



Review

Carbon Capture Materials in Post-Combustion: Adsorption and Absorption-Based Processes

Abdulrahman Allangawi ¹, Eman F. H. Alzaimoor ¹, Haneen H. Shanaah ¹, Hawraa A. Mohammed ¹, Husain Saqer ¹, Ahmed Abd El-Fattah ^{1,2} and Ayman H. Kamel ^{1,3,*}

¹ Department of Chemistry, College of Science, University of Bahrain, Zallaq P.O. Box 32038, Bahrain
² Department of Materials Science, Institute of Graduate Studies and Research, Alexandria University, El-Shatby, Alexandria 21526, Egypt
³ Department of Chemistry, Faculty of Science, Ain Shams University, Cairo 11566, Egypt
* Correspondence: ahmohamed@uob.edu.bh or ahkamel76@sci.asu.edu.eg

Abstract: Global warming and climate changes are among the biggest modern-day environmental problems, the main factor causing these problems is the greenhouse gas effect. The increased concentration of carbon dioxide in the atmosphere resulted in capturing increased amounts of reflected sunlight, causing serious acute and chronic environmental problems. The concentration of carbon dioxide in the atmosphere reached 421 ppm in 2022 as compared to 280 in the 1800s, this increase is attributed to the increased carbon dioxide emissions from the industrial revolution. The release of carbon dioxide into the atmosphere can be minimized by practicing carbon capture utilization and storage methods. Carbon capture utilization and storage (CCUS) has four major methods, namely, pre-combustion, post-combustion, oxyfuel combustion, and direct air capture. It has been reported that applying CCUS can capture up to 95% of the produced carbon dioxide in running power plants. However, a reported cost penalty and efficiency decrease hinder the wide applicability of CCUS. Advancements in the CCSU were made in increasing the efficiency and decreasing the cost of the sorbents. In this review, we highlight the recent developments in utilizing both physical and chemical sorbents to capture carbon. This includes amine-based sorbents, blended absorbents, ionic liquids, metal-organic framework (MOF) adsorbents, zeolites, mesoporous silica materials, alkali-metal adsorbents, carbonaceous materials, and metal oxide/metal oxide-based materials. In addition, a comparison between recently proposed kinetic and thermodynamic models was also introduced. It was concluded from the published studies that amine-based sorbents are considered assuperior carbon-capturing materials, which is attributed to their high stability, multifunctionality, rapid capture, and ability to achieve large sorption capacities. However, more work must be done to reduce their cost as it can be regarded as their main drawback.

Keywords: carbon capture; methods and processes; absorption; adsorption; carbon emission; global warming



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1. Introduction

Recently, the world has been facing serious problems concerning climate change and global warming, which are the results of the industrial growth and anthropogenic activities. The increased the demand for energy consumption, transportation, and water treatment emits numerous greenhouse gases (GHGs) including carbon dioxide, nitrous oxide, and methane gas. The emission of GHGs eventually contributes to global warming [1–3]. They are the major contributors to the elevation of the average temperatures in the earth due to their ability to capture the heat from the atmosphere. In fact, the greenhouse effect is a natural process where GHGs trap the heat from the sun into the atmosphere, while maintaining the earth's average temperature in a livable range, which is around 33 °C [4]. As a result of the growth in industrialization, GHGs are emitted in excessive amounts into

the atmosphere, thereby increasing their levels in it. The increased level of GHGs burdens the natural greenhouse effect by capturing more radiation than the normal rates, which will cause elevated temperatures around the earth [3].

The concentration of carbon dioxide in the 1800s was around 280 ppm. In year 2022, it reached 420.99 ppm [5]. Rise in CO₂ emissions indicates its significance as compared to the other GHGs, being the most abundant GHG in the atmosphere with contribution of about two-third [6]. The major sources of CO₂ emission worldwide are electricity, transportation, industrial manufacturing including cement production, residential (heating and wood fires), and agriculture other with emissions contribution of 27, 28, 22, 12, and 11% of CO₂, respectively [7–11]. Global warming and climate change have long-term environmental problems such as the loss of biodiversity, weather change, average global temperature rise, polar ice melting, and increased weather events such as droughts, floods, and hurricanes [12].

The world today is aiming towards decreasing carbon emissions, either directly or indirectly to reach net-zero emissions [13,14]. There are multiple ways to reach net-zero carbon emissions. For instance, increasing the efficiency of power plants, where the maximum electricity is produced while contributing to the lowest CO₂ emission. This can be achieved by applying new technologies in which less amounts of fuel are required for the combustion process. Enhancing the efficiency while maintaining the low-cost is the most promising approach to lower carbon footprint [15]. Another approach includes using renewable energy sources such as wind, hydropower, solar cells, and nuclear energies. These sources are clean and do not contribute to carbon emissions. In addition, hydrogen energy could be used as fuel in transportation with little to no carbon emissions. Moreover, fossil fueled power plants are the highest CO₂ emitters, thus, replacing coal with natural gas would decrease carbon footprint. Furthermore, deforestations contribute to the carbon footprint by reducing the abundance of plants and/or biomass which could remove CO₂ naturally from the atmosphere by the photosynthesis process, therefore, reducing deforestation is another way to reduce the carbon footprint [16].

Reducing the demand for energy consumption is another way to reduce the carbon footprint. However, the energy demand is predicted to increase in the future because of the increased world population [17]. Therefore, instead of emitting CO₂ into the atmosphere during the industrial processes or energy production, practicing carbon capture utilization and storage (CCUS) is a key solution in this period of increased carbon emissions [18]. CCUS is a technique with multiple methods to capture CO₂ emitted from industrial processes. Carbon is not only captured but also utilized in other fields such as storage purposes. For example, after capturing CO₂ as a gas, it could be compressed into liquid form and transported for storage purposes either at the bottom of the ocean or under appropriate geological structures. The captured carbon could be utilized in industrial processes such as the Enhanced Oil Recovery (EOR) by injecting CO₂ into a depleted oil and gas reservoirs, or by conversion of CO₂ into synthetic fuels [19].

In this review, we highlight the various modes used for carbon capture while focusing on the post-combustion and its carbon capture separation techniques such as the physical and chemical adsorption and absorption, as summarized in Figure 1. The selected studies that were discussed in detail are all recent (from 2016 to 2022). In addition, we will discuss the thermodynamic and kinetic models in the adsorption and absorption methods.

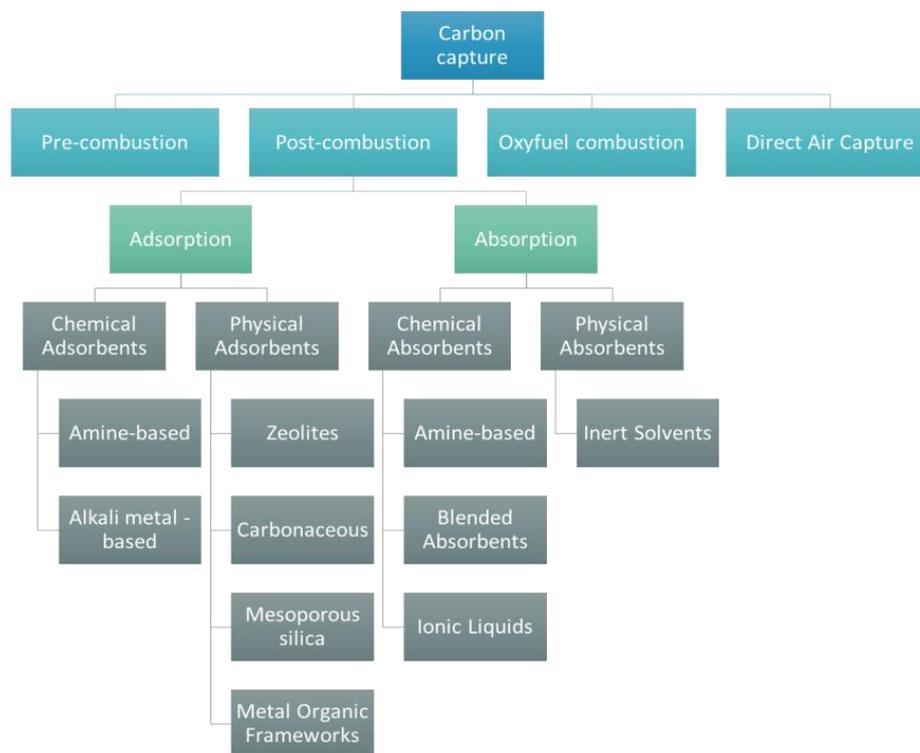


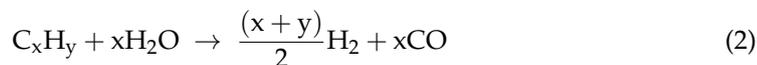
Figure 1. Summary of the adsorbents and the absorbents utilized in post-combustion carbon capture.

2. Carbon Capture Processes

There are four main methods for carbon capture. Namely, pre-combustion, post-combustion, oxyfuel combustion, and Direct Air Capture (DAC).

2.1. Pre-Combustion Carbon Capture

The pre-combustion process is based on removing carbon from the fuel before the combustion. The process begins with reacting fossil fuels with air or oxygen in a controlled gasifier unit to undergo gasification at high temperatures and pressures [20]. In the gasifier unit, the fossil fuel gets converted to a mixture of H₂ and CO gas called the synthesis gas. The gasification process can occur with or without the presence of steam as shown in Equations (1) and (2):



After gasification, the resultant synthesis gas is then passed through a water-gas shift reactor (WGSR). In the WGSR, the synthesis gas passes through water converting CO to CO₂ gas at low temperatures as shown in Equation (3) [21]:



After passing through the WGSR, the fuel gas mainly consists of high levels of CO₂ (15–60%) and H₂ [22]. Due to the high concentration of CO₂, the carbon capture process is now favorable and several chemical and physical methods can be implemented including adsorption, absorption, membrane techniques, and many more [23]. The end product of this process is a high-purity H₂ gas [21].

The carbon capture efficiency for the pre-combustion process is usually high due to having high concentrations of CO₂ in the fuel gas [24]. Moreover, the exit gas has a high pressure and therefore can be transported at low cost using small size equipment [25]. However, the need to implement a gasifier for this process is very costly and usually the plant's energy production efficiency is reduced after the implementation of this technique [26]. A schematic representation for the Pre-Combustion Carbon Capture process is illustrated in Figure 2.

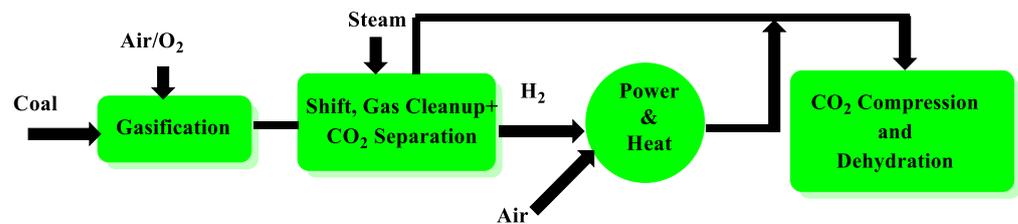


Figure 2. Pre-combustion capture process.

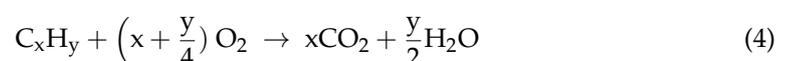
2.2. Post-Combustion Carbon Capture

Post-combustion carbon capture involves separating carbon dioxide from the flue gas (the gas emanated from combustion plants). The flue gas usually consists of nitrogen and carbon dioxide gas at high temperatures (120–180 °C), with smaller concentrations of steam sulfur dioxide, nitrogen oxide, and particulate fly ash [27]. As per the emission standards [28], the flue gas is cleansed from the toxic gases before its emission. The presence of carbon dioxide in smaller concentrations (3–20%) in the flue gas, as compared to the pre-combustion method, enforces the use of chemical sorption for separating the CO₂ gas [22]. As a result of the low concentration of carbon dioxide and therefore its partial pressure, highly efficient separation methods are required in this method. Aqueous solutions of monoethanolamine (MEA) are most commonly used as they efficiently absorb carbon dioxide and form carbamates [29]. Therefore, the post-combustion carbon capture process begins by scrubbing the flue gas in the vessel containing the absorber (most commonly MEA), then the CO₂-containing solvent is transferred to another vessel where the CO₂ is released, and the solvent used can then be recycled into the process [30]. The released CO₂ is then compressed and transported.

The post-combustion carbon capture methods are superior to the pre-combustion methods in their flexibility, as they can be integrated into existing power plants. Therefore, it is the preferable choice to existing plants [22]. However, a large increase in the electricity cost is expected due to the large energy input required for the solvent regenerating step and the compression of CO₂. For instance, coal plants can capture up to 800 tCO₂/day with increased electricity costs of 65% [31].

2.3. Oxyfuel Combustion

The oxyfuel combustion is a recently developed technology for carbon capture [32], it involved using a relatively pure oxygen stream instead of air for combustion. To employ the oxyfuel combustion method, an air separation unit is required to remove nitrogen gas from air to produce oxygen gas with a purity of 90 to 95% [33]. The pure oxygen stream is then used for the combustion of the fuel, converting it to a mixture of CO₂ and low amounts of water vapor as shown in Equation (4):



Separation of the CO₂ gas from the exhaust is relatively easy as no significant amount of nitrogen is present. The most common separation technique for the oxyfuel combustion are cryogenic air separation, temperature swing adsorption, pressure swing adsorption, and the use of membranes [34,35]. The oxyfuel combustion method is the simplest method

to implement in running facilities as the main requirement is switching the air used for combustion to oxygen. Moreover, it is advantageous as it has low NO_x emission and low CO_2 separation cost [36,37]. However, the main drawback is in the high cost of the air separation unit, which makes it heavily dependent on a high capital cost [38–40]. A schematic representation of Pre-Combustion Carbon Capture process is illustrated in Figure 3.

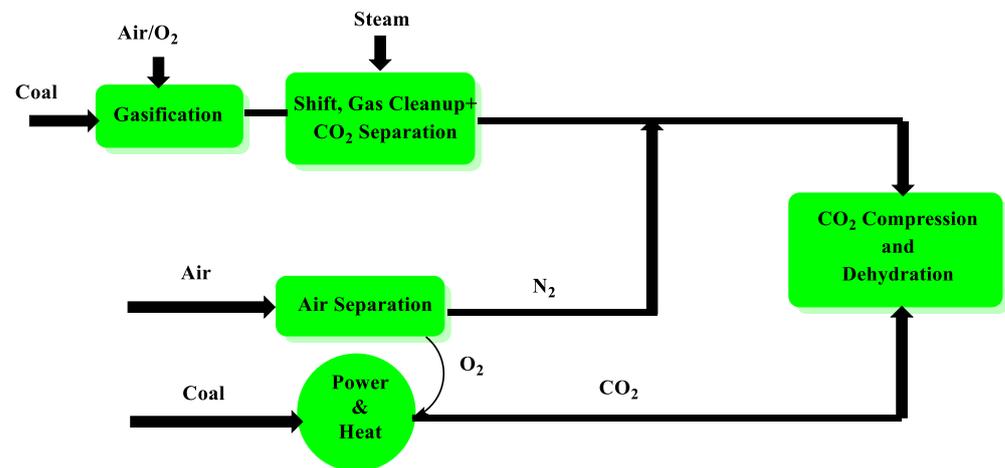


Figure 3. Oxyfuel-combustion capture process.

2.4. Direct Air Capture (DAC)

DAC technology is an alternative climate change mitigation technology that selectively captures CO_2 from the ambient air by a chemical adsorbent. A concentrated stream of CO_2 is then generated for disposal or reuse, while at the same time, the adsorbent is regenerated, and the CO_2 -depleted air is released back to the atmosphere. Typical process conditions of carbon capture and storage (CCS) technology are summarized in Table 1.

Table 1. Typical carbon capture and storage (CCS) technology conditions.

Carbon Capture and Storage (CCS) Technology	Typical Pressure (Bar)	Temperature ($^{\circ}\text{C}$)	CO_2 Concentration (%)
Pre-combustion	14–70	200–450	15–60
Post-combustion	1	–55	17–70
Oxyfuel Combustion	1	40–60	3–20
Direct Air Capture	1	25	~0.04

The choice of which to implement is affected by several factors such as the concentration and partial pressure of CO_2 , the content of impurities and pollutants, and the cost of implementing the method [41]. For instance, if the CO_2 is of high pressure and high concentration (15–50%), the most preferable mode of carbon capture is pre-combustion, where CO_2 would be captured before the combustion of the fuel, as the fuel gas naturally has higher concentrations of CO_2 [42]. However, for a relatively low concentration of CO_2 (13–15%) and low partial pressure, the post-combustion mode is highly recommended and could be implemented in an existing power plant to capture low concentrations of CO_2 from the flue gas [43].

3. Post-Combustion Carbon Capture Based on the Adsorption Process

The sequestration and capture of CO_2 emitted into the atmosphere by adsorption processes have been widely investigated and implemented. It is employed to overcome the limitations associated with conventional absorption methods, such as the low capac-

ity of solvents at high temperatures and pressures, and the corrosive nature of these adsorbents [41].

The adsorption technique is highly effective in the separation and remediation of different contaminants. It is based on the use of solid surface materials (adsorbents) to remove or separate pollutants (adsorbate) [42–44]. The different interactions between the adsorbent and the adsorbate classify the adsorption into two mechanisms. Weak interactions via Van der Waals forces, dipole-dipole forces, and the London force result in the physisorption mechanism [45]. Whereas, the chemisorption mechanism occurs due to the strong chemical interaction such as the covalent, chelation, complex formation, and other chemical bonds between the contaminant and the adsorbent [46].

In the case of carbon dioxide, the gaseous molecules are bound to the surface of the adsorbent [47]. Various organic/inorganic-based adsorbents have emerged as promising candidates for the removal of carbon dioxide [43,48]. For example, amine-based adsorbents [49,50], metal oxides [51,52], and alkali metal-based materials have been employed for chemisorption-based carbon capture. This is attributed to the fact that these materials have different functionalization on their surfaces, which facilitates the electrostatic interactions between the adsorbent and the adsorbate [53]. Despite having different active sites on their surfaces, many studies have shown that these materials exhibit low selectivity and adsorption capacities for carbon dioxide at a low partial pressure. Therefore, many attempts have recently been made to modify the surfaces of these materials by the addition of a new basic functionalization to enhance the capturing of carbon dioxide that has an acidic nature [54]. Additionally, many studies have been reported for the physisorption sequestration of CO₂ by different porous and mesoporous materials such as zeolites [55,56], carbonaceous materials [57,58], and silica materials [59,60]. It is well known that the pores within the materials provide rapid and simple mass attraction of the analyte on the surface of the adsorbent. It is worth mentioning that physisorbents are extensively employed for the sequestration of carbon dioxide at high concentrations. Moreover, the metal-organic framework (MOF) gained popularity in the removal of carbon dioxide by both physisorption and chemisorption [61,62]. Table 2 summarizes the advantages and disadvantages of these adsorbents.

The selection of a specific adsorbent is very crucial for the adsorption performance. Tremendous effort has been made to set systematic criteria for the selection of CO₂ adsorbents including the adsorption capacity and selectivity for CO₂, adsorption and desorption kinetics, regeneration of sorbents, and adsorbents cost [63]. Adsorbents with high adsorption capacities are most favorable in achieving good carbon capture results. The selectivity of CO₂ ensures the purity of the captured CO₂. Rapid adsorption/desorption kinetics are preferable as they have a direct influence on the amount of adsorbent required. A statistical study on the relation of the sorbent price to its utilization has shown that the most used carbon capture sorbents are in the range of \$10/kg. This is due to the economical and cost-effective characteristics of these materials [64].

Many parameters play an important role in controlling the adsorption process, including the pH, temperature, contact time, concentration of carbon dioxide, and adsorbent dosage. These parameters are optimized for increasing the effectiveness of capturing carbon [65].

This section of the review provides a detailed background for researchers interested in different adsorbents used for the capturing and separation of carbon dioxide in the post-combustion method. Furthermore, it presents some of the emerging techniques and latest studies related to these sorbents.

Table 2. Pros and cons of different types of carbon dioxide adsorbents.

Type of Adsorbent	Adsorbents	Advantages	Disadvantages
<i>Chemisorbents</i>	Amine-based sorbents	Low regeneration energy High adsorption capacity in case of high amine and nitrogen content Stable materials Fast adsorption of carbon dioxide Multiuse sorbents	Expensive synthetic material
	Metal oxides and metal oxides-based sorbents	Common for pre-combustion of CO ₂ Cost-effective Abundant materials Low toxic substance Durable after various cycles The operation temperature is moderate to high	Require long reaction time Require high energy for regeneration
	Alkali-metal adsorbents	Low regeneration energy Cost-effective Ability to operate at low temperature below 200 °C	Slow operation adsorbents Durable Irreversible adsorbents in the presence of SO ₂ and HCl
<i>Physisorbents</i>	Zeolites	High adsorption capacity Porous materials Large surface area High stability	Low selectivity of CO ₂ Large decrease in adsorption with slight increase in temperature
	Carbonaceous materials	Excellent thermal stability Tolerance to moisture Cost-effective Low adsorption operating temperature Abundancy Good conductivity Large surface area Suitable pore sizes and volumes	Low for selectivity to CO ₂ High thermal sensitivity
	Mesoporous silica materials	Tuneable structure Good thermal and mechanical stability Large surface area Porous structures Low cost	Low adsorption capacity in the absence of functionalities
	MOFs	Uniform and tuneable structures Large surface area Ultrahigh porosity Easy functionalization Chemical and thermal stability	Low adsorption capacity at low pressure Sensitive to moisture Sensitive to mixture of gases Expensive generation procedures

3.1. Chemisorbents

3.1.1. Amine-Based Adsorbents

Functionalized amine-based adsorbents have been widely explored for the efficient chemisorption of carbon dioxide, because of their advantageous characteristics and properties, including the low energy required for synthesis, high adsorption capacities, and selectivity to carbon dioxide resulting from the immobilization of high contents of amines and nitrogen in the adsorbents. Moreover, they have been widely used as adsorbents because of their rapidity, recyclability, and stability [66,67]. In addition, they are water-tolerant species and have been used as alternatives to tackle the drawbacks of the amine adsorbents [68,69]. Therefore, these materials were synthesized with supporting porous and mesoporous materials to improve the performance in capturing carbon dioxide [70–73]. The most common amine sources used in solid sorbents are shown in Figure 4.

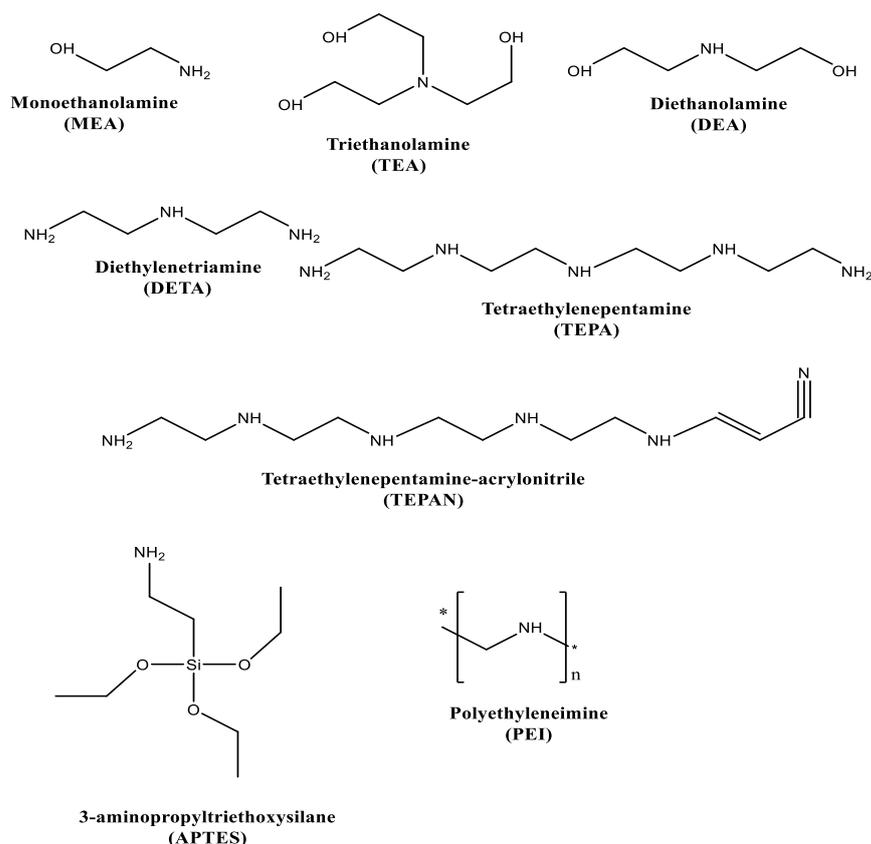


Figure 4. Common amine adsorbents.

Despite their advantages, these materials are costly in their production [74]. The chemical reaction between amine groups and carbon dioxide is explained by the zwitterion mechanism, which was firstly proposed by Caplow [75]. This mechanism is applicable for primary and secondary amines due to the availability of hydrogen for deprotonation, unlike tertiary amines, which are bonded to three alkyl groups. Therefore, tertiary amines are not used for the capturing of carbon dioxide as no reaction can occur. The zwitterion mechanism is a two step mechanism, involving the formation of a zwitterion as an intermediate, which is then deprotonated by basic catalysts [76]. The reaction of sterically hindered primary and secondary amines results in the formation of bicarbonates (Figure 5), where it usually has a high CO₂ adsorption capacity [77].

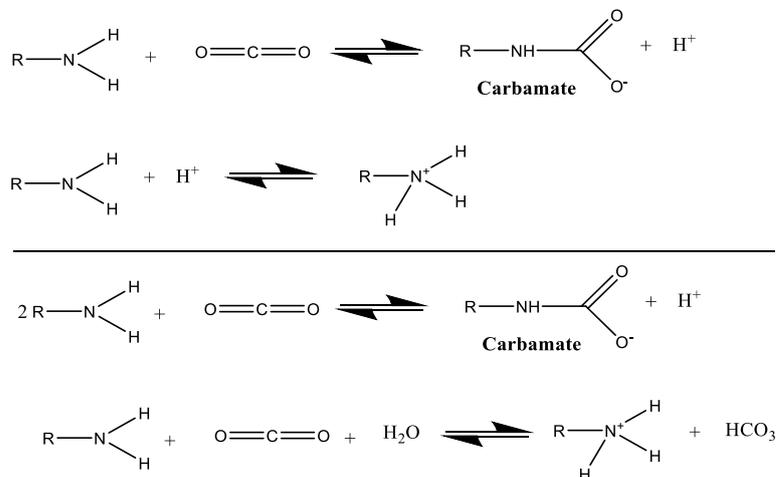


Figure 5. The reaction of a primary or secondary amine with carbon dioxide in the presence of water.

Many recent studies were documented for the fabrication and usage of various amine-based adsorbents in post-combustion carbon capture. Zhou et al. [78], constructed different monolithic adsorbents with excellent carbon dioxide adsorption capacities and mechanical strength. The synthesized mesoporous MCM-41 immobilized by an organic polymer showed a large surface area ($\sim 1088 \text{ m}^2 \text{ g}^{-1}$) available for mass diffusion and interaction with carbon dioxide. The 70TMM-550 monolithic adsorbent impregnated with tetraethylenepentamine (TEPA) was reported as a reversible adsorbent under mild conditions. In addition, it achieved the highest adsorption capacity of 151.1 mg g^{-1} at $75 \text{ }^\circ\text{C}$ and under 1 atm. This is because when the temperature increases, the amine chains will stretch, and more active sites will be available for the adsorption of carbon dioxide which will increase the adsorption capacity. However, the study also revealed that at higher temperatures ($90 \text{ }^\circ\text{C}$), the thermodynamic equilibrium limits the adsorption of CO_2 on the binding sites of amines and the adsorption capacity recorded was decreased to 146 mg g^{-1} . Figure 6 shows the effect of temperature on the adsorption process. The recyclability of the adsorbent was also tested, and the results obtained show that the adsorption capacity reported for this adsorbent decreased gradually by 2.8% after five cycles [78].

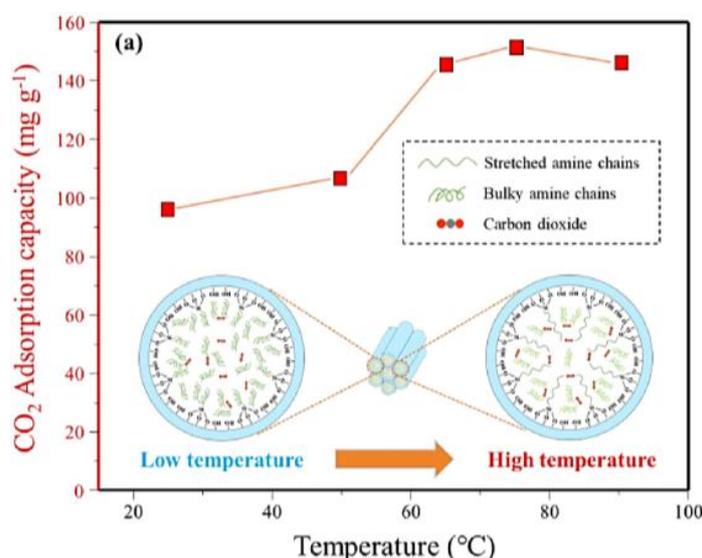


Figure 6. The effect of the operation temperature on the adsorption of CO_2 on 70TMM-550 adsorbent. Reproduced with permission from [78].

Furthermore, Chisitiga et al. [79] developed novel water-soluble adsorbents named Ethylenediamine-grafted polysuccinimide (EDA-PSI). Their work was conducted using Methyl Amine (MA) and Mono-Ethanol Amine (MEA) as water-soluble amines to improve the porosity and increase the surface area. The results showed increases in adsorption capacities by increasing the concentration of MA and MEA in the sample. The highest adsorption capacity was obtained by the 100% MA grafted sample ($44.2 \text{ g CO}_2/\text{kg Ads}$).

Further studies have extensively explored functionalized amine-based adsorbents on mesoporous and macroporous silica for achieving high selectivity of carbon dioxide. A study by Ra et al. [80], showed enhanced adsorption by immobilizing Pentaethylenhexamine (PEHA) on macroporous silica (MPS). The fabricated adsorbent 2.0PO-PEHA/MPS achieved an adsorption capacity of 1.8 mmol g^{-1} at $50 \text{ }^\circ\text{C}$ as shown in Figure 7. The adsorbent was found to be stable after 20 regeneration cycles.

Moreover, Ahmed et al. [81] investigated the effect of functionalizing various forms of tetraethylenepentamine (TEPA) with different concentrations in mesoporous Si-MCM-41 using gravimetric analysis. The investigation included the impact of temperature on the adsorption capacity. At 50% wildtype, an adsorption capacity of 54.65 mg/g (in $25 \text{ }^\circ\text{C}$ and 1 bar) was recorded. The study concluded that the increase in temperature from 25 to $75 \text{ }^\circ\text{C}$ was significantly efficient in increasing the adsorption capacity, where it was recorded that

at 75 °C and 1 bar the adsorption capacity reached 70.41 mg/g. The chemisorption process of carbon dioxide on the amine-based adsorbents was confirmed by the FT-IR spectra, which showed peaks attributed to the formation of carbamates.

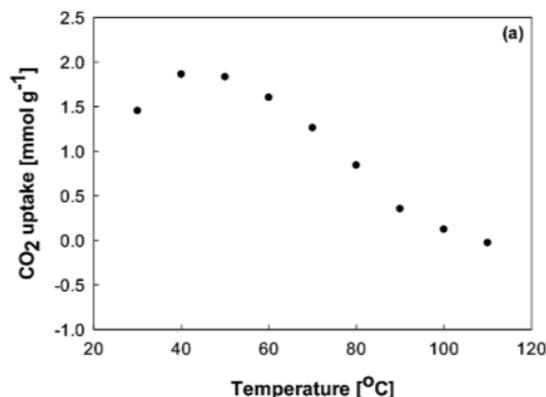


Figure 7. The effect of temperature on the adsorption capacity of 2.0PO-PEHA/MPS. Reproduced with permission from [80].

The amine-functionalized carbonaceous materials (CMs) are well-recognized for post-combustion carbon capture. Atta-Obeng et al. [82] synthesized different sorbents of CMs functionalized with polyethyleneimine (PEI) to evaluate the change in the adsorption capacity. Conclusive results demonstrated that the surface area and the adsorption capacity increased with the increase in amine impregnation. However, after 5% loading of amine, the adsorption started decreasing and this was attributed to the blockage of the pores of CMs due to the higher contents of amine. The surface area reported after impregnation increased from 2.8 to 1341 m² g⁻¹.

The CO₂ adsorption capacities of L350 with 5% PEI reached 2 mmol g⁻¹. Moreover, Lourenco et al. [83] compared the adsorption capacities of CO₂ at different functionalities of -OH, -COOH, modified -OH with DETASi, and modified-COOH with DETASi on a multi-walled carbon nanotube (MWCNT). The functionalities were modified with N1-(3-trimethoxysilylpropyl) diethylenetriamine (DETASi) to improve the adsorption properties. The results revealed that no adsorption occurred for the standard MWCNT and OH-functionalized MWCNT. However, a small adsorption percentage of 0.1% was reported for the COOH-modified MWCNT at 1 bar and 30 °C. Additionally, the results obtained showed an enhanced adsorption percentage after modification with DETASi. Furthermore, the results showed that COOH-MWCNT functionalized with DETASi achieved the highest adsorption percentage of 2.11%.

3.1.2. Alkali-Metal/Metal Oxide-Based CO₂ Adsorbent

Alkali-metal-based CO₂ adsorbent can be prepared by adding alkali-metal (i.e., Na, K, Al, or Li) carbonates to various inorganic supports such as carbon materials, zirconia, ceramics, silica, and alumina. They have gained prominence for carbon capture due to their unique characteristics, including low regeneration energy, low cost, and low operation temperatures. Despite these advantages, they have certain drawbacks including slow reaction rates, low disabilities, and irreversibility in the presence of SO₂ and HCl [66,84].

Lithium orthosilicate (Li₄SiO₄) was examined by Seggiani et al. [85]. The CO₂ adsorption capacity was examined after the addition of 30% K₂CO₃ or Na₂CO₃ wildtype. Both Li₄SiO₄-carbonate adsorbents had CO₂ adsorption capacities of 5.23 mmol g⁻¹ at low CO₂ partial pressures of 0.04 bar and optimal adsorption temperatures of 580 °C.

Lithium oxosilicate (Li₈SiO₆) was studied by Durán-Muoz et al. as a CO₂ adsorbent [86]. Over a large temperature range (T ≥ 650 °C), the Li₈SiO₆ adsorbent demonstrated a very high sorption capacity of roughly 11.79 mmol g⁻¹ with an efficiency of 71.1%.

According to Ma et al. [87], alkali metal-doped porous carbon materials, such as Li⁺ metal-doped porous carbon material (PC-Li), Na⁺ metal-doped porous carbon material (PC-Na), and K⁺ metal-doped porous carbon material (PC-K), demonstrated a CO₂ adsorption capacity of 8.43–12.46 mmol g⁻¹, which demonstrates that the interaction between the carbon surface and CO₂ molecules is significantly influenced by the doping of alkali metals into the carbon surface.

The post-combustion CO₂ capture using the alkali-metal-based CO₂ adsorbents at high temperatures and low concentrations is technically and economically advantageous because they do not need further cooling procedures. However, these alkali metal-based CO₂ adsorbents' carbonation reaction characteristics heavily depend on the support materials, the adsorbent surface area, the physical qualities of adsorbents, and the distribution of the active ingredients. Most of the recently reported data are simulated and not specific to a certain mode of combustion of carbon dioxide. It is clear that this type of adsorbent is still under investigation [41].

3.2. Physisorbents

3.2.1. Zeolites

Zeolites are microporous (<2 nm) crystalline structures with large surface areas, and are composed of aluminosilicates and have various applications in catalysis and adsorption fields [88]. Figure 8 represents a schematic representation of zeolite [89]. Zeolites are negatively charged frameworks which tend to host cations such as alkali metals in their pores to balance the negative charge, which results in an electric field mechanism during the physisorption process. In previous studies, a directly proportional relation was reported between the number of cations in zeolite pores and the carbon dioxide adsorption capacity. This is due to the increase in basicity with the increased number of cations, hence it facilitates the electrostatic interaction between carbon dioxide and the cations.

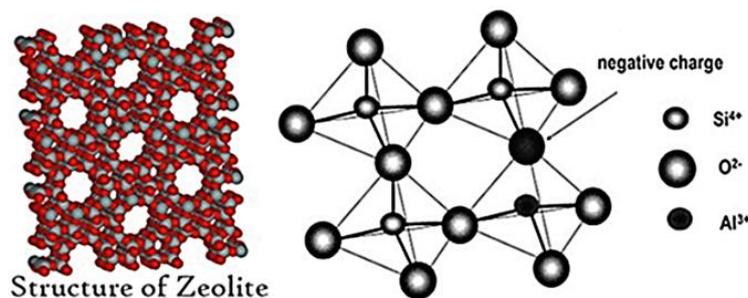


Figure 8. The zeolite structure. Reproduced with permission from [89].

Zeolites have been widely utilized as efficient porous adsorbents for different contaminants. They exhibit several unique characteristics including having a large surface area, low cost, ease in fabrication, and tunability [90]. The large surface area and the existence of pores attracted researchers to examine the carbon dioxide adsorption capability of these materials [63]. The results obtained have shown high carbon dioxide adsorption capacities. However, the results have shown a decrease in the CO₂ adsorption capacity with the increase in temperature above 30 °C, and no adsorption performance was obtained above 200 °C. Additionally, it is unselective for carbon dioxide in the presence of moisture in the flue gas [90].

Many studies were published in the literature documenting the use of zeolites and their derivatives as CO₂ adsorbents. Figure 9 represents a schematic representation for physisorption of CO₂ on zeolite.

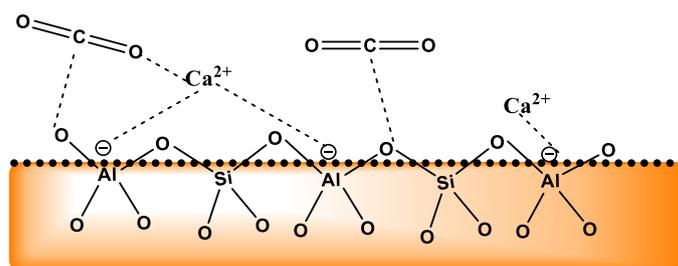


Figure 9. Physisorption CO₂ on zeolite.

A lithium low silica X type (Li-LSX) zeolite was tested as an adsorbent for post-combustion carbon capture [91]. The adsorption capacity of CO₂ was found to be 4.43 mmol g⁻¹ and the adsorption percentage was reported to be 14% at 60 °C. The adsorbent was stable during 85 sorption cycles and at 35 h period. Panda et al. [92] worked on enhancing the mesopore volume and surface area for better adsorption results. The investigation included the synthesis of three different forms of the hierarchical zeolites 4A (HZ4A) derived from the zeolite 4A (Z4A) using the post synthetic modification procedures. The results showed that the modified mesoporous structure of HZ4A-1–3 exhibits a higher CO₂ adsorption capacity as compared to the parent zeolite framework. In addition, it achieved low water adsorption capacity, mild desorption temperature (13 °C less than the original) and stability up to 10 cycles. The results are affected by the existence of mesopores which contribute to the fast diffusion of carbon dioxide. Hwang et al. [93] compared the efficiency of the commercial zeolites in capturing CO₂ with novel synthesized zeolitic 4A type materials at different temperatures from 283 to 303 K and pressure ranges from 0.1 to 1500 kPa. The synthesized material of zeolitic 4A type was fabricated using alkali fusion and hydrothermal synthesis methods. The zeolitic 4A type exhibited the micropore volume and large surface area to volume ratio. This facilitates the sequestration of CO₂ within the pores. The reported results showed that the zeolitic 4A displayed a higher adsorption capacity of 5.9 mmol g⁻¹ as compared to that of commercial zeolites, which was found to be 3.6 mmol g⁻¹ at 293 K and 1500 kPa.

The synthesis of the functionalized amine-based zeolite adsorbents emerged due to their excellent adsorption characteristic. Liang et al. [94] developed different amine-immobilized HY zeolites for adsorption applications. The amines used were monoethanolamine (MEA) and ethylenediamine (ED). The carbon dioxide adsorption capacity was measured at different temperatures of 30, 60, and 90 °C. The highest adsorption capacity of 1.76 mmol·g⁻¹ was recorded for the 20% ED@HY Zeolite sample at 90 °C, this was attributed to the higher content of amine as compared to other amine@HY zeolite samples. Panda et al. [95] constructed a novel type of composite adsorbent by amine functionalization of binder-containing zeolite 4A bodies. The purpose of their study was to observe the impact of amine modification on the adsorption properties of binder-containing zeolites. Different amine functionalities were used for applying modifications, such as propylamine (PA), butylamine (BA), pentylamine (PEA), iso-propylamine (IPA), iso-butylamine (IBA), and iso-pentylamine (IPEA). Among the prepared adsorbents, the iso-butylamine-modified binder-containing zeolite 4A bodies (IBA-Z4A) displayed the highest CO₂ adsorption of 2.56 mmol g⁻¹ at 25 °C and 1 bar. In addition, IBA-Z4A showed the highest selectivity to carbon dioxide and nitrogen gas. A good justification of these results is attributed to the increase in basicity and electron density at the N atom of the amines which enhances the adsorption of CO₂.

3.2.2. Carbonaceous Materials

Carbonaceous materials are physisorbents formed from carbon. They have been increasingly implemented in the adsorption of carbon dioxide due to their large surface area, superior pore sizes and volumes, thermal stability, low cost, low adsorption temperature

(below 100 °C), and good conductivity. Nevertheless, their selectivity to carbon dioxide is low and they are highly sensitive to changes in temperature [63,74,96].

Different types of carbonaceous materials were reported in the literature including activated-carbon (ACs), carbon nanotubes (CNTs), and graphene-based materials. This part of the review provides brief introductions to each type of these materials along with recent studies of their CO₂ adsorption performance.

Activated carbons (ACs) are mesoporous amorphous materials with micropores (less than 2 nm) and nanopores (2–50 nm) [97]. Owing to their large surface area and porosity, they are applicable in various applications. The modification of the surface of activated carbons by functionalization is a well-known strategy as it contributes to better hosting/diffusion of molecules [98]. Many types of functionalization can be employed in ACs such as hydroxyl, carboxylic acid, ketones, graphitic, pyridinic, and pyrrolic N functionalization [99,100].

The synthetic routes for the preparation of ACs includes the use of high content carbon precursors. The use of coal, natural biomass, and biowaste as precursors is popular to synthesize green activated carbon [101]. The synthetic procedure of activated carbons (ACs) adsorbents includes two steps: carbonization and activation. The carbonization is a step in which the precursors are pyrolyzed to extract the carbon materials at elevated temperatures (below 700 °C) and under an inert atmosphere. This is followed by the activation of carbon by either physical or chemical activation processes to achieve porosity and improve the surface area [102–104].

Nowadays, the effect of activation on the adsorption capacity has been thoroughly investigated. Zafanelli et al. [105], worked on 3D-printed monolith-activated carbons to examine the efficiency of the adsorption process, and to evaluate different activation conditions and their roles in enhancing the carbon capture process. Besides, the study involves the examination of selectivity to carbon dioxide. The activation conditions included the burn-off level at a range of temperatures (313 and 373 K), and a partial pressure of 120 kPa. The results suggested high burn-off during the activation to improve the adsorption capacity as it was found to be 3.17 mol/kg at 313 K and 120 kPa, which is greater than that of low burn-off. However, the lower burn-off during activation resulted in high selectivity to carbon dioxide. Jiang et al. [106] compared the efficiency of activated carbon with different materials for post-combustion carbon capture. The materials used in the experimental comparison are commercial adsorbents (monoethanolamine) and a chemical adsorbent (polyethyleneimine/silica). The efficiency of the adsorption of CO₂ by activated carbon increased from 50.5% to 50.9% when the adsorption temperature raised from 348 K to 378 K. The results showed that the chemical adsorbent polyethyleneimine/silica has almost the same efficiency as activated carbon. The commercial adsorbent monoethanolamine achieved a 3% lower capturing efficiency as compared to AC.

Carbon nanotubes (CNTs) are needle-shaped structural materials with diameters ranging from 0.5 to 50 nm. They are synthesized from sp² hybridized graphitic carbon. There are three types of CNTs, classified based on their diameters including single-walled CNTs (SWCNT), double-walled, and multiwalled-CNTs (MWCNT). Figure 10 illustrates the different structures of CNTs [107]. Recent studies have utilized CNTs and impregnated CNTs as adsorbents in the sequestration of carbon dioxide in post-combustion carbon capture. Osler et al. [108] evaluated the performance of MWCNTs and chitosan/MWCNTs on the adsorption efficiency. The amount of CO₂ adsorbed by MWCNTs was found to be 0.4 mg g⁻¹, and it was increased after impregnation with chitosan as it achieved 3 mg g⁻¹ at 45 °C and 1.1 bar. Moreover, Krishnamurthy et al. [109] found a high percentage of selectivity (more than 95%) to CO₂, using a 3D printed sorbent containing polyethyleneimine (PEI) and multiwalled carbon nanotubes (MWCNT).

Graphene is a carbon-allotrope in a two-dimensional honeycomb-shape lattice nanostructure. The graphene-based materials including graphene oxide (GO), and reduced graphene oxide (rGO) have been widely used for capturing carbon [110].

Nagarajan et al. [111] studied the effect of different parameters such as the time, dosage of adsorbent, concentration of CO₂, adsorption thermodynamics, and temperature on the CO₂ adsorption performance of a synthesized solar reduced graphene oxide (SRGO). The synthesized material was developed using a modified Hummer's method. The adsorption capacity achieved was found to be $1.893 \times 10^{-3} \text{ mol g}^{-1}$ at 60 min. The Freundlich isotherm was found to best fit the adsorption results. The results obtained showed that the adsorption reaction is a pseudo second-order reaction.

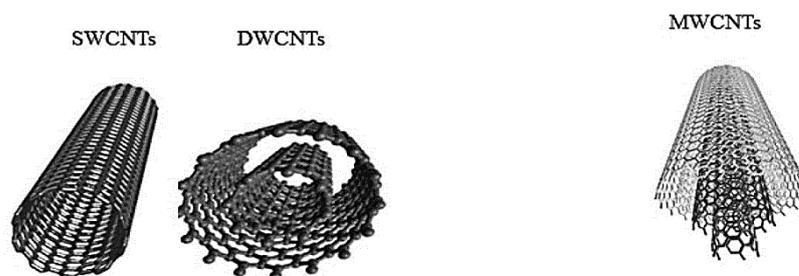


Figure 10. Different types of CNTs adsorbents. Reproduced with permission from [107].

3.2.3. Mesoporous Silica

Recently, the mesoporous silica materials were studied due to their large surface area and good porosity. Most mesoporous silica materials were functionalized with amines, due to the absence of active sites on the silica, which is considered as a problem hindering carbon capture. Recently, amine functionalization was used to impregnate the silica materials in order to enhance the adsorption properties [63].

3.2.4. Metal Organic Frameworks (MOFs)

MOFs and MOFs-functionalized materials are new classes of materials that have emerged predominantly in the last decade. They are characterized by their unique properties including ultrahigh porosity, large surface area supported with a high number of active sites, uniform and tunable structures, easy functionalization, and thermal stability [112]. MOFs are crystalline porous materials composed of metal ions bonded to organic ligands via coordinate covalent bonds. These materials are also called coordination polymers or metal organic polymers [113]. They have a wide range of applications in the catalysis [114–116], adsorption [117,118], and sensing fields [119–122]. Although having many advantages, they have certain inadequacies in the adsorption, such as the low adsorption capacity in low pressure, sensitivity to moisture and a mixture of gases, and their high synthetic cost which limit their use [96].

Impregnated MOF-based adsorbents have attracted researchers due to their excellent physisorption and chemisorption characteristics for post-combustion carbon capture. Gaikwad et al. [123] evaluated the adsorption efficiency of different amine-functionalities such as polyethyleneimine (PEI), tetraethylenepentamine (TEPA), and diethylenetriamine (DETA), and impregnated in MOF-177 to enhance the adsorption capacity. The results showed that TEPA-impregnated MOF-177 displayed a significant improvement (4.8 times) in CO₂ capturing as compared to the unmodified MOF-177 at 298 K. However, both PEI and DETA-functionalized frameworks exhibited negligible improvements. The study also revealed that the adsorption capacity was increased with the increase in temperature as it reached 4.6 mmol/g at 328 K for TEPA-impregnated MOF-177. Furthermore, Quan et al. [124] synthesized diamine-appended metal-organic framework (MOF)/polymer composite hollow fiber sorbent for post-combustion carbon capture. The results showed that the 2-ampd-Mg₂(dobpdc) fiber sorbents captured higher amounts of CO₂ (2.5 mmol CO₂/g-MOF) at a relatively low pressure. Furthermore, Wu et al. [125] investigated the adsorption efficiency of a copper-based metal-organic framework with two types of pores. The first type is occupied with Cu open metal sites (OMS) while the second type was occupied with –CH₂ moieties from the organic linkers in narrower-sized pores. The CO₂ uptake value

reported at 298 K was 4.63 mmol/g at 100 kPa and 2.92 mmol/g at 15 kPa. This value outperformed adsorption performances of other documented MOFs. The availability of strong electrostatic interaction sites caused by the presence of dense Cu OMS in the first channel has resulted in the presence of CO₂-hosting molecules.

Qazvini et al. [126] attempted to overcome the limitations associated with MOFs-based adsorbents. Therefore, his study was focused on the synthesis of MOFs adsorbent materials that can be implemented on large-scale industrial applications with an affordable production cost and long-term chemical stability. The successful synthesis resulted in the formation of MUF-16 ([Co(Haip)₂], Haip₂ = 5-aminoisophthalic acid), a hydrogen-bonded water-stable microporous material coated with polymeric poly(vinylidene difluoride) (PVDF). The fabricated MUF-16 showed a good sensitivity to carbon dioxide as the amount of CO₂ uptake was found to be 47.8 and 61.1 cm³ /g of CO₂ at 1 and 20 bar, respectively.

A comparison between the adsorbents discussed in detail was provided in Table 3 with additional information regarding the surface area (m²/g), pore size (nm), and important parameters for adsorption, regeneration cycles, and adsorption capacity Q_{max}.

Table 3. Adsorbents for carbon dioxide capture.

Type of Adsorbent ^a	Adsorbent ^b	Surface Area (m ² /g)	Pore Size (nm)	Operation Parameters		Regeneration Cycles	Adsorption Capacity Q _{max}	Ref.
				Pressure (bar)	Temp. (°C)			
Chemical adsorbents	70T-MM-550 monolithic adsorbent impregnated with TEPA	10.46	0.02	1	75	5	151.1 mg g ⁻¹	[78]
	PAA-100% MA	2.94	30.9	1.1	40	-	44.2 g kg ⁻¹	[79]
	2.0PO-PEHA/MPS	472	-	-	50	20	1.8 mmol g ⁻¹	[80]
	50 wt.% TEPA-functionalized Si-MCM-41	11	1.8	1	75	-	70.41 mg g ⁻¹	[81]
	Si-MCM-41	993	3.1	1	25	-	54.65 mg g ⁻¹	[82]
	L350 PEI 5%	1341	-	-	30	-	2 mmol g ⁻¹	[83]
	L350	2.8	-	-	30	-	1.54 mmol g ⁻¹	[83]
COOH-MWCNT/DETASi	74	1.9–63	0.9	30	-	0.48 mmol g ⁻¹	[83]	
Physical adsorbents	Li-LSX zeolite	662	0.08–0.18	0.15	60	85	4.43 mmol g ⁻¹	[91]
	HZ4A-1–3 with urea	126	0.4–5.5	1	40	10	2.86 mmol g ⁻¹	[92]
	Basalt based zeolite 4A	726	-	15	20	-	5.9 mmol g ⁻¹	[93]
	20% ED@HY Zeolite	-	-	-	90	8	1.76 mmol g ⁻¹	[94]
	IBA-Z4A	32	3.8	1	25	10	2.56 mmol g ⁻¹	[95]
	3D-printed monolith activated carbons	-	-	1.2	40	-	3.17 mol kg ⁻¹	[105]
	chitosan/MWCNTs	-	-	1.1	45	-	3 mg g ⁻¹	[108]
3D-printed PEI/(MWCNT)	27	30	-	90	-	0.064 mol kg ⁻¹	[109]	
Hybrid adsorbents	20% TEPA-impregnated MOF-177	585	-	1	55	-	4.6 mmol g ⁻¹	[123]
	2-ampd-Mg ₂ (dobpdc)	-	-	1	40	-	2.5 mmol g ⁻¹	[124]
	Copper based MOF-11	-	-	1	25	-	4.63 mmol g ⁻¹	[125]

^a Type of Adsorbent: Hybrid adsorbents = adsorbents having both physisorption and chemisorption characteristics; ^b Adsorbent: PAA-100% MA = Polyaspartamide adsorbent impregnated with 100% methyl amine; 2.0PO-PEHA/MPS = two mole ratio of propylene oxide-pentaethylenhexamine on macroporous silica; L350 PEI 5% = 5% loading of polyethyleneimine-functionalized carbonaceous material; L350 = carbonaceous material; Li-LSX = lithium low silica X type zeolite; HZ4A-1–3 = hierarchical zeolite 4A (HZ4A) with urea to zeolite weight ratio 1:3; COOH-MWCNT/ DETASi multi-walled carbon nanotube modified with carboxyl group and N1-(3-trimethoxysilylpropyl)diethylenetriamine; 20% ED@HY Zeolite = 20% ethylenediamine loaded proton type Y zeolite; IBA-Z4A = iso-butylamine-modified binder-containing zeolite 4A bodies; 3D-printed PEI/(MWCNT) = 3D printed sorbent containing polyethyleneimine and multiwalled carbon nanotubes; 2-ampd-Mg₂(dobpdc) = diamine 2-(aminomethyl)piperidine infused into Mg-MOF with 4,4'-dioxidobiphenyl-3,3'-dicarboxylate.

4. Post-Combustion Carbon Capture Based on the Absorption Process

Over the last few decades, a lot of research was devoted towards improving and optimizing carbon-capturing solvents, and advancements have been made in increasing the efficiency and lowering the energy input requirements.

There are some ideal characteristics that should be present in ideal adsorbents including:

1. Relatively low cost;
2. High absorption rate;
3. High capacity of absorbing CO₂;
4. Low regeneration energy;
5. Non-degradable;

6. Salt formed must be unstable at the regeneration temperature;
7. Non-corrosiveness.

Unfortunately, most solvents do not have all the desired properties of an ideal absorbent, this is a major limitation which researchers are actively trying to overcome [127]. Sorbents can capture carbon via physical and chemical absorption mechanisms. The difference between physical and chemical absorption mechanisms depends on the state in which carbon is present. In short, physical absorption is the process of absorbing CO₂ through Van der Waals non-covalent weak forces, thus it is considered a chemically inert process. Whereas chemical absorption is a process in which CO₂ reacts chemically to the absorbent, and thus it strongly attaches to it, resulting in carbon capture. Moreover, the absorbent can then be heated to release the captured CO₂ [43]. It is well agreed that physical absorption is to be used when the partial pressure of CO₂ is high, whereas chemical absorption is best at low partial pressures of CO₂ [128,129].

4.1. Chemical Absorbents

4.1.1. Amine-Based Absorbents

Amine-based absorbents are recognized as one of the most widely used absorbents in post-combustion carbon capture, as they have relatively high efficiency and low toxicity. This method was first introduced during the 1930s and was heavily developed [130]. Nowadays, alkanolamines such as ethanolamine (EA), di-ethanolamine (DEA), and methyl di-ethanolamine (MDEA) are widely used for capturing carbon [43], which are shown in Figure 4.

Solutions of EA, DEA, and MDEA have shown effectiveness in capturing CO₂. For instance, Park et al. [131,132] have shown that the tertiary amine (MDEA) is less efficient than the secondary (DEA) and primary (EA) amines in capturing carbon. Tertiary, secondary, and primary amines differ in the way in which the mechanism occurs as mentioned previously in Section 3.1.1, therefore, it is expected that the efficiency would differ. The mechanism of primary and secondary amines is shown in Figure 5. However, tertiary amines do not react with carbon dioxide directly, as water must be involved in the reaction. A schematic representation for this reaction is shown in Figure 11.

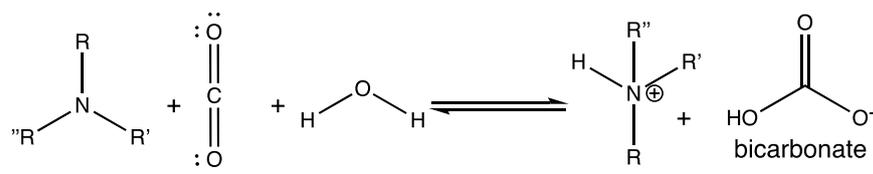


Figure 11. Tertiary amines react with carbon dioxide in the presence of water to give bicarbonate.

Capturing carbon dioxide by amine-based solvents has its pros and cons. In terms of the advantages of the method, it operates at a low temperature and pressure with high efficiency. Furthermore, since the amine-solvents are aqueous, they have a low viscosity. Finally, they are commercially available and cheap. On the other hand, the regeneration of the absorbents is very costly, as high energy inputs are required to do so [131]. Non-aqueous amine-based sorbents were developed in recent years (Table 4). The major advantage of such sorbents is the obvious reduction in the energy required to regenerate the sorbent once more. Non-aqueous solvents were used in a recent study, namely 2-Methoxyethanol (2ME) and 2-ethoxyethanol (2EE), and MEA and DEA were dissolved in them. The obtained results were promising as the capacity of absorption reached after 60 min was 91.98%, 90.00%, and 71.14% for MEA/2ME, MEA/2EE, and DEA/2ME, respectively. Using aqueous solutions as a benchmark for comparison, the latter solutions were reported to be generated with 55% less energy compared to the corresponding aqueous solutions. This rather noticeable reduction in energy was attributed to relatively low-heat capacity of the solvents compared to the water [133].

Table 4. Summary of the studies on amine-based sorbents [131,133].

Sorbent	Efficiency (Kg CO ₂ /Kg Sorbent)	Time (min)	Number of Cycles	Temperature (°C)	Reference
MEA/H ₂ O	61.40	50	2	30	[131]
DEA/H ₂ O	81.67	55	2	30	[131]
MDEA/H ₂ O	90.48	35	2	30	[131]
MEA/2ME	91.98	60	3	40	[133]
MEA/2EE	90.00	60	3	40	[133]
DEA/2ME	73.14	60	3	40	[133]

4.1.2. Blended Absorbents

The usual amine-based solvents have great performances in absorbing carbon dioxide, yet their performance could be enhanced through a process called blending of solvents. During the past few years, this field has attracted the attention of researchers due to the enhanced features that could be achieved by blending such solvents. For instance, combining the solvents at a proper rate would increase the ability capturing carbon [43].

In a study performed by Magnone et al. [134], the performances of twenty-one amine-based solvents were studied thoroughly. It was found that blending N-methyl diethanolamine along with DEA achieved an increase in the absorption of carbon dioxide, which reached up to 500%. In another research conducted by Artanto et al. [135], it was found that mixing 25% 2- amino-2-methyl-1-propanol (AMP) wildtype with 5% of Piperazine (PZ) wildtype, the carbon capture performance increased to a level in which it could replace EA.

Although, blended solvents possess promising features, more research must be devoted to overcome the main challenges such as the high-cost and corrosiveness [43].

4.1.3. Ionic Liquids

Recently, numerous studies have emerged utilizing ionic liquids in the carbon capture [127]. Ionic liquids could be defined as liquids which contain a cation and an anion. The anion is usually a large organic species whereas the cation is normally an inorganic counterpart [136].

Ionic liquids are classified into two main types, the first of which are called room temperature ionic liquids (RTILs), whereas the second is called the task specific ionic liquids (TSILs). Although they are both ionic liquids, they differ in terms of their behavior. RTILs behave according to Henry's Law, where the absorption occurs physically. Whereas, TSILs absorb carbon dioxide physically and chemically, resulting in a higher carbon capture efficiency. However, when carbon dioxide is absorbed chemically, more energy is required to break up the newly formed chemical bonds for the release of CO₂ and for the recyclability of the solvent [137].

Nowadays, a wide variety of solvents are under investigation. Vadillo et al. [138] found that 1-Ethyl-3-methylimidazolium methyl sulphate ([emim][MS]) absorbs carbon dioxide physically, whereas changing the anion to acetate ([emim][Ac]) would lead to the chemisorption of carbon dioxide. [emim][Ac] was preferred in the carbon capture due to the high surface tension, angle of contact, and the relative low viscosity.

Ionic liquids have a large advantage in that they have extremely low vapor pressures (approximately 0). Moreover, due to the availability of a wide range of applicable ions, many combinations of ionic liquids can be developed. Therefore, the corresponding degradability, toxicity and other factors could be controlled [136]. Furthermore, recently published studies indicated that ionic liquids are promising in this field due to their relative chemical and thermal stabilities [127]. The main disadvantage of ionic liquids is their high cost as they are ten to twenty folds more expensive than other solvents [5].

4.1.4. Alkali Material Absorbents

Hydroxides of metals, especially the sodium ones, have been used for a long time to capture carbon dioxide and many studies were implemented to investigate the best possible routes in using such sorbents. Among the studies, a highly efficient system for capturing carbon dioxide and converting it into a green carbonate via solid NaOH was reported by Ruiz et al. In this study, a whole system was prepared, and its efficiency was investigated in real situations and on a laboratory scale. The results have shown that utilization of solid NaOH is of the lowest costs compared to other technologies and it has the lowest possible life cycle impact [139]. Metal hydroxides are also fused inside membranes to capture CO₂. In research, bipolar membrane electro dialysis (BMED) and hollow fibre membrane contactor (HFMC) filled with NaOH solution were compared in terms of the efficiency of CO₂ absorption and it was revealed that (HFMC) is more efficient as it has shown a maximum absorption of 90.85%. The study can be illustrated according to Figure 12 [140].

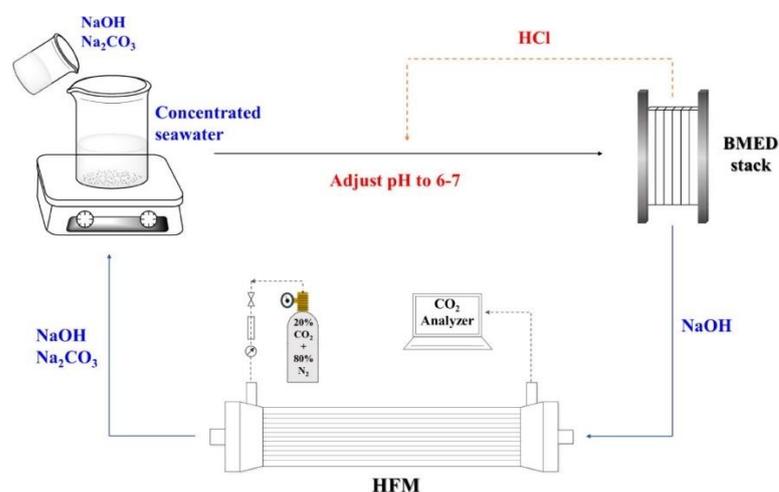


Figure 12. An illustrative scheme of the process of absorption of CO₂ using HFMC and BMED membranes filled with NaOH with permission of [140].

The corrosive ability of alkaline metal hydroxides, as well as the energy required to regenerate it, is relatively high among the drawbacks in using such solutions in capturing CO₂ from the atmosphere. In recent studies, inhibition of such ability was investigated to provide a solution for this grueling issue by changing the solvent. Glycerol is a byproduct in biodiesel industries, and its ability to circumvent such issues was investigated by Valeh-e-Sheyda and Nafchi. It was reported by the latter that the efficiency of capturing CO₂ reached the maximum of 98.40% when the 77% of NaOH was mixed with 15% glycerol. The experiments were conducted in the range of 25–45 °C [141].

Regeneration energy, capacity, reagent cost as well as the corrosive ability of the sorbent must be kept in mind. An alkali solution (NaOH, KOH), amine-based (MEA, DEA . . . etc.), and sodium carbonate were compared in a recent study according to these criteria. In terms of cost, amine-based solutions are of the highest cost whereas sodium carbonate is the least. The capacity of the sorbents is quite close to each other, yet alkali solutions are of the highest capacity reported. The energy required to regenerate the solvent is a priority: had it been very high, it would not serve the ultimate end efficiently, even if it had a high capacity. 3.2–4.3 MJ/Kg CO₂ is the range for all the reported solvents. Sodium carbonate requires the least amount of energy to be regenerated as 3.2–3.8 MJ/Kg CO₂ are needed, whereas alkali solution regeneration energy lays in the middle of the sorbents. Namely, it needs 3.5–3.9 MJ/Kg CO₂ to be regenerated and finally, the highest required energy is reported to be of amine-based solutions 3.9–4.2 MJ/Kg CO₂. The previous results could be summarized in Table 5 and Figures 13 and 14 [142].

Table 5. Comparison between different sorbents with permission of [142].

Type of Sorbent	Capacity (Kg CO ₂ /Kg Sorbent)	Regeneration Energy (MJ/Kg CO ₂)	Reagent's Cost (\$/tone of Reagent)	Corrosion
Amine (MEA, DEA, etc.)	0.40	3.9–4.3	1400–1800	Highly corrosive to pipes and equipment
Alkali Solutions (NaOH, KOH)	0.55	3.5–3.9	400–450	Corrosive to pipes and equipment due to high pH
Sodium Carbonate	0.42	3.2–3.8	225–240	Non-corrosive

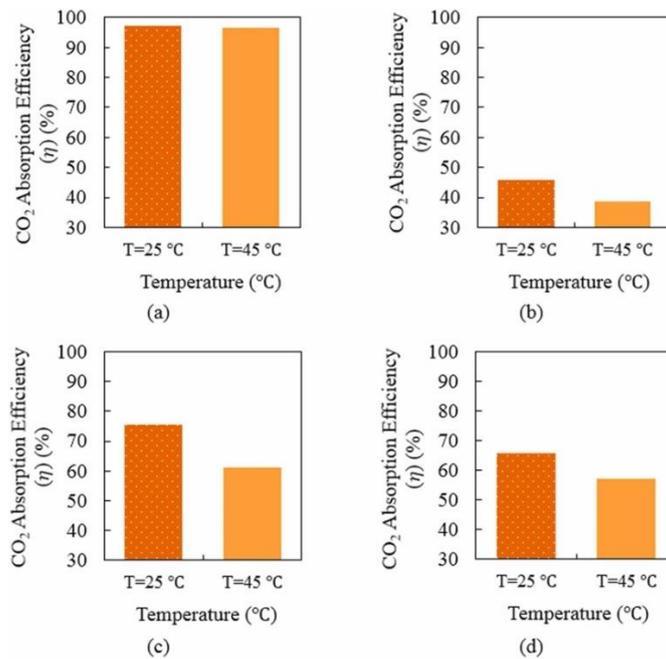


Figure 13. Effect of temperature and composition on the efficiency of CO₂ (a) [NaOH-GLY]: (0.5 M-8 wt.%), Gas Flow Rate = 100 mL/min, (b) [NaOH-GLY]: (0.2 M-8 wt.%), Gas Flow Rate = 200 mL/min, (c) [NaOH-GLY]: (0.5 M-4 wt.%), Gas Flow Rate = 200 mL/min, (d) [NaOH-GLY] with permission of [142].

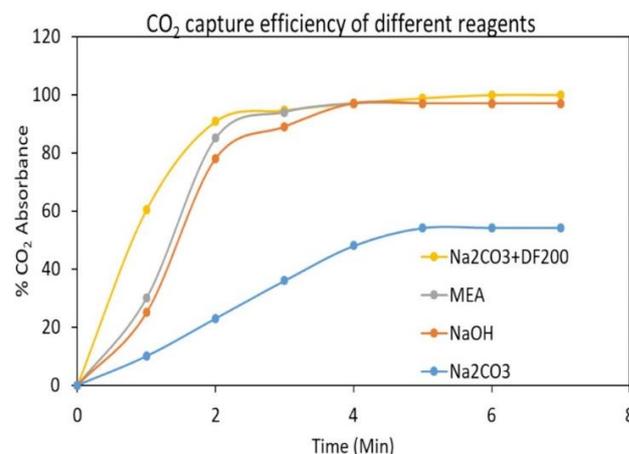


Figure 14. Comparison of CO₂ absorption efficiency of different sorbents, with the permission of [142].

Many solvents were used in this rather developing method, and it has been applied due to their relatively low vapor pressure as it reaches approximately zero, thus they would not contaminate the atmosphere from any side. Since ionic liquids are composed of ions, there are many to be investigated and they might one day achieve the aim with the

highest possible efficiency. Since the option of choosing ions is highly abroad, the related degradability, toxicity, and other factors could be controlled [136]. Many researches have indicated that ionic liquids are promising in this field due to their relative chemical and thermal stability [127]. Away from the bright side of the ionic liquids, the main problem that needs to be circumvented is their cost. They are more expensive than the usual solvents that are employed [5].

4.2. Physical Absorbents

Physical absorption occurs through the interaction of an inert solvent and carbon dioxide. The process occurs usually through water or organic absorbents such as methanol, dimethyl ether physical absorption is usually favorable at high pressure and temperature conditions [43].

In a recent theoretical study, it was reported that upon the combination of two polymers, namely poly carbonate (PC) and poly(ethylene glycol) bis(2-ethylhexanoate) (PEGB), carbon dioxide could be absorbed easily as compared to the pristine polymers. This was attributed to the increase in hydrogen bonding. In another study, Ref. [143] investigated the ability of green solvents to capture carbon dioxide. The researchers employed a zwitterionic natural deep eutectic solvents (NADESs) based on N,N,N-trimethylglycine (TMG) and carboxylic acids (oxalic, glycolic, and phenylacetic). Results showed that the maximum carbon dioxide capture capacity was observed when the conditions of phenylacetic acid/TMG are 313.15 K and 4 MPa, as 45.5 mg of carbon dioxide is absorbed by 1 g of the solvent. Nanoparticles could be used to capture carbon as well. Elhambakhsh et al. [144] employed Fe₃O₄ nanoparticles to absorb carbon dioxide through physical and chemical absorption by varying the coating of the nanoparticles. It was found that Fe₃O₄.SiO₂-lysine achieved the highest possible carbon dioxide absorption capacity.

In general, the advantages of physical absorption are the high efficiency of capturing carbon, as well as the ease of incorporation into existing plants. On the other hand, the main disadvantages are that they have low contact areas between the gas and liquid and they are sensitive to NO_x, SO_x, and other contaminants [144].

5. Mechanisms, Thermodynamics, and Kinetics of Absorption and Adsorption

5.1. Absorption

In absorption, the gas is physically or chemically dissolved in a material, and an actual mass transfer occurs between the absorbate and the absorbent. The two types of absorption, physical and chemical absorption, differ in the mechanism that binds carbon dioxide to the absorbent. However, in both mechanisms, the absorbed carbon dioxide can be regenerated and recovered. Physical absorption is based on Henry's Law, where the amount of dissolved gas is directly proportional to the partial pressure of the gas. The physical process depends on the temperature and pressure, where the optimum conditions need to be set in the process. Therefore, to achieve high efficiencies, physical absorption is usually applied in pre-combustion carbon capture, where the partial pressure of carbon dioxide is high. The drawback of physical absorption lies in the recovery of carbon dioxide from the absorbent, where large amounts of energy are needed for the regeneration of carbon dioxide, and occasional loss of solvent occurs due to high volatility. Chemical absorption, on the other hand, involves a chemical reaction between carbon dioxide and the absorbent material. The products and the mechanism differ based on the absorbing species. Chemical absorption and physical absorption both share the same disadvantages [21,145,146].

Equilibrium and rate-based models are the two most frequently used models for carbon dioxide absorption [147]. Equilibrium models assume a vapor-liquid equilibrium at each stage. However, since it is difficult to achieve physical equilibrium while mass transfers between the solvent and the gas phase, rate-based models are considered more accurate. However, the reaction between primary amines with carbon dioxide involves fast mass transfer due to the corresponding large reaction rate, making it suitable for equilibrium models. More accurate data are obtained from rate-based models by adding

ratio coefficients of physical and chemical mass transfer to compensate equilibrium computations [148].

5.2. Adsorption

Adsorption is a physical process used to separate CO₂ by attaching gas molecules to the surface of the adsorbent (solid material). The adsorption success is measured by the capacity, selectivity, and regeneration of the adsorbate [149]. Adsorbates can be classified as carbonaceous material or non-carbonaceous material. The former includes graphene, activated carbon, activated carbon fibers, and porous carbon, while the latter includes silicas, zeolites, MOFs, porous polymers, and alkali metal-based substances [150]. The two dominant mechanisms of adsorption are physisorption and chemisorption. Sometimes, the adsorbate can be both physisorbed and chemisorbed on the same adsorbent. The main difference between the two types is in the interaction itself between the adsorbent and the adsorbate. If the force binding the adsorbent and the adsorbate is a Van der Waals force, such as the dipole-dipole or London dispersion forces, the adsorption is considered as physisorption. However, if an intramolecular bond occurs by a nucleophilic attack on the electropositive carbon atom, then the adsorbent is said to be chemisorbed. The energy difference between physisorption and chemisorption is about 40–50 kJ/mol. It is safe to assume that the maximum borderline for physisorption to be 50 kJ/mol [151,152]. Typically, it is expected that chemisorption is more selective and has high adsorption capacities, as compared to physisorption, since the latter consists of weak interactions [153].

In order to deeply understand the extent of adsorption, adsorption isotherms of the process are studied [154]. Many types of isotherms have been formulated over the years, with Langmuir, Freundlich, Toth, and Sips being the major isotherms for adsorption studies, which are summarized in Table 6. While isotherms help in investigating the mechanism of adsorption, kinetic models study the rate and order of adsorption. Kinetic models include diffusion kinetic models and adsorption kinetics models. The main difference between the two models is the rate-determining step, where the diffusion through porous adsorbents is the rate-determining step in the former and the adsorption of the molecules on the surface is the rate-determining step for the latter [154,155]. A summary of the kinetic models is illustrated in Figure 15. Rehman et al. [156], synthesized an amine-functionalized organic metal framework (MOF) that followed a pseudo-second-order reaction and proposed the rate-determining step to be the chemical adsorption step. Moreover, Nagarajan et al. [109] proposed solar-reduced graphene oxide to follow pseudo-second-order kinetics for the physical adsorption of carbon dioxide.

Table 6. Summary of the major adsorption isotherms.

Isotherm	Description	Non-Linear Expression	Notes	References
Langmuir	Adsorption occurs as a monolayer and every active site on the surface can adsorb a single molecule	$q_e = \frac{Q_0 \cdot b \cdot C_e}{1 + b \cdot C_e}$	-	[157,158]
Freundlich	Compatible with heterogeneous surfaces and allows the adsorption of multiple layers	$q_e = K_F \cdot C_e^{\frac{1}{n}}$	-	[158]
Toth	An empirical form of Langmuir isotherm with less limitations	$q_e = \frac{K_T \cdot C_e}{(a_T + C_e)^{\frac{1}{t}}}$	When $t = 1$, the expression is reduced to Langmuir model	[158]
Sips	Compatible with heterogeneous surfaces and combines Langmuir and Freundlich models	$q_e = \frac{K_s \cdot C_e^{\frac{1}{n}}}{1 + a_s \cdot C_e^{\frac{1}{n}}}$	K_s, a_s Sips constants	[159]

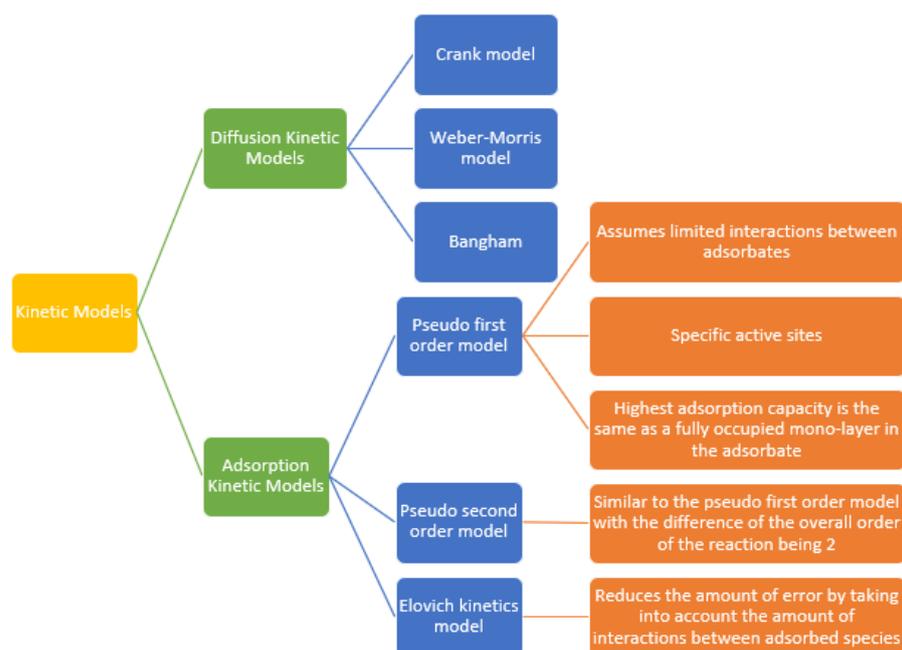


Figure 15. Diffusion kinetic models and adsorption kinetic models.

6. Conclusions, Opportunities, and Challenges

Over the previous few decades, various technologies included in this review showing promise for CO₂ mitigation, each with its own operational requirements, benefits, and downsides. Before the industrial application can be used, there are still significant obstacles to overcome. Absorption is the most developed post-combustion capture process, according to several research groups, including EPRI (Palo Alto, Santa Clara, CA, USA). Among the assessment of post-combustion CCS, 57% apply absorption, 14% rely on adsorption, 8% use membranes, and 21% use mineralization or bio-fixation. Since absorption gas separation was widely used in the various petrochemical industries, this outcome was in line with predictions. All other systems require more work before being applied on a big basis. Chemical use, temperature swings, or pressure swings for regeneration are not involved in membrane separation. It exhibits a strong potential to develop into a sustainable and eco-friendly CO₂ capture technology. CO₂ capture has proven to have long-term steady performance in pilot-scale trials. Further research will encourage its use on an industrial scale by lowering operational costs, optimizing selectivity, permeability, and antifouling, and extending membrane life.

With heat pinch, process integration and improvements, and/or creating adsorbents with a greater CO₂ capacity and low heat capacity are significant research priorities. Even though they are still in the early stages of research, the reduction of the energy penalty is of the utmost importance. To dramatically minimize the energy penalty and reach an energy-acceptable level for large-scale use, it is necessary to reevaluate every component of CO₂ collection methods.

At a cost of \$40–\$100 /ton of CO₂ captured, an amine absorption process that can absorb 90% of the CO₂ from flue gas will use roughly 30% of the power produced by the power plant [159]. Other key issues in absorption processes include corrosion and solvent degradations in addition to the high energy penalty. Amines are particularly corrosive to machinery such as the column, heat exchangers, reboiler, and pipes. The cost of operation will be greatly reduced by the development of next-generation solvents with low regeneration temperatures, which will also significantly reduce corrosion and deterioration. The usage of industrial waste heat will also assist solvents with low regeneration temperatures.

It seems that adsorption offers a significant amount of promise for future application among the variety of CCS systems. Although most of the experimental work used a syn-

thetic combination of CO₂ and N₂, the adsorption uptake of CO₂ has been explored in the greatest depth. Since water vapor, SO_x, and NO_x are present in substantial concentrations in flue gas, it is important to consider their potent chemisorption on adsorbents and the resulting permanent reduction in adsorption capacity. Before advocating for their extensive usage as CCS, more research is necessary to understand how impurities affect adsorption processes and the physicochemical features of the adsorbents. Further research is also necessary to understand how contaminants cause adsorbents to degrade. For current applications, it is important to pre-treat flue gas to remove contaminants to fully utilize the available ad- and absorbents. For the large-scale CCS application, it is necessary to investigate the additional equipment needed as well as the higher capital and operating costs. Since these systems would partially avoid the expenditures of the pre-treatment stage that is otherwise necessary in CCS systems, research on systems that effectively and simultaneously abate NO_x, SO_x, and CO₂ is necessary. It is necessary to design new adsorbents or adsorbents.

For post-combustion CO₂ capture, the two most common forms are fixed bed and fluidized bed. These two variants have larger columns that are more suited for capturing CO₂ from major emission sources like power plants. Numerous small, low-concentration sources with a wide variety of flue gas compositions and impurity profiles are responsible for the CO₂ emissions from numerous industrial sectors, including chemical refineries and iron and steel factories. A significant piping network and compression power will be needed if a centralized CCS plant is used. To handle these minor industrial emissions, it is vital to create flexible, compact capture devices that can use waste heat from various process units while still having high efficiency and low operating and capital costs.

Despite the anticipated operational problems and expense increases, upscaling and integrating the already used procedures has received little attention. Available techniques rely on small-scale experimental units. A 500 MW fossil fuel-fired power plant releases roughly 8000 tons of CO₂/day, which is present in millions of cubic meters of the flue gas. Such amounts and volumes create significant difficulties for CCS design. While retrofitting will require significant equipment adjustments, scaling up to the massive amounts of CO₂ and flue gas produced by burning fossil fuels still poses a significant barrier.

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