

Efficacies of Carbon-Based Adsorbents for Carbon Dioxide Capture

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Keywords: surface area, Adsorption, carbon nanomaterials, activated carbon, Carbon Dioxide Capture

Abstract:

Carbon dioxide (CO₂), a major greenhouse gas, capture has recently become a crucial technological solution to reduce atmospheric emissions from fossil fuel burning. Thereafter, many efforts have been put forwarded to reduce the burden on climate change by capturing and separating CO₂, especially from larger power plants and from the air through the utilization of different technologies (e.g., membrane, absorption, microbial, cryogenic, chemical looping, and so on). Those technologies have often suffered from high operating costs and huge energy consumption. On the right side, physical process, such as adsorption, is a cost-effective process, which has been widely used to adsorb different contaminants, including CO₂. Henceforth, this review covered the overall efficacies of CO₂ adsorption from air at 196 K to 343 K and different pressures by the carbon-based materials (CBMs). Subsequently, we also addressed the associated challenges and future opportunities for CBMs. According to this review, the efficacies of various CBMs for CO₂ adsorption have followed the order of carbon nanomaterials (i.e., graphene, graphene oxides, carbon nanotubes, and their composites) < mesoporous -microporous or hierarchical porous carbons < biochar and activated biochar < activated carbons.

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Review

Efficacies of Carbon-Based Adsorbents for Carbon Dioxide Capture

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Abstract: Carbon dioxide (CO₂), a major greenhouse gas, capture has recently become a crucial technological solution to reduce atmospheric emissions from fossil fuel burning. Thereafter, many efforts have been put forwarded to reduce the burden on climate change by capturing and separating CO₂, especially from larger power plants and from the air through the utilization of different technologies (e.g., membrane, absorption, microbial, cryogenic, chemical looping, and so on). Those technologies have often suffered from high operating costs and huge energy consumption. On the right side, physical process, such as adsorption, is a cost-effective process, which has been widely used to adsorb different contaminants, including CO₂. Henceforth, this review covered the overall efficacies of CO₂ adsorption from air at 196 K to 343 K and different pressures by the carbon-based materials (CBMs). Subsequently, we also addressed the associated challenges and future opportunities for CBMs. According to this review, the efficacies of various CBMs for CO₂ adsorption have followed the order of carbon nanomaterials (i.e., graphene, graphene oxides, carbon nanotubes, and their composites) < mesoporous -microporous or hierarchical porous carbons < biochar and activated biochar < activated carbons.

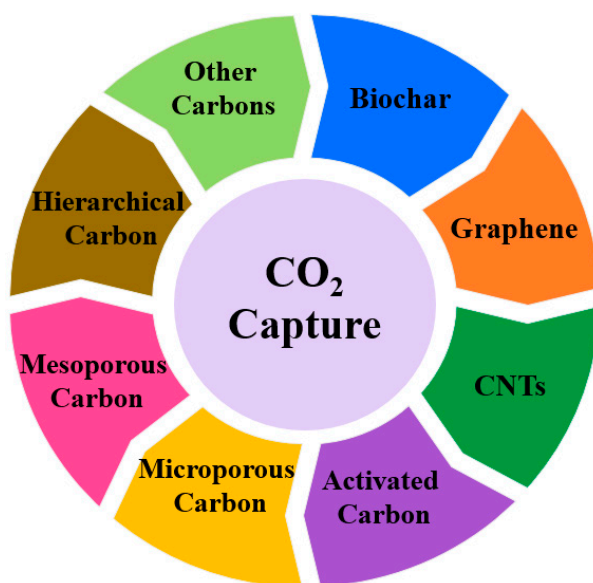
Keywords: CO₂ capture; activated carbon; carbon nanomaterials; adsorption; surface area

1. Introduction

Fossil fuels supply more than 98% of the world's energy demands [1]. Due to the burning of fossil fuels in industrial activities, the concentration of CO₂ has been increasing in the atmosphere significantly [2]. For example, CO₂ concentration hits up to 415.26 ppm at the Mauna Loa Observatory in Hawaii [3]. It is estimated that, in 2050, the atmospheric CO₂ concentration will reach up to 550 ppm [3]. Therefore, the increased concentration of CO₂ in the atmosphere causes global warming and significant environmental problems [3–5]. Hence, there is a great urgency to reduce the CO₂ level from the atmosphere through the utilization of different technologies. The intergovernmental panel on climate change has recommended three fundamental steps for carbon capture and storage for combating carbon dioxide emissions. These involve (i) separation through capture, (ii) transportation, and (iii) storage of CO₂ [6]. Although enough progress has been made on transportation and storage of CO₂, progress is still going on the capture of CO₂ through different processes [7]. Membrane separation techniques have been utilized for the capture of CO₂ at low pressure. However, these kind of technologies often suffers from high operating costs, and they are non-energy efficient to compress the

feed gas [8]. Technologies for the removal of CO₂ from ambient air have been recently demonstrated using different solid or liquid sorbents, which can contribute to “negative carbon emission”, although there remains much room for their improvements [9,10]. On the other hand, porous-based materials are very promising materials to adsorb CO₂. Hence, compared to the liquid adsorption-based technology (such as amine-based adsorption technology), CO₂ capture via solid-state materials (e.g., adsorption technology) is very cost-effective, easy to design, has a functional surface, hydrophobicity, need low energy consumption, simple operation, and easy regeneration of adsorbents [11–15]. Solid adsorbents are alkaline metal oxides and hydroxides, zeolite, metal-organic frameworks, porous polymers, and carbon-based materials (CBMs), such as activated carbon, biochar, nanocarbons (carbon nanotubes (CNTs) and graphene), mesoporous, and microporous carbons, and so on. Among them, CBMs have great potential in the capture of CO₂ due to their high surface area, well-defined porosities, larger pore volume, chemical stability, and easy handling [3,11–19].

Scheme 1 demonstrates a brief summary of CBMs, which are used for the adsorption of CO₂. Although there are many reviews on CO₂ capture, however, to our best knowledge, none of them has discussed the overall efficacy of CBMs for adsorption of CO₂. Therefore, the main objective of this review was to demonstrate the comparative analysis of the efficacies of different CBMs for CO₂ adsorption from the air at different temperatures and pressures. The subsequent objective of this review was to provide an overview of the performance of CBMs together with the major associated challenges and future opportunities for the potential applications of CBMs as CO₂ adsorbents. Hence, we believed that this review would be very helpful for the different researchers and stockholders for the understanding of the recent trends of CBMs performances for CO₂ capture through adsorption technology.



Scheme 1. CBMs (carbon-based materials) for CO₂ capture through adsorption technology.

2. Efficacy of CBMs for CO₂ Capture

CBMs are considered as the top performance material for CO₂ adsorption from the air [15]. CBMs have specific properties, which are highly required for efficient CO₂ capture. There are many types of carbon-based adsorbents, but they can be broadly classified as biochar, nanocarbons materials (e.g., graphene, CNTs, nanocarbons), activated carbons (ACs), different microporous, mesoporous, and hierarchical carbons with or without doping with other inorganic, organics, metal components, or metal atoms, and so on. All of these CBMs have a significant surface area, pore density, volume, pore size, high stability, and sustainability properties, which are prime requirements for efficient CO₂ capture. Therefore, this review has covered the performances of biochar, different nanomaterials, such as graphene, graphene oxides, and carbon nanotubes (CNTs), ACs, microporous, mesoporous, and

hierarchical porous carbon materials together with their composites. The following subsections have addressed CO₂ capture efficacies using those CBMs.

2.1. Biochar for CO₂ Capture

Recently, among various adsorptive materials (e.g., AC, graphene, carbon fibers, etc.), biochar has gained considerable attention as an eco-friendly and cost-effective material for CO₂ capture and sequestration, as catalysts, as greenhouse gas capturing material, as water treatment and, as soil remediation materials [20–22]. Biochar is a carbon-rich material, which is prepared from natural resources having high surface area, hydrophobic nature, and easy regeneration capability [23]. These properties make the biochar an attractive material for the researcher's various applications [24,25]. Biochar can be synthesized from cheap and easily available biomass feedstocks and wastes from different industries (e.g., dairy manure, forestry, agricultural) and many other bio-wastes [26–28]. Biomass resources are composed of C, O, H structures and some of the inorganic materials in their complex matrix together with different heteroatoms (e.g., N, P, or S) [21,29]. However, the quality and yield of biochar depend on several parameters, such as feedstock material and operational conditions.

Biochar can be prepared through different processes, such as gasification (where different biochar, gaseous fuel, such as syngas, and tar (oil) are produced); torrefaction (where biomass is thermally treated for a short period at low-temperature usually 473–573 K); hydrothermal carbonization (where biochar is produced in the presence of water, low oxygen content, high pressure, usually 14–22 MPa, and low temperature at 393–573 K); pyrolysis process (where biomass is thermally converted into its basic graphitic structure at 473–1473 K in a limited or inert atmosphere) [30–32]. Figure 1 shows a simple overview of biochar production from biomass using different thermochemical processes. Hence, the porous biochar is produced [24,33,34].

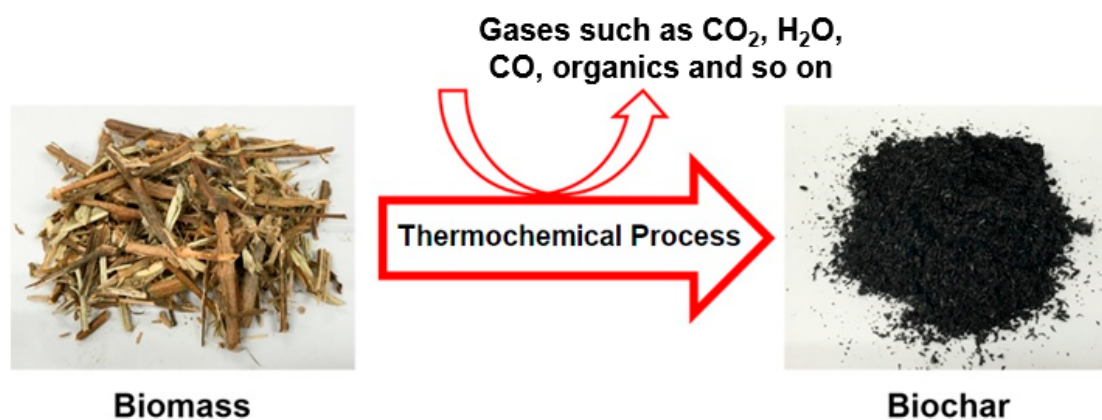


Figure 1. A general overview of biochar production from different biomasses.

Owing to the unique structure and surface properties of biochar, it can act as an excellent adsorbent for the capture of several gases. In a study, Mohd et al. [35] reported that adsorption of toxic gases on biochar surface took place mainly through the physisorption process. The surface of biochar contains macro and micropores, which act as a storage place for gas molecules [35]. Table 1 shows the CO₂ intake capacity of biochar at 1 bar atmospheric pressure and two different temperatures. It is clear from the table that chemically activated biochar prepared from Vine shoots were capable of adsorbing a higher amount of CO₂ (6.08 mmol/g at 1 bar and 273 K) compared to physically activated biochar (4.07 mmol/g at 1 bar and 273 K) [36,37]. In another study, Ello et al. [37] prepared biochar and biochar activated with KOH at 1133 K for 1 h from Africa palm shells. They reported higher CO₂ adsorption capacities (6.3 mmol/g at 273K and 4.4 mmol/g at 298 K and 1 bar, respectively). On the other hand, different CO₂ intake capacities were also reported for chemically activated biochars from rice husk (3.71 mmol/g) [38], pine nutshell (5.0 mmol/g) [39], wheat flour (3.48 mmol/g) [40], vine shoots (2.46 mmol/g) [36], coconut

shells (4.23 mmol/g) [11], Jujun grass (hydrochar, 4.9 mmol/g) [41], and Camellia Japonica (Hydrochar, 5.0 mmol/g) [41] at 298 K and 1 bar pressure. Moreover, single-step pyrolysis and activation of various biomasses to produce biochar and activated biochar were also reported by Serafin et al. [42]. They found that CO₂ adsorption capacities of pomegranate peels, carrot peels, and fern leaves were 4.00, 4.18, and 4.12 mmol/g at 298 K, respectively, and 6.89, 5.64, and 4.52 mmol/g at 273 K, respectively, at 1 bar. Zhang et al. [43] produced amine functional group doped activated biochar from black locust. They reported a CO₂ adsorption capacity of 5.05 mmol/g at 298 K and 1 bar. Similarly, Rouzitalab et al. [44] used urea to synthesize amine-functionalized activated biochar from the walnut shell in the presence of KOH, and they observed record CO₂ adsorption capacity of 7.42 mmol/g at 298 K and 1 bar.

Table 1. CO₂ capture performances by top performance biochar produced from different biomasses and at different conditions. The surface area is based on Brunauer–Emmett–Teller (BET).

Biochar Derived from	BET Surface Area (m ² /g)	Pressure (Bar)	Adsorption Capacity (mmol/g) at 273 K	Adsorption Capacity (mmol/g) at 298 K	Reference
Vine shoots	767	1	4.07	1.58	[36]
Vine shoots	1305	1	6.04	2.46	[36]
Vine shoots	1439	1	6.08	1.98	[37]
African palm shells	1250	1	6.3	4.4	[37]
Rice husk	2695	1	6.24	3.71	[38]
Pine nut shells	1486	1	7.7	5.00	[39]
Wheat flour	1438	1	5.70	3.48	[40]
Coconut shells	1172	1	6.04	4.23	[11]
Jujun grass	1512	1	-	4.9	[41]
Jujun grass	3144	1	-	4.1	[41]
Camellia Japonica	1353	1	-	5.0	[41]
Camellia Japonica	3537	1	-	2.8	[41]
Pomegranate peels	585	1	6.89	4.00	[42]
Carrot peels	1379	1	5.64	4.18	[42]
Fern leaves	1593	1	4.52	4.12	[42]
Black locust	2511	1	-	5.05	[43]
Walnut shell	1315	1	-	7.42	[44]
Pine cone	1680	1	-	4.7	[45]
Saw dust	394.12	1	-	3.7	[46]
Mg loaded Walnut shell	292	1	-	3.7	[47]
Pristiene Walnut shell	997	1	-	3.2	[47]

However, CO₂ adsorption capacity can significantly vary with the changing of the surface morphology of biochar, i.e., the surface area, micropore volume, and size, together with the effects of temperature and pressure [24,42]. For example, Deng et al. [39] reported that biochar having a pore size of 0.33–0.63 nm played an important role in the higher CO₂ adsorption. It was also reported that the control of micropores had greater importance for adsorbing high CO₂ compared to surface area and total pore volume [39,42]. Figure 2 shows the presence of functional groups and porous structures (mesoporosity and microporosity) of biochar materials. Metal oxyhydroxide biochar composites have also been used to increase the adsorption capacity of biochar. For example, Lahijani et al. [47] reported that Mg-loaded biochar showed a higher CO₂ adsorption capacity (3.7 mmol/g) than that of raw biochar (3.2 mmol/g) at 298 K and 1 atm. This phenomenon can be explained by the fact that the incorporation of metals (i.e., Mg, Al, Ni, and Fe) onto the biochar surface will increase basic sites on the surface of biochar, which enhances the adsorption capacity of acidic CO₂ [47].

Therefore, it can be summarized that biochar and activated biochar/biochar-based adsorbents are low-cost, renewable, and promising materials for the adsorption of CO₂. However, still there remain various challenges, especially which can prevent the practical and large-scale application of biochar-based adsorbents for CO₂ removal, which need to be addressed. First of all, the robustness and stability of biochar-based adsorbents have not been fully demonstrated, despite the fact that high adsorption capacities and long-term cyclic operation are critical to ensure the economics and practicality of the technology [48]. Secondly, the production process should be simple, cost-efficient, and eco-friendly to develop highly efficient CO₂ adsorbents. Thirdly, both physical and chemical

modification methods have been carried out in laboratory-scale experiments. However, most studies are explorative in nature, and the effectiveness of the methods for large-scale biochar modification and application is still unclear. Finally, a new type of modified biochar should keep continuing to develop with larger surface area, well-defined porosity, together with surface functional groups, and it is also necessary to produce biochar from low-cost materials, such as agricultural wastes.

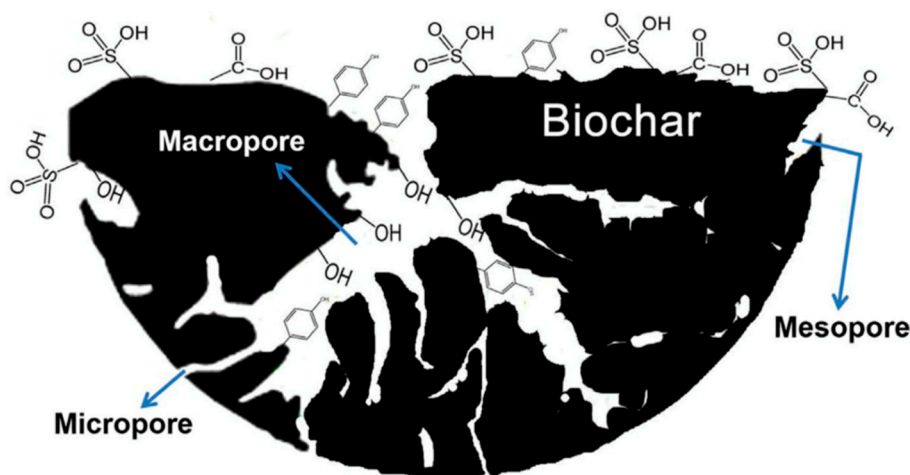


Figure 2. Morphology and the presence of functional groups in biochar. Reproduced with permission from [24]; Elsevier and Copyright Clearance Center, 2017.

2.2. Graphene, Graphene Oxide, and Carbon Nanotubes (CNTs) for CO₂ Capture

CBMs can be dimension-less and less than 100 nm but in many forms. Nanomaterials are extensively used for different applications, owing to their downsized unique properties. They can be used as catalysts supports, adsorption, energy conversion, charge storage device preparation, filtration, electrode materials, conductive materials, and so many [49]. Graphene-based nanomaterials are also used for CO₂ capture [49]. The development of new adsorbents with high capacity and high selectivity for reducing energy-related CO₂ emissions is a topic of utmost global importance because of its implications in climate change mitigation. Recent advances in materials science and engineering suggest that graphene-based adsorbents are wonder material with many attractive properties and can deliver viable solutions to the challenges of developing cost-effective, energy-efficient, and high-volume adsorption-based CO₂ capture technologies. To date, a wide range of graphene materials has been investigated to curb CO₂ emissions from static sources of fossil fuel combustion. Table 2 represents the CO₂ adsorption performance by graphene, graphene oxide, CNTs, and composite materials. Graphene-based materials, such as graphene oxide, have different oxygen-containing functional groups, which can show higher chemical reactivity over pristine graphene [50]. The introduction of different heteroatoms (e.g., N, boron B, aluminum Al, sulfur S, and so on) in graphene can increase the adsorption capacity of CO₂. For example, Liu et al. [51] prepared N and B-doped graphene aerogels, which showed CO₂ capture capacities of 2.9 mmol/g at 273 K and 1.0 bar pressure. On the other hand, Bhanja et al. [52] did a modification of graphene oxide with 2,6-diformyl-4-methyl phenol. They reported that this material could capture CO₂ up to 8.10 mmol/g at 273 K. Recently, graphene-based monoliths have been prepared following a one-step water-based method, which has shown an excellent CO₂ capture performance of 2.1 mmol/g at 298 K and 1 bar [53]. On the other hand, Huang et al. [54] synthesized a hybrid composite based on polyethyleneimine (PEI)-modified graphene oxide and ZIF-8. This composite showed a higher CO₂ capture capacity of 8.08 mmol/g at 273 K and 1 bar. Rahimi et al. synthesized bundles of double-walled CNTs with an inner diameter of 8 nm, and they reported excellent CO₂ adsorption capacity (i.e., 3.5 mmol/g at 308 K and 1 bar) [55]. An improved innovative hydrate-based CO₂ capture was observed by the rational surface modification of CNTs by Zhao et al. [56]. However, the maximum CO₂ capture performance (up to 8.75 mmol/g at 196 K and

1 bar) was observed by Jonathan et al. [57] by synthesizing a new composite based on single-walled carbon nanotube (SWCNT@HKUST-1).

Table 2. CO₂ capture performances, recently reported by graphene, graphene oxide, carbon nanotubes (CNTs), and their composites.

Adsorbent	BET Surface Area (m ² /g)	Pressure (Bar)	Adsorption Capacity (mmol/g) at 273 K	Adsorption Capacity (mmol/g) at 298 K	Reference
Reduced graphene oxide	1300	1	3.35	2.45	[49]
BN-graphene	170	1	2.9	2.6	[51]
Imine-functionalized graphene oxide	190	2	8.1	2.1	[52]
N-functionalized graphene	979	1	5.8	2.7	[58]
Polyethyleneimine (PEI)-modified graphene oxide	29	1	-	2.0	[59]
Graphene-based monolith	328	1	-	2.1	[53]
PEI-graphene oxide@ZIF-8	190	1	8.08	-	[54]
DWCNTs	423	1	-	3.5 (at 308 K)	[55]
PEI-purine-CNTs	-	1	-	3.9 (at 323 K)	[60]
PEI-CNT aerogels	62	1	-	3.3 (at 343 K)	[61]
SWCNT@HKUST-1	1714	1	-	8.75 (at 196K)	[57]
Chitosan-polybenzoxazine nanocomposite aerogels	710	1	6.70	5.72	[62]

On the other hand, Alhwaige et al. [63] synthesized chitosan aerogels with graphene oxide nanosheets, which showed CO₂ capture capability up to 4.14 mmol/g. Few other aerogels and cross-linked composites have been also reported, which have shown CO₂ adsorption capacity up to 5.72 mmol/g at 298 K and 1 bar [62].

Therefore, based on the above description, it can be clearly said that graphene, graphene oxide, and CNTs have CO₂ capture ability, specifically in terms of high storage, excellent selectivity, rapid uptake, easy regeneration, and good reproducibility and stability. However, the maximum adsorption capacity comes from polyethyleneimine-modified graphene and graphene oxide compared to other graphene, graphene oxides, and CNTs. In comparison to other competing adsorbents, a key advantage of these material systems is that many different functional groups or heteroatoms can be attached to their surface, allowing custom-tailoring of surface properties without sacrificing the remarkable intrinsic characteristics of the graphene core. However, a number of technological limitations and practical challenges have to be tackled in order to produce next-generation graphene-based adsorbents with the capability of being applied on an industrial scale for efficient and effective CO₂ separation from flue gases. Henceforth, future applications of such kinds of materials for CO₂ capture need further consideration with mainly focusing on the significant improvement in the adsorption capacity as well as the low-cost production of these materials.

2.3. Activated Carbons (ACs) for CO₂ Capture

Activated carbon is a high-porosity material, which is useful in adsorption and separation of many gas mixtures [64,65]. Perhaps, ACs have widely been used for CO₂ capture compared to other types of CBMs. This is because they have high surface area (SA), pore-volume, and submicroscopic pores [5,66,67]. ACs are not degraded in acidic and basic conditions [68]. Hence, they possess excellent performance in CO₂ uptake. Table 3 summarizes the CO₂ capture performances by different ACs.

Table 3. CO₂ capture performances by different activated carbons (ACs).

Adsorbent	BET Surface Area (m ² /g)	Pressure (Bar)	Adsorption Capacity (mmol/g) at 273 K	Adsorption Capacity (mmol/g) at 298 K	Reference
AC beds	3537	18	-	20.66	[69]
N-doped ACs	1535	1	7.0	4.80	[70]
Starch-based ACs	3350	1	4.4	3.4	[71]
Polyurethane foam-based AC	1360	1	5.85	-	[67]
Polyacrylonitrile-based AC fibers	1565	1	-	2.74	[72]
N and S-doped ACs	2040	1	7.76	5.19	[73]
Celtuce leaves-derived AC	3404	1	6.04	4.36	[74]
Longan shells-derived AC	3260	1	5.60	4.30	[75]
Slash pine-derived AC	906	1	4.93	3.86 (at 288K)	[76]
Coconut shell-derived AC	1327	1	5.60	3.90	[77]
Black locust-derived AC	2511	1	5.86	3.75	[44]
Starch and cellulose, sawdust	1260	1	6.10	4.8	[28]
Empty fruit bunch-derived AC	1720	1	5.22	3.70	[78]
Lignin-derived AC	3500	1	8.20	4.8	[79]
Pitch-based N-doped AC	1505	1	7.10	4.58	[80]

ACs can be derived from biomass through pyrolysis but requires either physical or chemical activation. Physical activation can be performed using steam/water vapor, air, or CO₂. On the other hand, carbon can also be chemically activated by various chemicals to increase the surface area, as well as add (or remove) specific surface functional groups. When carbon is activated with ammonia at high temperatures, nitrogenous groups are added, and acidic oxygen groups are removed, which significantly improves basicity (Shafeeyan et al., 2020) [81].

However, different precursors, such as biomasses, coal, and petroleum pitch, are used for the production of ACs. However, mostly used precursors are biomasses, coal, and petroleum pitch [82]. For example, Shao et al. [71] synthesized ACs from coal tar pitch with an extremely high surface area of 3537 m²/g. This AC could capture CO₂ up to 20.66 mmol/g at 298 K and 18 bar. On the other hand, ACs can also be prepared from different biomass precursors. For instance, Chen et al. [67] synthesized N-doped microporous-ACs from coconut shells by using urea as an activating agent. They found the CO₂ capture capacity of 7.0 and 4.8 mmol/g at 273 and 298 K, respectively, at 1 bar. An ultrahigh-surface area of ACs (3350 m²/g) was achieved by using starch as a source of a precursor. These ACs could capture CO₂ up to 3.4 mmol/g at 298 K and 1 bar [72]. On the other hand, polyurethane foam-based AC was synthesized by Ge et al. [67], whose adsorption capacity was 5.85 mmol/g at 273K and 1 bar. In another study, the CO₂ removal capacity of polyacrylonitrile-based AC fibers at 298K and 1 bar was reported to be 2.74 mmol/g [72]. It is reported that each year, around 140 billion metric tons of biomasses are produced from agriculture resources [73]. So, the proper utilization of agricultural wastes together with other biomass sources, such as food residues, nutshells, cellulose craft, lignin, sawdust, rice husk, chips, logs, wood processing residues, marine microalgae, and pitch, for the production of ACs in an environmentally friendly, as well as an economic way, could be an alternative solution. Such an example is given in Figure 3, where celtuce leaves were pyrolyzed at a high temperature, followed by a chemical activation process [74].

In summary, it can be mentioned that ACs materials are excellent materials for the adsorption of CO₂ with higher adsorption capacity, as well as they can be prepared from low-cost materials. ACs have higher potential for commercial applications as they have higher adsorption capacity, high surface area, microporosity, mesoporosity, and stability. Hence, AC is one of the top performance CBMs for the CO₂ capture.

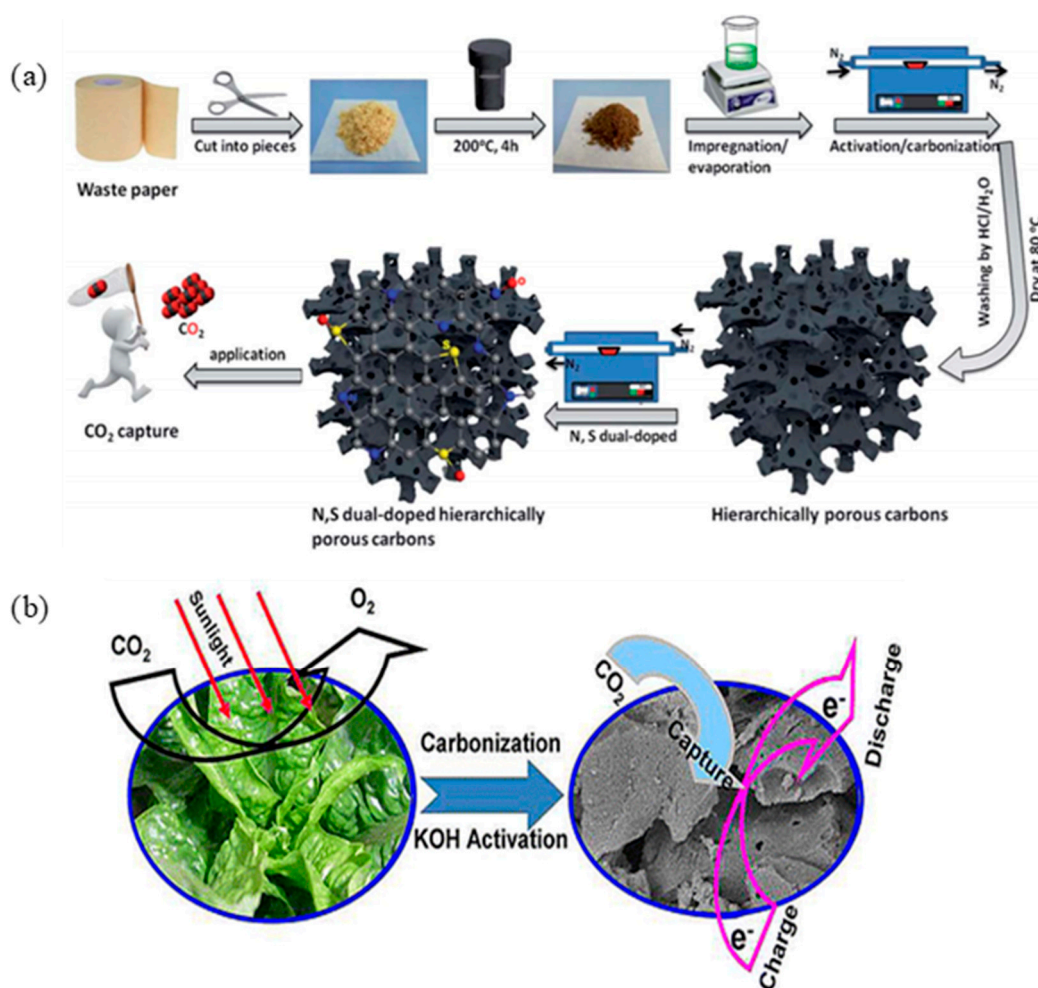


Figure 3. ACs (activated carbons) preparation from (a) waste paper and (b) biomass [73,74]. Reproduced with permissions from the references of [73,74]; Copyright © 2019, Royal Society of Chemistry and Copyright © 2012, American Chemical Society; respectively.

2.4. Microporous, Mesoporous, and Hierarchical Porous Carbons for CO₂ Capture

Porous carbon materials have versatile properties, such as high Brunauer–Emmett–Teller (BET) surface area, adjustable pore structure, cost-effective, and easy regeneration [83]. Generally, there are three different types of porous carbon materials, i.e., microporous (<2 nm), mesoporous (2–50 nm), and macroporous (>50 nm), but hierarchical porous carbon (HPC) consists all of these properties [84]. For example, Lizen et al. [85] synthesized super porous carbon materials with 95% mesoporosity using polypyrrole as a precursor material. They mentioned about the ultra-high surface area (i.e., 2800–4000 m²/g) and pore volume (i.e., 2.5–3.6 cm³/g). However, their CO₂ capture capacity was found to be 2.8 mmol/g at 298 K. On the other hand, it was found that the mesoporosity was significantly increased by using sodium amide (NaNH₂) during activation and doping with magnesium (Mg) and nitrogen (N₂). These materials showed excellent CO₂ uptake performance (3.68–6.31 mmol/g at 273 K) [86–88]. On the other hand, Park et al. [89] synthesized 3D ordered mesoporous carbon and observed the CO₂ capture capacity of 5.53 mmol/g. Recently, a newly designed porous geopolymer template was developed by Pei et al. [90], which was based on the metakaolin. This AC had an excellent CO₂ capture performance of 26.30 mmol/g at 273 K and 30 bar (Table 4). HPC ordered materials have great potential for high CO₂ capture as they have great interest due to their many advantages, such as high microporosity, high surface area, higher microporous quantity, and so on. For example, HPC with a prominent BET surface area up to 2734 m²/g had higher CO₂ capture performance up to 27 mmol/g at

30 bar and 300 K [91]. Hence, carbon nanomaterials can possess a hierarchical porous structure and contain both macropores and micropores structure. These properties of carbon, together with the high surface area, are very important for higher CO₂ capture [92].

Table 4. CO₂ capture performances by microporous, mesoporous, and hierarchical porous carbons.

Adsorbent	BET Surface Area (m ² /g)	Pressure (bar)	Adsorption Capacity (mmol/g) at 273 K	Adsorption Capacity (mmol/g) at 298 K	Reference
Mesoporous carbon	3934	1	-	2.8	[85]
NaNH ₂ -activated mesoporous carbon	3325	1	6.31	3.66	[86]
Mg and N-doped mesoporous carbon	541	1	3.68	-	[87]
N-doped mesoporous carbon	984.91			4.23 (at 303 K)	[88]
Ordered mesoporous carbon nitrides	232	30	5.63		[89]
Ordered mesoporous carbon	2255	1	3.0	2.1	[93]
Ultramicroporous carbon	882	1	5.91	4.30	[94]
Mesoporous carbon nanospheres	1240	1	4.76	2.36	[95]
Microporous carbon	1551	30	26.30	-	[90]
N-doped microporous carbon	664	1	5.0	4.0	[96]
Ultramicroporous carbon	1059	1	5.87	3.82	[97]
Microporous carbon aerogel	1871	1	-	3.0	[98]
N-doped microporous carbon	1060	1	-	4.24	[99]
Microporous carbon beads	1755		6.15	4.25	[100]
N-doped microporous carbon	1381	1	5.91	3.86	[101]
Ultra microporous carbon	335	1	-	1.82 (at 303 K)	[102]
S-doped microporous carbon	1567	1	-	4.5	[103]
N-doped porous carbon	467	1	-	3.13	[104]
Ultra microporous carbon nanoplates	800	1	-	5.2	[105]
Yeast-based porous carbon	1348	1	-	5.0	[106]
Sponge-like porous carbon	1143	1	5.6	4.0	[107]
Hierarchical porous carbon	2734	30	-	27.0 (at 300 K)	[91]
Hierarchical porous carbon nitride	550	1	-	2.9	[108]
Hierarchical porous carbon	2698	1	-	3.7	[109]
Hierarchical nanosheet	1555.7	1	4.62	3.10	[110]
N-doped hierarchical porous carbon	1455.1	1	6.22	4.05	[111]
Waste wool-derived N-doped hierarchical porous carbon	1352	1	3.72	2.78	[112]
N-doped hierarchical porous carbon	2799	1	5.3	4.4	[113]
Si-doped porous carbon	1500	1	7.8	4.0 (at 296 K)	[114]

Porous carbon materials have drawn great attention due to the remarkable pore structure, high specific surface area, large pore volume, excellent property of adsorption, and separation. When the material is highly microporous, it may result in a long equilibrium time for CO₂ adsorption. Large mesopores enable faster transfer of gas from the bulk phase to micropores and, thus, result in faster equilibrium [113,114]. Although microporous and mesoporous content has been found to be the best indicator of CO₂ capture performance, a large pore volume values originating from a distinct large mesoporous peak can improve CO₂ performance as well. So, utilizing the hierarchical porous carbon materials by adjusting various templates and catalysis with large pore volume and high surface area would be the best candidate for reducing the emission of CO₂ to the environment.

3. Comparative Analysis of CBMs Performances

CBMs are found to be very effective in the capture of CO₂ at various conditions with varying degree of adsorption capacity. We know that different adsorbents have been produced at different conditions using different precursors. Based on rough estimation, it can be mentioned that biochar and activated biochar are cheap materials compared to any other CBMS. Table 5 lists the rough lower and higher prices of each CBMs, although the actual cost may vary depending on several factors, such as purity, quality, quantity, and so on. Based on the table, it can be seen that carbon-based

nanomaterials, such as graphene, graphene oxide, and CNTs, have a higher cost compared to other types of CBMs. Besides, the further modification of those materials can significantly increase the cost, such as composite materials preparation and fabrication for the end-use. However, their average CO₂ adsorption capacity values were 5.13 ± 1.62 and 3.23 ± 1.13 mmol/g, respectively, at 273 and 298 K, which was even lower than that of cheap materials, such as biochar at both temperatures (Figure 4). These results indicate that graphene, graphene oxide, and CNTs have lower CO₂ adsorption capacity compared to biochar and activated biochar and even compared with other types of CBMs.

Table 5. Rough prices of different carbon-based adsorbents [115]. Price varies based on purity, quantity, quality, and type of materials.

Adsorbents	Lower Price (\$/kg)	Higher Price (\$/kg)
Biochar/activated biochar	0.4	0.90
Activated carbons	2.90	8.20
CNTs	1000	10,000
Graphene	50	200
Graphene oxide	200	400
Other carbons	Depends on processing	Depends on processing

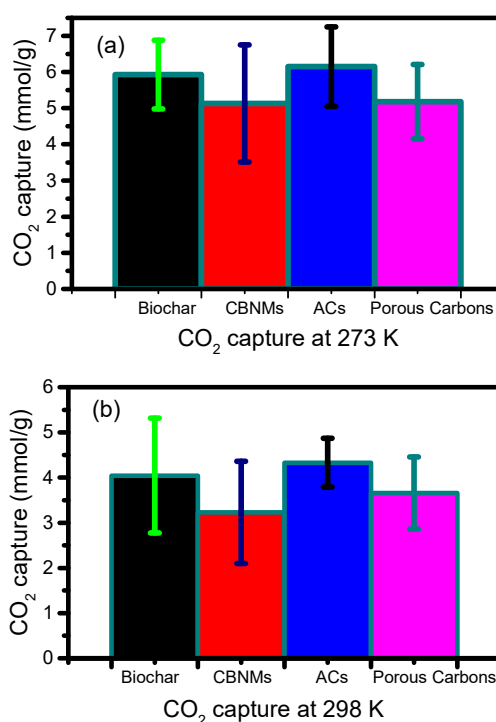


Figure 4. Average (with standard deviation) CO₂ capture performance by different carbon-based materials at two different temperatures, i.e., 273 K and 298 K, respectively. Biochar refers to biochar and activated biochar; CBNMs refers to graphene, graphene oxide, CNTs, and their composites; porous carbon refers to micro, meso, and hierarchical porous carbons. Each set of data refers to the average value (with standard deviation) at the adsorption capacities of each type of material, which was generated from Tables 1–4.

On the other hand, biochar and activated biochar have higher CO₂ capture performance over graphene, graphene oxides, and CNTs, although some special cases can cease this estimation. On the right side, different meso-micro and hierarchical porous carbons have slightly lower CO₂ adsorption capacities than that of biochar, and they have higher efficacy over graphene, graphene oxides, and CNTs. Hence, biochar and activated biochar have a higher potential for the capture of CO₂ than hierarchical porous carbons.

However, ACs have been found very effective among all types of CBMs with the higher average CO₂ capture performances (6.15 ± 1.10 , 4.33 ± 0.54 mmol/g, respectively, at 273 and 298 K) at both temperatures (Figure 4). These average values indicate that ACs have higher CO₂ capacities over biochar, activated biochar, hierarchical porous carbons, graphene, graphene oxide, and CNTs. These are mainly due to their high surface area and the properties of ultra-microporous structures. Therefore, ACs are the top performance materials for the capture of CO₂. However, there might have some other form of carbons that can overcome these estimations, but grossly ACs are the highly efficient materials for CO₂ capture. Hence, for CO₂ capture, CBMs follow the order of carbon nanomaterials (i.e., graphene, graphene oxides, CNTs, and their composites) < meso-micro or hierarchical porous carbons < biochar and activated biochar < activated carbons.

4. Future Challenges and Opportunities

Although enough progress has been done towards the synthesis of CBMs and application for CO₂ capture, still there is a lack of studies. For example, it is highly necessary to consider the effects of different parameters, such as the presence of moisture, foreign ions, environmental conditions, neutral and ionic species, and so many, for the effective capture of CO₂ and to measure the overall efficacy of CBMs from the atmosphere [116]. Therefore, further investigations are needed in many areas. They are:

- i. Developments of the novel composite to improve the capture performance of CO₂ of CBMs.
- ii. A need to properly understate the CO₂ interactions with CBMs. For this reason, new analytical tools are needed to develop.
- iii. Ensuring the regeneration efficiency for repeatable applications. Regeneration mechanisms also need to study in detail.
- iv. Development of new technologies for the efficient capture of CO₂.
- v. A highly efficient carbon-based catalyst needs to develop for the conversion of CO₂ into valuable fuels, such as methane.
- vi. Low-cost materials with high adsorption capacity need to develop.
- vii. Most of the CBMs have been used for CO₂ capture on a lab-scale basis, i.e., from ambient air. However, studies are not enough. Therefore, more studies are required.
- viii. Other types of materials, such as metal-organic frameworks, porous silica, resin, amine derivatives sorbents, and new types of materials, need to produce with lower cost for the scale-up process.
- ix. These coatings of sorbents can help for faster heat and mass transfer, as well as can reduce energy losses. Therefore, these kinds of sorbents need to develop.
- x. Detailed kinetics of sorption and mechanisms need to be focused on more clearly.
- xi. Combining together and application of the different existing technologies can reduce the cost of the capture of CO₂.

5. Conclusions

CBMs are very efficient in the capture of CO₂ from the air at different temperatures and pressures due to their specific properties, including high surface area, mesoporosity, microporosity, micropore volume, well-defined pore size distributions, and high stability, at different environmental conditions. Among different CBMs, activated carbons and activated biochar are found to be the top performance materials for the capture of CO₂ in an environmentally friendly way. Although extensive research has been carried out for the development of different suitable carbon-based materials for CO₂ capture, still there is a lack of research for future studies on the development of low-cost suitable adsorbent material. In our opinion, CBMs have a good future for CO₂ capture if all the properties can be merged into one material, which can compete with metal-organic frameworks. Therefore, the future focus should be given on the increase in the adsorption capacity, as well as materials properties, in order to sustain in the long future.

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