

Review article

Activated carbon from biomass: Preparation, factors improving basicity and surface properties for enhanced CO₂ capture capacity – A review

K. Malini, D. Selvakumar^{*}, N.S. Kumar

Defence Bioengineering and Electromedical Laboratory (DEBEL), DRDO, CV Raman nagar, Bangalore 560093, India



ARTICLE INFO

Keywords:

AC
CO₂ adsorption
Nitrogen doped
Metal oxide

ABSTRACT

There has been a concerted and continued effort to enhance the CO₂ capture capacity of activated carbon (AC) by adopting various physical and chemical treatments on the AC materials. This review is aimed for the compilation of works performed by various researchers on the synthesis of AC from biomass and two major modification works performed on them to improve their basicity for the application towards CO₂ adsorption. The different methods of preparation of ACs utilizing biomass as starting materials have been reviewed. The effects of carbonization and activation on the surface properties of the ACs were discussed. Basicity of AC plays a vital role in the adsorption of CO₂ along with the activation of carbon obtained from the carbonization of biomass. The improvement of basicity of ACs by i) nitrogen incorporation and ii) metal oxide impregnation, the various methods adopted to incorporate the above components and their effect on CO₂ capture have been discussed in detail.

1. Introduction

The life-threatening problems, such as climate changes and global warming faced by the human beings in this 21st century is the outcome of elevated release of CO₂ to the atmosphere. The major sources of CO₂ pollutions are anthropogenic activities such as fossil fuel combustion, deforestation, industrial emissions etc. The concentration of atmospheric CO₂ has reached 412 ppm in the year 2021 and it is responsible for an average raise in temperature by 1.2 °C [1]. The resultant effects are melting of glaciers, rise in sea level, heat waves etc. which will disrupt the usual balance of nature.

The continuous increase in the CO₂ concentration in atmosphere has to be curbed in an effective manner. CO₂ can be either directly absorbed from the atmosphere or collected from flue gas streams following efficient techniques. The captured CO₂ is either stored using appropriate methods (Carbon Capture and Sequestration) or used to convert into useful chemicals (Carbon Capture and Utilization). A number of techniques such as absorption, membrane separation and adsorption are being used for the removal of CO₂ [2]. Adsorption using liquid ammonia was the widely used technique, but due to its high cost of regenerations, high volatility and high alkalinity researchers were on the study to develop an alternative way. Later on, a cost-effective as well as efficient technique was developed, which is by using the process of adsorption

technique. Adsorption involves use of several adsorbents such as AC [3], zeolites [4], mesoporous silica [5], Metal Organic Frameworks (MOFs) [6] and Covalent Organic Frameworks (COFs) [7]. AC possesses significant advantage over the other adsorbents as it can be obtained from natural and cost-effective sources. It has high surface area, porosity, pore volume those form important factors for better adsorption, in addition to their very easy processability.

A great variety of carbon precursors are available such as petroleum coke, polymers, wood, coal and biomass. Among them, different kinds of biomass such as chitosan, shells, seeds, rice husk, saw dust etc. serve as better carbon precursors as they are inexpensive and can be easily processed to prepare ACs [8–10]. The adsorption capacity of the AC is enhanced when the number of basic sites, such as nitrogen as well as metal oxides on the carbon increases [11]. For instance, the N-doped AC prepared by the stepwise crosslinking of melamine and ZnCl₂/NaCl with polyethylene terephthalate (PET) resulted in an enhanced CO₂ adsorption capacity due to the enhanced nitrogen content in the carbon as well as the enhanced basicity [12]. The N-doped AC not only serves as better CO₂ adsorbents but also as supercapacitors as well as catalyst for oxygen reduction [13–15]. For example Kaare et al. prepared AC from wood biomass followed by nitrogen doping on the AC using dicyandiamide (DCDA). This N-doped AC was used as a catalyst for oxygen reduction [16,17]. Similarly, Li et al. prepared N-doped AC which showed

^{*} Corresponding author.

E-mail address: ghanaselva.debel@gov.in (D. Selvakumar).

<https://doi.org/10.1016/j.jcou.2022.102318>

Received 3 September 2022; Received in revised form 21 October 2022; Accepted 3 November 2022

Available online 16 November 2022

2212-9820/© 2022 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

excellent electrochemical performance, where corncob was used as carbon precursor and urea as nitrogen source [18]. In another study conducted by Ying Zhao, it can be seen that the CO₂ is adsorbed due to the presence of Ba²⁺ ions as well as uncoordinated nitrogen species trapped in a porous surface making a highly polar host and thereby electrostatic interaction is occurred between CO₂ and the porous surface [19]. These basic sites react with the Lewis acidic CO₂ molecules, thereby enhancing the chemisorption of CO₂ molecule. The basicity of AC can be improved either incorporating/doping nitrogen onto the carbon framework or by incorporating basic metal ions or basic metal oxides on the carbon. However, related review articles are lacking in literatures on this topic, where the role of basicity in the adsorption of CO₂ is discussed. Existing reviews mainly focus on the preparation of carbon, its activation using different activating agents and the role of surface properties on the carbon capture. Therefore in this review we mainly focus various methods to improve basic sites on the AC for an enhanced CO₂ capture capacity.

2. Carbon capture technologies

Many technologies are commercially used to capture carbon dioxide from gaseous stream. The production of synthesis gas, ammonia, hydrogen are the processes, which involves separation of CO₂ from the gas streams on a large scale [20]. The major technologies involved are mainly, as follows:

2.1. Post-combustion

where CO₂ is captured from flue gases after combustion. In this process the flue gas is passed through a gas separation unit in which CO₂ is removed. The obtained gas stream, which is rich in CO₂ further undergo compression and hydration for transporting and storing, while the remaining flue gases such as N₂ and O₂ are evolved to the atmosphere. The gas separation involves processes such as absorption, adsorption and membrane separation. A major disadvantage of this method is the low partial pressure of CO₂ in flue gases, which is of about 0.03–0.15 bar. This is due to the fact that the flue gas evolved from the combustion system will be usually at atmospheric pressure and the flue gas themselves contain a very low concentration of CO₂. Post-combustion procedure requires a large amount of flue gas to process and it produces a large volume of impurities also. Regardless of these drawbacks, it is the most suitable process that can be used in gas-fired power plants. Also it can retrofitted without any change in its configuration in the coal-fired power plants [21]. Fig. 1 exhibits schematic representation of Post-Combustion CO₂ capture.

2.2. Oxyfuel

where the combustion of carbonaceous fuel takes place in pure oxygen atmosphere instead of air, which in turn will increase the

concentration of CO₂ in the flue gas. This process eliminates nitrogen from the flue gas and combustion of hydrocarbon or the carbonaceous fuel occurs in a completely pure oxygen atmosphere [23] at a combustion temperature of 3500 °C, which is comparatively high for typical power plant materials. The products obtained by the combustion of flue gas in oxyfuel technology are highly concentrated CO₂ and water vapour, from which CO₂ is removed by dehydration and purification under low temperature. Due to the different fuels used, such as SO_x, HCl, NO_x etc., and the diluents used in the oxygen streams there are chances for creating impurities. Similarly, the air leakage in the system is also prone to increase the impurities in the system. CO₂ captured using the oxy-combustion system is compressed and transported using aluminium, iron or steel pipelines. Fig. 2 represents the schematic diagram for oxyfuel process.

2.3. Pre-combustion

where CO₂ is captured from the reformed synthesis gas of an upstream gasification unit. In the pre-combustion process, a primary fuel is reacted with oxygen, or air and/or steam to produce CO and H₂ which is called synthesis gas or syngas. A catalytic reactor also called a shift converter is included in the combustion unit where CO is made to react with steam to produce CO₂ and more H₂. This CO₂ formed can be separated, compressed and made available for transport and storage, whereas the remaining H₂ can be used as in applications such as boilers, fuel cells, furnaces, gas turbines and engines [23]. The commonly used CO₂ capture method is absorption using a physical or chemical solvent. Chemical solvents like tertiary amine methyldiethanolamine (MDEA) degases CO₂ from the syngas at a partial pressure of about 1.5 MPa, while physical solvent processes extracts CO₂ at higher partial pressures. Adsorption is another method, which is used to separate the gases at both high and low temperature. For example, water gas shift reaction uses solid adsorbents for the conversion of CO combined with CO₂

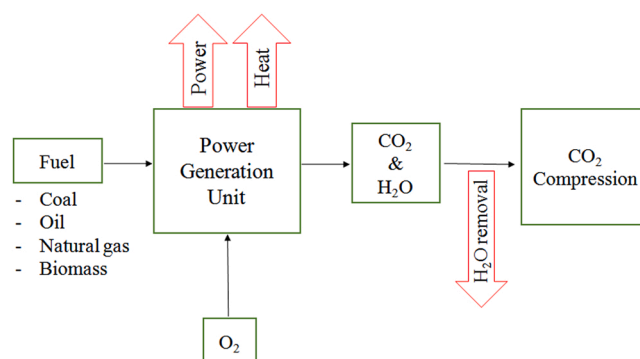


Fig. 2. Schematic representation of Oxyfuel process [22].

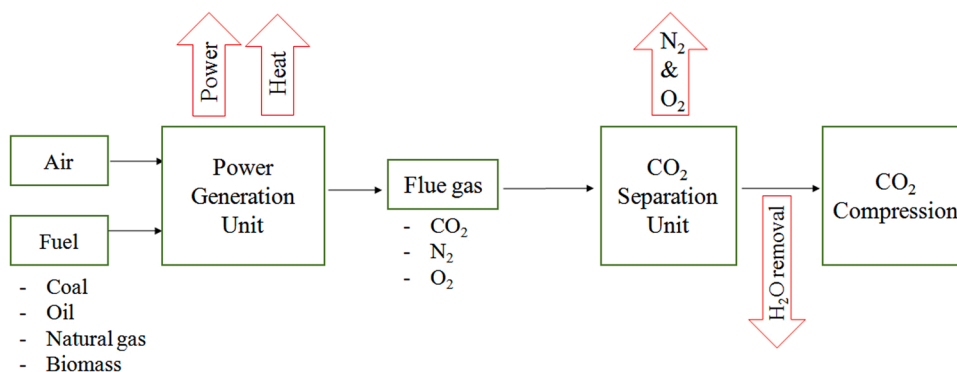


Fig. 1. Post-Combustion CO₂ capture process [22].

removal. Other possible methods are membrane technology and low temperature separation processes (e.g. cryogenic distillation) [24]. Fig. 3 represents the schematic diagram for pre-combustion process.

Among the CO₂ separation processes used in the pre-combustion as well as post combustion technologies, adsorption carries a lot of advantages such as i) reduction in the cost of CO₂ capture ii) higher efficiency of carrying CO₂ iii) lesser conditions for regeneration iv) faster rate of reaction v) minimum pressure drop [25]. For adsorption, AC acts as the suitable material which adsorbs CO₂ from a mixture of gases. Industrial applications such as urea production, extractant synthesis, beverages, fire extinguishers etc., use AC as the adsorbent. The characteristics of AC including cost effectiveness, higher surface properties, ease of availability etc., makes it a better adsorbent for pre-combustion as well as post-combustion CO₂ capture [26].

3. Preparation of AC from biomass

Different kinds of precursors are used to produce porous carbon materials such as hybrid organic-inorganic composites, synthetic polymers and biomass. However, the use of synthetic hybrid composites and synthetic polymers often suffer from extreme use of raw chemicals as well as highly complicated synthesis process [27]. Biomass is a renewable biogenic organic-inorganic energy source, which is produced by natural and anthropogenic processes, where it is naturally formed as the vegetation in land or water by photosynthesis reaction and the anthropogenic activity, which involves the processing of these natural constituents [28]. The major advantage of using biomass as the carbon precursor is its ease of processability, economical benefit as well as recyclability [29]. The benefits of biomass over other carbon precursors are, they are naturally abundant, renewable, environmental friendly, sustainable and has a greater surface area and complex pore structure [27]. However, preparation of activated carbon from certain sulfur containing biomasses such as oak and corn stover releases sulfur to the surroundings resulting in environmental hazards [30,31]. The commonly used biomass involves cellulosic based precursors, such as coconut shell, palm kernel shell, lotus stalk, date seeds, leaves, barks, sugarcane bagasse, rice husk, algae, etc. Biopolymers such as, glucose, chitin, chitosan, gelatin, starch have also been used as renewable carbon sources. The structural, surface properties as well as the chemical composition of AC vary according to the source of biomass used for their preparation [32]. Preparation of AC from the biomass involves two main

steps, i.e., i) carbonization of the biomass in the absence of oxygen at a temperature below 800 °C followed by ii) activation of the carbon for improving the microstructural properties such as, surface area, porosity, pore volume and pore diameter.

3.1. Carbonization

Carbonization is the process in which the carbon content of the sample is enriched by thermally treating the precursor in an oxygen free environment, which results in the removal of the non-carbonaceous species from the carbon network structure. The exclusion of oxygen is important so as to prevent the oxidation of the carbon as well as to limit the formation of water and other gases. Carbonization generally involves the formation of carbon, which has lower surface area, pore volume and pore diameter but still has an influence in the final product. The final product depends mainly on the carbonization temperature, flow rate of inert gas, heating rate and the dwell time. As the carbonization temperature increases the amount of carbon content simultaneously increases but the yield is decreased due to higher ash content. Similarly lower the heating rate, higher will be the carbon content due to a higher degree of dehydration. In addition, the increase in the dwell time helps to develop greater number of pores in the carbon. Furthermore, if the flow rate of inert gas is too low, it takes more time to create an inert atmosphere in the furnace which in turn results in the ashing of sample due to the presence of oxygen. Table 1 represents the yield of carbon content as well as ash content and moisture content at different carbonization temperatures for various biomass.

3.2. Activation

Next important factor, which affects the physico-chemical properties and yield of the final product is the method of activation of carbon. As the surface area and pore volume of AC increases, the number of adsorbing sites increases and as a result CO₂ adsorption also increases. Thus the enhancement in the surface properties such as surface area, porosity, pore volume, and pore diameter as well as the incorporation of surface functional groups can be achieved by the process of activation. Activation can be performed in two ways, viz., physical activation and chemical activation methods. Physical activation uses steam or CO₂ as the activating agents while in chemical activation the activating agents used are certain chemicals such as ZnCl₂, KOH, K₂CO₃, H₃PO₄, etc.

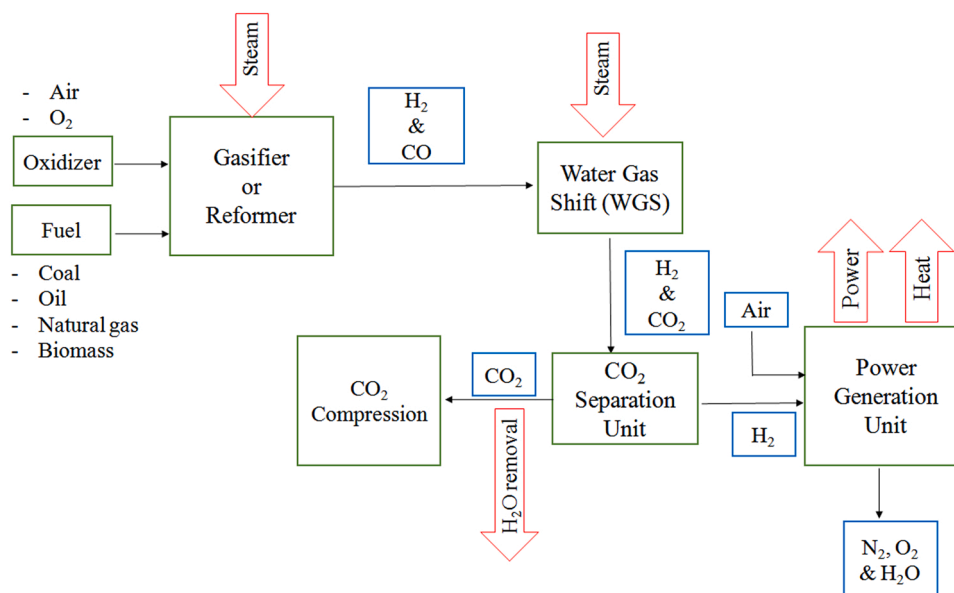


Fig. 3. Schematic representation of Pre-combustion process [22].

Table 1

Yield of carbon content as well as ash content and moisture content at different carbonization temperatures for various biomass.

| Carbon Precursor | Carbonization temperature (°C) | Carbon yield (%) | Ash content (%) | Moisture content (%) | Ref |
|-------------------|--------------------------------|------------------|-----------------|----------------------|------|
| Palm shell | 300 | – | 0.85 | 7.40 | [33] |
| Coconut Shell | 300 | – | 4.20 | 6.80 | [33] |
| Palm Kernel Shell | 350 | – | 2.6 | 6 | [34] |
| Paw paw trunk | 400 | 69 | 10.20 | 3.50 | [35] |
| Rubber wood | 500 | 80 | 8.00 | 4.00 | [36] |
| Sugarcane Bagasse | 680 | 19.5 | 3.3 | 8.4 | [37] |
| Coconut leaves | 700 | 35 | 0.16 | 0.59 | [38] |
| Spruce bark | 700 | 41 | 2.70 | – | [39] |

Physical activation of biomass with CO₂ will proceed through certain reactions (Eq. 1), which results in higher surface area and pore volume [40].



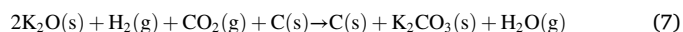
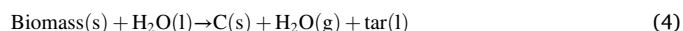
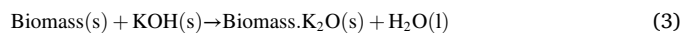
CO₂ activation results in the formation of microporous carbons, while steam activation results in meso and macroporous carbons [41]. The activation depends on factors such as, activation temperature and activation time. Ogungbenro et al. prepared AC from date seeds using CO₂ as the activating agent [42]. The different activation time and temperature used in the study led to a significant alteration in the textural characteristics as well as CO₂ capture capacity of as formed ACs. Prolonged activation time resulted in the pore damage reducing the surface area and pore volume. Activation temperature at 900 °C gave a surface area of 723.72 m²/g for the resulting AC. CO₂ activation along with NH₃ modification demonstrated by Zhang et al. produced AC with enhanced surface area and improved nitrogen content [43]. The surface area of the sample increased from 224 m²/g (for the untreated biochar) to 627 m²/g (AC).

Another method of physical activation is using steam. The activation proceeds through the following reaction (Eq. 2)

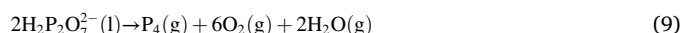


Steam activation is an effective activation technique, which results in the decrease of acidic and increase of phenolic functional groups. Also, steam activation has an effect on pore size distribution and elemental composition. Heo et al. prepared steam AC using cellulose fiber [44]. The carbonized material was activated at 800 °C using steam showed an adsorption capacity of 3.77 mmol/g and a good CO₂/N₂ selectivity due to the enhanced interaction energy between CO₂ and carbon. However, the activation of carbon using a combination of steam and CO₂ is always preferred over activation using either steam or CO₂ alone. Roman et al. reported the preparation of AC using olive stones as the carbon precursor and steam, CO₂ and combination of both for the activation of carbon. The surface area of steam activated sample was 1074 m²/g and the CO₂ activated sample was 572 m²/g while a CO₂/steam combined activation resulted in a surface area of 1187 m²/g [45]. This is due to the fact that the combination of CO₂ and steam results in the increase in their partial pressures. As a result the interaction between them and carbon gets improved, enhancing the porosity of the carbon.

Activation using chemical activating agents is the widely used activation technique for the preparation of AC due to their simple and convenient methodology, among which KOH is commonly used one. The process of KOH activation proceeds through the following reactions (Eqs. 3 to 7). The evaluation of volatile species enhances the microstructural properties of the ACs.



The surface area and porosity of the KOH AC depends on the ratio of KOH to the carbon as well as on the residence time. For example, Sun et al. prepared AC from raw hemp stem using different ratios of KOH such as 1, 3 and 5 at an activation temperature of 800 °C. Among the three ratios, carbon:KOH of ratio 1:3 was the optimal ratio to produce AC with enhanced surface area (2879 m²/g). The impregnation ratio 1:1 produced higher microporous material while the ratio 1:5 produced a material with diminished microporosity due to the intense chemical reaction [46]. Zinc chloride is another chemical activating agent, which is mainly mixed in situ with the biomass for the preparation of AC. At lower activation temperature (400 °C to 500 °C), ZnCl₂ acts as a strong dehydrating agent, while higher activation temperature (above 500 °C) results in the decomposition ZnCl₂ to zinc and chlorine resulting in the improved porosity and surface area of the AC [47,48]. The use of ZnCl₂ as the activating agent also improves the carbon content through the formation of aromatic graphitic structures. However, as the amount of ZnCl₂ used increases the yield is reduced [49]. Spagnoli et al. reported the synthesis of AC from cashew nut shell using ZnCl₂ as the activating agent with an impregnation ratio 1.5:1 (ZnCl₂: cashew nut shell) at activating temperatures 400 °C and 500 °C. The results showed that as the activation temperature increased from 400 °C to 500 °C, there occurred an enhancement the surface characteristics as well as the adsorption capacity [50]. Phosphoric acid is another activating used to improve the surface properties of AC. Olivares et al. reported that during the activation process, H₃PO₄ polymerizes to form polyphosphoric acid [51]. The monomer H₃PO₄ dehydrates to form P₂O₅ and further reacts with carbon to form P and CO₂, while the polyphosphoric acids decompose into steam, P and O in the gaseous state.



The gases formed in the above reactions create porosity on the carbon framework. Table 2 represents surface characteristics as well as CO₂ adsorption of the ACs prepared from biomass using various activating agents. Once the chemical activation process is completed, the AC are washed thoroughly with hot deionized water, in order to remove excess ZnCl₂, KOH or H₃PO₄ on the carbon which otherwise tend block the pores of the carbon and thus prevent the CO₂ adsorption process [52].

In certain cases the carbonization and activation are combined in a single step. The carbon precursor is mixed with the activating agent and is carbonized at a high temperature in an inert atmosphere to obtain the AC [66]. For example, Lee et al. prepared N-doped AC by mixing chitosan with urea (nitrogen source), KOH (activating agent) and carbonized at 700–1000 °C. Here the activating agent was mixed with the carbon precursor before carbonization. In another study, Thote et al. prepared AC from soybean where the precursor was mixed with ZnCl₂ which served as the activating agent and was carbonized at 600 °C [67].

4. Modification of AC to improve basicity

The basicity of AC is one of the important factors, which affect the adsorption as well as selectivity of CO₂ over N₂. Since CO₂ is acidic in nature, strong basic functional groups such as nitrogen or basic metal oxides can donate the lone pair of electrons resulting in the enhancement of chemisorption of CO₂. The major advantages and disadvantages

Table 2Surface characteristics as well as CO₂ adsorption of the ACs prepared from biomass using various activating agents.

| Carbon precursor | Activating agent | Activating temperature (°C) | BET surface area (m ² /g) | Pore volume (cc/g) | CO ₂ adsorption (mmol/g) capacity | Adsorption temperature (°C) & pressure (bar) | Ref |
|-------------------------------|------------------------------------|-----------------------------|--------------------------------------|--------------------|--|--|------|
| Date seeds | CO ₂ | 900 | 723.72 | 0.26 | 3.20 | 20, 1.013 | [42] |
| Cherry stones | CO ₂ | 885 | 1045.00 | 0.48 | 2.60 | 25, 1.013 | [53] |
| Rice husk | CO ₂ | 900 | 1097.00 | 0.83 | 3.1 | 25, 1.013 | [54] |
| Walnut shell | CO ₂ | 500 | 810.85 | 0.34 | 1.58 | 20, 1.013 | [55] |
| Cellulose fiber | Steam | 800 | 863.00 | 0.34 | 3.77 | 25, 1.013 | [44] |
| Willow | Steam | 800 | 840.60 | 0.57 | – | – | [56] |
| Walnut shell | Steam | 850 | 1361.00 | 0.94 | – | – | [57] |
| Cherry stones | Steam | 850 | 998.00 | 0.53 | 2.4 | 25, 1.013 | [53] |
| Olive stones | Steam & CO ₂ | 850 | 1187.00 | 0.70 | – | – | [45] |
| Coconut shells | Steam & CO ₂ | 900 | 2194.0 | 1.29 | – | – | [58] |
| Commercial AC FPV | KOH | 850 | 2406.00 | 0.46 | 3.67 | 25, 1 | [59] |
| Tea seed shell | KOH | 700 | 1503.20 | 0.64 | 3.15 | 25, 1 | [60] |
| Argan hard shells | KOH | 850 | 1889.63 | 0.87 | 5.63 | 25, 1 | [61] |
| Argan hard shells | NaOH | 850 | 1826.96 | 0.96 | 3.73 | 25, 1 | [61] |
| Chitosan | LiCl-ZnCl ₂ molten salt | 1000 | 2025.00 | 1.15 | 5.6 | 25, 1 | [62] |
| Citrus aurantium Waste Leaves | ZnCl ₂ | 800 | 937.00 | 0.57 | 6.5 | 25, 1 | [63] |
| Raw bamboo | H ₃ PO ₄ | 500 | 1492.00 | 0.93 | 1.45 | 25, 1 | [64] |
| Subabul wood | H ₃ PO ₄ | 800 | 823.00 | 0.26 | 4.52 | 25, 1.013 | [65] |

in the modification of AC to improve the basicity are tabulated in Table 3.

4.1. Nitrogen doped AC

The acidic nature of CO₂ derives it to get adsorbed on basic groups such as nitrogen containing groups. Moreover, when the graphene layer of AC is doped with nitrogen atoms, it is doped flat on to the surface of the AC, which is more stable as compared to oxygen containing functional groups (e.g., OH, COOH, and CO). When nitrogen is doped on to the carbon framework, the carbon atoms are replaced with nitrogen atoms to form a pentagonal or hexagonal shape with adjacent carbon atoms on the graphene layer. Thus, nitrogen when incorporated on to the AC commonly available in three different forms such as pyridinic, pyrrolic, and graphitic which contributes towards the higher microporosity and surface area resulting in an enhanced CO₂ capture capacity [68]. A pyridinic-N atom is included in a hexagonal structure, which is bonded to two carbon atom and has a sp² hybridization, which can donate one p electron to the π system. Pyrrolic-N atom is consisted in a pentagonal structure and is bonded to two carbon atoms with a sp³ hybridization, which will donate two p electrons to the π system. Graphitic-N is the species for which nitrogen is sp² hybridized and bonded with three carbon atoms [69]. Both pyridinic and pyrrolic N exist at the edges of graphitic carbon layers, while graphitic N exist inside the graphitic carbon layer. Oxidized-N and aminic-N are other nitrogen species observed in AC besides these three N species [70]. The formation of these nitrogen species can be controlled by changing the carbonization temperature. Aminic-N is formed at a carbonization

Table 3

Advantages and disadvantages in the modification of AC to improve basicity.

| Advantages | Disadvantages |
|--|---|
| Improvement in the lone pair of electrons which functions as Lewis bases | Byproducts formed during the modification reaction bring chemical waste to the environment Higher energy consumption as it requires high temperature for the surface modification to incorporate functional groups |
| Improvement in the CO ₂ adsorption capacity | |
| Enhancement in textural properties such as surface area and pore volume | |
| Improvement in the carbon, nitrogen and oxygen contents | |

temperature below 300 °C while around 600 °C pyridinic and pyrrolic nitrogens existed. As the carbonization temperature increases above 700 °C, the presence of graphitic nitrogen increases while the existence of all other nitrogen species diminishes [70,71]. Among these nitrogen species the pyridinic and pyrrolic nitrogen shows the maximum CO₂ adsorption capacity since the lone pair of electrons on pyridinic as well as pyrrolic nitrogen species are available for donation to the Lewis acidic CO₂ molecule enhancing the chemisorption of CO₂. Among these two, the pyridinic nitrogen shows improved basicity than pyrrolic nitrogen and thus the maximum CO₂ adsorption capacity since the lone pair of electrons in the pyrrolic nitrogen engages in delocalization while that of pyridinic nitrogen can share its lone pair of electrons [72]. Thus the increase in the number of pyrrolic as well as pyridinic nitrogen on the AC results in the enhancement of CO₂ capture capacity of the same. The amount of nitrogen doped in to the AC can be found out by using CHN analysis which gives quantitative information about the amount of C, H and N available on the sample. The qualitative as well as quantitative identification of nitrogen species present on the N-doped AC can also be performed using XPS analysis. The ratio of the peak intensities of N 1 s and C 1 s from the XPS spectra gives the amount of nitrogen content on the AC. The deconvoluted N 1 s spectrum gives the qualitative information about the species of nitrogen present on the sample. Each nitrogen species possess characteristic binding energies in the XPS spectra. Pyridine, pyrrole, graphitic nitrogen and oxidized nitrogen has binding energies 398.5 ± 0.4 eV, 400.5 ± 0.4 eV, 401.2 ± 0.4 eV and 402.9 ± 0.4 eV respectively [73]. For instance, Khan et al. prepared N-doped AC from chitosan for electrocatalytic and photocatalytic application. The XPS studies for the samples exhibited the presence of pyridinic-N, pyrrolic-N, graphitic-N, and N – O at the binding energies 398.4 eV, 399.9 eV, 400.8 eV, and 401.8 eV, respectively [70]. Fig. 4 represents the interaction between CO₂ and N-doped AC. The incorporation of nitrogen into the carbon framework can be performed through three processes, viz., (i) by amine functionalization (ii) by in-situ nitrogen doping and (iii) single-step nitrogen doping. The doping of nitrogen on AC helps in the improvement of surface properties of the AC. This is due to the fact that the incorporation of a heteroatom into the carbon framework, besides an increased basicity, causes defects in the carbon structure creating pores in the carbon network structure during pyrolysis [74].

4.1.1. Amine functionalization

In this process, the porous AC was modified with amine functionalization resulting in a more basic amine grafted AC, which improves the

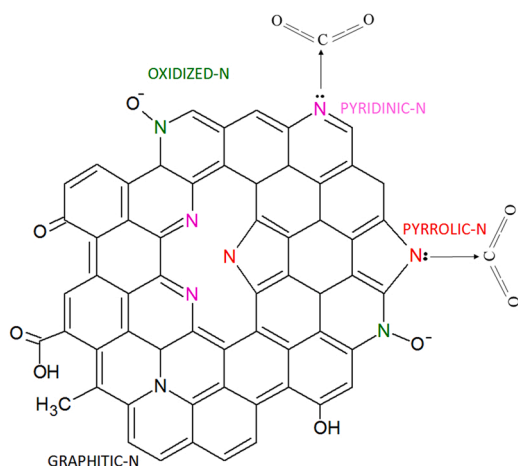


Fig. 4. Interaction between CO₂ and N-doped AC.

CO₂ adsorption extensively. When the carbon comes in contact with ammonia, the oxides on the carbon reacts with ammonia to form ammonium salt, and the amine groups undergoes dehydration or dehydrogenation producing nitriles, amides and pyridinic and pyrrolic functionalities [75]. Heidari et al., synthesized AC from eucalyptus wood using H₃PO₄ as activating agent, modified by ammonia. Nitrogen doping was dependent on the temperature and the maximum nitrogen incorporation happened for samples aminated at 800 °C. The nitrogen content of the modified AC reached 7.76% from a value of 0.52%. The basicity of the sample was determined by finding the pH at point zero charge (pH_{pzc}) and was found that the value increased after amine modification resulting in the improvement of basicity of AC. The surface area and total pore volume of the ammonia modified carbon was found to be 2079 m²/g, 1.292 cm³/g respectively whereas for the unmodified carbon it was 1889 m²/g, 1.178 cm³/g respectively which showed that the surface area and the porous nature of the AC were improved due to the ammonia modification. It had a significant effect on the CO₂ adsorption capacity also [76]. The unmodified carbon showed an adsorption capacity of 2.98 mmol/g while the ammonia modified carbon exhibited an enhanced adsorption capacity of 3.32 mmol/g. Ammonia decomposes at high temperature to produce NH₂, NH radicals and atomic H which reacts with carbon to form CH₄, (CN)₂, HCN, and H₂ [77]. Since these gases evolved through the surface of the AC, the BET surface area as well as porosity of the samples increases resulting in the increment of CO₂ adsorption capacity. But the use of ammonia is being reduced as it is lost at higher activation temperature and also due to the unpleasant odor during activation process [76,78]. The most common amine used for nitrogen doping on AC was urea. Dilokekunakul et al., prepared AC from bamboo waste and nitrogen doping was performed using urea. The sample prepared showed an enhanced nitrogen content of 3.87% and an adsorption capacity of 2.63 mmol/g while the reference sample had a nitrogen content of 0.57% and an adsorption capacity of 2.52 mmol/g [79]. Similarly Rajasekaran et al. in 2021, developed an AC from coconut shell, modified using tetraethylene pentamine (TEPA) as the dopant. The unmodified carbon showed a nitrogen content of 0.72% and a surface area of 1246 m²/g while the N-doped carbon exhibited a nitrogen content of 4.34% and a surface area of 1078 m²/g. The N-doped carbon also showed an excellent CO₂ adsorption capacity of 9.9 mmol/g. Here also the surface basicity and the microporosity of the N-doped carbon synergistically tailors the adsorption of CO₂ on to the AC [80].

4.1.2. In-situ nitrogen doping

In-situ nitrogen doping can be performed by carbonization of nitrogen containing compounds such as melamine, gelatin, etc. These compounds, already possess nitrogen in their chemical structure, which

when carbonized will be grafted on to the carbon framework. Chitosan is another biomass which serves as both carbon and nitrogen source. The synthesis of N-doped AC was carried out using chitosan as the carbon/nitrogen precursor by Fujiki et al. Chitosan was mixed with different alkali carbonates for activation, and carbonized. The AC using Rb₂CO₃ as the activating agent at an activation temperature of 600 °C showed a surface area of 1496 m²/g, pore volume of 0.63 cc/g, nitrogen content 3.15% and CO₂ capture capacity of 4.88 mmol/g [81]. Similarly, Alabadi et al. synthesized AC by the co-carbonization of gelatin and starch. Here gelatin served as the carbon & nitrogen source. Therefore, its carbonization along with starch resulted in the formation of AC with improved surface properties, nitrogen content and thus CO₂ enhanced capture capacity [82].

4.1.3. Single step nitrogen doping

Another method of nitrogen incorporation is the single step N-doping, where the carbon precursor is mixed with a nitrogen source such as urea or melamine before carbonization. Here carbonization will result in the doping of nitrogen from the nitrogen source on to the carbon framework. Nitrogen doped AC was prepared using sugarcane bagasse, where it is mixed with urea that serves as the nitrogen source in a study by Han et al. In this study, the N-doped AC possessed a nitrogen content of 1.98% with an enhanced surface area and pore volume and possessed a CO₂ capture capacity of 4.8 mmol/g [83]. This suggested that the incorporation of nitrogen had a significant effect on the texture properties as well as the CO₂ adsorption capacity of the AC. In a recent study, Zgrzebnicki et al. mixed polyfurfuryl alcohol with urea which served as the nitrogen dopant for the preparation of N-doped AC. The surface area as well as the pore volume of the N-doped AC was found to be 616 m²/g and 0.26 cm³/g respectively. Here also the doping of nitrogen had a strong influence on the pore structure and basicity of the AC which in turn enhanced the CO₂ adsorption capacity from 0.8 mg/g to 1.8 mg/g [84]. However, in some cases addition of nitrogen source to the carbon precursor can reduce the surface area as well as the CO₂ adsorption capacity. Malini et al., prepared AC from chitosan using hexamethylene tetramine (HMT) as an additional nitrogen source. The adsorption capacity of chitosan derived AC was greater than that of chitosan/HMT derived AC. The deterioration in the surface area, pore volume as well as CO₂ capture capacity can be ascribed to the hydrogen bonding interaction between chitosan and HMT which results in the reduction of free volume of the polymer network. Also, the increase in the pH due to the addition of HMT to chitosan causes the physical crosslinking of chitosan polymer which in turn decreases the surface area of the AC [85].

Table 4 represents the various N-dopants on AC and their effect on surface properties as well as the CO₂ adsorption capacity.

Here in the study by Quan et al., the adsorption capacity of N-doped AC is seen to be lower than the undoped counterpart [60]. In this case, the specific surface area of the AC was considered as the dominant factor than the basicity for CO₂ capture and the undoped carbon possessed the maximum specific surface area. The decrease in the surface properties for the N-doped ACs was due to the collapsing of pores during the thermal process for nitrogen doping.

4.2. Metal oxide doped AC

Another important criteria to enhance the basicity, surface chemistry as well as the CO₂ capture capacity other than nitrogen doping is the incorporation of basic metal oxide on to the AC surface. The adsorption as well as selectivity of CO₂ over N₂ is enhanced by the electrostatic interaction between the CO₂ molecule and the impregnated metal ion. The commonly used metal oxides are alkaline earth metal oxides such as MgO, CaO, etc., and transition metal oxides such as CuO, NiO, CoO etc. The mechanism of adsorption of CO₂ on to the metal impregnated AC was illustrated in Fig. 5. The metal oxides are commonly impregnated on to the AC surface through wet impregnation method. The carbon precursor is mixed with metal oxide solutions and prior to a high

Table 4
Surface properties and CO₂ adsorption capacity for various N-doped ACs.

| Carbon precursor | N source used | Amine functionalization/ In-situ nitrogen doping | N content (%) | BET surface area (m ² /g) | Pore volume (cc/g) | CO ₂ adsorption capacity (mmol/g) | Adsorption temperature (°C) & pressure (bar) | Ref |
|------------------------|---------------|--|---------------|--------------------------------------|--------------------|--|--|------|
| Eucalyptus wood | Ammonia | Amine functionalization | 7.76 | 2079 | 1.29 | 3.22 | 30, 1 | [76] |
| Cotton stalk | Ammonia | Amine functionalization | 0.71 | 434.92 | 0.19 | 1.81 | 20, 1.013 | [78] |
| Black locus | Ammonia | Amine functionalization | 7.21 | 2511 | 1.35 | 5.05 | 25, 1 | [86] |
| Microalgae | Ammonia | Amine functionalization | 2.57 | 1509 | 0.82 | 4.03 | 25, 1.013 | [87] |
| Bamboo waste | Urea | Amine functionalization | 3.87 | 532 | – | 2.63 | 25, 1 | [79] |
| Coconut shell | Urea | Amine functionalization | 1.23 | 1535 | 0.96 | 4.80 | 25, 1 | [88] |
| Rice husk | Chitosan | Amine functionalization | – | 1496 | 0.78 | 3.68 | 25, 1 | [89] |
| Tea seed | Melamine | Amine functionalization | 3.41 | 1187.93 | 0.52 | 2.75 | 25, 1 | [60] |
| Chitosan | – | In-situ N doping | 3.15 | 1496 | 0.63 | 4.88 | 25, 1 | [81] |
| Gelatin and starch | – | In-situ N doping | 3.00 | 1636 | 0.51 | 3.84 | 25, 1 | [82] |
| Chitosan | – | In-situ N doping | 4.59 | 1381 | 0.57 | 3.86 | 25, 1.013 | [90] |
| Microalgae and glucose | – | In-situ N doping | 1.47 | 1940 | 0.82 | 4.50 | 25, 1 | [91] |
| Prawn shell | – | In-situ N doping | 6.00 | 554.7 | 0.17 | – | – | [92] |
| Sugarcane Bagasse | Urea | Single step N doping | 1.98 | 1113 | 0.51 | 4.80 | 25, 1 | [83] |
| Coconut shell | Glucosamine | Single step N doping | 4.61 | 984.91 | 0.65 | 4.23 | 30, 1 | [93] |
| Glucose | Melamine | Single step N doping | 2.07 | 3247 | 3.09 | 4.95 | 25, 1 | [94] |

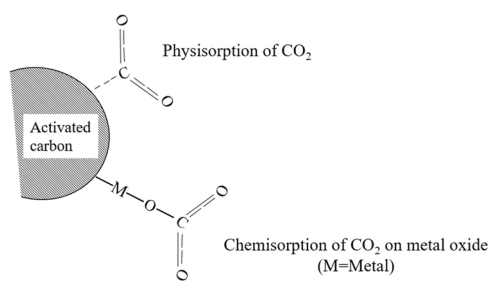


Fig. 5. Mechanism of metal oxide impregnated AC.

temperature carbonization process or the AC is mixed with metal oxide solution and then is calcined at a higher temperature. For example, Botome et al. prepared AC using CCA (chromated copper arsenate) treated wood pyrolyzed at 700 °C for CO₂ capture and the sample showed an adsorption capacity of 1.88 mmol/g [95]. The impregnation of metal oxide on the AC makes a significant effect on the structural as well as CO₂ adsorption property depending on the amount of metal loading. If the metal loading is considerably low, there won't be any improvement in the adsorption capacity. While significantly high amount of metal loading will lead to the clogging of pores resulting in the lowering of surface area and pore volume. Hosseini et al. suggested that the catalytic surfaces produced on the Cu or Zn modified AC provides active sites to capture CO₂. Lesser adsorption energy is needed for the chemisorption oxygen atoms of CO₂ on cationic Cu²⁺ and Zn²⁺ since there is a shorter distances between these cations and CO₂ molecule [96]. Investigations on the effect of metal impregnation on carbon before and after activation showed that, when transition metal oxides such as CrO₃, CoO, Co₃O₄, etc., were added to the carbon before activation process these metals acted as catalysts for the degasification reaction resulting in the formation of meso and micropores on the carbon. The development of wider mesopores results in the dispersion of metal species while the micropore formation results in the deposition of metal oxides on the surface improving the efficiency of the AC [97,98]. On the other hand doping of these metal oxides after activation of the carbon results in the reduction of surface properties due to the blocking of pores on the surface by the metal ions. Moradi et al. developed Fe-impregnated AC for hydrogen storage where the AC before metal impregnation had a surface area of 1640 m²/g and a pore volume of 0.93 cc/g which reduced to 1511 m²/g and 0.81 cc/g respectively after impregnation [99].

On comparison of the CO₂ adsorption capacity of metal oxide impregnated AC derived from palm-kernel shell studied by Hidayu et al., it was found out that CeO₂ impregnated AC showed the maximum adsorption capacity than that of TiO₂ and BaO impregnated AC. Here metal Ce donate the oxygen atoms to oxidize with CO₂ enhancing the CO₂ adsorption [100]. The metal oxide impregnation on AC was confirmed from the XRD studies. The XRD patterns for AC showed two broad peaks at 2θ= 20–30° and 40–50°, while in the case of metal oxide impregnated AC these two broad peaks disappeared and substituted with additional diffraction peaks of metal oxide. In a similar study by Hidayu et al., where the AC was impregnated with different metal oxides, the BaO impregnated AC showed the higher and MgO showed the lowest CO₂ adsorption capacity [101]. Here the loading of MgO resulted in the blockage of pores and thus the decrease in the adsorption capacity. On the other hand impregnation of BaO improved the basicity of AC, which in turn increases the electrostatic interaction between CO₂ and BaO resulting in the chemisorption of CO₂. In a recent report, Malini et al. impregnated barium oxide in various ratios onto AC derived from chitosan using wet impregnation method followed by thermal treatment at under nitrogen atmosphere. The studies showed that 10 wt% barium oxide loaded AC exhibited improved surface properties as well as CO₂ adsorption capacity while an increase in the concentration of barium oxide resulted in the decline CO₂ adsorption properties [102]. The amounts of BaO loaded in to the carbon was quantitatively confirmed using the UV-Visible spectroscopic method, which was found to be 5.2% for 10 wt% barium oxide loaded AC as consistent with the EDS mapping and spot analysis results. The structural and CO₂ adsorption property of ACs mixed with various metal salts are tabulated in Table 5.

5. Conclusion and way forward

Global warming is the major concerns faced by the human being in this century and the main cause for that is the increased CO₂ concentration in the atmosphere. The most important way to control the increasing level of CO₂ is Carbon Capture and Sequestration, which uses adsorption as the significant method. Use of AC helps to adsorb the CO₂ in an effective way. In this review the recent works on the synthesis of AC from biomass using different carbonization and activation processes have been summarized. The surface characteristics as well as CO₂ capture can be improved by increasing the basicity of the AC either by nitrogen doping or by metal impregnations. The various nitrogen dopants as well as metal oxides used in the recent studies, as well as their effect on the surface characteristics and CO₂ capture capacity were compared,

Table 5Structural and CO₂ adsorption property of ACs mixed with various metal salts.

| Carbon precursor | Metal impregnated | BET surface area (m ² /g) | Pore volume (cc/g) | CO ₂ adsorption capacity (mmol/g) | Adsorption temperature (°C) & pressure (bar) | Ref |
|-------------------|--------------------------|--------------------------------------|--------------------|--|--|-------|
| Wood | Chromium copper arsenate | 1215 | 0.750 | 1.88 | 25, 1 | [95] |
| Coconut shell | CuO | 1339 | 0.540 | 0.37 | 25, 1 | [103] |
| Saw dust | MgO | 306 | – | 2.70 | 50, 1 | [104] |
| Persian ironwood | CuO | 1918 | 1.570 | 6.78 | 30, 1 | [105] |
| Whitewood | MgO | 760 | 0.399 | 1.11 | 25, 1 | [106] |
| Palm kernel shell | BaO | 1260 | 0.670 | – | | [101] |
| Nypha fruticans | CuO & MgO | 727.7 | 0.260 | – | | [107] |
| Chitosan | BaO | 259.01 | 0.027 | 1.95 | 25, 1 | [102] |

tabulated and discussed.

There are still many challenges faced in the field of CO₂ adsorption by biomass derived AC. The large scale production of porous AC from biomass is yet to be investigated. The production cost of the precursors, other chemicals as well as the experimental setup has to be thoroughly examined. The bulk production of the AC material should meet the conditions such as efficiency of CO₂ capturing capacity and environmental sustainability. Another study should be conducted on the conversion of side products produced during the fabrication of the AC material on account of pollution control. Lastly, there is a dearth of scientific information regarding the conversion of adsorbed CO₂ into useful products. Therefore more studies on the practical application of CO₂ conversion need to be conducted.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

No data was used for the research described in the article.

Acknowledgement

The authors gratefully acknowledge Director, DEBEL-DRDO, Bangalore in providing the necessary facilities to conduct this work. One of the authors, MK thankfully acknowledges a research fellowship from DRDO, the Government of India.

References

- [1] H.H. Ahmad, et al., Evaluation of catastrophic global warming due to coal combustion, paradigm of South Asia, *Int. J. Innov. Sci. Technol.* 3 (4) (2021) 198.
- [2] K.S. Lakhi, et al., Energy efficient synthesis of highly ordered mesoporous carbon nitrides with uniform rods and their superior CO₂ adsorption capacity, *J. Mater. Chem. A* 5 (31) (2017) 16220.
- [3] Y. Ji, et al., A high adsorption capacity bamboo biochar for CO₂ capture for low temperature heat utilization, *Sep. Purif. Technol.* (2022), 121131.
- [4] J. Zhou, et al., Scalable fabrication of high-selective SSZ-13 membranes on 19-channel monolithic supports for efficient CO₂ capture, *Sep. Purif. Technol.* (2022), 121122.
- [5] Oliveira, D.E., et al., CO₂ Capture over MCM-41 and SBA-15 Mesoporous Silicas Impregnated with Chitosan, *Industrial & Engineering Chemistry Research*, 2022.
- [6] J.J. You, et al., A cage-based metal-organic framework with a unique tetrahedral node for size-selective CO₂ capture, *J. Solid State Chem.* (2022), 123140.
- [7] Y. Zeng, et al., Carbon dioxide capture: Covalent organic frameworks for CO₂ capture, *Adv. Mater.* 28 (15) (2016) 3032.
- [8] J. Song, et al., Superior carbon-based CO₂ adsorbents prepared from poplar anthers, *Carbon* 69 (2014) 255–263.
- [9] Y. Gao, et al., High surface area and oxygen-enriched activated carbon synthesized from animal cellulose and evaluated in electric double-layer capacitors, *RSC Adv.* 5 (40) (2015) 31375.
- [10] X. Zhang, et al., High temperature ammonia modification of rice husk char to enhance CO₂ adsorption: influence of pre-deashing, *RSC Adv.* 5 (128) (2015), 106280.
- [11] J.J. Li, et al., K⁺-enhanced electrocatalytic CO₂ reduction to multicarbon products in strong acid, *Rare Met.* 41 (3) (2022) 723.
- [12] Song, C., et al., Converting poly (ethylene terephthalate) waste into N-doped porous carbon as CO₂ adsorbent and solar steam generator. *Green Energy & Environment*, 2020.
- [13] A.L. Rimmel, et al., Nickel and Nitrogen-Doped Bifunctional ORR and HER Electrocatalysts Derived from CO₂, *ACS Sustain. Chem. Eng.* 10 (1) (2021) 134.
- [14] S. Ratso, et al., CO₂ turned into a nitrogen doped carbon catalyst for fuel cells and metal–air battery applications, *Green. Chem.* 23 (12) (2021) 4435.
- [15] X. Liu, et al., Controlled growth of unusual nanocarbon allotropes by molten electrolysis of CO₂, *Catalysts* 12 (2) (2022) 125.
- [16] K. Kaare, et al., Biomass-derived graphene-like catalyst material for oxygen reduction reaction, *ChemNanoMat* 7 (3) (2021) 307.
- [17] K.T. Kaare, et al., Highly active wood-derived nitrogen-doped carbon catalyst for the oxygen reduction reaction, *ACS Omega* 5 (37) (2020) 23578.
- [18] B. Li, et al., Nitrogen-doped activated carbon for a high energy hybrid supercapacitor, *Energy Environ. Sci.* 9 (1) (2016) 102.
- [19] Y. Zhao, et al., Two comparable Ba-MOFs with similar linkers for enhanced CO₂ capture and separation by introducing N-rich groups, *Rare Met.* 40 (2) (2021) 499.
- [20] P. Markewitz, et al., Worldwide innovations in the development of carbon capture technologies and the utilization of CO₂, *Energy Environ. Sci.* 5 (6) (2012) 7281.
- [21] P. Feron, et al., CO₂ capture process principles and costs. *Oil Gas. Sci. Technol.* 60 (3) (2005) 451.
- [22] Riboldi, L., Assessment of pressure swing adsorption as CO₂ capture technology in coal-fired power plants. 2016.
- [23] E. Rubin, H. De Coninck, TNO (2004): Cost Curves for CO₂ Storage, Part, IPCC special report on carbon dioxide capture and storage, 2, Cambridge University Press, UK, 2005, p. 14. TNO (2004): Cost Curves for CO₂ Storage, Part.
- [24] A.M. Yousef, et al., New approach for biogas purification using cryogenic separation and distillation process for CO₂ capture, *Energy* 156 (2018) 328.
- [25] A. Mukherjee, et al., Review of post-combustion carbon dioxide capture technologies using activated carbon, *J. Environ. Sci.* 83 (2019) 46.
- [26] R. Saxena, et al., Carbon dioxide capture and sequestration by adsorption on activated carbon, *Energy Procedia* 54 (2014) 320.
- [27] J. Li, et al., Selective preparation of biomass-derived porous carbon with controllable pore sizes toward highly efficient CO₂ capture, *Chem. Eng. J.* 360 (2019) 250.
- [28] J. Serafin, et al., Highly microporous activated carbons from biomass for CO₂ capture and effective micropores at different conditions. *J. CO₂ Util.* 18 (2017) 73.
- [29] L. Luo, et al., Heteroatom self-doped activated biocarbons from fir bark and their excellent performance for carbon dioxide adsorption, *J. CO₂ Util.* 25 (2018) 89.
- [30] S. Cheah, et al., Speciation of sulfur in biochar produced from pyrolysis and gasification of oak and corn stover, *Environ. Sci. Technol.* 48 (15) (2014) 8474.
- [31] J. Ouyang, et al., Biomass-derived activated carbons for the removal of pharmaceutical micropollutants from wastewater: a review, *Sep. Purif. Technol.* 253 (2020), 117536.
- [32] S. Manocha, et al., Activated carbon from biomass, *AIP Conf. Proc.* 1538 (1) (2013) 120.
- [33] I. Mustafa, et al., Palm shell-derived activated carbon adsorbent is better than that of coconut shell: comparative studies of cod adsorption from palm oil mill effluent, *Carbon* 15 (2) (2022) 738.
- [34] A.S. Nwosi-Anele, et al., Production, activation and characterisation of PKS-biochar from *elaeis guineensis* biomass activated with HCl for optimum produced water treatment, *Int. J. Recent Eng. Sci.* 9 (1) (2022).
- [35] N. Udeh, et al., Production and characterization of paw-paw trunk activated carbon, *Am. Acad. Sci. Res. J. Eng., Technol., Sci.* 87 (1) (2022) 9.
- [36] Sasmita, A., et al., CO adsorption performance of rubber wood activated carbon. *Materials Today: Proceedings*, 2022.
- [37] M. Alhassan, et al., Comparative studies of CO₂ capture using acid and base modified activated carbon from sugarcane bagasse. *Biofuels* 9 (6) (2018) 719.

- [38] R. Abd Rashid, et al., FeCl₃-activated carbon developed from coconut leaves: characterization and application for methylene blue removal, *Sains Malays.* 47 (3) (2018) 603.
- [39] G.S. dos Reis, et al., Application of design of experiments (DoE) for optimised production of micro-and mesoporous Norway spruce bark activated carbons, *Biomass- Convers. Biorefin.* (2021) 1.
- [40] M.J. Prauchner, et al., Tailoring biomass-based activated carbon for CH₄ storage by combining chemical activation with H₃PO₄ or ZnCl₂ and physical activation with CO₂, *Carbon* 110 (2016) 138.
- [41] J. Pallares, et al., Production and characterization of activated carbon from barley straw by physical activation with carbon dioxide and steam, *Biomass- Bioenergy* 115 (2018) 64.
- [42] A.E. Ogungbenro, et al., Activated carbon from date seeds for CO₂ capture applications, *Energy Procedia* 114 (2017) 2313.
- [43] X. Zhang, et al., Nitrogen enriched biochar modified by high temperature CO₂-ammonia treatment: Characterization and adsorption of CO₂, *Chem. Eng. J.* 257 (2014) 20.
- [44] Y.J. Heo, et al., A role of steam activation on CO₂ capture and separation of narrow microporous carbons produced from cellulose fibers, *Energy* 91 (2015) 142.
- [45] S. Román, et al., Control of pore development during CO₂ and steam activation of olive stones, *Fuel Process. Technol.* 89 (8) (2008) 715.
- [46] W. Sun, et al., Hemp-derived activated carbons for supercapacitors, *Carbon* 103 (2016) 181.
- [47] Z. Liu, et al., Preparation and characterization of activated carbon fibers from liquefied wood by ZnCl₂ activation, *BioResources* 11 (2) (2016) 3178.
- [48] S.C. Wang, et al., Fine activated carbon from rubber fruit shell prepared by using ZnCl₂ and KOH activation, *Appl. Sci.* 11 (9) (2021) 3994.
- [49] D. Angin, et al., Production and characterization of activated carbon from sour cherry stones by zinc chloride, *Fuel* 115 (2014) 804.
- [50] A.A. Spagnoli, et al., Adsorption of methylene blue on cashew nut shell based carbons activated with zinc chloride: the role of surface and structural parameters, *J. Mol. Liq.* 229 (2017) 465.
- [51] M. Olivares-Marín, et al., Thermal behaviour of lignocellulosic material in the presence of phosphoric acid, *Influ. Acid. Content Initial Solut. Carbon* 11 (44) (2006) 2347.
- [52] R. Hoseinzadeh Hesari, et al., Comparison of oil palm shell-based activated carbons produced by microwave and conventional heating methods using zinc chloride activation, *J. Anal. Appl. Pyrolysis* 104 (2013) 176.
- [53] N. Álvarez-Gutiérrez, et al., Cherry-stones-based activated carbons as potential adsorbents for CO₂/CH₄ separation: effect of the activation parameters, *Greenh. Gases: Sci. Technol.* 5 (6) (2015) 812.
- [54] M. Li, et al., Preparation of a dual pore structure activated carbon from rice husk char as an adsorbent for CO₂ capture, *Fuel Process. Technol.* 186 (2019) 35.
- [55] Mesfer Al, et al., Synthesis and characterization of high-performance activated carbon from walnut shell biomass for CO₂ capture, *Environ. Sci. Pollut. Res.* 27 (13) (2020) 15020.
- [56] M. Kottowski, et al., Effect of steam activated biochar application to industrially contaminated soils on bioavailability of polycyclic aromatic hydrocarbons and ecotoxicity of soils, *Sci. Total Environ.* 566–567 (2016) 1023.
- [57] J.F. González, et al., Porosity development in activated carbons prepared from walnut shells by carbon dioxide or steam activation, *Ind. Eng. Chem. Res.* 48 (16) (2009) 7474.
- [58] K. Yang, et al., Preparation of high surface area activated carbon from coconut shells using microwave heating, *Bioresour. Technol.* 101 (15) (2010) 6163.
- [59] J. Sreńscek-Nazzal, et al., Advances in modification of commercial activated carbon for enhancement of CO₂ capture, *Appl. Surf. Sci.* 494 (2019) 137.
- [60] C. Quan, et al., Nitrogen-doping activated biomass carbon from tea seed shell for CO₂ capture and supercapacitor, *Int. J. Energy Res.* 44 (2) (2020) 1218.
- [61] O. Boujibar, et al., CO₂ capture using N-containing nanoporous activated carbon obtained from argan fruit shells, *J. Environ. Chem. Eng.* 6 (2) (2018) 1995.
- [62] P. Wang, et al., Molten salt template synthesis of hierarchical porous nitrogen-containing activated carbon derived from chitosan for CO₂ capture, *ACS Omega* 5 (36) (2020) 23460.
- [63] S. Balou, et al., Synergistic effect of nitrogen doping and ultra-microporosity on the performance of biomass and microalgae-derived activated carbons for CO₂ capture, *ACS Appl. Mater. Interfaces* 12 (38) (2020) 42711.
- [64] I.S. Ismail, et al., Production and characterization of bamboo-based activated carbon through single-step H₃PO₄ activation for CO₂ capture, *Environ. Sci. Pollut. Res.* 29 (9) (2022) 12434.
- [65] Malleh, D., et al., Synthesis, Characterization and Evaluation of Porous Carbon Adsorbents Derived from Waste Biomass for CO₂ Capture. Available at SSRN 4053261.
- [66] D.W. Lee, et al., Straightforward synthesis of hierarchically porous nitrogen-doped carbon via pyrolysis of chitosan/urea/KOH mixtures and its application as a support for formic acid dehydrogenation catalysts, *ACS Sustain. Chem. Eng.* 5 (11) (2017) 9935.
- [67] J.A. Thote, et al., In situ nitrogen enriched carbon for carbon dioxide capture, *Carbon* 48 (2) (2010) 396.
- [68] L. Spessato, et al., Nitrogen-doped activated carbons with high performances for CO₂ adsorption, *J. CO₂ Util.* 61 (2022), 102013.
- [69] X. Wang, et al., An introduction to the chemistry of graphene, *Phys. Chem. Chem. Phys.* 17 (43) (2015) 28484.
- [70] A. Khan, et al., Chitosan-based N-doped carbon materials for electrocatalytic and photocatalytic applications, *ACS Sustain. Chem. Eng.* 8 (12) (2020) 4708.
- [71] S. Kundu, et al., The formation of nitrogen-containing functional groups on carbon nanotube surfaces: a quantitative XPS and TPD study, *Phys. Chem. Chem. Phys.* 12 (17) (2010) 4351.
- [72] X. Zhu, et al., Efficient CO₂ capture by porous, nitrogen-doped carbonaceous adsorbents derived from task-specific ionic liquids, *ChemSusChem* 5 (10) (2012) 1912.
- [73] E. Raymundo-Piñero, et al., The role of different nitrogen functional groups on the removal of SO₂ from flue gases by N-doped activated carbon powders and fibres, *Carbon* 41 (10) (2003) 1925.
- [74] J. Chen, et al., Outstanding supercapacitor performance of nitrogen-doped activated carbon derived from shaddock peel, *J. Energy Storage* 39 (2021), 102640.
- [75] M.G. Plaza, et al., Development of low-cost biomass-based adsorbents for postcombustion CO₂ capture, *Fuel* 88 (12) (2009) 2442–2447.
- [76] A. Heidari, et al., Evaluation of CO₂ adsorption with eucalyptus wood based activated carbon modified by ammonia solution through heat treatment, *Chem. Eng. J.* 254 (2014) 503.
- [77] H.P. Boehm, et al., Carbon as a catalyst in oxidation reactions and hydrogen halide elimination reactions, *Fuel* 63 (8) (1984) 1061.
- [78] Z. Xiong, et al., Influence of NH₃/CO₂ modification on the characteristic of biochar and the CO₂ capture, *BioEnergy Res.* 6 (4) (2013) 1147.
- [79] W. Dilokekunakul, et al., Effects of nitrogen and oxygen functional groups and pore width of activated carbon on carbon dioxide capture: Temperature dependence, *Chem. Eng. J.* 389 (2020), 124413.
- [80] N. Rajasekaran, et al., The synergistic character of highly N-doped coconut-shell activated carbon for efficient CO₂ capture, *ChemistrySelect* 6 (34) (2021) 9149.
- [81] J. Fujiki, K. Yogo, The increased CO₂ adsorption performance of chitosan-derived activated carbons with nitrogen-doping, *Chem. Commun.* 52 (1) (2016) 186.
- [82] A. Alabadi, et al., Highly porous activated carbon materials from carbonized biomass with high CO₂ capturing capacity, *Chem. Eng. J.* 281 (2015) 606.
- [83] J. Han, et al., The N-doped activated carbon derived from sugarcane bagasse for CO₂ adsorption, *Ind. Crops Prod.* 128 (2019) 290.
- [84] M. Zgrzebnicki, et al., N-doped activated carbon derived from furfuryl alcohol—development of porosity, properties, and adsorption of carbon dioxide and ethene, *Chem. Eng. J.* 427 (2022), 131709.
- [85] K. Malini, et al., Nitrogen doped activated carbon derived from chitosan/hexamethylenetetramine: structural and CO₂ adsorption properties, *J. Porous Mater.* 29 (2022) 1539.
- [86] C. Zhang, et al., Enhancement of CO₂ capture on biomass-based carbon from black locust by KOH activation and ammonia modification, *Energy Fuels* 30 (5) (2016) 4181.
- [87] H. Luo, et al., Preparation of N-doped activated carbons with high CO₂ capture performance from microalgae (*Chlorococcum* sp.), *RSC Adv.* 6 (45) (2016) 38724.
- [88] J. Chen, et al., Enhanced CO₂ capture capacity of nitrogen-doped biomass-derived porous carbons, *ACS Sustain. Chem. Eng.* 4 (3) (2016) 1439.
- [89] S. He, et al., Facile preparation of N-doped activated carbon produced from rice husk for CO₂ capture, *J. Colloid Interface Sci.* 582 (2021) 90.
- [90] X. Fan, et al., Chitosan derived nitrogen-doped microporous carbons for high performance CO₂ capture, *Carbon* 61 (2013) 423.
- [91] M. Sevilla, et al., High-performance CO₂ sorbents from algae, *RSC Adv.* 2 (33) (2012) 12792.
- [92] F. Gao, et al., Nitrogen-doped activated carbon derived from prawn shells for high-performance supercapacitors, *Electrochim. Acta* 190 (2016) 1134.
- [93] A. Yauri, et al., Reusable nitrogen-doped mesoporous carbon adsorbent for carbon dioxide adsorption in fixed-bed, *Energy* 138 (2017) 776.
- [94] A. Rehman, et al., Tunable nitrogen-doped microporous carbons: Delineating the role of optimum pore size for enhanced CO₂ adsorption, *Chem. Eng. J.* 362 (2019) 731.
- [95] M.L. Botomé, et al., Preparation and characterization of a metal-rich activated carbon from CCA-treated wood for CO₂ capture, *Chem. Eng. J.* 321 (2017) 614.
- [96] S. Hosseini, et al., Adsorption of carbon dioxide using activated carbon impregnated with Cu promoted by zinc, *J. Taiwan Inst. Chem. Eng.* 52 (2015) 109.
- [97] M. Alvim-Ferraz, et al., Micropore size distribution of activated carbons impregnated after carbonization, *J. Porous Mater.* 10 (1) (2003) 47.
- [98] Alvim-Ferraz, et al., Impregnated active carbons to control atmospheric emissions: influence of impregnation methodology and raw material on the catalytic activity, *Environ. Sci. Technol.* 39 (16) (2005) 6231.
- [99] S. Moradi, Low-cost metal oxide activated carbon prepared and modified by microwave heating method for hydrogen storage, *Korean J. Chem. Eng.* 31 (9) (2014) 1651.
- [100] A. Hidayu, et al., Impregnated palm kernel shell activated carbon for CO₂ adsorption by pressure swing adsorption, *Indian J. Sci. Technol.* 10 (2) (2017).
- [101] A. Hidayu, et al., Preparation and characterization of impregnated activated carbon from palm kernel shell and coconut shell for CO₂ capture, *Procedia Eng.* 148 (2016) 106.
- [102] K. M., et al., Effect of barium activation on chitosan derived carbon: enhancement of CO₂ adsorption capacity. *International Journal of Environmental Analytical Chemistry*, 2021.
- [103] H. Yi, et al., Simultaneous Removal of SO₂, NO, and CO₂ on metal-modified coconut shell activated carbon, *Water, Air, Soil Pollut.* 225 (5) (2014) 1965.
- [104] W.J. Liu, et al., Mesoporous carbon stabilized MgO nanoparticles synthesized by pyrolysis of MgCl₂ preloaded waste biomass for highly efficient CO₂ capture, *Environ. Sci. Technol.* 47 (16) (2013) 9397.

- [105] M. Nowrouzi, et al., Superior CO₂ capture performance on biomass-derived carbon/metal oxides nanocomposites from Persian ironwood by H₃PO₄ activation, *Fuel* 223 (2018) 99.
- [106] S. Shahkarami, et al., Enhanced CO₂ adsorption using MgO-impregnated activated carbon: impact of preparation techniques, *Ind. Eng. Chem. Res.* 55 (20) (2016) 5955.
- [107] W.N.R.W. Isahak, et al., Enhanced physical and chemical adsorption of carbon dioxide using bimetallic copper–magnesium oxide/carbon nanocomposite, *Res. Chem. Intermed.* 44 (2) (2018) 829.