

Review

Nitrogen enriched biochar used as CO₂ adsorbents: a brief review

Yuanting Qiao, Chunfei Wu*

School of Chemistry and Chemical Engineering, Queens University Belfast, Belfast, UK BT7 1NN



ARTICLE INFO

Keywords:

Biochar
CO₂ adsorbents
Nitrogen functionalities

ABSTRACT

It is widely acknowledged that the increasing CO₂ concentration has led to the rise of temperature in the earth. Thus, capturing CO₂ to alleviate environmental catastrophic is becoming important and urgent. Among the CO₂ sorbents reported, solid adsorbents are advantageous in CO₂ adsorption, CO₂/N₂ selectivity, easy operation and good regeneration ability. Biochar-based sorbents are promising for CO₂ capture because they are self-sufficient in energy requirements, wide availability, renewability, low cost, and high porous structure. In addition, N-containing functional groups are used to improve the capability of CO₂ adsorption of biochar. This review aims to evaluate the preparation and performance of nitrogen-enriched biochar for CO₂ capture. Throughout this review paper, the current N-containing precursors and biomass, as well as the technologies for the preparation of N-rich biochar are discussed. It is concluded that cheaper and more sustainable ways should be proceeded to produce N-rich biochar in the field of CO₂ capture research.

1. Introduction

The atmospheric content of CO₂ concentration has been more than 400 ppm, and CO₂ is a dominant (accounting for 90%) global anthropogenic greenhouse gas (CO₂ Emissions from Fuel Combustion 2017 Highlights 2017). Fossil fuel combustion, the main energy source, occupies the largest share of the annual CO₂ emissions with over 33 GtCO₂ in 2015 (Dlugokencky, 2017). To prevent the increase in global temperature, it is essential to control the annual CO₂ emissions (Siegelman et al., 2017). Therefore, many technologies have been researched to remove CO₂ from ambient air, industry plants, animals and human beings' activities (Li et al., 2013). Among the variety of routes designed for CO₂ capture from various CO₂ sources, adsorption is regarded as a promising technology (Samanta et al., 2012). According to the nature of interactions between the adsorbents and CO₂, adsorption can be classified into physical adsorption and chemical adsorption (Younas et al., 2016). A variety of porous solids such as zeolites (Walton et al., 2006, Siriwardane et al., 2005), mesoporous silica (Harlick and Sanyal, 2006, Knowles et al., 2005), metal organic frameworks (MOFs) (Llewellyn et al., 2008, Millward and Yaghi, 2005, Keskin et al., 2010), porous carbons (Sevilla and Fuertes, 2011, Sevilla et al., 2011) and porous organics (de Jonge and Mittelmeijer-Hazeleger, 1996) have been studied for CO₂ removal. In contrast to absorption processes based on a liquid absorbent like monoethanolamine (MEA) (Abu-Zahra et al., 2007, Glasscock et al., 1991), diethanolamine (DEA) (Glasscock et al., 1991, Haji-Sulaiman et al., 1998) and potassium carbonate (Cullinane and Rochelle, 2004), a solid adsorbent is used to bind the CO₂ on its sur-

faces with many advantages including greater capacity, high selectivity, flexible handling and easy regeneration (Samanta et al., 2012, Qi et al., 2011). The regeneration of adsorbents depends on Temperature swing adsorption (TSA), pressure swing adsorption (PSA), and vacuum swing adsorption (VSA). PSA systems have been applied in industrial feed mixtures such as steam reformer off the gas, landfill gas, and natural gas, where the feed gas at high pressure and low temperature offers the driving force between the desorption pressure and the adsorption pressure. Chung et al. (Ho et al., 2008) illustrated the PSA using the "short-cut" method that PSA systems rely on batch sorption vessels with a fixed volume, as shown in Figure 1.

Activated carbon is one of the most solid adsorbents that are applied in the PSA unit (Shen et al., 2015). The preparation of activated carbon normally contains heat treatment of carbon materials such as biomass, coal, oil and peat, as well as activation steps including both chemical and physical activation (Ioannidou and Zabaniotou, 2007). The chemical activation relied on the chemical activating agent such as KOH, NaOH, H₃PO₄, K₂CO₃, ZnCl₂, etc, which are usually expensive and bad for the environment (Shafeeyan et al., 2010). In terms of industrial application, activated carbons are commonly produced from biomass via KOH activation. Thus, single-step preparation or only activation of biomass with steam without extra carbonisation or pyrolysis step is more appealing, which has also been shown to produce good quality adsorbents (Zhang, 2015).

Biochar is a solid carbon material, which has been successfully applied to improve soil quality (Sohi et al., 2010, Lehmann et al., 2011), remove contaminants in water and soil (Ahmad et al., 2014), reduce greenhouse gas emissions (Bamdad et al., 2018, Jung et al.,

* Corresponding authors. Dr Chunfei Wu, Tel: +44 2890975573.
E-mail address: c.wu@qub.ac.uk (C. Wu).

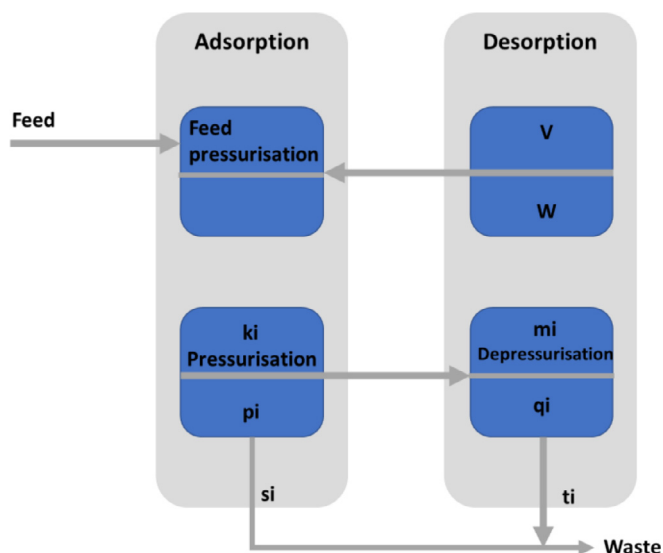


Figure 1. Short-cut method of VSA/PSA process (Ho et al., 2008). The processes of pressurization and adsorption and the processes of depressurization and desorption are combined. CO₂ is adsorbed at higher pressure and desorbed at lower pressure, under adiabatic conditions. The adsorption and desorption can be modeled by the Langmuir isotherm. K_i/m_i , amount of component i in the bulk gas; s_i/t_i amount of component i in the expelled gas; p_i/q_i , amount of component i on the adsorbent. W , the weight of the adsorbent; V , the volume of the adsorbent.

2019, Mohd et al., 2013), and reduce energy production (Zhang et al., 2019, Lehmann et al., 2006), etc. (Ahmed et al., 2016, Keiluweit et al., 2010, Rittl et al., 2018). Currently, biochar is also acknowledged as an eco-friendly and cheap CO₂ adsorbent, which is nearly ten times cheaper than others such as MOFs and commercial activated carbon (Mohd et al., 2013, Parshetti et al., 2015, Dissanayake et al., 2020) due to the cheap and environmental-friendly source of biomass materials such as bamboo (Wei et al., 2012), fungi (Wang et al., 2012), yeast (Shen et al., 2012), chitosan (Wang et al., 2020), nutshell (Deng et al., 2014), palm shells (Ello et al., 2013), coconut shell (Yang et al., 2011), coffee ground (Plaza et al., 2012), cassava peel (Moreno-Piraján and Giraldo, 2010), celtuce leave (Wang et al., 2012), potato starch and cellulose (Sevilla and Fuertes, 2011), of which are most waste. Moreover, biochar is usually prepared by pyrolysis at moderate temperatures (usually below 700 °C) in an oxygen-deficient or oxygen-free environment (Balahmar et al., 2017). The pyrolysis process is attractive as it has the following advantages: (1) Biochar can usually satisfy energy requirements with extra energy production in the form of heat or biofuel (Matovic, 2011). (2) Biomass is renewable, the most abundant, worldwide available, inexpensive and environmentally friendly; thus, biochar is cheap and environmental friendly (Ioannidou and Zabaniotou, 2007, Plaza et al., 2014). (3) Biochar shows well in high surface area, which is beneficial for CO₂ capture (Ok et al., 2015).

Generally, the CO₂ adsorption of biochar depends on both physical and chemical properties such as the porosity, basicity of biochar surface, surface functional groups, presence of alkali and alkali earth metals, hydrophobicity, polarity, and aromaticity (Chiang and Juang, 2017). These properties are influenced by the route of preparation, carbon source, activation, and modification such as chemical modification, physical modification, impregnation with elements, or grafting, as well as pretreatment/post-treatment of the feedstock (Igalavithana et al., 2017). Nitrogen has been reported to enhance the good adsorption and selectivity of porous carbon (Ahmed et al., 2016) because N-rich functional groups can enhance the surface affinity between basic sites and CO₂, as well as microporous structure, large pore volume and surface area in some cases (Z-l et al., 2013, Ma et al., 2013). For

example, amazonian wastes (nutshells waste) improved by nitrogen flow, have been reported to produce N-rich porous carbon used for CO₂ adsorbents (Serafin et al., 2021). The highest capacity of CO₂ adsorption reached at 298 K with 3.67 mmol g⁻¹. A pinewood derived biochar was investigated with amine activation (tetraethylenepentamine, TEPA) and showed the capacity of CO₂ capture up to 2.79 mmol g⁻¹ (Chatterjee et al., 2018).

To date, several reviews have discussed the modification with nitrogen groups to enhance the CO₂ capture of activated-carbon-based adsorbents (Shafeeyan et al., 2010, Saha and Kienbaum, 2019). The main objective of this paper is to analyse the modification of biochar with N-containing groups and the possible N-rich biomass sources to produce biochar, as well as the performance and the mechanism of the N-rich biochar used as CO₂ adsorbents.

2. Nitrogen source for the N-rich biochar

N-functional groups introduced into biochar have been applied in many fields such as adsorbents for heavy metal (Jia et al., 2002) and SO₂ (Shao et al., 2018), catalysis (Guo et al., 2016), energy storage (Yaumi et al., 2017), etc (Leng et al., 2020). There are two main sources of nitrogen. One is introducing the nitrogen-containing functionalities to modify the biochar; the other is the direct use of the nitrogen-rich biomass.

2.1. N-containing functionalities

Usually, ammonia, amine groups (including primary amine, secondary amine and tertiary amine), and polymer-based amine are used to introduce N into biochar. Amine groups strongly and selectively bind CO₂ via chemisorptive interactions with CO₂ molecules by forming a carbamate (Xiong et al., 2013). Ammonia is widely used as the N functionalities. Zhang et al. used black locust to produce ammonia-doped biochar, AC-KOH-N, with activation of KOH and ammonia (NH₃) under N₂, at 830 °C (Zhang et al., 2016). At 1 bar, CO₂ adsorption reached 5.05 mmol g⁻¹ at 25 °C and 3.37 mmol g⁻¹ at 50 °C. CO₂/N₂ selectivity of AC-KOH-N calculated by the IAST method was 30.75 at 25 °C and 1 bar, and CO₂ adsorption of AC-KOH-N was fully reversible and stable after 10 cycles.

As urea is a cheap and non-toxic amine group, it is also commonly used to introduce nitrogen into porous material. Cansado et al. has compared activated carbon with the treatment of sodium hydroxide and urea, and the results showed that the urea treatment could lead to better porosity and a basic character; whereas, the treatment with sodium hydroxide showed little influence on the nature of activated carbon (Cansado et al., 2012). Rouzitalab et al. used walnut shell, activated by urea and following KOH, to produce biochar, which shows CO₂ adsorption capacity of 7.42 mmol g⁻¹, and CO₂/N₂ selectivity of 12.7 at 25 °C and 1 bar (Rouzitalab et al., 2018).

Melamine has also been used as a nitrogen source to modify a water chestnut for the prepare N-rich biochar through KOH activation at 600 °C-900 °C (Wei et al., 2018). The resulting samples showed highly developed micropores, outstanding surface area (3401 m² g⁻¹) and a high nitrogen content (4.89 at.%), leading to CO₂ adsorption capacity up to 6.0 mmol g⁻¹ at 0 °C and 1 bar and 4.7 mmol g⁻¹ at 25 °C and 1 bar.

2.2. N-rich biomass

Compared to the N-containing functionalities, biomass derivatives as precursors are more sustainable and available (Zhao et al., 2010). Some biomass samples that have a high content of nitrogen have been concluded in Table 1 (Leng et al., 2020). Microalgae occupies the highest N-content with 13.94%, and its turning biochar is 6.57%–12.93%. Chitosan also performs well with the 9.4% N-content in biomass and 8.9-9.1% N-content in produced biochar. In addition, the porous carbon

Table 1
Nitrogen content and form of nitrogen in biomass and derived porous carbon (Leng et al., 2020).

Biomass	N(w%)	Form	Porous carbon N(w%)	Form	Application	Ref.
Sludge	5.9	Protein-N	2.1–3.1	Pyridinic-N	Adsorbents for ammonium in water	(Tang et al., 2019)
Sewage sludge	6.2	-	2.1–7.1	-	Adsorbents for heavy metal	(Agrafioti et al., 2013)
Wood sawdust	0.41	-	0.56–0.71	-	Catalyst for esterification and transesterification	(Chellappan et al., 2018)
Organic xerogel	0.41	-	0.28–5.84	-	Adsorbents for heavy metal	(Veselá and Slovák, 2014)
Alfalfa	0.53	-	0.15–5.7	-	Adsorbents for bisphenol A and sulfamethoxazole in water	(Choi and Kan, 2019)
Rice Husk	2.4	-	4.0–4.9	-	Renewable solid bio-fuel source	(Abbas et al., 2018)
Rice Husk	-	-	0.01–1.05	-	Galaxolide adsorbents	(Zhang et al., 2019)
Wheat straw	-	-	0.01–0.52	-	Galaxolide adsorbents	(Zhang et al., 2019)
α -amylase	-	-	1.39–8.60	C–N	Adsorbents for aromatic compounds	(Zhang et al., 2014)
Chitin	-	-	2.86–10.13	-	-	-
Zein	-	-	2.50–14.92	-	-	-
Microalgae	13.94	Pyrrolic-N, pyridinic-N	6.57–12.93	C–N–C, pyrrolic-N, pyridinic-N, quaternary-N	Nitrogen-containing compounds such as indole, quinoline, isoquinoline and phenanthridine	(Maliutina et al., 2018)
Gelatin	-	-	9.26–0.88	Pyridinic, pyrrolic/pyridone, quaternary, and pyridine-N-oxide	Supercapacitors	(Xu et al., 2012)
Pine-cone	-	-	1.9–2.0	-	Rremoving tetracycline	(Wu et al., 2021)
Chitosan	9.4	-	8.9–9.1	-	-	(Zhao et al., 2010)
Glucosamine	6.5	-	6.6–6.7	Pyridinic and aromatic graphene structure	-	(Zhao et al., 2010)
Cotton stalk	1.09	–NH, –NH ₂ , protein-N	0.47–1.28	N–H, N–COO, C–N, C = N, pyridinic-N	CO ₂ adsorbents	(Zhang et al., 2014)
Cotton stalk	1.15	protein-N	1.02–1.09	N–H, C–N, C = N, amine-N, pyridinic-N	CO ₂ adsorbents	(Xiong et al., 2013)
Walnut shell	4.5	-	0.34–1.54	-	CO ₂ adsorbents	(Lahijani et al., 2018)
Rice Husk	0.38	-	0.33–0.52	C–N, N = O, pyridinic-N	CO ₂ adsorbents	(Zhang et al., 2015)
London plane leaves	0.2	-	0.4–2.5	Pyridinic and pyridonic	CO ₂ adsorbents	(Zhu et al., 2015)
Pine-cone	0	-	0.5–1.3	Pyrrolic	CO ₂ adsorbents	(Zhu et al., 2016)
Soybean staw	1.52	-	1.34–1.46	-	CO ₂ adsorbents	(Zhang et al., 2016)
Digestate from Anaerobic Digestion	1.82	-	1.88–2.30	-	CO ₂ adsorbents	(Qiao et al., 2020)

derived from Zein reaches up to 14.92%. Most nitrogenous groups in the biomass exit in the form of both inorganic N-functional groups (e.g. NH₄-N, NO₂-N, and NO₃-N) (Liu et al., 2018) and organic N-functional groups (e.g. pyridinic-N, pyrrolic-N, quaternary-N, pyridinic-N-oxide, graphitic-N, amine-N, amide-N, nitrile-N, etc.) (Yuan et al., 2018). After pyrolysis, nitrogen-rich components may convert into pyridinic-N, pyrrolic-N, quaternary-N, and possibly pyridinic-N-oxide (Chen et al., 2017). Generally, the higher nitrogen content leads to the higher nitrogen content of porous carbon. However, the pyrolysis may also lead to the loss of nitrogen in the biomass as the nitrogen-containing groups may convert into nitrogen-containing gases (e.g. NH₃). Among the nitrogen-containing biomass including cotton stalk, walnut shell, rice husk and london plane leaves have been used to produce biochar as CO₂ adsorbents. However, these biomass are not outstanding nitrogen content of biomass, more possibilities can be further explored.

3. Preparation of N-rich biochar

Biochar is mainly activated carbon through physical and chemical methods. In chemical activation, the precursor is carbonised using chemical agents such as KOH, NaOH, H₃PO₄, K₂CO₃, ZnCl, etc. In terms of industrial application, activated carbons are commonly produced from biomass via KOH activation. However, the chemical activation via washing procedures eliminates the excess activating agent from the biochar. In contrast, physical activation is benign to the environment with activating agents such as CO₂, H₂O or air as. The disadvantages of the activation technologies relate to the remarkable loss of mass, nitrogen, and other heteroatoms. Generally, N-rich porous carbons have been prepared through some methods: (1) In-situ pyrolysis of N-containing functional groups or N-rich biomass. (2) Post-modification with N-containing functional groups.

3.1. In-situ pyrolysis

In-situ pyrolysis of N-containing functional groups and biomass are the most promising way to prepare N-rich biochar. It is required to mix the N-containing functional groups and biomass before pyrolysis through the methods such as the impregnation method, gaseous activation, mixing, etc. Impregnation is normally used to chemically modify the adsorbents. For example, the amine is typically dissolved in a polar solvent such as methanol or ethanol and subsequently mixed with the porous carbon (Chen et al., 2014). Madzaki et al. compared biochar from raw sawdust without the modification to the amine-modified biochar through the amine impregnation with monoethanolamine (MEAs) (Madzaki and KarimGhani, 2016). It was shown that the impregnation reduced the BET surface area of biochar attributed to the pore filling effects of the nitrogen. In addition, the impregnation method did not enhance basic functionalities linked to the surface of the biochar. Thus, the modified biochar showed less CO₂ adsorption compared to the biochar without modification, although it had a higher N-content but lower BET surface area.

To overcome these disadvantages, ammonia treatment was explored to introduce the N-functionalities to porous carbon. Generally, gaseous activation was proved to increase porosity between 700 and 800°C, which can be attributed to high reaction rates of steam with carbon (Gergova and Eser, 1996). In addition, ammonia is used as a modification method. For example, Zhang et al. reported a cotton stalk-derived biochar prepared by pyrolysis and modification by gaseous NH₃ (Zhang et al., 2014). The surface area of CA-char was the highest at 627.15 m² g⁻¹, and its CO₂ adsorption capacity was 2.18 mmol g⁻¹ at 20°C when N content was 1.52%. Using the method, CN 800 was obtained from soybean straw by modification of CO₂-NH₃ mixture at 800°C, processing CO₂ adsorption of 88.89 mg g⁻¹ (Zhang et al., 2016).

Another challenge that lies in the activation technologies is the significant mass loss during activation. Mixing between solids is also one efficient way to introduce the nitrogen groups to avoid mass loss. Our group has also proposed a one-step method to obtain N-rich biochar derived from anaerobic digestion digestate used as a CO₂ adsorbent (Qiao et al., 2020). The N-rich biochar was obtained by pyrolysis of a mixture of the biomass and urea, with the CO₂ capacity up to 1.22 mmol g⁻¹. In this work, the low BET surface area limited the CO₂ capacity, which may be linked to blocked pores. However, both the porous property and functionalities are important to CO₂ capture.

Peiyu et al. used a "mixed molten salt" method to receive hierarchical N-rich activated carbons (N-ACs) derived from chitosan with a molten salt template of LiCl-ZnCl₂ (Wang et al., 2020). This simple one-step carbonization method is also advantageous in terms of avoiding significant mass loss. The CO₂ adsorption capacity of N-ACs was 7.9/5.6 mmol•g⁻¹ at 0°C/25°C under 1 bar pressure, respectively.

Generally, the process of biochar production used for CO₂ capture is conducted by two steps including carbonization and activation, which means harsh and multiple processes are used. But if the biochar is prepared through a single-step process, its costs could be decreased.

3.2. Post modification

Biochar from coffee grounds was reported to be treated by three methods as follows: (i) KSHC, dispersion of the biochar in an alcohol solution of 3-aminopropyltrimethoxysilane (APTES), (ii) KPHC, through the polycondensation of C₆H₅NH₂, and (iii) KMHC, hydrothermal treatment with melamine solution of biochar at 160 °C for 24 h (Liu and Huang, 2018). KMHC led to the highest CO₂ adsorption (117.51 mg/g) among three prepared adsorbents, possibly due to the presence of high microporosity, good N content (5.1 wt%) with active sites (pyrrolic nitrogen). These sorbents also showed surpassing renewability and cyclability.

Nguyen et al. prepared a biochar (AMBC, porous nitrogen-doped biochar) sorbent at lower pyrolysis and modification temperature with

higher CO₂ adsorption (Nguyen and Lee, 2016). The preparation method was also based on the gas modification but a little complex, with the following steps: (1) slow pyrolysis of chicken manure for 1 h at 450°C; (2) chemical treatment from HNO₃ and anhydrous ammonia gas for 1 h at 450°C; (3) reaction with sodium- α -l-gulopyranuronate to form solid beads. The AMBC beads performed a high capacity of CO₂ adsorption (10.15 mmol g⁻¹ at 20°C) with a specific surface area (328.6 m² g⁻¹) and CO₂/N₂ selectivity (79.1). Another important performance was the stability in that the CO₂ adsorption capacity kept 85% after ten regeneration cycles.

To simplify the preparation procedure, Serafin et al. used a one-step method of combining carbonization with activation to make use of Amazonian wastes (nutshells waste), including Andiroba (AD), Biochar Brazilian nut (BBN), Brazilian nutshell (BNS), Cascara Cupuassu (Cas-Cup), COSC Cupuago (CosCup), Hueso Assai (HA), to produce biochar-based CO₂ adsorbents (Serafin et al., 2021). The highest capacity of CO₂ adsorption at 298 K with 3.67 mmol g⁻¹ was investigated on Cascara Cupuassau-derived biochar.

Riya et al. described pinewood-derived biochar via a two-stage activation process including sonication treatment and amine-activation (tetraethylenepentamine, TEPA) near room temperature (Chatterjee et al., 2018). The optimum capacity of CO₂ capture was 2.79 mmol g⁻¹ at 70 °C, 0.15 atm. The method of post-modification is related to high consumption of energy or cost because of high temperatures, corrosive materials, blocked pores.

From table 2, the highest capacity of CO₂ capture is 10.15 mmol/g at 20°C for AMBC. Because of the existence of CO₂ and N₂ in flue gas from fossil-fuel power plants, CO₂/N₂ selectivity is a key factor for the development of biochar-based adsorbents. The highest CO₂/N₂ selectivity is also obtained using AMBC, with 79 at 20°C. However, the highest BET surface area is KNWS-xy with 4230 m² g⁻¹ and the highest N-content with 8.99% is from UCAD 1:1. Researchers have discussed the co-effect of BET surface area, N-functionalities on the CO₂ adsorption (Wei et al., 2012, Gupta and Kua, 2017). During the preparation of AMBC, the chemical treatment of the biochar with HNO₃ and NH₃ enhanced the presence of amine groups on its surface, thus leading to the increased capacity of CO₂ capture. Therefore, it is desirable to directly convert biomass into porous carbon with good CO₂ capacities. In addition, the comparison between the sample before and after nitrogen enrichment proves that N-functionalities have a larger contribution to CO₂ adsorption compared to BET surface area. In all the cases shown in table 2, CO₂ adsorption has been improved after nitrogen is enriched, while in some cases like US0.5-EH 1:1-T2.5 (Chatterjee et al., 2018), BET surface area decreased after the introduction of nitrogen.

In terms of preparation methods, the post-modification method requires more steps and the possibility of pore blockage. Thus the in-situ method is a preferred method (Rouzitab et al., 2018).

4. Mechanism of CO₂ adsorption on N modified biochar

Nitrogen atoms can replace carbon atoms in carbon materials as nitrogen atoms are close to C atoms in the periodic table. The covalent radius of carbon is 0.77 Å, while the nitrogen is 0.74 Å (Lv et al., 2018).

When the heteroatomic nitrogen is introduced into a porous carbon, the surface conjugate structure and electron distribution of the carbon carrier, as well as the electrical neutrality of carbon materials, are changed (Wu et al., 2019). N-containing groups were reported to perform well in CO₂ adsorption, CO₂/N₂ selectivity, and initial isosteric heats of CO₂ adsorption (Q_{st}) with improved surface properties (Wickramaratne et al., 2014).

The nitrogen in porous carbon mainly contributes to the chemical adsorption of CO₂ instead of the physical adsorption of CO₂ (Chen et al., 2013). Primary and secondary amines formed various urea linkages in the reactions between the N-containing groups and CO₂ (Sayari et al., 2012, Sethia and Sayari, 2014). As shown in Fig. 2, primary amines form open-chain urea with CO₂ (Route a, Fig. 2), which is regarded as

Table 2
Summary for representative reported CO₂ adsorbents of N-rich biochar at 1 bar.

Sample Name	Before Nitrogen enrichment			After Nitrogen enrichment			Ref.
	Biomass	BET Surface area/ m ² g ⁻¹	CO ₂ adsorption/ mmol g ⁻¹	BET Surface area/ m ² g ⁻¹	CO ₂ adsorption/ mmol g ⁻¹	CO ₂ /N ₂ selectivity	
N-AC-3-1000	Chitosan	-	-	2025	5.6 at 25°C	-	(Wang et al., 2020)
CasCup	Nutshell waste	-	-	1624	5.13 at 0°C, 3.67 at 20°C,	48 at 20°C	(Serafin et al., 2021)
US0.5-EH	Pinewood	312.31	0.3 at 70 °C	261.68	2.79 mmol/g at 70 °C and 0.15 atm	-	(Chatterjee et al., 2018)
1:1-T2.5							
AC-KOH-N	Black locust	1175	1.85 at 25°C	2511	5.05 at 25°C	31 at 25°C	(Zhang et al., 2016)
KNWS-xy	Walnut shell	2.19	-	4230	7.42 at 25°C	13 at 25°C	(Rouzitalab et al., 2018)
ANCs-3-700	Water chestnut	15	-	3401	4.7 at 25°C	-	(Wei et al., 2018)
A-char	Cotton stalk	224	-	627	2.18 at 20°C	-	(Zhang et al., 2014)
PC3-700	Pine cones	-	-	2090	-	-	(Zhu et al., 2016)
NSD 850	Raw sawdust	-	1.08 at 30°C	3.17	1.02 at 30°C	-	(Madzaki and KarimGhani, 2016)
CN 800	Soybean straw	0.04	0.96 at 30°C	491	2.02 at 30°C	-	(Zhang et al., 2016)
UCAD 1:1	Digestate from Anaerobic Digestion	-	-	6.89	1.22 at 25°C	-	(Qiao et al., 2020)
KSHC	Coffee grounds	34	0.14 at 35°C	1684	2.04 at 35°C	-	(Liu and Huang, 2018)
KPHC				992	2.22 at 35°C	-	
KMHC				990	2.67 at 35°C	74 at 35°C	
AMBC	Chicken manure	34.6	3.72 at 20°C	328.6	10.15 at 20°C	79 at 20°C	(Nguyen and Lee, 2016)
GSK1-700	Starch, Pristine gelatin	1294	3.3 at 25°C	1636	3.84 at 25°C	51 at 25°C	(Alabadi et al., 2015)

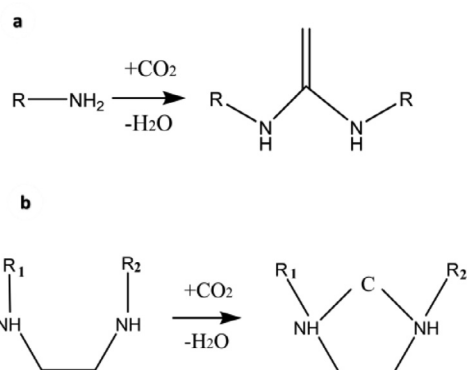
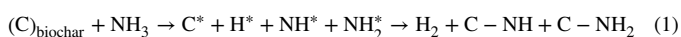


Fig. 2. The mechanism of reaction between amines and CO₂ (Abbas et al., 2018).

the main reaction. As for adsorbents containing ethylenediamine units, the mechanism will be the reaction between secondary amines and CO₂ to obtain cyclic urea (Route b, Fig. 2) (Sayari et al., 2012).

For example, the enhancement of CO₂ adsorption by ammonia treatment depended on the C–N and C=N groups introduced by modifications (Przepiórski et al., 2004). In detail, NH₃ decomposes to produce various free radicals including NH₂^{*}, NH^{*}, and H^{*} when the temperature is around 500 °C. Then these radicals react with the active sites on the surface of biochar to form N- functionalities such as amines, amides, imides, lactams, nitriles, or pyridine- or pyrrole-like functional groups as shown in the following routes (Scheme 1) (Li et al., 2019).



5. Conclusion

In terms of N sources, N-containing functionalities and N-rich biomass are introduced into biochar to enhance CO₂ adsorption. Ammonia, urea and polymer-based amine have been applied as the functionalities, while microalgae and chitosan are significantly N-rich biochar. The preparation methods include in-situ pyrolysis and post-modification

with N- containing functional groups. The further design may lie in the combination of both the nitrogen-rich functionalities and nitrogen-rich biomass groups together. As most of the methods for preparing biochar based CO₂ adsorbents require at least two steps including pyrolysis and modification. Thus, a simpler process is desired, for example, the one-step in-situ method of combining carbonization with activation to make use of N-compounds in biomass to obtain active biochar for CO₂ capture. Biochar based adsorbents for CO₂ capture have shown high activity, good selectivity, stability after regeneration cycles and nontoxicity to the environment.

Declaration of Competing Interest

There are no conflicts of interest to declare.

Acknowledgment

The authors gratefully acknowledge financial support from the China Scholarship Council (student number 201706880031). This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 823745.

References

- Abbas, Q, Liu, G, Yousaf, B, Ali, MU, Ullah, H, Munir, MAM, et al., 2018. Contrasting effects of operating conditions and biomass particle size on bulk characteristics and surface chemistry of rice husk derived-biochars. *Journal of analytical and applied pyrolysis* 134, 281–292.
- Abu-Zahra, MR, Niederer, JP, Feron, PH, Versteeg, GF., 2007. CO₂ capture from power plants: Part II. A parametric study of the economical performance based on mono-ethanolamine. *International journal of greenhouse gas control* 1 (2), 135–142.
- Agrafioti, E, Bouras, G, Kalderis, D, Diamadopoulos, E., 2013. Biochar production by sewage sludge pyrolysis. *Journal of Analytical and Applied Pyrolysis* 101, 72–78.
- Ahmad, M, Rajapaksha, AU, Lim, JE, Zhang, M, Bolan, N, Mohan, D, et al., 2014. Biochar as a sorbent for contaminant management in soil and water: a review. *Chemosphere* 99, 19–33.
- Ahmed, MB, Zhou, JL, Ngo, HH, Guo, W., 2016. Insight into biochar properties and its cost analysis. *Biomass and Bioenergy* 84, 76–86.
- Alabadi, A, Razaque, S, Yang, Y, Chen, S, Tan, B., 2015. Highly porous activated carbon materials from carbonized biomass with high CO₂ capturing capacity. *Chemical Engineering Journal* 281, 606–612.

- Balahmar, N, Al-Jumaily, AS, Mokaya, R., 2017. Biomass to porous carbon in one step: directly activated biomass for high performance CO₂ storage. *Journal of Materials Chemistry A* 5 (24), 12330–12339.
- Bamdad, H, Hawboldt, K, MacQuarrie, S., 2018. A review on common adsorbents for acid gases removal: Focus on biochar. *Renewable and Sustainable Energy Reviews* 81, 1705–1720.
- Cansado, I, Mourão, P, Falcão, A, Carrott, MR, Carrott, P., 2012. The influence of the activated carbon post-treatment on the phenolic compounds removal. *Fuel Processing Technology* 103, 64–70.
- Chatterjee, R, Sajjadi, B, Mattern, DL, Chen, W-Y, Zubatiuk, T, Leszczynska, D, et al., 2018. Ultrasound cavitation intensified amine functionalization: A feasible strategy for enhancing CO₂ capture capacity of biochar. *Fuel* 225, 287–298.
- Chellappan, S, Nair, V, Sajith, V, Aparna, K., 2018. Synthesis, optimization and characterization of biochar based catalyst from sawdust for simultaneous esterification and transesterification. *Chinese journal of chemical engineering* 26 (12), 2654–2663.
- Chen, C, Kim, J, Ahn, W-S., 2014. CO₂ capture by amine-functionalized nanoporous materials: A review. *Korean Journal of Chemical Engineering* 31 (11), 1919–1934.
- Chen, H, Sun, F, Wang, J, Li, W, Qiao, W, Ling, L, et al., 2013. Nitrogen doping effects on the physical and chemical properties of mesoporous carbons. *The Journal of Physical Chemistry C* 117 (16), 8318–8328.
- Chen, W, Yang, H, Chen, Y, Xia, M, Chen, X, Chen, H., 2017. Transformation of nitrogen and evolution of N-containing species during algae pyrolysis. *Environmental science & technology* 51 (11), 6570–6579.
- Chiang, Y-C, Juang, R-S., 2017. Surface modifications of carbonaceous materials for carbon dioxide adsorption: A review. *Journal of the Taiwan Institute of Chemical Engineers* 71, 214–234.
- Choi, Y-K, Kan, E., 2019. Effects of pyrolysis temperature on the physicochemical properties of alfalfa-derived biochar for the adsorption of bisphenol A and sulfamethoxazole in water. *Chemosphere* 218, 741–748.
- CO₂ Emissions from Fuel Combustion 2017 Highlights. International Energy Agency; 2017.
- Cullinane, JT, Rochelle, GT., 2004. Carbon dioxide absorption with aqueous potassium carbonate promoted by piperazine. *Chemical Engineering Science* 59 (17), 3619–3630.
- de Jonge, H, Mittelmeijer-Hazeleger, MC, 1996. Adsorption of CO₂ and N₂ on soil organic matter: nature of porosity, surface area, and diffusion mechanisms. *Environmental Science & Technology* 30 (2), 408–413.
- Deng, S, Wei, H, Chen, T, Wang, B, Huang, J, Yu, G., 2014. Superior CO₂ adsorption on pine nut shell-derived activated carbons and the effective micropores at different temperatures. *Chemical Engineering Journal* 253, 46–54.
- Dissanayake, PD, You, S, Igalavithana, AD, Xia, Y, Bhatnagar, A, Gupta, S, et al., 2020. Biochar-based adsorbents for carbon dioxide capture: A critical review. *Renewable and Sustainable Energy Reviews* 119, 109582.
- Dlugokencky ET, P. P. ESRL Global Monitoring Division - Global Greenhouse Gas Reference Network. 2017.
- Elo, AS, de Souza, LKC, Trokourey, A, Jaroniec, M., 2013. Development of microporous carbons for CO₂ capture by KOH activation of African palm shells. *Journal of CO₂ Utilization* 2, 35–38.
- Gergova, K, Eser, S., 1996. Effects of activation method on the pore structure of activated carbons from apricot stones. *Carbon* 34 (7), 879–888.
- Glasscock, DA, Critchfield, JE, Rochelle, GT., 1991. CO₂ absorption/desorption in mixtures of methyldiethanolamine with monoethanolamine or diethanolamine. *Chemical Engineering Science* 46 (11), 2829–2845.
- Guo, D, Shibuya, R, Akiba, C, Saji, S, Kondo, T, Nakamura, J., 2016. Active sites of nitrogen-doped carbon materials for oxygen reduction reaction clarified using model catalysts. *Science* 351 (6271), 361–365.
- Gupta, S, Kua, HW., 2017. Factors determining the potential of biochar as a carbon capturing and sequestering construction material: critical review. *Journal of Materials in Civil Engineering* 29 (9), 04017086.
- Haji-Sulaiman, M, Aroua, M, Benamor, A., 1998. Analysis of equilibrium data of CO₂ in aqueous solutions of diethanolamine (DEA), methyldiethanolamine (MDEA) and their mixtures using the modified Kent Eisenberg model. *Chemical Engineering Research and Design* 76 (8), 961–968.
- Harlick, PJ, Sayari, A., 2006. Applications of pore-expanded mesoporous silicas. 3. Triamine silane grafting for enhanced CO₂ adsorption. *Industrial & Engineering Chemistry Research* 45 (9), 3248–3255.
- Ho, MT, Allinson, GW, Wiley, DE., 2008. Reducing the cost of CO₂ capture from flue gases using pressure swing adsorption. *Industrial & Engineering Chemistry Research* 47 (14), 4883–4890.
- Igalavithana, AD, Mandal, S, Niazi, NK, Vithanage, M, Parikh, SJ, Mukome, FN, et al., 2017. Advances and future directions of biochar characterization methods and applications. *Critical reviews in environmental science and technology* 47 (23), 2275–2330.
- Ioannidou, O, Zabaniotou, A., 2007. Agricultural residues as precursors for activated carbon production—A review. *Renewable and Sustainable Energy Reviews* 11 (9), 1966–2005.
- Jia, Y, Xiao, B, Thomas, K., 2002. Adsorption of metal ions on nitrogen surface functional groups in activated carbons. *Langmuir* 18 (2), 470–478.
- Jung, S, Park, Y-K, Kwon, EE., 2019. Strategic use of biochar for CO₂ capture and sequestration. *Journal of CO₂ Utilization* 32, 128–139.
- Keilueit, M, Nico, PS, Johnson, MG, Kleber, M., 2010. Dynamic Molecular Structure of Plant Biomass-Derived Black Carbon (Biochar). *Environmental Science & Technology* 44 (4), 1247–1253.
- Keskin, S, van Heest, TM, Sholl, DS., 2010. Can Metal–Organic Framework Materials Play a Useful Role in Large-Scale Carbon Dioxide Separations? *ChemSusChem* 3 (8), 879–891.
- Knowles, GP, Graham, JV, Delaney, SW, Chaffee, AL., 2005. Aminopropyl-functionalized mesoporous silicas as CO₂ adsorbents. *Fuel Processing Technology* 86 (14–15), 1435–1448.
- Lahijani, P, Mohammadi, M, Mohamed, AR., 2018. Metal incorporated biochar as a potential adsorbent for high capacity CO₂ capture at ambient condition. *Journal of CO₂ Utilization* 26, 281–293.
- Lehmann, J, Gaunt, J, Rondon, M., 2006. Bio-char sequestration in terrestrial ecosystems—a review. *Mitigation and adaptation strategies for global change* 11 (2), 403–427.
- Lehmann, J, Rillig, MC, Thies, J, Masiello, CA, Hockaday, WC, Crowley, D., 2011. Biochar effects on soil biota—a review. *Soil biology and biochemistry* 43 (9), 1812–1836.
- Leng, L, Xu, S, Liu, R, Yu, T, Zhuo, X, Leng, S, et al., 2020. Nitrogen containing functional groups of biochar: An overview. *Bioresource technology* 298, 122286.
- Li, B, Duan, Y, Luebke, D, Morreale, B., 2013. Advances in CO₂ capture technology: A patent review. *Applied Energy* 102, 1439–1447.
- Li, K, Chen, W, Yang, H, Chen, Y, Xia, S, Xia, M, et al., 2019. Mechanism of biomass activation and ammonia modification for nitrogen-doped porous carbon materials. *Bioresource technology* 280, 260–268.
- Liu, L, Tan, Z, Ye, Z., 2018. Transformation and transport mechanism of nitrogenous compounds in a biochar “preparation–returning to the field” process studied by employing an isotope tracer method. *ACS Sustainable Chemistry & Engineering* 6 (2), 1780–1791.
- Liu, S-H, Huang, Y-Y., 2018. Valorization of coffee grounds to biochar-derived adsorbents for CO₂ adsorption. *Journal of Cleaner Production* 175, 354–360.
- Llewellyn, PL, Bourrelly, S, Serre, C, Vimont, A, Daturi, M, Hamon, L, et al., 2008. High Uptakes of CO₂ and CH₄ in Mesoporous Metal–Organic Frameworks MIL-100 and MIL-101. *Langmuir* 24 (14), 7245–7250.
- Lv, Q, Si, W, He, J, Sun, L, Zhang, C, Wang, N, et al., 2018. Selectively nitrogen-doped carbon materials as superior metal-free catalysts for oxygen reduction. *Nature communications* 9 (1), 1–11.
- Ma, L, Bai, R, Hu, G, Chen, R, Hu, X, Dai, W, et al., 2013. Capturing CO₂ with amine-impregnated titanium oxides. *Energy & fuels* 27 (9), 5433–5439.
- Madzaki, H, KarimGhani, WAWA., 2016. Carbon dioxide adsorption on sawdust biochar. *Procedia engineering* 148, 718–725.
- Maliutina, K, Tahmasebi, A, Yu, J., 2018. Pressurized entrained-flow pyrolysis of microalgae: Enhanced production of hydrogen and nitrogen-containing compounds. *Bioresource technology* 256, 160–169.
- Matovic, D., 2011. Biochar as a viable carbon sequestration option: Global and Canadian perspective. *Energy* 36 (4), 2011–2016.
- Millward, AR, Yaghi, OM., 2005. Metal–Organic Frameworks with Exceptionally High Capacity for Storage of Carbon Dioxide at Room Temperature. *Journal of the American Chemical Society* 127 (51), 17998–17999.
- Mohd, A, Ab Karim Ghani, WW, Resitanim, NZ, Sanyang, L, 2013. A review: carbon dioxide capture: biomass-derived-biochar and its applications. *Journal of dispersion science and technology* 34 (7), 974–984.
- Moreno-Piraján, J, Giraldo, L, 2010. Study of activated carbons by pyrolysis of cassava peel in the presence of chloride zinc. *Journal of Analytical and Applied Pyrolysis* 87 (2), 288–290.
- Nguyen, M-V, Lee, B-K., 2016. A novel removal of CO₂ using nitrogen doped biochar beads as a green adsorbent. *Process Safety and Environmental Protection* 104, 490–498.
- Ok, YS, Chang, SX, Gao, B, Chung, H-J., 2015. SMART biochar technology—a shifting paradigm towards advanced materials and healthcare research. *Environmental Technology & Innovation* 4, 206–209.
- Parshetti, GK, Chowdhury, S, Balasubramanian, R., 2015. Biomass derived low-cost microporous adsorbents for efficient CO₂ capture. *Fuel* 148, 246–254.
- Plaza, M, González, A, Pis, J, Rubiera, F, Pevida, C., 2014. Production of microporous biochars by single-step oxidation: Effect of activation conditions on CO₂ capture. *Applied energy* 114, 551–562.
- Plaza, MG, González, AS, Pevida, C, Pis, JJ, Rubiera, F., 2012. Valorisation of spent coffee grounds as CO₂ adsorbents for postcombustion capture applications. *Applied Energy* 99, 272–279.
- Przepiórski, J, Skrodziewicz, M, Morawski, A., 2004. High temperature ammonia treatment of activated carbon for enhancement of CO₂ adsorption. *Applied Surface Science* 225 (1–4), 235–242.
- Qi, G, Wang, Y, Estevez, L, Duan, X, Anako, N, Park, A-HA, et al., 2011. High efficiency nanocomposite sorbents for CO₂ capture based on amine-functionalized mesoporous capsules. *Energy & Environmental Science* 4 (2), 444–452.
- Qiao, Y, Zhang, S, Quan, C, Gao, N, Johnston, C, Wu, C., 2020. One-pot synthesis of digestate-derived biochar for carbon dioxide capture. *Fuel* 279, 118525.
- Rittl, TF, Butterbach-Bahl, K, Basile, CM, Pereira, LA, Alms, V, Dannenmann, M, et al., 2018. Greenhouse gas emissions from soil amended with agricultural residue biochars: Effects of feedstock type, production temperature and soil moisture. *Biomass and Bioenergy* 117, 1–9.
- Rouziatalab, Z, Maklavany, DM, Rashidi, A, Jafarinejad, S., 2018. Synthesis of N-doped nanoporous carbon from walnut shell for enhancing CO₂ adsorption capacity and separation. *Journal of environmental chemical engineering* 6 (5), 6653–6663.
- Saha, D, Kienbaum, MJ., 2019. Role of oxygen, nitrogen and sulfur functionalities on the surface of nanoporous carbons in CO₂ adsorption: a critical review. *Microporous and Mesoporous Materials* 287, 29–55.
- Samanta, A, Zhao, A, Shimizu, GKH, Sarkar, P, Gupta, R., 2012. Post-Combustion CO₂ Capture Using Solid Sorbents: A Review. *Industrial & Engineering Chemistry Research* 51 (4), 1438–1463.
- Sayari, A, Belmabkhout, Y, Da'na, E., 2012. CO₂ deactivation of supported amines: does the nature of amine matter? *Langmuir* 28 (9), 4241–4247.
- Sayari, A, Heydari-Gorji, A, Yang, Y., 2012. CO₂-induced degradation of amine-containing adsorbents: reaction products and pathways. *Journal of the American Chemical Society* 134 (33), 13834–13842.

- Serafin, J, Ouzzine, M, Junior, OFC, Sreńscek-Nazzal, J., 2021. Preparation of low-cost activated carbons from amazonian nutshells for CO₂ storage. *Biomass and Bioenergy* 144, 105925.
- Sethia, G, Sayari, A., 2014. Nitrogen-doped carbons: remarkably stable materials for CO₂ capture. *Energy & Fuels* 28 (4), 2727–2731.
- Sevilla, M, Fuertes, AB., 2011. Sustainable porous carbons with a superior performance for CO₂ capture. *Energy & Environmental Science* 4 (5), 1765–1771.
- Sevilla, M, Valle-Vigón, P, Fuertes, AB., 2011. N-doped polypyrrole-based porous carbons for CO₂ capture. *Advanced Functional Materials* 21 (14), 2781–2787.
- Shafeeyan, MS, Daud, WMAW, Houshmand, A, Shamiri, A., 2010. A review on surface modification of activated carbon for carbon dioxide adsorption. *Journal of Analytical and Applied Pyrolysis* 89 (2), 143–151.
- Shao, J, Zhang, J, Zhang, X, Feng, Y, Zhang, H, Zhang, S, et al., 2018. Enhance SO₂ adsorption performance of biochar modified by CO₂ activation and amine impregnation. *Fuel* 224, 138–146.
- Shen, W, He, Y, Zhang, S, Li, J, Fan, W., 2012. Yeast-based microporous carbon materials for carbon dioxide capture. *ChemSusChem* 5 (7), 1274–1279.
- Shen, Y, Linville, JL, Urgun-Demirtas, M, Schoene, RP, Snyder, SW., 2015. Producing pipeline-quality biomethane via anaerobic digestion of sludge amended with corn stover biochar with in-situ CO₂ removal. *Applied Energy* 158, 300–309.
- Siegelman, RL, McDonald, TM, Gonzalez, MI, Martell, JD, Milner, PJ, Mason, JA, et al., 2017. Controlling Cooperative CO₂ Adsorption in Diamine-Appended Mg₂(dobpc) Metal–Organic Frameworks. *Journal of the American Chemical Society* 139 (30), 10526–10538.
- Siriwardane, RV, Shen, M-S, Fisher, EP, Losch, J., 2005. Adsorption of CO₂ on zeolites at moderate temperatures. *Energy & Fuels* 19 (3), 1153–1159.
- Sohi, SP, Krull, E, Lopez-Capel, E, Bol, R., 2010. A review of biochar and its use and function in soil. *Advances in agronomy* 105, 47–82.
- Tang, Y, Alam, MS, Konhauser, KO, Alessi, DS, Xu, S, Tian, W, et al., 2019. Influence of pyrolysis temperature on production of digested sludge biochar and its application for ammonium removal from municipal wastewater. *Journal of Cleaner Production* 209, 927–936.
- Veselá, P, Slovák, V., 2014. N-doped carbon xerogels prepared by ammonia assisted pyrolysis: Surface characterisation, thermal properties and adsorption ability for heavy metal ions. *Journal of Analytical and Applied Pyrolysis* 109, 266–271.
- Walton, KS, Abney, MB, LeVan, MD., 2006. CO₂ adsorption in Y and X zeolites modified by alkali metal cation exchange. *Microporous and Mesoporous Materials* 91 (1–3), 78–84.
- Wang, J, Heerwig, A, Lohe, MR, Oschatz, M, Borchardt, L, Kaskel, S., 2012. Fungi-based porous carbons for CO₂ adsorption and separation. *Journal of Materials Chemistry* 22 (28), 13911–13913.
- Wang, P, Zhang, G, Chen, W, Chen, Q, Jiao, H, Liu, L, et al., 2020. Molten salt template synthesis of hierarchical porous nitrogen-containing activated carbon derived from chitosan for CO₂ capture. *ACS omega* 5 (36), 23460–23467.
- Wang, R, Wang, P, Yan, X, Lang, J, Peng, C, Xue, Q., 2012. Promising porous carbon derived from celctue leaves with outstanding supercapacitance and CO₂ capture performance. *ACS applied materials & interfaces* 4 (11), 5800–5806.
- Wei, H, Chen, J, Fu, N, Chen, H, Lin, H, Han, S., 2018. Biomass-derived nitrogen-doped porous carbon with superior capacitive performance and high CO₂ capture capacity. *Electrochimica Acta* 266, 161–169.
- Wei, H, Deng, S, Hu, B, Chen, Z, Wang, B, Huang, J, et al., 2012. Granular bamboo-derived activated carbon for high CO₂ adsorption: the dominant role of narrow micropores. *ChemSusChem* 5 (12), 2354–2360.
- Wickramaratne, NP, Xu, J, Wang, M, Zhu, L, Dai, J, Jaroniec, M., 2014. Nitrogen enriched porous carbon spheres: attractive materials for supercapacitor electrodes and CO₂ adsorption. *Chemistry of Materials* 26 (9), 2820–2828.
- Wu, J, Wang, L, Ma, H, Zhou, J., 2021. Investigation of element migration characteristics and product properties during biomass pyrolysis: a case study of pine cones rich in nitrogen. *RSC Advances* 11 (55), 34795–34805.
- Wu, Q, Zhang, G, Gao, M, Huang, L, Li, L, Liu, S, et al., 2019. N-doped porous carbon from different nitrogen sources for high-performance supercapacitors and CO₂ adsorption. *Journal of Alloys and Compounds* 786, 826–838.
- Xiong, Z, Shihong, Z, Haiping, Y, Tao, S, Yingquan, C, Hanping, C., 2013. Influence of NH₃/CO₂ modification on the characteristic of biochar and the CO₂ capture. *Bioenergy Res* 6, 1147–1153.
- Xu, B, Hou, S, Cao, G, Wu, F, Yang, Y., 2012. Sustainable nitrogen-doped porous carbon with high surface areas prepared from gelatin for supercapacitors. *Journal of Materials Chemistry* 22 (36), 19088–19093.
- Yang, H, Gong, M, Chen, Y., 2011. Preparation of activated carbons and their adsorption properties for greenhouse gases: CH₄ and CO₂. *Journal of natural gas chemistry* 20 (5), 460–464.
- Yaumi, A, Bakar, MA, Hameed, B., 2017. Reusable nitrogen-doped mesoporous carbon adsorbent for carbon dioxide adsorption in fixed-bed. *Energy* 138, 776–784.
- Younas, M, Sohail, M, Leong, L, Bashir, MJ, Sumathi, S., 2016. Feasibility of CO₂ adsorption by solid adsorbents: a review on low-temperature systems. *International journal of environmental science and technology* 13 (7), 1839–1860.
- Yuan, S, Tan, Z, Huang, Q., 2018. Migration and transformation mechanism of nitrogen in the biomass–biochar–plant transport process. *Renewable and Sustainable Energy Reviews* 85, 1–13.
- Zhang, C, Song, W, Ma, Q, Xie, L, Zhang, X, Guo, H., 2016. Enhancement of CO₂ capture on biomass-based carbon from black locust by KOH activation and ammonia modification. *Energy & Fuels* 30 (5), 4181–4190.
- Zhang, S, et al., 2015. One-step, template-free synthesis of highly porous nitrogen/sulfur-codoped carbons from a single protic salt and their application to CO₂ capture. *Journal of Materials Chemistry A* 3, 17849–17857. doi:10.1039/C5TA03575A.
- Zhang, M, Shu, L, Shen, X, Guo, X, Tao, S, Xing, B, et al., 2014. Characterization of nitrogen-rich biomaterial-derived biochars and their sorption for aromatic compounds. *Environmental pollution* 195, 84–90.
- Zhang, Q, Wang, J, Lyu, H, Zhao, Q, Jiang, L, Liu, L., 2019. Ball-milled biochar for galaxolide removal: Sorption performance and governing mechanisms. *Science of the Total Environment* 659, 1537–1545.
- Zhang, X, Wu, J, Yang, H, Shao, J, Wang, X, Chen, Y, et al., 2016. Preparation of nitrogen-doped microporous modified biochar by high temperature CO₂-NH₃ treatment for CO₂ adsorption: effects of temperature. *RSC Advances* 6 (100), 98157–98166.
- Zhang, X, Zhang, S, Yang, H, Feng, Y, Chen, Y, Wang, X, et al., 2014. Nitrogen enriched biochar modified by high temperature CO₂-ammonia treatment: Characterization and adsorption of CO₂. *Chemical Engineering Journal* 257, 20–27.
- Zhang, X, Zhang, S, Yang, H, Shao, J, Chen, Y, Feng, Y, et al., 2015. Effects of hydrofluoric acid pre-deashing of rice husk on physicochemical properties and CO₂ adsorption performance of nitrogen-enriched biochar. *Energy* 91, 903–910.
- Zhang, Z, Zhu, Z, Shen, B, Liu, L., 2019. Insights into biochar and hydrochar production and applications: a review. *Energy* 171, 581–598.
- Zhao, L, Baccile, N, Gross, S, Zhang, Y, Wei, W, Sun, Y, et al., 2010. Sustainable nitrogen-doped carbonaceous materials from biomass derivatives. *Carbon* 48 (13), 3778–3787.
- Zhu, B, Qiu, K, Shang, C, Guo, Z., 2015. Naturally derived porous carbon with selective metal-and/or nitrogen-doping for efficient CO₂ capture and oxygen reduction. *Journal of Materials Chemistry A* 3 (9), 5212–5222.
- Zhu, B, Shang, C, Guo, Z., 2016. Naturally Nitrogen and Calcium-Doped Nanoporous Carbon from Pine Cone with Superior CO₂ Capture Capacities. *ACS Sustainable Chemistry & Engineering* 4 (3), 1050–1057.
- Z-I, LIU, Yang, T, ZHANG, K, Yan, C, W-p, PAN., 2013. CO₂ adsorption properties and thermal stability of different amine-impregnated MCM-41 materials. *Journal of Fuel Chemistry and Technology* 41 (4), 469–475.