Chapter 8
Engineering Biochar-Based Materials for Carbon Dioxide Adsorption and Separation

Shuai Gao, Jack Shee, Wei Chen, Lujiang Xu, Chengyu Dong, and Bing Song

Abstract Increasing emissions of carbon dioxide, the primary greenhouse gas, are the main contributor to climate change. Developing an effective carbon capture, storage and utilization approach is paramount to overcoming global warming. Emerging research in engineered biochars provides a promising means of utilizing highly abundant lignocellulosic biomass as a precursor for carbon capture. Given appropriate production and modification of its physiochemical properties, biochar can be used as a cost-effective and selective adsorbent for CO_2 capture. In this chapter, the engineering of biochar for CO_2 capture is reviewed. The effects of different modification processes on the material properties of biochars (i.e. specific surface area, pore volume, pore size, hierarchical pore structure and surface chemistry) and their impacts to CO_2 uptake are discussed. Feedstock type, thermochemical conditions of pyrolysis and surface chemical modification via functional groups all play significant roles in determining the texture, porosity, aromaticity and hydrophobicity of biochar, which are key factors to increase CO_2 adsorption capacity.

Keywords Climate change · Carbon capture · Engineered biochar · Porous structure · Functional groups

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Z. Fang et al. (eds.), *Production of N-containing Chemicals and Materials from Biomass*, Biofuels and Biorefineries 12,
https://doi.org/10.1007/978-981-99-4580-1_8

8.1 Introduction

The increasing emission of greenhouse gases, especially CO_2, is responsible for various unwanted environmental changes such as the rise of sea level, drought, desertification, global warming and ocean acidification. Based on NOAA's Global Monitoring Lab's observation, atmospheric carbon dioxide concentration sharply increased from around 300 ppm in the 1960s to more than 400 ppm in the 2020s. The International Panel on Climate Change (IPCC) further predicts that atmospheric CO_2 concentration will reach 570 ppm by 2100, resulting in a mean temperature increase of 1.9 °C [1]. This will lead to a significant impact on the global environment and further exacerbate adverse conditions. Thus, developing sustainable technologies for mitigating CO_2 emissions to overcome global warming has become a priority as stated in the fifth assessment report of the IPCC. Carbon capture has been highlighted as a straightforward means that can directly decrease the distribution of CO_2 in the atmosphere if appropriate absorbent and scalable techniques are employed [2].

In 2005, IPCC identified three possible intervention phases during the process of carbon emissions by significant stationary sources: precombustion carbon capture, oxy-fuel process, and post-combustion carbon capture [3]. Among them, post-combustion capture is the only technology that can be applied to existing large point sources (e.g., power plants and cement manufacturing plants) and therefore is a promising approach in the short and medium term with low technological risk. More specifically, CO_2 separation technologies involve most commonly four processes, (1) absorption; (2) adsorption; (3) gas separation membranes; and (4) cryogenic distillation [3]. Adsorption, due to the low energy consumption, easy regeneration of adsorbent, adaptability at a wide range of temperatures and pressures, as well as lack of unfavourable by-product formation, has been considered a feasible process for CO_2 capture at an industrial scale. Materials used for adsorption sit at the heart of any adsorption process. Zeolites, activated carbons, porous silicas, engineered carbon nanomaterials and metal-organic frameworks have been studied for carbon capture in the last few years [4]. However, none of the above-mentioned materials can be practically applied for CO_2 capture without improving their selectivity of CO_2 adsorption in cost-effective ways via appropriate engineering processes.

Biochar is defined as a carbon-rich, porous solid produced by the thermal decomposition of biomass in a process with the absence or limited access to oxygen at moderate temperatures (normally below 700 °C) [5]. As biochars can be prepared from abundant biomass such as crop residues, wood wastes, animal manure, food wastes, municipal solid wastes, and sewage sludge, it is sustainable and widely accessible to end users at low cost. Given the variety of raw materials and tuneable preparation conditions, biochars can be purposely prepared with abundant surface functional groups ($C{-}O$, $C{=}O$, $-COOH$, and $-OH$, etc.), which provide modifiable sites for the synthesis of various functionalized carbon materials, making biochar a versatile precursor amenable for many uses. Hence, engineering biochars is more promising than developing other carbon-based materials. For instance,

Table 8.1 Main distinctions between biochar and activated carbon (Adapted from [6–8])

	Biochar	Activated carbon
Main source	Biomass	Coal, asphalt, biomass
Carbon content	40–90%	80–95%
Structure	Amorphous carbon with abundant surface functional groups, nanostructures, or porosity	Amorphous carbon with abundant porosity
Production method	Pyrolysis of biomass at medium temperature (400–600 °C) and then modification with physical or chemical methods	Carbonization of main source at high temperature (700–1000 °C) under physical or chemical activation
Average energy demand	6.1 MJ/kg	97 MJ/kg
Average unit price (2017)	US $5/kg	US $5.60/kg
Estimated break-even price (2009)	US $246/ton	US $1500/ton

compared with activated carbon, biochar exhibits significant advantages in energy demand and production cost (Table 8.1),

In the past few years, the great potential of using biochars and related engineered materials for environmental applications has garnered much attention. Carbon capture by biochars as well as enhancing the adsorption capacity by structural modification and surface functionalization have been of great interest to the research community. In this chapter, the advantages of using biochar and related engineered materials for CO_2 adsorption and separation have been evaluated. The factors related to the CO_2 uptake of biochar as well as the engineering strategies targeting CO_2 separation are also discussed. Upon overview and discussion of the recent advances, the chapter concludes with key challenges and perspectives to advise development towards a sustainable approach to reducing carbon emissions.

8.2 Recent Advances in Using Biochar as an Adsorbent for Carbon Capture

Biochar is a low-cost and sustainable adsorption medium generated from natural biomass or agricultural waste. In industrial applications, biochars can be produced as a major product or by-product, accompanied by various liquid and gas flows (e.g., syngas and bio-oil). At present, the estimated amount of biochar produced by fast pyrolysis of biomass is 220 million tons/year (with an estimated 10% of biochar). With the continuously growing demand for biorefinery products, this amount is expected to increase sharply in the next 30 years [9]. Table 8.2 presents an overview

Table 8.2 Production capacity of selected types of biomass/biochar (Adapted from [11])

Type of Sample	Country/Region	Year	Production Capacity (tons/year)
Lignin	Global	2019	100,000,000
Oil tea	China	2018	56,250,000
Wood pellets	Global	2020	52,700,000
Animal waste (manure)	Vietnam	2017	26,361,000
Coconut	Indonesia	2019	17,130,000
Whitewood	Finland	2019	11,800,000 m^3/year
Olive	Spain	2020	6,560,000
Oats	Russian Federation	2020	4,761,000
Almond	U. S. A.	2020	2,003,000
Coconut shell	Malaysia	2005	577,000
Pine sawdust	Mexico	2019	280,000
Pine cones	Andalusia	2012	55,000

of the production capacity of some significant types of biomass or biochars throughout the world. Due to the wide availability of biomass, biochars are about 10 times cheaper than other CO_2 adsorbents [10]. However, raw biochars have limited CO_2 adsorption capacity and various modification techniques are required to improve the performance of biochars for carbon capture.

Many studies have demonstrated that having a microporous structure allows for more active sites on the biochar; enhancing the CO_2 adsorption capacity. For instance, a novel activated carbon prepared from bamboo by KOH activation with enhanced specific surface area (SSA) showed a 15% CO_2 adsorption capacity up to 1.50 mmol g^{-1} at 25 °C [12]. In addition, biochars prepared from food waste, wood waste gasification and KOH + CO_2 activation showed that the development of a microporous structure contributed to a high CO_2 adsorption capacity (q_{max} = 3.23 mmol g^{-1} at 25 °C) [13]. The CO_2 adsorption performances of wood pellet-derived biochar with steam and KOH activation were compared [14]. The KOH-activated biochar exhibited a higher CO_2 uptake (50.8 mg g^{-1}) than that of steam-activated biochar (38.3 mg g^{-1}) which supports the statement that a higher percentage of micropores contributes to higher CO_2 uptake. It was also found that carbon capture from microporous biochar produced via KOH activation may be lower in high humidity conditions since water molecules occupy available micropore sites, acting as a competitive inhibitor. Thus, it is important to remove water from the gas stream before the CO_2 adsorption process, while it is even more preferred to enhance the stability and adsorption efficiency of biochar in conditions with high relative humidity.

It has been widely accepted that surface functionalization of biochars will improve the capture of acidic CO_2. Specifically, biochars with N-functional groups provide active sites for the uptake of CO_2 through both chemical and physical adsorption. For instance, pyridinic-N, pyrrolic-N, and primary, secondary and tertiary amines can all react with CO_2. The presence of these N-functional groups (Fig. 8.1) increases the alkalinity of biochar, promoting Lewis acid-base interactions,

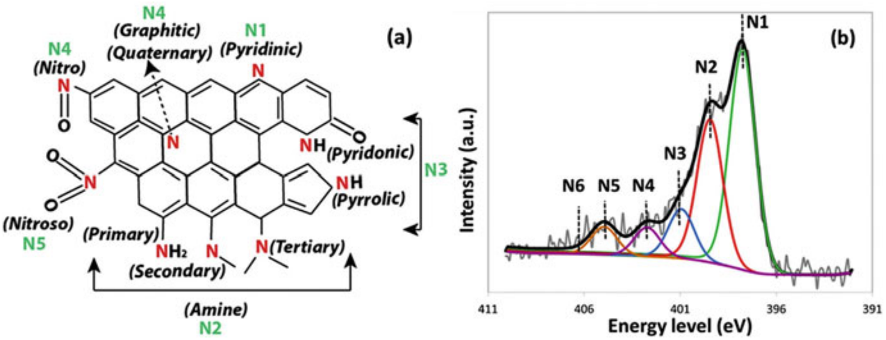

Fig. 8.1 (**a**) Schematic of nitrogen functionality on carbon surface and (**b**) XPS peak deconvolution results of nitrogen (N-1 s). Reprinted with permission from [17]. Copyright © 2022, Elsevier

thus enhancing the CO_2 adsorption [15]. Coffee grounds were used as the raw material for the preparation of biochars for CO_2 adsorption through ammoxidation and KOH activation. The biochars with nitrogen-doping by melamine and KOH activation exhibited high microporosity and developed more pyrrolic nitrogen as active adsorption sites contributing to high CO_2 uptake (2.67 mmol g^{-1} at 35 °C). In addition, the prepared biochar showed high stability (total decrease of ca. 6% in 10 cycles) and high selectivity of CO_2 over N_2 ($CO_2/N_2 = 74.2$) [16]. This excellent performance was attributed to a high proportion of micropore volume ($V_{micro}/V_{total} = 82\%$), increased nitrogen doping (5.1 wt%) and specific pyrrolic nitrogen (active adsorption sites).

Lignin was used as a precursor for the preparation of hierarchical porous carbon by KOH activation and NH_3 was selected as the source for N-doping [17]. The obtained biochar showed a large SSA (1631–2922 m^2 g^{-1}) and a highly developed porous structure with both micropores and mesopores. NH_3 activation introduced basic functional groups including mainly pyridinic as well as amino and pyrrolic/pyridonic type of functionality with a total nitrogen content of 5.6–7.1 at.%. All these properties are beneficial for CO_2 adsorption (5.48 mmol g^{-1} at 25 °C) and separation ($CO_2/N_2 = 37–433$), as well as a consistent working capacity (up to 10 cycles).

Recently, a simple method to prepare N-doped biochar for carbon capture was reported where the importance of amine and nitrile content was highlighted [18]. Bagasse and hickory chips were used as the raw materials and processed with pyrolysis at 450 or 650 °C under an N_2 atmosphere followed by ball milling with $NH_3{\cdot}H_2O$. The dehydration of oxygen-containing functional groups including carboxyl and hydroxyl transferred to nitrogen species such as $–NH_2$ and $C \equiv N$ on the surface of the prepared biochar. Meanwhile, a lower pyrolysis temperature (450 °C) was found to contribute to doping more nitrogen on the biochar surface compared to a higher pyrolysis temperature (600 °C). One possible explanation is that low pyrolysis temperature may result in higher concentration of oxygen-containing functional groups, thus more nitrogen-containing functional groups can be retained. Nevertheless, biochars (pyrolysis at 450 °C) with nitrogen-containing functional groups enhanced the CO_2 uptake by 31.6–55.2% compared with those of green and ball-milled biochars.

Recent efforts have also evaluated biochars as a potential adsorbent for cyclic adsorption processes. Karimi et al. [11] comprehensively reviewed studies on cyclic adsorption processes (e.g., pressure/temperature/vacuum swing adsorption) which highlighted the application of biochars as a raw material used for engineered adsorbents in large-scale applications of gas adsorption and separation. Biomass waste (olive and cheery stone) was used as the raw material for preparing adsorbent for the separation of CO_2 and CH_4 [19]. The precursor was calcinated with CO_2 in the atmosphere at a high temperature followed by loading in a bench-scale pressure swing adsorption (PSA) setup equipped with a fixed-bed adsorption column. The result showed that the olive stone-derived adsorbent was comparable with the commercial carbon adsorbent and presented a high sorbent selection value for efficient separation of CO_2/CH_4 gas mixture at given conditions. Karimi et al. [20] evaluated municipal solid wastes-derived biochars for carbon capture. The samples were activated using H_2SO_4 and thermal treatment at 400 °C and 800 °C, respectively. It has been found that the combination of H_2SO_4 treatment and activation at 800 °C contributed to the best CO_2 adsorption capacity with an uptake (2.6 mmol g^{-1} at 40 °C and 2.5 bar) comparable with commercial carbon materials. The following scale-up process carried out in a conceptual PSA unit confirmed that municipal solid wastes derived biochars exhibited excellent performance as a source of material for carbon capture under conditions of post-combustion operation.

8.3 Key Engineering Strategies Targeting Biochar for Carbon Dioxide Adsorption and Separation

The CO_2 adsorption capacity of biochar is the amount of CO_2 uptake per unit weight of biochar, which mainly depends on its physio-chemical properties including composition, SSA, pore volume, pore size, surface functional groups, presence of alkali and alkali earth metals and hydrophobicity. These properties of biochar are significantly influenced by the type of feedstocks and the thermal treatment conditions as well as the use of additives and activation methods, which are further discussed in the following subsections.

8.3.1 Strategies for Modifying the Physical Properties of Biochar

The van der Waals force and pore filling mechanism play important roles between CO_2 molecules and the solid phase of biochar [21, 22], thus increasing the SSA and pore volume as well as optimising the pore size and distribution (hierarchical pore structure) are the main strategies for modifying the physical properties of biochar.

8.3.1.1 Increasing the Specific Surface Area

Increasing the SSA means providing biochars with a wider surface for active sites responsible for carbon capture, thus contributing to a larger adsorption capacity. A positive relationship can be seen between the SSA ($R^2 = 0.6475$), micropore area ($R^2 = 0.9032$), and the CO_2 adsorption capacity of biochars (Fig. 8.2). Many reports have concluded that a high SSA of adsorbents presents a superior CO_2 adsorption capacity.

Creamer et al. [23] investigated the effect of SSA of biochar on CO_2 adsorption performance. Sugarcane bagasse and hickory wood were used as the precursor for the preparation of biochars at higher pyrolysis temperatures with a large SSA and excellent CO_2 capture performance (73.50 mg g^{-1} and 61.0 mg g^{-1} at 25 °C). Physical adsorption played an important role by bonding CO_2 to the surface of biochar, thus SSA was an important contributor to CO_2 adsorption. Huang et al. [24] prepared biochars by microwave pyrolysis of rice straw for CO_2 capture and reported the high correlation (correlation coefficient: 0.84) of the SSA with the CO_2 uptake of biochar. The prepared biochar exhibited a CO_2 adsorption capacity of up to 80 mg g^{-1} at 20 °C. Sun et al. [25] prepared engineered biochar from wood waste by pyrolysis in molten salts. It was found that high temperature (800 °C) and ternary carbonate contributed to the largest SSA (476 m^2 g^{-1}) and highest CO_2 capacity

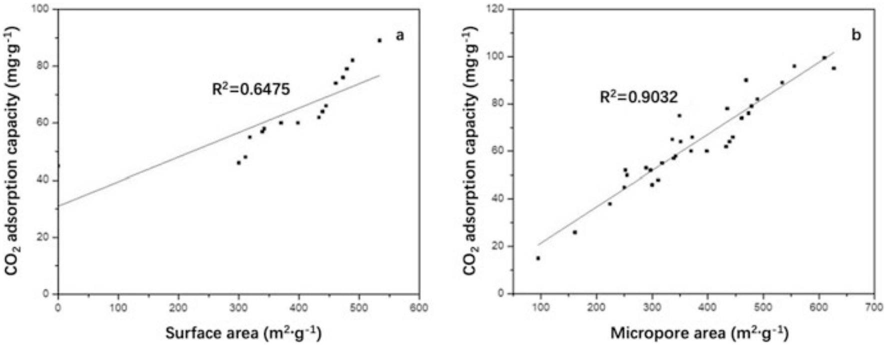

Fig. 8.2 Relationship between the SSA (**a**), micropore area (**b**), and CO_2 adsorption capacity of biochar. Reprinted with permission from [26]. Copyright © 2022, Elsevier

(4.5 mmol g^{-1}, 0 °C, 100 kPa) of the resultant biochar. The high selection parameter (S) in both PSA and vacuum swing adsorption (VSA) processes and high recovery rate (89%) of the molten salt showed great potential for repurposing biowaste as green and efficient adsorbents for carbon capture.

8.3.1.2 Increasing Pore Volume and Optimising Pore Size

During biomass pyrolysis, the release of volatile organic matter causes the formation of porous structures in the resulting biochar. This behaviour is related to the above-mentioned SSA. In addition, the specific pore structure (e.g., volume and size) can also alter the carbon capture capacity. The CO_2 uptake was found to closely follow a linear correlation with the size of pores $\leq$1.5 nm at the ambient pressure [27]. At 1 bar, pores <0.8 nm contributed the most to the CO_2 uptake and at 0.1 bar pores $\leq$0.5 nm were preferred. The coefficients of determination between the CO_2 uptake at a certain pressure and the cumulative pore volume of pores less than or equal to a certain pore diameter are shown in Fig. 8.3a. It agrees well with the CO_2 adsorption performance of bamboo-derived activated carbon [28], where the volume of micropores in the range of 0.33–0.82 nm demonstrates a positive correlation with CO_2 adsorption in Fig. 8.3b.

The type of biomass or feedstock is one of the main factors that may influence the pore volume and pore size of biochar. Specifically, biochars produced from biomass materials that are high in cellulose are known to develop more pores that are less than 2 nm during the pyrolysis, while pyrolysis of biomass materials that are high in lignin results in pores larger than 50 nm [29]. In addition, higher pyrolysis and activation temperatures result in the widening of the pore size [30]. It is worth noting that over-pyrolysis and activation of biochar may lead to excess widening of the pore

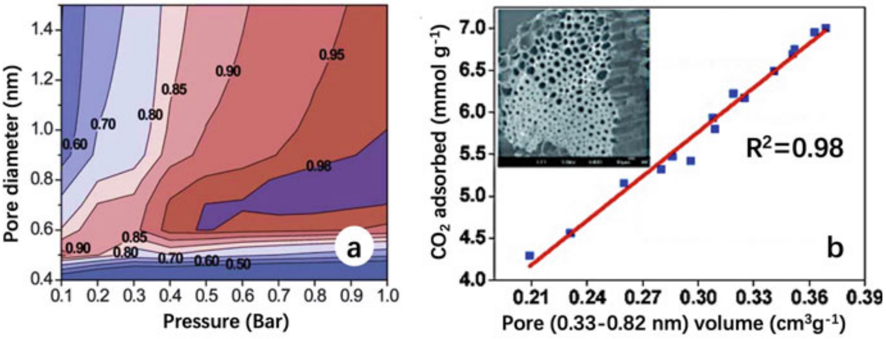

Fig. 8.3 (**a**) Coefficient of determination between CO_2 uptake between 0.1 bar and 1.0 bar (x-axis) and the volume of pores smaller to threshold size (y-axis) and (**b**) volume of micropores in the range of 0.33–0.82 nm has a good linear relationship with CO_2 adsorption on bamboo-derived activated carbon. Reprinted with permission from [27]. Copyright © 2022, RSC. Reprinted with permission from [28]. Copyright © 2023, John Wiley and Sons

which may be detrimental to the CO_2 adsorption capacity as micropores are more desirable for gas adsorption.

Igalavithana et al. [31] prepared different types of biochars from pine sawdust and paper mill sludge and investigated the effect of porous structure on carbon capture performance. It was found that the SSA and microporosity, especially the micropores of 0.5 nm diameter played an important role in CO_2 adsorption (positively correlated to carbon capture with $r = 0.960$ and $p = 0.039$). The study demonstrated that the feedstock, pyrolysis temperature and activation method (steam activation) had a great effect on the textural, surface, and structural properties of biochar as well as the resulting carbon capture performance.

8.3.1.3 Developing a Hierarchical Pore Structure

The International Union of Pure and Applied Chemistry defines pores with a diameter $>$ 50 nm as macropores, those with a diameter between 2 nm and 50 nm as mesopores, and those with a diameter of $<$2 nm as micropores [32]. Micropores with a pore size of $<$1 nm predominantly affect CO_2 adsorption. However, hierarchical structures with balanced and cross-linked macro-, meso- and micro-porosity also play a significant role in the adsorption process [33]. Feng et al. prepared biochars from corn straw with a hierarchical-functionalized structure and explored its adsorption properties of CO_2 with both experimental data analysis and molecular dynamics simulation [34]. The results showed strong evidence of a link between one-step activation with H_2O and the construction of functional groups on the biochar surface, however, the two-step activation with H_2O and NH_3 was beneficial to the enhancement of pore formation and aromatization of biochar. The adsorption sites of CO_2 were mainly generated from micropores with a diameter of less than 0.7 nm, while the mesopores provided a significant contribution to the total adsorption capacity due to the creation of a concentration gradient for diffusion based mass transfer. In another study, hierarchically porous carbon was prepared from an ocean pollutant (*Enteromorpha prolifera*) via hydrothermal carbonization, KOH activation and HF washing [35]. The intrinsic sponge structure of the precursor, hydrolysis of hemicellulose, carbon gasification, KOH activation and inorganic compounds together contributed to the hierarchical carbon with micropores, mesopores and macropores (Fig. 8.4). As a result, the diffusion of CO_2 into the bulk carbon skeleton was accelerated by the presence of meso- and macropores in the adsorbent, thus improving the kinetics of adsorption.

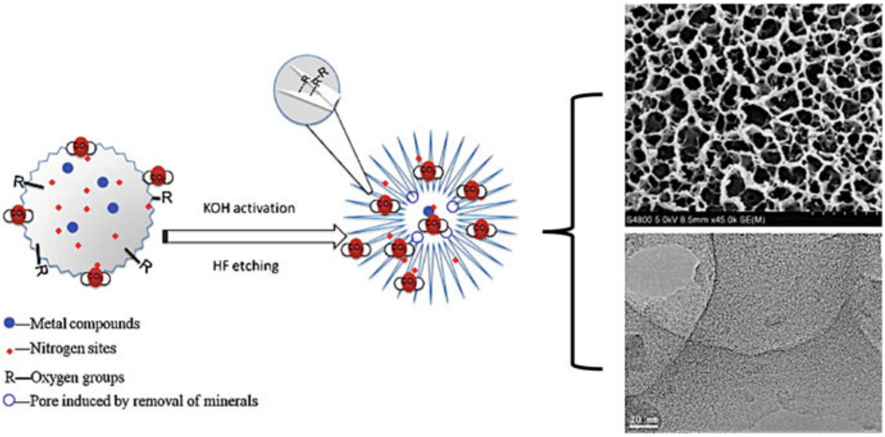

Fig. 8.4 Diagram of porosity formation and enhanced CO_2 capacity of KOH activated and hydrothermally treated ocean waste-derived biochar. Reprinted with permission from [35]. Copyright © 2022, Elsevier

8.3.2 Strategies for Functionalizing Biochar for High-Performance CO_2 Adsorption and Separation

The uptake of CO_2 by biochar surface is also influenced by the functionality (chemical properties) of the biochar including alkalinity, presence of surface functional groups, mineral composition, hydrophobicity, etc. Thus, the CO_2 adsorption capacity of biochar can be optimised by introducing functional groups and elements with a strong affinity for acidic gas.

8.3.2.1 Introducing Basic Functional Groups

The reaction between the acidic CO_2 molecules and basic nitrogen-containing functional groups is well accepted as the main contribution to CO_2 capture. Pyridone, pyrrole, amine, pyridine-N-oxide, quaternary-N, cyanide, and pyridine groups with different basic strengths are common N species on the carbon surface. Among them, pyridone, pyridine and pyrrole are well reported to enhance CO_2 adsorption due to various interactions including hydrogen bonding and Lewis acid-base interactions [36, 37]. Figure 8.5 summarises different methods (agents) for introducing various N-containing functional groups.

The direct pyrolysis of nitrogen-rich precursors is a sustainable method for doping nitrogen atoms into the carbonaceous matrix of biochar, which is conducive to the application of the carbon capture [39, 40]. Nitrogen-doped microporous carbon was prepared from chitosan and K_2CO_3 as a nitrogen-containing precursor and activation agent, respectively [41]. The high CO_2 uptake by the porous carbon was attributed to the large pore volume, well-defined microporosity and high

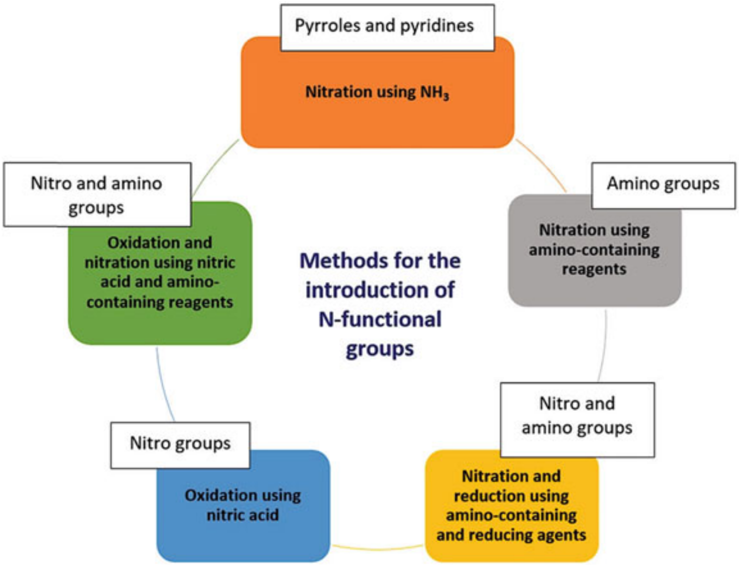

Fig. 8.5 Different methods for introducing various N-containing functional groups. Reprinted with permission from [38]. Copyright © 2022, Elsevier

nitrogen content. In the XPS analysis of N-containing functional groups, the dominant peak belonged to pyridone, and pyridine contributed less. As for pyridone nitrogen, the *p* orbital in –OH produces a *p*–*π* conjugation effect with the *π* bond and as consequence, the Lewis basicity of the nitrogen located in the *ortho*-position of –OH with a stronger negative charge is enhanced. Thus, pyridonic nitrogen was attributed as the main active site for CO_2 capture. Density functional theories calculation also confirmed that the pyridone groups exhibited the maximum energy of adsorption contributed by the H bond between the H atom of the –OH and the O atom of the CO_2 with high electronegativity [37].

Sawdust was impregnated with a urea phosphate solution and kept for 24 h, then carbonized at a high temperature (600–900 °C) under N_2 followed by hot water washing and drying [42]. The obtained N-doped biochar exhibited a large SSA (1189 $m^2\ g^{-1}$), high micropore volume (0.433 $cm^3\ g^{-1}$), high nitrogen content (4.24 at.%) with the main basic functional groups including pyridinic and pyrrolic N, and decent CO_2 adsorption capacity (1.34 mmol g^{-1} at 30 °C and 1 bar). These results confirmed that the adsorption of CO_2 was related to the synergistic effect of SSA, micropore volume and N-containing functional groups [43]. Specifically, due to the strong polarity and improvement for acid-base reaction, pyridinic N was more conducive to CO_2 adsorption than other types of N species. On the other hand, pyrrolic N can promote the hydrogen-bond interaction between the biochar surface and CO_2 (Fig. 8.6). In addition, a high pyrolysis temperature (900 °C) was found to transfer some nitrogen groups into aromatic nitrogen-containing groups and weaken the alkalinity of the biochar.

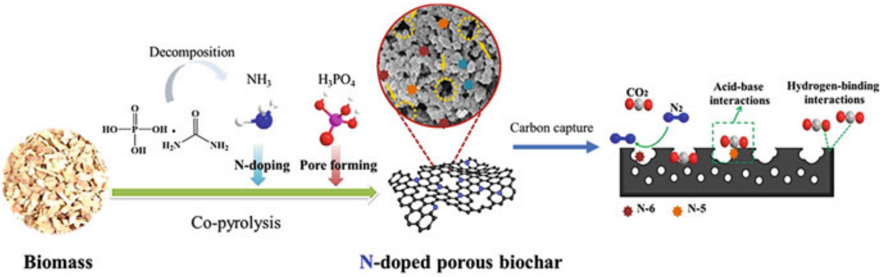

Fig. 8.6 One-step method for preparation of microporous N-doped biochar from plant biomass using urea phosphate (N-5: pyrrolic N; N-6: pyridinic N). Adapted from [42]. Copyright © 2022, Elsevier

CO_2 adsorbent was prepared from biomass waste by three ammoxidation methods and KOH activation (400 °C for 1 h and 600 °C for 1 h under an N_2 atmosphere) [16]. In particular, the process of using melamine contributed to the smallest SSA (990 m^2 g^{-1}) but the highest nitrogen content (5.1%) and the largest CO_2 capacity (117.5 mg g^{-1} at 35 °C) of the resultant biochar. The study suggests that N-functional groups (mainly pyrrolic nitrogen) rather than the SSA are considered to be the dominant factor for CO_2 adsorption. The high value (49.9 kJ mol^{-1}) of adsorption enthalpy of biochar doped with pyrrolic nitrogen indicates that the interaction (e.g., hydrogen bonding or intermolecular force) between adsorbent and CO_2 was enhanced, resulting in the improved carbon capture performance.

Xie et al. [44] investigated the bean dregs-based porous carbon for CO_2 capture. A significant increase of C and N contents in the hydrothermally treated biochar was found and the pyridinic-N and pyrrolic-N accounted for more than 60% of the total N-containing groups. As a result, the isosteric heat of adsorption at the low CO_2 uptake stage was much higher than the value of interaction between CO_2 and pure carbon-based materials, indicating that the adsorption of CO_2 on N-rich biochar is not completely physical and may occur via intermolecular forces and covalent bonds. Nuclear magnetic resonance spectroscopy data verifies that interactions between N-containing species and CO_2 result in the formation of new chemical bonds (Fig. 8.7).

Apart from pyridone, pyridine and pyrrole, other N-containing groups including Amine-N ($-$ NH_2 and C–N) and N=N [45, 46] were also investigated for their performance of carbon capture. It was found that all these functional groups presented the ability to interact with CO_2, and most of them can be regenerated except for the C-N.

8.3.2.2 Introducing Oxygenated Functional Groups

It has been reported that hydrogen bonding plays a critical role in the interaction between adsorbate and adsorbent when oxygenated functional groups are presented

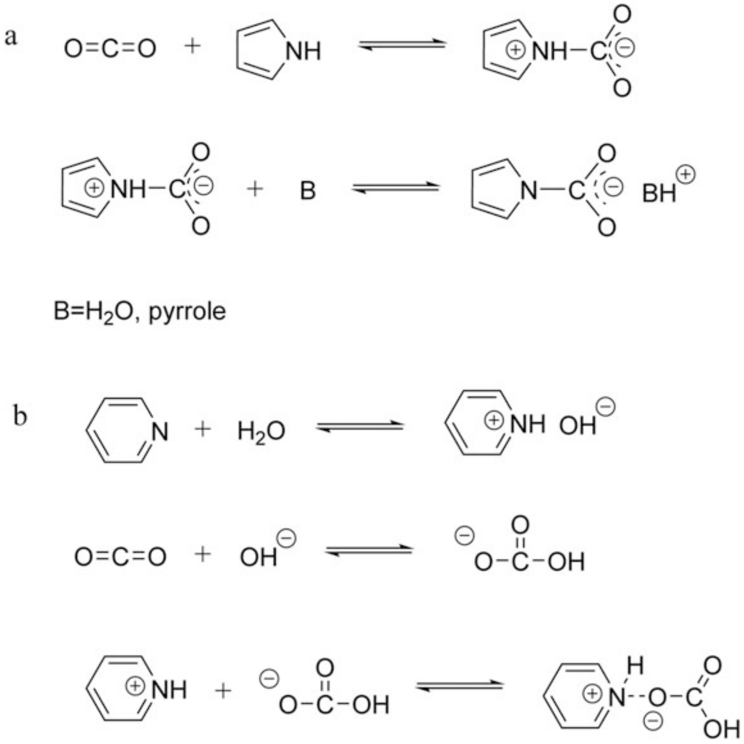

Fig. 8.7 Adsorption mechanism of CO_2 on (**a**) pyrrolic-N and (**b**) pyridine-N. Reprinted with permission from [44]. Copyright © 2023, John Wiley and Sons

on the surface of the adsorbent [38, 47]. Although most oxygen-containing functional groups (e.g., –COOH, –OH, C=O, phenolic, lactone, and peroxide groups) are acidic which would inhibit the capturing of acidic CO_2, following studies found that the adsorption of CO_2 may be enhanced by the functional groups including –OH and –COOH, when they were presented on the carbon skeleton. Xing et al. [48] reported the influence of introducing O-containing functional groups to the adsorbent matrix (by chlorination and followed by HNO_3 oxidation) on the CO_2 adsorption capacity of carbide-derived carbon (CDC). It was found that the CO_2 adsorption capacity per unit SSA was positively related to the oxygen content of the carbons, suggesting that the CO_2 uptake was significantly facilitated by the doping of O-containing groups. Quantum chemical calculation further supports that the introduction of oxygen atoms into the carbon surface promotes hydrogen bonding between the CO_2 molecules and the carbon surface (Fig. 8.8). In addition, the binding energy difference between oxygenated and non-oxygenated complexes roughly agreed with the difference in CO_2 adsorption heat between the pristine CDC and oxygenated CDC. The findings indicate that acidic O-containing groups of carbon adsorbents can also facilitate CO_2 adsorption.

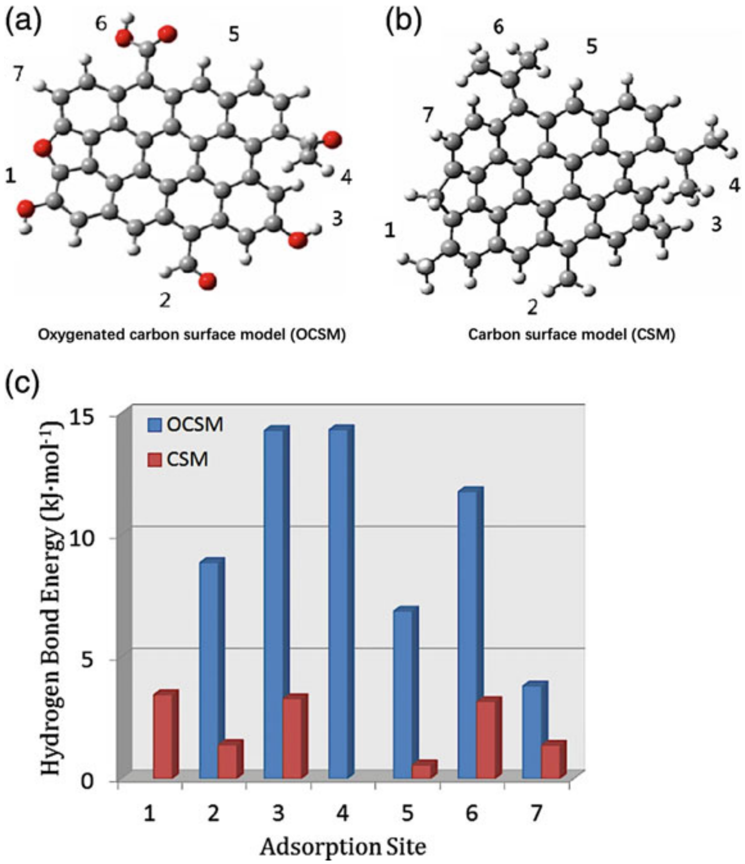

Fig. 8.8 Theoretical models for (**a**) oxygen-containing carbon surface and (**b**) pure carbon surface (red ball: oxygen atom; grey ball: carbon atom; small white ball: hydrogen atom). (**c**) Hydrogen bond energies at different adsorption sites. Reprinted with open access from [48] under the terms of the creative commons attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0)

8.3.2.3 Loading Alkaline and Alkaline Earth Metals

It has been demonstrated that the carbon frameworks with open metal sites tend to have a high affinity for CO_2 [49]. The basic nature of metal oxide and carbon framework may improve the selectivity of adsorbent on CO_2 and suppress the adsorption of other gases such as N_2 and CH_4. This is because metal oxyhydroxides tend to bond with acidic CO_2 when polar surfaces are in contact. Creamer et al. [50] prepared biochar/metal (Al, Mg and Fe) oxyhydroxide composites using cottonwood as the precursor and evaluated their capacity to uptake CO_2. The treatment with a sequence of metal ions impregnation and pyrolysis at 600 °C prepared biochar loaded with metal oxyhydroxide nanoparticles. The CO_2 uptake by biochar/metal oxyhydroxide composites was attributed to the surface adsorption mechanisms contributed by both carbon matrix and metal oxyhydroxide particles. The high CO_2 uptake by AlOOH–biochar (71 mg g^{-1} at 25 °C) is roughly equal to commercial adsorbents, and together with the low-cost regeneration at 120 °C (90% and 99% desorption) suggests that metal oxyhydroxide–biochar composites can be used for carbon capture with high efficiency at a low cost. Lahijani et al. [51] further investigated the impact of pyrolysis temperature (500 °C, 700 °C and 900 °C) and type of metal oxide (Mg, AL, Fe, Ni, Na and Ca) on the carbon capture ability of the modified biochar prepared from walnut shell. It was found that increasing the pyrolysis temperature was effective to enhance the SSA and porosity of the biochar. In particular, the largest SSA (397 m^2g^{-1}) and highest pore volume (0.198 $cm^3\ g^{-1}$) were obtained by preparing the sample at 900 °C. Meanwhile, the loading of basic metal sites onto the metal/biochar composite surface enhanced the adsorption of acidic CO_2 gas in the order of Mg $>$ Al $>$ Fe $>$ Ni $>$ Ca $>$ green-biochar $>$ Na. In addition, Mg-loaded biochar exhibited high stability and reusability upon 10 cycles of CO_2 adsorption and desorption with almost no compromise in its carbon capture performance.

8.3.3 Summary

In addition to the above-mentioned strategies to engineer biochars for improved CO_2 adsorption and separation, studies have indicated that biochars with hydrophobic and non-polar characteristics may enhance CO_2 uptake by restraining the interference of H_2O (polar molecule) [8, 52]. The carbonization process can reduce the concentration of O, H, N and S in the biochar matrix, thus increasing the degree of hydrophobicity by increasing the degree of aromaticity, resulting in a high potential to adsorb CO_2 when competing with water molecules in humid conditions [29]. In summary, CO_2 adsorption on biochars is a complex interaction that may be affected by multiple factors including van der Waals forces, hydrogen bonds, micropore filling phenomenon as well as Lewis acid-base reaction when functional groups (N and O) presented on the surface of adsorbents. Therefore, tuning the properties of biochars and developing their surface functionality to enhance the above-mentioned interactions is critical to engineering biochars with improved CO_2 adsorption capacity and selectivity.

8.4 Challenges and Perspectives

The use of biochars as a widely accessible and low-cost adsorbent for CO_2 capture promises chances for valuable application of biomass resources and an alternative approach for reducing carbon emissions, thus contributing to the achievement of our sustainable development goals. As an emerging research area of interest, the practical use of biochars for carbon capture is yet to be realised with efforts addressing challenges in all aspects from the initial biochar preparation and engineering to the application of CO_2-saturated biochar in real practices. Based on the above overview, some key challenges and corresponding perspectives are given as follows.

Biochar is a complex material with variants in raw materials and preparation methodologies. This provides possibilities for preparing versatile products for multiple purposes including CO_2 adsorption. However, there is a key challenge to developing standardised protocols for biochar preparation and engineering towards targeted purposes. Addressing this challenge will require a fundamental understanding of the correlations among feedstock of biomass, engineering strategies (e.g., activation and modification), the physiochemical properties of biochar and the CO_2 uptake capability. The emerging application of artificial intelligence (AI) techniques such as machine learning in biomass valorization is promising to assist in identifying these correlations based on a considerable amount of experimental data.

Overall, achieving ideal adsorption performance will require engineering biochar by both physical and chemical means. This also means extra costs and the possible use and/or emission of toxic chemicals. From the perspective of life-cycle analysis, the process of biochar preparation and engineering is carbon emissive, despite the facts (1) producing and storing biochar is considered a negative emission process [53] and (2) the adsorption and storage of CO_2 in biochar further contribute to emission reduction. Life-cycle analysis is thus highly recommended to detail the emission portfolios.

Enabling and promoting the practical application of biochar as a CO_2 adsorbent also expects a shift from Carbon Capture & Storage to Carbon Capture & Utilization, whilst re-utilizing engineered biochar for carbon capture in a circular manner. This calls for efforts in (1) improving the reusability of biochar, and (2) developing proof-of-concept of integrated biochar carbon capture and CO_2 utilization or valorization. Recent drastically progressing technologies such as electrochemical CO_2 reduction [54] and the use of CO_2 for algae cultivation [55] have provided wide opportunities for the post-adsorption valorization of CO_2.

8.5 Conclusions and Future Outlook

Engineered biochars with their enhanced inherent properties are promising sustainable materials for CO_2 capture. Specifically, the specific surface area, micropore area and volume, hierarchical pore structure, presence of functional groups (e.g., N-containing functional groups) and hetero elements are great contributing factors to CO_2 adsorption capacity. Thus, strategies of biochar modification through physical and chemical processes will significantly improve the aforementioned properties, thereby enhancing the CO_2 uptake of biochar.

On the other hand, the practical use of biochar is yet to be realised in all aspects from the initial biochar preparation and engineering to the application of CO_2

capture in large-scale production. Hence, future studies should focus on developing standardised biochar preparation and engineering protocols towards specific carbon capture scenarios with a complete life-cycle analysis. The high-value utilization of biochar as byproducts from biorefinery or lignin residue after valerization of cellulose and hemicellulose is suggested to increase the overall competitiveness of bioenergy. Novel technologies and biochar-based materials such as nano-biochar composites and biomass-derived carbon foam should be developed to enhance the CO_2 adsorption capacity of biochar. Study on the adsorption and reaction mechanism of CO_2 with specific functional groups of biochar is preferred as it not only helping understand the adsorption process but also paving the way for CO_2 conversion on carbon capture and utilization. Moreover, industrial-scale application of biochar for CO_2 capture should also be highlighted as well as developing proof-of-concept of integrated biochar carbon capture and CO_2 utilization.

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