_2, or NH_3 at the same time. It can be hypothesized that the mechanism of N-dopant formation using ammonium salts is analogous to that of ammonia purge, where the NH_3 molecules first bind to defective sites terminated with oxygen functional groups and subsequently are converted to the corresponding N-dopants.

N-doping with organic additives is a convenient one-pot approach to acquiring N-doped biochar because it simply needs organic additives and homogeneous

mixing of the organic material [27]. Urea is the most popular choice among all organic nitrogen additives because it has nitrogen and carbon contents and could be utilized to introduce carbon substrates and nitrogen atoms. N-doped biochar associated with urea activation usually exhibits high specific surface area owing to the decomposition of urea in the organic materials during pyrolysis [27]. This could be caused by the thermal instability of mixed urea opening pores and releasing NH_3 [27]. For operating conditions with organic additives, the temperature reaction of reaction should be sensibly regulated because nitrogen-rich sources at the specified peak temperatures, such as melamine and urea, incline to decompose into different intermediate products [27]. During the initial pyrolysis stage, carbon nitrides are formed at 300 °C, and various aminated moieties (i.e., C–N, N–H, and $–NH_2$) appeared on the biochar surface [27]. These N-based moieties can be coalesced and decomposed into the carbonized biomass lattice to produce a variety of nitrogen-bonding configurations (i.e., graphitic N, pyrolytic N, and pyridinic N) when the temperature is raised above 400 °C [27]. As the temperature rises above 700 °C, only a considerable portion of graphitic nitrogen remains. In addition, urea cannot disperse to the internal macrostructure of the organic materials, implying that initial modifications to the size of particles and/or the size of pores might promote the introduction of nitrogen content.

Sulfurization treatment is frequently utilized to introduce sulfur-containing functional groups (e.g., S=O, C=S, or C–S) to the carbon sorbents' surface [21]. The introduction of sulfur into carbon materials is achieved through reactions of carbon with sulfurizing agents such as dimethyl disulfide, H_2S, SO_2, K_2S, Na_2S, and elemental S [21]. Analogous to the nitrogenation treatment, sulfuration of carbon surfaces can also be achieved through different chemical reaction pathways that usually need acid or heat treatments [21]. A significant amount of sulfur (up to > 30% *wt.*) could bind to most carbon-sulfur surface groups in the form of thiocarbonyl groups [21]. On top of the advantage of introducing sulfur-containing functional groups, depending on the treatment conditions, the porous structure of carbon can be modified by sulfuration treatment with notable increases or decreases in pore volume and certain surface areas [21]. The reduction in pore volume and surface areas might be caused by sulfur-containing particles blocking the pores.

Carbonaceous Engineering Nanocomposites

Biochar can bind to carbonaceous materials with functional groups that are eligible to establish strong bonds with contaminants present in an aqueous media and on biochar surfaces. The most frequently used agents are carbon nanotubes (CNTs), carbonaceous nanomaterials, amines, and polysaccharides. This modification could be accomplished by mixing biochar with amino-rich polymers, such as chitosan or polyethyleneimine, or through simple chemical reactions. Among bulk carbon

materials, carbon nanotubes (CNTs) and graphene (G) are generally utilized in composite synthesis because of the strong binding affinity through chemical oxidation with –COOH and –OH groups. Because of the fairly high specific surface area and the porous structure of biochars [19], they can be employed as hosts to stabilize and distribute carbon nanomaterials, expanding the range of potential applications.

Microorganism–Biochar Composites

Biochar-immobilizing microorganisms (BIM) are precisely coordinated by impregnating pollutant-degrading microorganisms together with biochar, which enriches the degrading bacteria to form biofilms and improves the mass transfer of pollutants from the polluted environment to the degrading microbial community [13]. Biochar's porous structure provides space for the reproduction and growth of microorganisms. It could also offer a small amount of nutrients to protect the growth of microorganisms from the influence of external environmental factors. In particular, biochar could increase biosorption by changing environmental conditions and reducing pollutant concentrations to protect the growth of microorganisms from excessive pollutant concentrations. As a result, BIM is a potentially useful method to improve treatment of wastewater.

Worked like living cells, immobilized microorganism could physically or chemically prevent cells from their initial position in the external environment. Since BIM technique was originated from fixed enzyme technology, it employs similar immobilization approach. However, no general immobilization approach available at the moment, and the suitable immobilization approach needs to be decided according to the product characteristics and living habits of the objective microorganism. The fixation methods consist of cross-linking, covalent bonding, entrapment, and adsorption. Among them, embedding and adsorption methods account for most of the BIM preparation.

The adsorption method is based on the interaction of nonspecific forces (adhesion force and surface tension) between microbial surface functional groups and biochar (such as –C=O, –COOH, and –OH), to achieve the microbial colonization in biochar [13]. The adsorption method has the advantages of simple operation, low cost, and little effect on cell activity, and has been generally used in immobilization technology. The fixed substrate of the adsorption method, though, could be reused, the interactions between substrates and microorganisms are unstable and weak, causing the microorganisms to fall off easily [13]. Thus, this method is suitable for the fixation of living cell organisms [13].

Microorganisms are trapped in a polymeric carrier mesh. The grid structure could prevent the microorganisms from seeping out of the carrier, and small molecule products and substrates in the external environment could easily exit and enter the carrier [13]. Materials for embedding include synthetic polymers (eco-friendly decomposition ability and mechanical strength) and natural polymers

(low microbial toxicity and high fixed density). The method has wide application, high particle strength, and low toxicity to microorganisms. However, it is not suitable for the degradation of macromolecular pollutants because only small molecular substrates can enter the interior of the particle. In addition, the diffusion of oxygen is affected as the mass transfer resistance increases, and the carriers cannot be reused. These are the reasons that most current studies only used polyvinyl alcohol and sodium alginate. Thus, this method has a wider scope of application than the adsorption method, and is more suitable for industrial applications that require stability [13].

The chemical covalent bonding, which works between the groups on the surface of the solid phase and the functional groups on the microbial cells [13], is utilized in the covalent bonding method to immobilize the cells. The technique also possesses the merits of good stability and tight binding. However, it gives a violent reaction when combining the groups. In addition, the operation is difficult to control and complicated, and only limited number of relevant cases have been studied so far.

1.4 Sustainability Considerations

In terms of biochar modification, eco-friendly methods without using toxic reagents are strongly encouraged. Magnetic modification, acid/base modification, and mineral modification are recommended because the reagents employed in these processes are either nontoxic or natural [17]. However, some new modification strategies involve the use of toxic substances, which may increase occupational safety risks. For example, while methanol can successfully introduce carbonyl groups to biochar surfaces, the compound can damage the optic nerve function (permanent blindness may be caused by ingesting 10 mL of pure methanol). In another example, a recent study investigated the possibility of employing biochar-supported nanoscale zero-valent iron (nZVI) to adsorb metals and catalyze the degradation of trichloroethylene. Toxic sodium borohydride ($NaBH_4$) was utilized in the reduction of Fe (II) to nZVI, but the potential risks were ignored. Though carbon nanotubes or grafting graphene onto the biochar's surface can successfully improve the affinity of biochar to organic pollutants with aromatic rings, its practical adoption to niche applications might be hindered by the complex procedure of nanocomposite creation. It has been argued that more modification methods and eco-friendly synthesis for producing engineered biochar should be suggested to reduce the environmental impact and cost.

It is worth noting that if the organic material itself contains pollutants (e.g., certain types of phytoremediation biomass, wood, and sewage sludge), the associated risks of pollutant release should not be ignored. Co-pyrolysis of uncontaminated

biomass and contaminated organic materials could be a feasible method to lessen the possible risks of pollutant leaching. It is a trend that in co-pyrolysis processes, plastics have been utilized to promote hydrophobicity and facilitate electrostatic interactions between pollutants and biochar adsorbents in wastewater. But the latest studies have also suggested that, in some cases, co-pyrolysis of organic materials and plastics adds to the risk of microplastic release and migration, as the plastic material breaks down into smaller fragments during the pyrolysis process. Reducing the risks from traditional pollutants might lead to increased risks from new pollutants such as microplastics. Care should be taken to avoid such risks when choosing pyrolysis conditions and organic materials for production. Until recently, research regarding this topic has been very limited, but it will be necessary to create operational boundaries and safe practices.

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