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Review Article

Novel Systems and Membrane Technologies for Carbon Capture

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Due to the global menace caused by carbon emissions from environmental, anthropogenic, and industrial processes, it has become expedient to consider the use of systems, with high trapping potentials for these carbon-based compounds. Several prior studies have considered the use of amines, activated carbon, and other solid adsorbents. Advances in carbon capture research have led to the use of ionic liquids, enzyme-based systems, microbial filters, membranes, and metal-organic frameworks in capturing CO_2. Therefore, it is common knowledge that some of these systems have their lapses, which then informs the need to prioritize and optimize their synthetic routes for optimum efficiency. Some authors have also argued about the need to consider the use of hybrid systems, which offer several characteristics that in turn give synergistic effects/properties that are better compared to those of the individual components that make up the composites. For instance, some membranes are hydrophobic in nature, which makes them unsuitable for carbon capture operations; hence, it is necessary to consider modifying properties such as thermal stability, chemical stability, permeability, nature of the raw/starting material, thickness, durability, and surface area which can enhance the performance of these systems. In this review, previous and recent advances in carbon capture systems and sequestration technologies are discussed, while some recommendations and future prospects in innovative technologies are also highlighted.

1. Introduction

The continuous increase in gaseous emissions is a major environmental challenge that bedevils our planet as well as the global populace. Climate change and global warming are resultant effects of the release of CO_2, CH_4, chlorofluorocarbons (CFCs), O_3, and NOx into the atmosphere [1, 2]. The greenhouse gas contributions of chlorofluorocarbons/methane are far higher than those of CO_2 when compared on the basis of unit mass [2]. However, due to the release of CO_2 from fossil fuels, which is the primary source (98%) of the global energy demand, most of the efforts to combat the menace of greenhouse gases are concentrated on CO_2 capture technologies [3]. In the year 2013, the high greenhouse gas concentrations in the earth's atmosphere were quite alarming; also, the CO_2 concentration was 396 ppm (i.e., about 142% of the estimated CO_2 concentration in the preindustrial era [4]. Findings from the Global Atmosphere Watch (a greenhouse gas bulletin) showed that CO_2 concentration experienced the highest increase between 2012 and 2013, compared to those reported for previous years. However, this was judged to have been caused by the reduction in CO_2 uptake in the biosphere. From 2013 to date, the increase in greenhouse gas emissions caused by a rapid rise in population density, industrial activities, and anthropogenic activities has given rise to unprecedented repercussions/effects ranging from environmental pollution to health deterioration, water contamination/pollution, ecodestruction, loss of aquatic life, and undesirable climate change. At a climate conference held in Paris (i.e., the COP21) in December 2015, a total of 195 countries instituted a resolution on the first-ever-historic legal-binding agreement on climate issues, where it was commonly agreed that the global temperature would be kept at an average increase of less than 2°C, which is slightly above what was obtainable in preindustrial times.

The resultant rise in the world's fossil fuel reserves alongside the rapid change in energy demands has led to the unavoidable global expansion of some existing plants, as well as the construction of new ones in order to boost production capacities as a preparatory measure to absorb the global energy shocks. This situation has extended into further years owing to the current state of industrial development and economic growth in different parts of the world, especially in the developed nations. According to the information provided by the Energy Information Administration (EIA), an arm of the US Department for Energy, while fossil fuels were projected to be the world's leading source of energy (80% of the world's energy) in the next two decades, energy consumption was predicted to also rise by 56% by 2040. According to the literature, the CO_2 emissions from power plants were predicted to rise by 46% in 2010 [5]. Furthermore, according to EIA reports, the combined CO_2 emissions from India and China from the use of coal are expected to triple that of the US by the year 2030 [6].

Three strategies are employed in trapping CO_2 emissions from fossil fuel-powered plants; the methods include oxy-, pre-, and post-combustion capture of CO_2 [7]. In pre-combustion capture, the gas is trapped from the parent mixture prior to undergoing combustion. Oxy-combustion capture has to do with capturing CO_2 during combustion, i.e., while burning gas in the air. In postcombustion capture, the gas is trapped from flue gas (a mixture of constituents such as nitrogen, water vapor, and oxygen), in a downstream unit retrofitted with a carbon capture system within the plant. The challenges associated with this process include low CO_2 partial pressure, high flue gas temperature, and the high amount of CO_2 in the flue gas [7, 8]. This also confirms why coal-fired power plants have been reported to be one of the largest stationary point sources of CO_2 emissions [9].

In the United States, policy implementation for CO_2 reduction exists at the local and state levels [10]. However, requests to build new coal-fired power plants are being denied regularly due to their lack of CO_2 controls at inception as well as their medium to high tolerance for CO_2 emission [11]. In 2009, 44.5% of US electricity was generated from coal, whereas, in 2008, CO_2 emissions from electricity generation accounted for about 40 and 34% of the global anthropogenic and GHG emissions [12, 13]. Globally, 31.2 Gt CO_2 emissions were told to have been released from fossil fuel combustion and cement production [14]; this value dropped by 1.3% in 2009 [15].

1.1. Some Related Reviews on Carbon Capture. In the study of Leung et al. [16], various aspects of carbon capture systems and some current state-of-the-art technologies for CO_2 capture, transport, separation, storage, leakage phenomena, monitoring, and life cycle analysis were discussed. They asserted that the choice of a specific CO_2 capture technology depends on the nature of the CO_2-generating plant and fuel source. Based on their discussions, absorption is the most preferred method for capturing CO_2 and according to them, it is due to the higher efficiency and cost-effectiveness of the process. Vakharia et al. [17] scaled up the performances of synthetic amine-doped thin-film composite membranes for CO_2 capture from flue gas, where they recorded CO_2 permeance > 700 GPU (1 GPU = 10^{-6} cm^3 (STP)/(s cm^2 cmHg)) with corresponding CO_2 selectivity above 140 at 330 K. Aaron et al. [18] carried out a review of some existing CO_2 capture technologies; they concluded that the most viable method for CO_2 capture is absorption using MEA. Other liquid absorbents, i.e., piperazine and anionic liquids, have also been discussed as potential candidates for carbon capture [19]. However, piperazine which flows and reacts faster with CO_2 than MEA has been proposed owing to its larger volatility relative to MEA; hence, its usefulness in CO_2 absorption is quite expensive and which is the reason for its noncommercialization [20]. The review conducted by Brunetti et al. [21] compares CO_2 separation involving membranes and other separation technologies, i.e., adsorption and cryogenic separation of CO_2. They highlighted that membranes are strongly affected by low CO_2 concentration and pressure from flue gas, which is a major hurdle in applying this technology.

Chemical absorption or scrubbing process is currently the technology most likely to be implemented in the near future but is rather energy-intensive. In recent years, membrane-based CO_2 separation appears to be a competitive substitution for conventional chemical absorption technologies. Wang et al. [22] reviewed the basic process design techniques for some CO_2 absorption processes using chemical solvents and membranes; they also highlighted the need to optimize some operational parameters, techniques for process modification, membrane module types, etc., in which the energy requirements and economic implications of both CO_2 capture technologies were scrutinized. However, they asserted that membrane-based separation lacks obvious advantages, in terms of energy requirement and cost, over MEA-based absorption where 90% CO_2 capture is feasible.

Based on the review carried out on carbon capture and utilization (CCU) by Koytsoumpa et al. [23], commercial applications of the thermal power and industrial sectors of pre- and postcombustion captured carbon were discussed. The focus of CCU is for the trapped CO_2 to serve as fuel or as a means of generating heat and power. Hence, they asserted that CCU combined with energy storage is an evolutionary approach for instilling the power to fuel concept, which in turn guarantees high market supplies of fuel and other chemicals. Furthermore, recent advances in supercritical CO_2 cycles for heat and power production were also presented.

Owing to the different types of absorption, adsorption, membrane, and cryogenic processes available for carbon capture operations, absorption still stands out as the most widely used method in commercial applications. Based on the content and composition of treated gas samples, different physical and chemical methods of adsorption are available for carbon dioxide and sulfur species removal from process streams [24–27]. For mixtures containing low amounts of carbon dioxide, chemical solvents are preferred to physical solvents; however, physical solvents give better results at high partial pressures. In addition, the thermal energy requirement for gas separation processes involving chemical solvents is much higher compared to those of physical solvents due to the addition of heat via the reboiler attached to the stripper column [25]. This is because, according to Henry's law, the loading capacities of physical solvents have a virtual linear relationship with the partial pressures of the components to be removed, which in turn allows for easy solvent regeneration by pressure throttling. The dissolution of carbon dioxide in the physical liquid solvent is attributed to the van der Waals or electrostatic interaction and is optimal at high pressure and low temperature, hence the need to optimize the process conditions for optimum CO_2 capture.

A review of the development of novel carbon capture technologies was conducted by Lockwood [28], where their energy requirements and cost implications were compared in terms of efficiency-penalty, cost of power, cost of the CO_2 capture process, and the current developmental status of new technologies. For operations that actually factor in the cost of CO_2 capture into the power generation process, chemical loop combustion or the oxyfuel-based Allam cycle offers great potentials to meet the economic requirements of the overall process. For retrofit designs, high performance is often associated with CO_2 capture. According to them, in the US, the post-, pre-, and oxyfuel combustion research programmes present some ambitious targets for new technologies to achieve a CO_2 capture cost of about $20 per tonne. Novel solvents are seen to tilt towards lower-cost involvements in terms of energy regeneration requirements as compared to those associated with conventional amine solvents, phase-change systems, ionic liquids, other non-aqueous solvents, and enzyme-activation systems which are all promising technologies. Alternatively, other commercial gas separation technologies involving solid sorbents, membranes, and cryogenic separation have also been widely investigated. Although there are obvious cost implications for postcombustion capture applications, these techniques may offer some measurable benefits to precombustion capture systems, especially in areas where higher CO_2 partial pressures are desired. Hence, the integration of the CO_2 capture step and the water gas-shift reaction occurs within the adsorbents or membranes. In oxyfuel combustion, pressurised systems have shown a high tendency for efficiency improvements within the supercritical CO_2 cycle at some unique conditions of combustion. Ceramic membranes for oxygen production were also recommended as a means of lowering costs relative to those obtained for cryogenic air separation. Dramatic energy saving can also be achieved via chemical looping strategies, as a result of the inherent avoidance of the possibility of a gas separation step. This technology offers significant scale-up options to companies and research institutes, where the focus is on low-cost oxygen carriers. Raza et al. [29] reviewed the various processes involved in the reduction of CO_2 emissions where it was mentioned that carbon capture and storage techniques hold high promises for reducing the global carbon footprint. Their thought pattern focused on a CCS technology that deals with the capture and storage of CO_2 in deep geological formations for the regulation of the earth's temperature. Some basic guidelines/principles for long-term CO_2 sequestration and storage were also discussed with considerations for the processes and mechanisms (buoyancy, pressure gradient, reservoir heterogeneity, dispersion, diffusion, mineralization, phase trapping, and adsorption by organic materials) involved alongside the various interactions stimulated by supercritical CO_2 injection into the subsurface of geological sites. According to the authors, the selection of apt geological sites for CO_2 storage is informed by the physical characteristics of CO_2 and its phase change tendencies as influenced by CO_2 transport/hydraulic pressure and temperature variation. Although CO_2 can exist as liquid, solid, or gas, it often exists as a supercritical fluid at geological formations whose depths are greater than 800 m and this is as a result of an increase in pressure and temperature at such depth [30, 31]. According to the review conducted by Sood and Vyas [32], CO_2 can be trapped from process facilities and transported to sedimentary basins, saline aquifers, and coal reservoirs for storage. The basic techniques highlighted include oxy-, pre-, and post-combustion strategies. Based on the storage capacities of the CCS technique, it is obvious that the storage capacities of CCS systems make them the most prospective candidates for carbon capture and storage owing to the huge tons of CO_2 storage capacities of the aforementioned sites. However, issues that bother on safety are paramount, especially when these sites are overburdened by excessive pressures that may subsequently result in hazards.

Despite all the efforts put into the well-appreciated past reviews as highlighted in some of the documented literature, it is evident that none seems to have looked into the collection of research works that have do with the application of hybrid systems/novel solvent systems and membrane technologies as the best potential candidates for carbon capture in lieu of the excellent properties they offer in those combinations. This then served as one of the major motivators for this study. Others include the scarcity of literature on the capture of several other carbonaceous compounds and the ill conceptualization of carbon capture in the light of CO_2 capture only.

To date, a lot of attention has been given to CO_2 capture due to its very high concentration in the earth's atmosphere relative to other gases; this has also led to the minimal attention received by other greenhouse gases, hence another motivation for this research, which serves to advocate for the focus on hybrid technologies for the trapping of CO_2 and other carbonaceous substances rather than paying attention to CO_2 only. Also, researchers are still searching for better strategies for curbing the global carbon footprint by trying out new measures that are not only highly efficient but also cost-effective and environmentally friendly. This is because, while a lot of the existing techniques are targeted at CO_2 capture, a myriad of these techniques lack high CO_2/carbon selectivity, stability, durability, etc. Hence, this paper seeks to uncover some of the advances made in carbon capture research, as well as consider possible ways of improving on the current technologies, all aimed at optimizing their performances towards ensuring a clean environment. Although somewhat efficient, the known/aforementioned CO_2 capture technologies are quite expensive, thus giving an estimate of about 70–80% of the overall cost of a full CCS system, capture, transport, and storage [33]. Therefore, significant R&D efforts are currently focused on the reduction of operating costs and energy penalties which must be borne out of strategic selection of the choice materials, such as hybrid technologies, without a compromise for low quality while optimizing the process conditions towards ensuring high carbon selectivity and separation. All of these alongside discourses on the use of modified hybrid systems/MOF-ionic liquid systems for multigas (CCl_3, CCl_4, CH_4, H_2Cl_2, CFCs, etc.) capturing are barely available with major attention given to conventional absorption/adsorption processes alongside oxy, pre-, and postcombustion capture processes for CO_2 sequestration because the term carbon capture is often seen to be limited to CO_2/CH_4 capture as evidenced by the available literature. Also, any carefree attitude in this regard/the neglect of other greenhouse gases will gradually result in the accumulation/build-up of these gases to the point that they begin to constitute serious problems.

1.2. Categories of Carbon Sequestration Technologies. The existing carbon capture technologies can be grouped into the following categories.

1.2.1. Physiochemical Absorption

(1) Physical Absorption: Selexol, Rectisol, Fluorinated Solvents, and Ionic Liquids. Physical absorption involves the reversible/nonreversible use of solvents that have high affinity for carbonaceous substances; these solvents include methanol, propylene carbonate, dimethyl ethers of polyethylene glycol, fluorinated solvents, and the most recent group known as ionic liquids. Ionic liquids (ILs) are liquid salts of cations and anions; they have boiling points of less than 100°C and have the ability to trap CO_2 from a mixture of gases [34–36] owing to their inherent properties, such as low volatility, high CO_2 solubility, thermal stability, and their susceptibility to structural tuning that allows for the attainment of certain advantageous properties [37–39]. Several studies involving ILs have been devoted to determining the extent of CO_2 solubility, selectivity and IL performance, as well as their thermal/chemical stability [34, 40]. Some advances on the use of amine-modified ILs or task-specific ILs (TSILs) [41, 42] have shown that these liquids have high affinity for CO_2. Although the literature has recorded some significant advances in the production of low-viscosity ILs, one common challenge associated with the use of TSILs/ILs is the high viscosity of the fluids after CO_2 entrainment during gas separation processes. Another solvent trapping process for CO_2 capture is the Rectisol process. The Rectisol process (Figure 1) uses cold methanol to trap acid gases such as CO_2 from contaminated gas streams [43–45]. The Fluor process employs propylene carbonate ($C_4H_6O_3$) and CO_2 partial pressure for removing CO_2, while the Selexol process makes use of dimethyl ethers of polyethylene glycol in trapping CO_2 at pressures ranging from 2.07 to 13.8 MPa.

The use of Purisol, Rectisol, Selexol, etc., is common in the oil and gas industry, and they are often preferred over chemical solvents at high acid gas partial pressures. Choosing the right solvent for natural gas sweetening seriously depends on factors such as gas composition, temperature, and partial pressure of gas, as well as the product specs. The works of Tennyson and Schaaf [46] and Kohl and Nielsen [45] are recommended for due consultation by readers. Over a wide range of conditions, aqueous amines are suitable for acid gas absorption from natural gas; however, these solvents still have some serious shortcomings, which include high energy costs for solvent regeneration [47], low CO_2/H_2S selectivity, corrosivity, and high volatility. This, however, sparked off the need for other viable alternatives which in turn ushered in the era of ionic liquids. Considering the past few decades, a huge chunk of studies have discussed the solubility of CO_2 relative to other acid gases in several ionic liquids [34, 48]. However, evidence has shown that, for high gas absorptivity of CO_2 in ILs, CO_2 solubility is trivial relative to the selectivity because the latter gives more credence to the degree of separation obtained from an absorption process [48]. In clear terms, considering the opinions of experts, despite the essentiality of both parameters, CO_2 selectivity is more dependable relative to its influence on the absorptivity of ILs. In another study, CO_2 absorption-desorption rates in polyionic liquids (hybrid system) were reported to be much faster compared to those of ionic liquids and the processes are totally reversible [49–51]. The absorptive potentials of ionic liquids, monomeric and polymeric materials, rely on the chemical and molecular structure of the ions/anions that make up the polar ends of the liquids [50]. Generally, ILs are characterized by low vapor pressures, nonflammability, chemical/thermal stability, tunable polarity, reliable electrolytic properties, and easy recycling [52].

A method to determine the bubble-point pressures of CO_2 and CH_4 at temperatures of 303.15 and 363.15 K and at pressures up to 14 MPa using the Peng–Robinson Equation of state and the van der Waal's mixing rule, in ionic liquids, was established by Ramdin et al. [53]. The solubility of CH_4 was estimated to be 10 times lower than that of CO_2 on a mole fraction basis. Furthermore, Henry's constants for CO_2 and CH_4 for all the ionic liquids (ILs) were used to determine the ideal CO_2/CH_4 selectivities which gave values comparable to those obtained for the Selexol, Purisol, Rectisol, Fluor, and sulfonate solvents. The estimated CO_2/CH_4 selectivity decreased at increased temperature and molecular weight. Genduso and Pinnau [54] also carried out a study that deals with the estimation of the sorption, diffusion, and plasticization properties of cellulose triacetate polymer films in a mixed-gas (CO_2/CH_4) environment.

(2) Chemical Absorption: Methanol Amine (MEA), Caustic Alkali, and NH_3. The Warrior Run coal-fired power station in the United States has a CO_2 capture capacity of about 150 t/d. Amongst the choice solvents for CO_2 capture, MEA is the most widely used amine amongst other members of

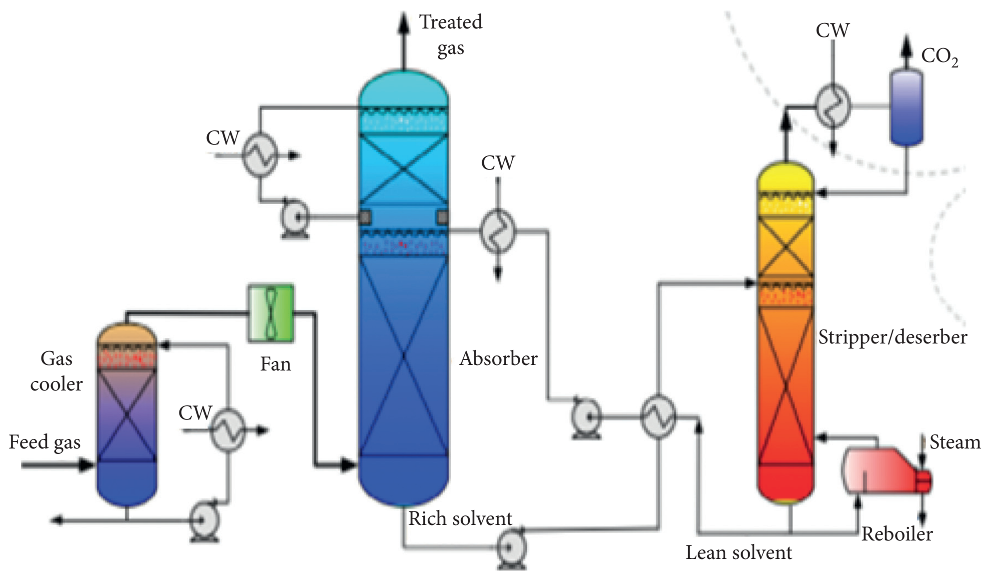

FIGURE 1: The Rectisol process for gas treatment (reprinted from Sanni et al. [27] and Salako et al. [43]).

the amine family because the CO_2 recovery rate and product purity are as high as 98% and 99%, respectively. However, one major demerit of this method is the tendency for MEA degradation when it is in contact with the oxidising environment of flue gas, whereas the energy requirement for the regeneration of the spent solvents can reduce energy costs by about 40% when compared with the cost incurred from using conventional MEA solvents. Hence, alternative solvents such as sterically hindered amines have been proven to possess good absorption and desorption features with minimal degradation or low solvent loss during carbon sequestration [27].

Till date, the most widely adopted technique for CO_2 capture from postcombustion processes/flue gas involves the use of aqueous solvents such as (MEA), diethanolamine (DEA), and methyl diethanolamine (MDEA) as well as hybrid systems which comprise of a mixture of more than one amine [55–57] or blends of amines and chemical solvents such as $Ca(OH)_2$ (Figure 2). Gas scrubbing, using alkanol amines, is one of the most widely adopted cost-effective strategies available on commercial scale for post-combustion CO_2 capture [58].

In order to overcome the limitations posed by amine-based solvents for stripping CO_2 from flue gas, they can (i) be doped with 0.1 M $Ca(OH)_2$ + 27.3–30% DEA at pressures of 2–2.7 bar for optimum CO_2 capture of about 98.3–99.6% (Figure 3) or (ii) be replaced with aqueous ammonia for CO_2 separation owing to its inherent lower heat of absorption. In addition, liquid ammonia (NH_4OH) is known to be able to trap impurities such as NO and SOx that are present in the gas stream. However, one major setback associated with the use of ammonia-based solvents is the recurring need of lowering the flue gas temperature prior to it being introduced in to the absorption column; this helps to abate the ammonia losses that would have ensued if the flue gas was introduced into the absorption column at higher temperature. High gas temperature increases the energy requirement of a large volume of flue gas that is yet to be treated [59]. Another limitation associated with the use of liquified ammonia for CO_2 capture is that the chilled ammonia may foul heat exchangers as a result of the deposition of ammonium bicarbonate from saturated liquids [7].

1.2.2. Cryogenic Separation. Cryogenic separation of CO_2 from a gaseous mixture is done via simultaneous cooling and condensation. Cryogenic separation is commercially adopted for streams with >90% CO_2 concentrations; however, the process is not economical for more dilute CO_2 streams. One major limitation of cryogenic separation of CO_2 is the amount of energy required to enforce refrigeration, especially for dilute streams. Also, dehydration of the gaseous stream is a necessary step prior to cooling because it helps to prevent plugging/blockages. In lieu of the aforementioned limitations, cryogenic separation of CO_2 engenders the production of liquid CO_2 as a transport fuel for ships [60]. Cryogenic operations are often compatible with highly pressured/concentrated gaseous mixtures, such as in pre-combustion or oxygen-fired combustion processes.

To date, cryogenic sequestration of CO_2 is deemed unrealistic owing to the high cooling costs incurred from the process; hence, there is a need for new developments/methods for cutting down the huge costs associated with cooling the gas. The work of Knapik et al. [61] suggests that the cold duty for a CO_2 separation protocol must come from an integrated liquefied natural gas (LNG) regasification or cryogenic air separation system, which takes advantage of an attached CO_2 liquefaction and separation module that helps to ensure the efficient denitrification of natural gas towards ensuring low energy consumption. Natural gas denitrification is a subject that is poorly addressed by the current body of literature; this then flags the extent of the urgency of research works that qualitatively address the subject matter. According to Knapik et al.

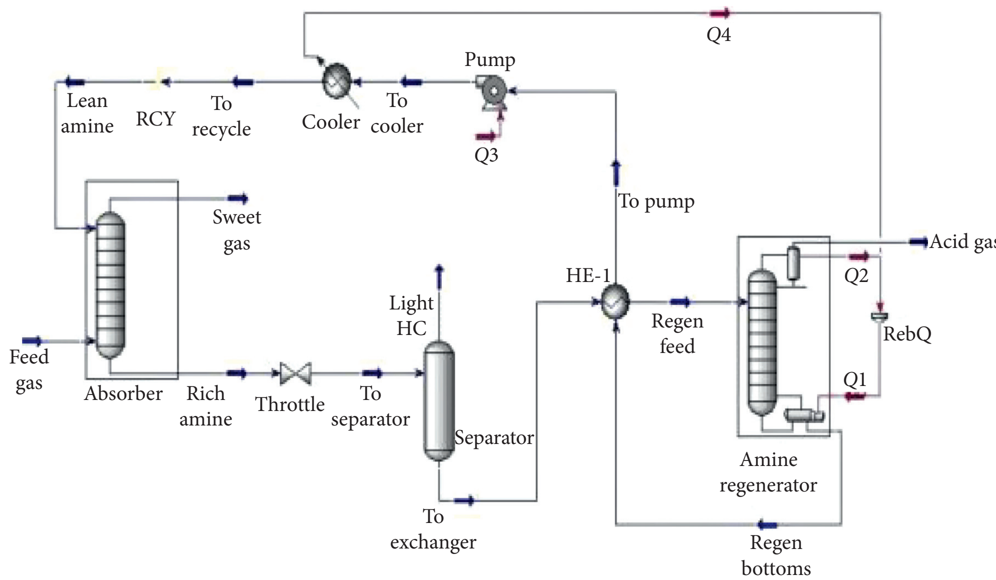

Figure 2: Process flow diagram for a DEA-Ca(OH)$_2$ gas scrubbing plant (adapted from Sanni et al. [27]).

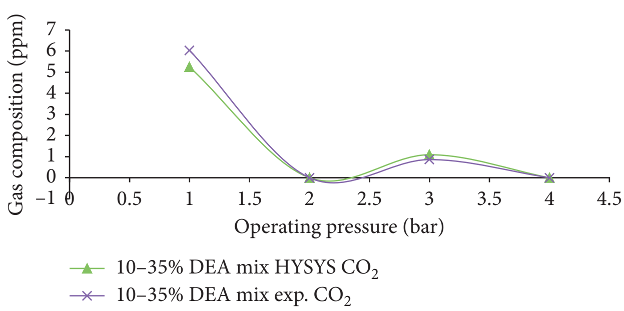

Figure 3: Operating pressure vs. CO_2 absorption using 0.1 M Ca(OH)$_2$ + 10–35% DEA (adapted from Sanni et al. [27]).

[61], the cryogenic separation of CO_2 considers the separation of liquid CO_2 from flue gas generated from oxy-fuel combustion. The outlet N_2 stream transiting from an N_2 removal unit (NRU) serves as the cold stream from the condenser that helps to liquefy CO_2. As a result of the low temperature generated from nitrogen expansion, the inclusion of an external refrigeration cycle is not required, and this makes the process somewhat economical. The amount of trapped CO_2 from the process is a function of the flue gas composition and operating pressure. Based on their findings, 83.07% CO_2 of 99.17% purity can be captured in this process. The energy required for separating the liquified CO_2 is 0.125 kWh/kg CO_2 or 449 kJ/kg CO_2. This novel CO_2 separation unit offers a unique opportunity to produce liquified CO_2 at moderate conditions; the integration of both cryogenic processes is technically and economically advantageous. Xu and Lin [62] successfully carried out the cryogenic separation of CO_2 from flue gas generated from natural gas. They asserted that the hybrid NRU-CO_2 capture installation is an innovative concept with good commercialization potential. The optimization of a cascaded thermodynamic system for separating CO_2 from liquified natural gas has been investigated [63], while the effect of multiple cryogenic desublimation on the dehydration and decarbonization of natural gas was studied by Ali et al. [64]. Song et al. [65] carried out a study that bothers on the cryogenic separation of CO_2 on Stirling coolers via heat integration.

1.2.3. Membrane Separation/Absorption. The performance of membranes for carbon capture processes is measured by the ease with which the component of interest adsorbs onto the surface of the membranes whilst allowing the permeation of other components. Membrane types include porous inorganic membranes, palladium-based, ceramic, polypropylene, polyphenylene oxide/polydimethylsiloxane (for gas separation), polymeric, zeolite, and MOF membranes, which cannot give high degrees of separation, and thus would require the integration of multiple stages and/or recycle streams. In lieu of this, problems such as process complications, energy consumption, and high costs often arise. Hence, solvent-assisted membranes are being developed to combine the best features of membranes and solvent scrubbing. Much development is required before membranes could be used on a large scale for carbon capture in power stations [44].

Polymeric membranes (Figure 4(a)) are classified as dense membranes which include polyimides, polysulfones, and cellulose acetate as well as their derivatives. Another group is one that comprises fixed-site carriers (FSC) (Figure 4(b)); they are made by coating polyvinyl amine on several supports. These membranes ensure high CO_2 selectivity and gas permeation/rejection by means of an integrated carrier within the membrane. The third group includes membranes fused with low-vapour-pressure liquids (e.g., K_2CO_3 or diethanolamine) as supports for housing the immobilized carrier within the membrane pores (Figure 4(c)). The three mechanisms (diffusion, sieving, and

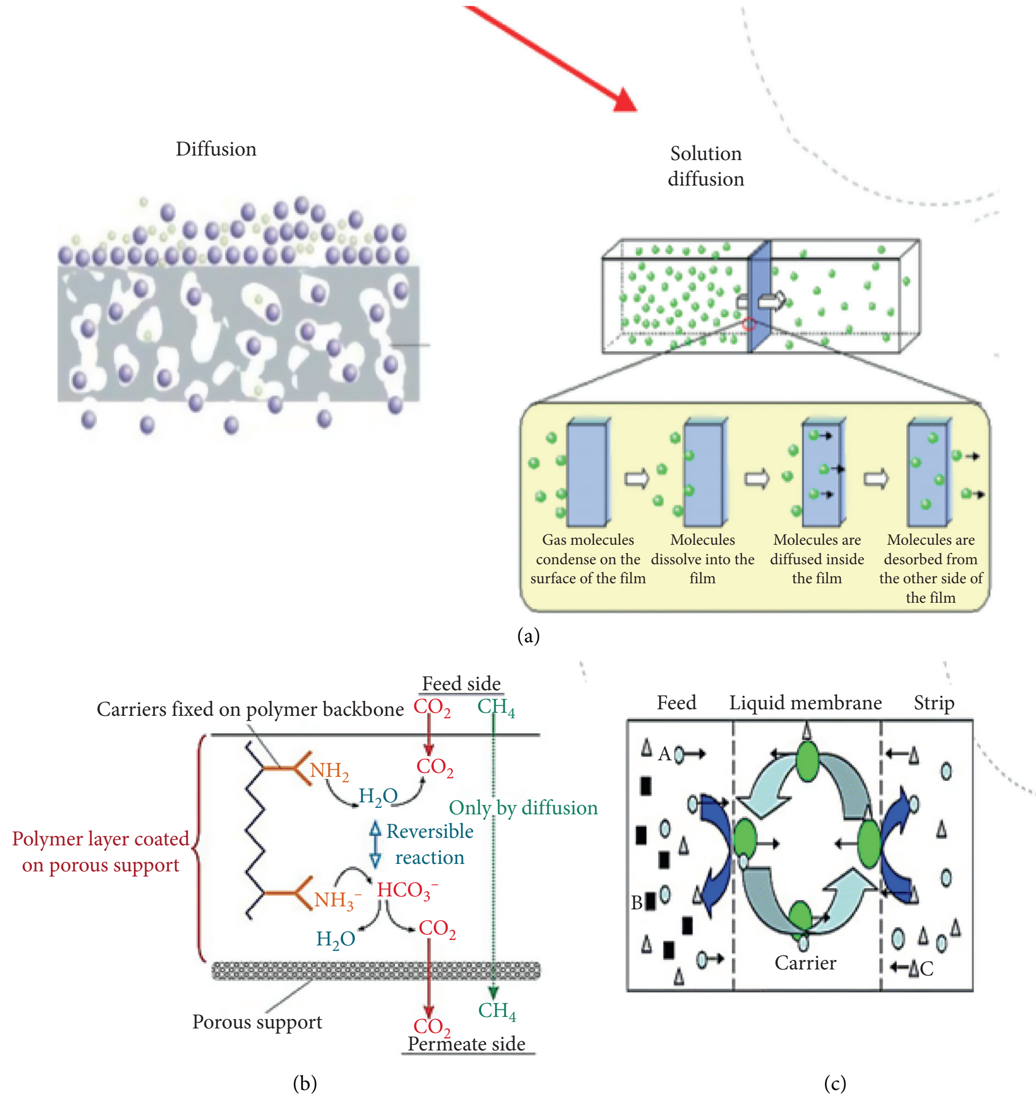

Figure 4: Schematic view of (a) dense polymeric membrane, (b) fixed-site carrier membrane, and (c) supported liquid membranes (adapted from Bolland [44]).

solution diffusion) responsible for gas adsorption in polymeric membranes are as illustrated in Figure 5.

In the study carried out by Tan et al. [66], a flexible microporous organic polymer (MOP) tagged BOP-1 was synthesized and functionalized using Cl and NH_2 moieties. Their findings revealed higher CO_2 uptake within a pressure limit of 1 bar, thus giving CO_2-trapped concentrations of 3.94 and 1.60 mmol/g at 273 and 298 K, respectively. At 273 K, the polymer selectivity for CO_2/CH_4 was abrupt, i.e., 568 at 0.02 bar. Considering the experimental and theoretical validations, they asserted that the $–CH_2–NH–$ linker within the polymer framework played a significant role in enhancing CO_2 polymer binding and was thus responsible for the flexibility of the entire framework. Amongst the diverse CO_2/CH_4 sequestration technologies, porous materials are very ideal candidates owing to their high energy efficiencies and low operating costs [67].

For MOFs, some major limitations in their use include the high energy requirement of the solvent regeneration process, thermal stability of the amine system during regeneration, and the presence of impurities that are present in the flue gas stream, which may have some significant effect on the chemical stability and sorption capacity/potential of the solvent [68, 69]. MOFs are a class of porous materials comprising of a network of metal ions/clusters of nodes connected by organic ligands; they have a wide application in gas separation processes [70, 71]. These materials have very high surface areas, ultrahigh porosity, and flexibility, which is imposed by the presence of ligands/connectors [70, 72–78]. One major merit of MOFs over other solid adsorbents lies in their adaptability to pore size tuning and framework functionalization, which are premeditated by carefully selecting suitable ligands, functionality/surface enhancers, metal ions, and the mode of activation. The limitations of MOFs are more pronounced in humid environments and this has led to a probe into understanding their mechanisms of operation during gas adsorption, which has further stimulated the development/integration of novel

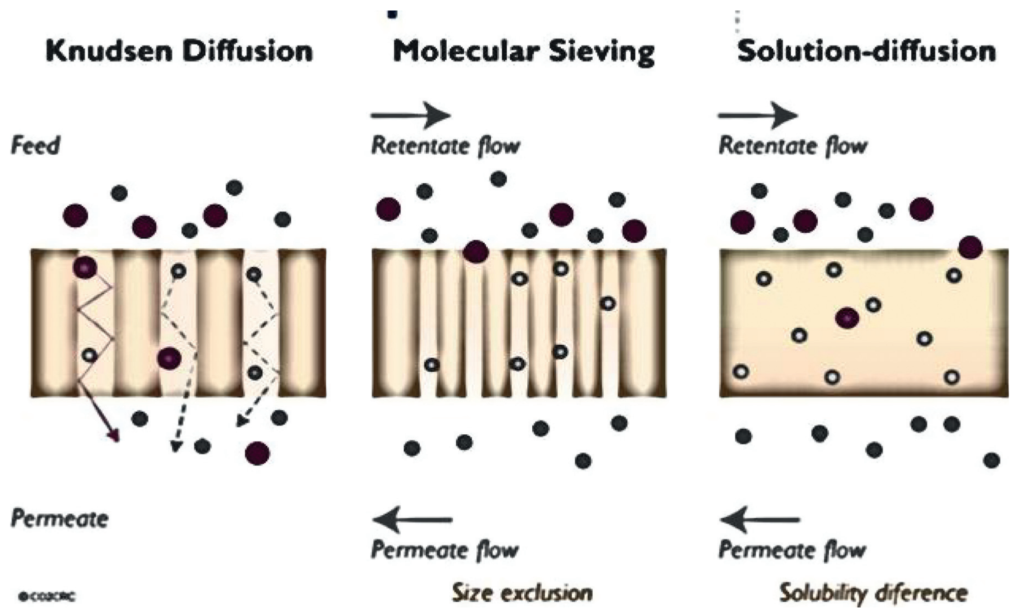

Figure 5: Mechanism of diffusion of gas through membrane pores (adapted from Bolland [44]).

structures, hybrid systems, and technologies as means of improving their adaptation to such environments. The strategies adopted in improving the performance of MOFs include the following.

(1) The Opening up of Metal Sites. This involves the removal of solvent molecules connected to metal nodes by the creation of a vacuum or application of heat after synthesizing the metal framework during chemical activation. The presence of open metal sites in MOFs impacts their CO_2 selectivity and the binding energy between adsorbed CO_2 molecules and the MOF surface. This helps to open metal centers/binding sites where CO_2 molecules can become attached and bind the pore surface via dipole-quadrupole interactions. A method that helps gain insight into the interactions between trapped CO_2 and the ionic force field generated by open metal sites in MOF-74 has been developed. The procedure adopted allows for the accurate estimation of the adsorption isotherms that enhance the subsequent evaluation of the hypothetical open metal sites in MOFs [79]; the findings corroborate the results of Kong et al. [80]. Some widely used MOFs include HKUST-1, M-MIL-100, M-MIL-101, and M-MOF-74, where M represents the metal site. In order to accurately determine the influence of open metal sites in MOFs, it is expedient to isolate the effects contributed by the organic ligand, the synthetic route, and the nature of the inherent functional groups present in the MOF framework. For M-MOF-74 subjected to low pressures, some authors have confirmed the suitability of light metal sites for its surface area enhancement alongside its CO_2 uptake [81]. An examination of the effect of metal centers in M-MOFs was done using a computational approach [81–83] that portrays Rh, Pd, Os, Ir, and Pt as ideal candidates for enhancing CO_2 capture within MOFs. Casey et al. [84] carried out an investigation on the adsorption mechanism and electrostatic force field created by metal centers comprising of Mo, Ni, Zn, Fe, Cu, and Cr in the isomers of HKUST-1. They observed that divalent metals such as Mg^{2+} helped to improve the binding potential of CO_2 which in turn enhanced CO_2 selectivity. It was also observed that the mode of activation of the metal matrix also influenced the MOF's affinity for CO_2; their results also support the findings in the work of Llewellyn et al. [85], in which they confirmed the effect of different activation methods on CO_2 loading using MIL-100 and MIL-101. The interaction of CO_2 and unsaturated Cr(III), V(III), and Sc(III) metal sites in MIL-100 framework was studied using variable-temperature infrared spectroscopy. The estimated adsorption enthalpies for Cr(III), V(III), and Sc(III) were −63, −54, and −48 kJ/mol, respectively; these are the highest ever-recorded CO_2 adsorption enthalpies on MOFs with open metal centers [86]. The work of Sumboon et al. [87] involves the synthetic characterization of M-DABCO metal series (M = Ni, Co, Cu, and Zn), in which they systematically tested the effect of different metal centers on surface area, pore volume, and CO_2 uptake. They asserted that, of all the tested metals, Ni-DABCO possessed the highest pore volume and specific surface area as a result of the high charge density concentration at the metal center. A close comparison of the M-DABCO with MIL-100(Cr) and an activated carbon (AC) sample showed that the presence of the unsaturated cations gave CO_2 uptake of 180 cm^3/g as compared to the values obtained for the Cr and AC samples which are 60 cm^3/g and 30 cm^3/g, respectively [88].

(2) Presynthetic Modification of Organic Ligands. Organic ligands/linkers are the functional bridges that help connect a network of metal nodes; hence, they are responsible for the final outlook of the framework structure, pore volume/pore window, and surface area, which are highly essential for the successful sequestration of CO_2. Ligand functionalization infuses some active functional groups into MOFs which

subsequently ease the organic ligand modification by the inducement of strong covalent interactions. Torrissi et al. [89] modelled the impact of some functional groups attached to ligands using the density functional theory (DFT). The inclusion of amine functional moieties in organic ligands has also been proven to have positive effects on open nitrogen sites within MOF frameworks [90]. The work of Keceli et al. [91] bothers on an amide modification of four biphenyl ligands. However, it was observed that varying the length of the alkyl amide group had a significant impact on the porosity, surface area, and CO_2 containment of the MOF. The activation procedure was also found to have influenced the surface area of the MOF, which was allotted to have been caused by solvent removal from the MOF framework. Yang et al. [92] synthesized three amino-functionalized MOFs from 2-aminoterephthalate (ABDC), Mg, Co, and Sr. The produced MOFs had low surface areas of 63, 71, and 2.5 m^2/g for Mg, Co, and Sr, respectively, which also culminated in low CO_2 uptake of about 1.4 mmol/g at 1 bar and 298 K. However, the MOFs demonstrated high selectivities for CO_2 with the highest being 396 as recorded for the Mg-ABDC, which also corresponds to a high heat of adsorption [92]. Shimizu et al. [93] made use of 3-amino-1,2,4-triazole ligands in designing a 3D MOF structure of characteristic area, pore volume, and CO_2 uptake of 782 m^2/g, 0.19 cm^3/g, and 4.35 mmol/g, respectively, at 1.2 bar and 273 K. Furthermore, the estimated enthalpy of adsorption of the Mg-ABDC was 40.8 kJ/mol at zero coverage, which is very close to the value (48.2 kJ/mol) obtained for a commercial zeolite (NaX) sample. Xiong et al. [94] employed nitrogen atoms and methyl functional groups supported on 5-methyl-1H-tetrazole ligands in synthesizing UTSA-49 framework. The synthesized MOF gave a CO_2 uptake and enthalpy of 13.6 wt.% at 1 bar, 298 K, and 27 kJ/mol, respectively. The results obtained from testing the effects of the triazolate ligands were found to be in close agreement with the findings of Gao et al. [95]. Hence, it becomes very pertinent to gain good insight into the mechanisms behind the synergistic effects offered by the pore-surface-imposed functional groups as well as their size exclusion effects owing to their potential in optimizing the performance of functionalized MOFs.

(3) Postsynthetic Functionalization of MOF-Metal Matrices. Postfunctionalization of MOFs helps guide against the limitations imposed by presynthetic functionalization. However, an accurate control of the process conditions is required, which is aimed at retaining the service life and stabilities of the unstable functional groups during solvothermal synthesis. In addition, the infusion of other functional groups into the synthetic mix may result in the distortion of the metal framework as a result of the improper mixing and steric hindrance that occur during crystallization, thus yielding undesired products. The insertion of functional groups at metal sites at the presynthetic stage of the framework casting may adversely affect the building blocks of the MOF, which may in turn lead to the structural deformation of the crystal lattice of the MOF [96–98]; hence, postsynthetic functionalization is considered a viable approach for combatting the highlighted shortcomings towards capacitating the resulting MOFs for high carbon/CO_2 capture. Some amine-moiety-modified solid adsorbents [99–102] and MOFs [103, 104] have shown improved CO_2 sorption over their unmodified counterparts. Lee et al. [105] grafted 16.7 wt.% diamine into MOF-74/Mg(dopbdc) at room temperature. The modified MOF exhibited a CO_2 uptake of 13.7 wt.% at 0.15 bar, while McDonald et al. [106] reported a CO_2 uptake of 12.1 wt.% for N, N′-dimethyl ethylenediamine grafted into Mg(dopbdc). The isosteric enthalpy of adsorption of CO_2 ranged from 49 to 51 kJ/mol, thus confirming chemisorption of CO_2 molecules, whose kinetics was determined by the formation of carbamic acid as identified using the Fourier transform infrared (FTIR) spectroscopy. The multicycle adsorption evaluation of the engrafted Mg(dopbdc) only revealed a 3% loss of CO_2 uptake after the 5^{th} cycle; however, the MOF was found to be hydrologically stable with a high CO_2 uptake. The work of Chernikova et al. [107] bothers on the synthesis of a nanoporous fluorinated MOF named "SIFSIX-3-M," where M = Zn, Cu, or Ni, which encompasses a periodic arrangement of fluorine moieties in an enclosed one-dimensional (1D) channel; the synthesized MOF was seen to have a remarkable CO_2 selectivity over CH_4 and H_2 in several gas mixtures. Tables 1 and 2 consist of properties of some MOFs measured at high and low pressures, respectively. Comparing the results in both tables shows that higher selectivities are somewhat guaranteed at low pressures than at high pressures. The highest recorded selectivity was obtained for UTSA-49 in Table 2, with a selectivity of 95.8% at 1 bar and 298 K.

Since studies on the sequestration of other carbonaceous substances are rare in the literature, the three processes itemized in "(1), (2), and (3)" can be tried for the different MOFs discussed in line with their capacities to trap CH_4, $CHCl_3$, CCl_4, CH_2Cl_2, and their compatibilities with the substances.

Reports have it that polymers of intrinsic microporosity (PIM) are also prospective starting materials for the synthesis of ultrapermeable thin-film composite (TFC) membranes. This is because PIMs are known to provide advantages including high fractional free volume (FFV), good mechanical and film-forming characteristics, and excellent processability which provide for high CO_2 selectivity of the material [135]. In lieu of the aforementioned properties, pristine PIMs are usually associated with shortcomings ranging from physical aging to low CO_2/N_2 selectivity (<20) which limit their industrial application. The detrimental aging effect of PIMs is somewhat evident in TFC assemblies, especially in situations where a 90% drop in CO_2 permeance was clearly ascribed to the physical aging of the composite material [136, 137]. In order to offset the aging problem associated with TFCs, a TFC membrane codoped with a polymer of intrinsic microporosity such as the PIM-1 was hybridized with nano-MOFs (i.e., MOF-74-Ni and NH_2-UiO-66 nanoparticles) and adopted for post-combustion CO_2 capture [138]. The design of the TFC membrane comprised of three layers, i.e., (i) a PIM-1@MOF mixed matrix CO_2-selective layer; (ii) an ultrapermeable polydimethylsiloxane (PDMS) gutter layer impregnated

Table 1: Properties of MOFs and MOF-based membranes measured at pressures of 8.5–224.99 bar.

		High-pressure separation data								
Nomenclature/ molecular formula	Feed composition ($CH_4/CO_2/H_2$)	X ($CO_2:CH_4:H_2$) (wt.%) or as given	BET surface area (m^2/g)	Langmuir surface area (m^2/g)	Adsorptive capacity (%)	P (bar)	T (K)	S_{CO2}	Q	Ref.
UiO(bpdc)	—	79.7 : 12.2 : 5.7	2646	2965	72.5	20	303			[108]
ZJU-32	—	49	3831	49	40		300			[109]
UPG-1	—	72 : 69 cc/g	410	514	11.9	9.8	298	24	24	[110]
Cu3 (H2L2) (bipy)2 .11H2O	—	77 cc/g			6.4	8.5	298			[111]
Cu_3 (H_2L_2) (etbipy) 2 .24H2O	—	77 cc/g			4.7	9.6	298			[111]
NU-111	—	350 : 284 cc/cc feed	4932		61.8	30	298		23	[112]
HTS-MIL-101	—	1112 mg/g	3482		52.8	40	298			[113]
DGC-MIL-101	—	1112 mg/g	4198		59.8	40	298			[113]
UTSA-62a	30/20/5	189 : 270 cc/cc of feed	2190		43.7	55	298		16	[114]
ZIF-7		10.3	312	355	20.9	10	298		33	[115]
{Ag3[Ag5(l3-3,5-Ph2tz)6] (NO3)2}n	—	0.025 : 0.35 mmol/g			12.3	10	298	10.5	19.1	[116]
Basolite® C 300	99.9%	16 mmol/g	1706.42		41.9	224.99	318		18	[117]
Basolite® F300	99.9%	16 mmol/g	1716.46		24.1	224.99	318		19	[117]
Basolite® A100	99.9%	8 mmol/g	1524.8		26.9	224.99	318		9	[117]
MIL-101(Cr)	99.99%	1.17 mmol/g	2549		24.2	30	303			[118]
HKUST-1	99.99%	1.82 mmol/g	1326		26.3	30	303			[118]
DMOF	—	2.5 mol/kg	1980		38.1	20	298	12[a]	20	[119]
DMOF-cl2	—	2.15 mol/kg	1180		26.4	20	298	17	21	[119]

*X = CO_2 uptake

with MOF nanosheets that provides for CO_2 permeance in the range of 10,000–11,000 gas permeation unit (GPU), thus allowing for less CO_2 transport resistance relative to the pristine PDMS gutter layers; and (iii) a third porous polymeric substrate-layer. Furthermore, by blending the nanosized MOF particles into the PIM-1, the resulting TFC membrane assembly gave high permeation of CO_2 in the region of 4660–7460 GPU with CO_2/N_2 selectivity ranging from 26 to 33 as compared with that of the pristine PIM-1, which gave CO_2 permeance of 4320 GPU with corresponding CO_2/N_2 selectivity of 19. In addition, the PIM-1–MOF-based TFC membrane was seen to exhibit enhanced resistance to aging effect, thus maintaining a constant CO_2 permeance in the region of 900–1200 GPU with CO_2/N_2 selectivity of 26–30 after 8 weeks.

Other works on PIM for CO_2 capture include the work of Bhavsar et al. [139] where ultrapermeable PIM thin-film nanocomposite membranes were anchored on microporous polyacrylonitrile (PAN) supports for effective CO_2 capture. Borisov et al. [136] also carried out an investigation of gas (CO_2/N_2) selectivity in thin-film PIM-1 composite membranes where they established the potential of the membrane for adsorbing both gases. However, it was also observed that the selectivity of the membrane for each gas decreased over the aging period of the membrane. Liang et al. [140] also allotted the performance of multilayer PIM composite hollow fibers to their intrinsic microporous multilayer gutters. In addition, the studies conducted by Tiwari et al. [141] and Swaidan et al. [142] bother on the examination of the aging period, plasticization, and CO_2 adsorptive performance of a synthetic thin-film and rigid PIM-1 membranes, respectively.

Three-phase mixed matrix membranes comprising of poly (ether-block-amide (PEBA), polyethylene glycol (PEG), and nanozeolite X were produced; the effects of the PEG and/or the nanozeolite on CO_2 and CH_4 permeabilities and CO_2/CH_4 selectivity of the membranes were examined. The CO_2 permeability and selectivity of the membranes were seen to increase with feed pressure and PEG loading. However, at a pressure of 8 bar, the PEBA membrane doped with 30% PEG and 10% nanozeolite X gave the best performance with CO_2 permeability and CO_2/CH_4 selectivity 95 Barrer and 45, respectively [143].

Synthetic ionic liquid (3-di-n-butyl-2-methylimidazolium chloride (DnBMCl)) was used in modifying a sample Pebax 1657 surface as a means of strengthening the carbon-carbon bond in the mixed polymer matrix [144]. By the coating method, ZIF-8 nanoparticles produced from different precursor ratios were doped in the matrix of the IL-Pebax 1657 system in order to fabricate the mixed matrix membranes (MMMs). Tests such as SEM, DSC, FTIR, 13C NMR, TGA, and gas permeation analysis were used to characterize and evaluate the performance of the MMMs. Based on the results of the gas permeation tests conducted, increased CO_2/CH_4, CO_2/N_2, and CO_2/H_2 selectivities were observed for the modified DnBMCl-MMM relative to the

Table 2: Properties of MOFs and MOF-based membranes measured at pressures of 0.91–1.01 bar.

Nomenclature/ molecular formula	Feed condition ($CO_2:N_2$)	X ($CO_2:CH_4:H_2$) uptake (wt.%)	Low-pressure separation data BET surface area (m^2/g)	Langmuir surface area (m^2/g)	Adsorptive capacity	P (bar)	T (K)	S_{CO2}	Q ($kJmol^{-1}$)	Ref.
rht-MOF-pyr		112 : 17 cc/g	2100		12.7	1	298		28	[120]
rht-MOF-1		90 : 16.4	2100		11	1	298		29	[120]
JLU-Liu22		170 cc/g	1487		15.6	1	298		30	[121]
SIFSIX-3-Co	15 : 85	62.6 cc/g	223		10	1	298		47	[122]
SIFSIX-3-Ni	—	64.5	368		10.3	1	298		59	[122]
{[$H_2N(CH_3)_2$]4 [Zn9O_2 (BTC)6 (H2O)$_3$].3DMA}cn	—	99 : 63 cc/g	844	1132	10.9	0.91	298		29	[123]
{[NH_2 $(CH_3)_2$, Cd(BTC)].DMA}n	—	32 : 23 cc/g	406	539	6.4	0.91	298	30	34.7	[123]
Ni-DOBDC		2.30 mol/kg	798		18.2	1	298			[124]
Py-Ni-DOBDC		1.64 mol/kg	409		12	1	298		16	[124]
UiO(bpdc)	—	8	2646	2965	8	1	303			[108]
ZJU-32	—	0.1 : 0.01	3831		4.8	1	300			[109]
Zn(5-mtz) (2-eim).(guest) [ZTIF-1]		49 : 13.16 cc/g	1430	1981	8.2	1	295	81	22.5	[125]
Zn(5-mtz) (2-pim).(guest) [ZTIF-2]		29.3 cc/g	1287	1461	3.8	1	295		20	[125]
UTSA-49 10 : 90; 15 : 85; 20 : 80		69 cc/g	710.5	1046.6	13.6	1	298	95.8		[126]
ZJNU-40 5 : 95		108 cc/g	2209		16.4	1.01	296		18.4	[127]
UPG-1	—	22	410	514	2.1	1	298	24	24	[110]
UiO-66(Zr100)		2.2 mmol/g	1390	1644	6.2	1	298		26	[128]
UiO-66(Ti32) and UiO-66(Zr/Ti)		2.3 and 4 mmol/g	1418	1703	6.4	1	298		28	[128]
UiO-66(Ti44)	—	2.3 cc/g	1749	2088	7.2	1	298		34	[128]
JLU-Liu1	—	34.7 : 0.5 cc/g	145	221	5.9	1	298		47.7	[129]
UTSA-62a 30/20/5		189 : 270 cc/ cc of feed	2190		8.1	1	298		16	[114]
Zn-DABCO	60–100 mg	1.87 mmol/g	1870	1902	7.2	1	298		22.4	[87]
Ni-DABCO	60–100 mg	2.17 : 0.51 mmol/g	2120	2219	8.1	1	298		25.8	[87]
Co-DABCO	60–100 mg	1.02 : 0.57 mmol/g	2022	2095	4.1	1	298		29.8	[87]
Mg/DOBDC	40 : 60 v/v	180 cc/g	1415.1		25	1	298		47	[88]
{Ag_3[Ag_5(l3-3,5-Ph_2tz)$_6$]$(NO_3)_2$}n	—	7-8 CO_2 molecules/ unit adsorbent (0.39 mmol/ g)			1.6	1	298	10.5	19.1	[116]
{Ag_3[Ag_5(l3-3,5tBu$_2$tz)$_6$]$(BF_4)_2$}n	—	0.37 mmol/g			1.6	1	298	14	15	[116]
Basolite® C 300		2 mmol/g	1706.42		9.4	0.95	318		18	[117]
Basolite® F300		0.5 mmol/g	1716.46		2,4	0.95	318		19	[117]
CPM-5			2187		8.8	1	298	16.1	36.1	[130]
ZIF-68 15 : 10 : 75 (CO_2:SO_2:N_2)		1.6 mol/kg	1220		41.3	0.9	298	30	33.3	[131]
Zn_4(bpta)2-1 -		41.95 cm^3/g		51	8.2	1.2	298	23	34.82	[132]
Cu_2L $(DMA)_4$ UHP-grade	UHP-grade 99.99%	160 cm^3/g	1433		22.2	1	296	41.6	35	[133]
bio-MOF-11	10 : 90 ($CO_2:N_2$)	147 cm^3/g	1148		22.2	1	273	123	33.1	[134]
bio-MOF-14	10 : 90 ($CO_2:N_2$)	44.8 cm^3/g		17	8	1	273	Extremely high	—	[134]

MM and pristine Pebax 1657 membranes. Also, they asserted that the inferior CO_2 separation ability exhibited by the MMMs in the mixed-gas condition compared to the situation where pure gas was adopted for the test was influenced by the effect of plasticization in the MMMs. In addition, the modified DnBM-Pebax 1657-ZIF-8 MMMs exhibited superior CO_2/CH_4 and CO_2/N_2 selectivities at feed pressures of 2 and 4 bar, respectively. The study by Sutrisna et al. [145] involves the comparison of the operational stability of Pebax modified with ZIF-8 for gas separation with flat sheet and composite hollow Pebax fibre membranes. Also, the modified ZIF-8 was found to be stable alongside the pristine ZIF-8 due to the hydrogen bonds and the polyamide chains present in both samples, and these were reported to have improved the stiffness of the linear glassy polymer chains, thus ensuring good operational stability of the membranes at high pressure for the flat sheet and hollow fibre membranes. In addition, the outstanding long-term stability of the hollow fibre membrane suggests that the ZIF-8/Pebax coating improved the aging resistance of the poly[1-(trimethylsilyl)-1-propyne] (PTMSP) gutter layer. The poly (ether-block-amide) (Pebax) mixed matrix membranes (MMMs) were prepared using size-tunable nanoparticles of ZIF-8 nanofillers (40, 60, 90, and 110 nm, i.e., ZIF-8-40, ZIF-8-60, ZIF-8-90, and ZIF-8-110) synthesized from 98% zinc acetate dehydrate ($Zn(COO)_2{\cdot}2H_2O$) and 98% 2-methylimidazole (Hmim, C_4H6N_2) [146]. The ZIF-8 nanofillers were produced in microemulsion by controlling the ratio of Zn^{2+} to Hmim (1 : 16, 1 : 8, 1 : 5, and 1 : 2). They were then uniformly distributed in the Pebax matrix without visible agglomerations/defects at loadings of 0–20 wt.% as confirmed by FESEM. Based on the results, the ZIF-8 significantly improved the CO_2 permeability and CO_2/N_2 selectivity of the MMM. The enhanced permeability of the MMM was attributed to the induced free/pore volume of the polymer caused by the integration of larger sized ZIF-8. The resulting increase in the selectivity of the MMM was allotted to the high surface area of the ZIF-8 nanofillers, which provided more active sites for CO_2 capture with improved resistance to mass transfer for N_2. For 5 wt.% loading of the ZIF8-90, the MMM had the best CO_2 separation performance with a permeability of 99.7 Barrer and CO_2/N_2 selectivity of 59.6, which both gave a marginal increase of about 25% when compared to the pristine Pebax membrane.

In the work of Beni and Shahrak [147], pristine zeolites (ZIF-8 and ZIF-90) were synthesized and compared with samples of both zeolites functionalized with Li, K, and Na cations. Based on the CO_2 adsorption tests conducted, the Li-functionalized zeolites gave the highest CO_2 uptake for both zeolites and these they allotted to have been enhanced by the interactions (i.e., electrostatic and dispersion interactions) that occurred between the adsorbate and adsorbent molecules which gave rise to higher binding energies. Simulation results also revealed that, at 1 bar and 298 K, the CO_2 uptakes for the Li-functionalized ZIF-8 and ZIF-90 increased by 7 and 9 times over their pristine counterparts, thus giving values of 6 and 9 mmol/g CO_2 uptake, respectively. The Li-functionalized-ZIFs exemplified chemisorption as informed by their calculated heats of adsorption which also provides vital information for efficient regeneration of the adsorbents in pragmatic situations.

1.2.4. Microbial and Algal Seed Coats: Contextualizing Regenerative Agriculture. Along farmlands on the East Coast of Australia, efforts are being put in place by farmers to test modern approaches of combatting climate change. One of such measures involves planting seeds that are coated with fungi and bacteria with the intent of capturing CO_2 from air [148]; according to reports, the plan is to sink billions of tons of carbon into farmlands. There are also speculations that the coated seeds exhibit a higher carbon capture potential than a carbon capture plant. A start-up firm, known as the Soil Carbon Company, is working on a modern technology whose origin is traceable to the University of Sydney where the annual projections on the carbon sequestration potential of the technology are 8.5 gigatons carbon or one-fourth of the global annual CO_2 emissions in a year. There are also projections that this technology can store trapped carbon for a longer time than some regenerative agricultural carbon capture technologies. Injecting microbes into crops on a farmland/plantation enhances the carbon storage capacity of plants since all plants make use of atmospheric carbon dioxide in their normal carbon cycles during photosynthesis; the absorbed carbon traverses the plant roots before ending up in the soil. However, some of the trapped carbon is fairly lost in the surrounding air. This then informed the idea of coating plant seeds with fungi and bacteria that can convert the trapped carbon into a form that can be stored much longer in soils over a long period of time, say hundreds of years. This technology is promising but is yet to gain full support for commercialization. Based on some findings, the process will enrich the soil and reduce the need for high amount of fertilizers.

Another technology that bothers on the use of microbes is microbial electrolytic carbon capture (MECC) which employs microbial electrolytic cells during wastewater treatment. The process/treatment brings about net negative carbon emissions from wastewater by simply converting the inherent CO_2 in water to calcite/limestone (CaCO3) [149] with the release of high amount of hydrogen gas that can be harnessed for other profitable ventures. CO_2 from anthropogenic sources contributes significantly to the regional dynamics of climate change as a result of the greenhouse gases released into the atmosphere from such processes. Most CO_2 mitigation practices are fossil fuel-based, which give off other compounds such as SOx and NOx during combustion. No doubt, a nation's economic growth relies on its capacity for energy generation and how energy efficient it is, i.e., in terms of energy production for transportation and production of industry goods and services. CO_2 from wastewater processing contributes a small percentage (i.e., about 15%) to the global greenhouse gas emissions [150]; presently, about 3% of the total electricity generated within the US is channeled to wastewater treatment facilities which have a capacity of 12 trillion gallons of wastewater per year.

MECC contributes significantly to sustainable energy practice, owing to the fact that it takes advantage of the properties of the organic constituents of wastewater for eliminating carbon-based compounds/CO_2 in order to produce a precipitate (calcite) alongside H_2 [151]. Operators of wastewater treatment facilities are held accountable for their greenhouse gas emissions during wastewater treatment by the Greenhouse Gas Protocol Initiative. For instance, the process is energy-intensive as it requires energy for the aeration process, which in turn releases volatile compounds from wastewater, during the agitation and transportation of polluted and recycled fluids within the entire process. The electricity used in wastewater treatment gives carbon dioxide, methane, and NOx gases; the aerobic treatment step gives off N_2O and CO_2, whereas the sedimentation and activated sludge steps produce CO_2 and CH_4.

1.2.5. Adsorption: Packed Beds (Alumina/Activated Carbon/Zeolite), Graphene, and Monolith-Molecular Sieves (Carbon-Coated Substrate and Carbon-Carbon Fibre Monolith). Solid adsorbents such as zeolite/activated carbon can be employed in trapping CO_2 from gaseous mixtures at high pressures/temperatures. During pressure swing adsorption (PSA), gas flows through one or more packed beds of adsorbent at high pressure until the concentration of the gas progressively attains equilibrium (Figure 6). Thereafter, the bed is regenerated by reversing the pressure, whereas, in temperature swing adsorption (TSA), sorbent regeneration or gas desorption occurs by an increase in temperature. The adsorption of CO_2 onto solid adsorbents is not considered economically viable for the recovery of large volumes of CO_2 from flue gas, due to the low capacity of these adsorbents as well as their CO_2 selectivities [152, 153]. However, hybrid systems or a combination of several carbon capture technologies may become necessary in order to make these processes economically viable.

Zeolites are aluminosilicates with well-defined micro/ultrasmall porous structures, thermal stability, recyclability, and chemical reactivity [154]. They are rated as high-performing adsorbents [155–158]. Some zeolite networks have been tested for their abilities to trap CO_2 under different humid conditions, and the adsorption process was simulated using the Monte Carlo simulation [159]. Although under wet conditions, a rise in CO_2 uptake of pure zeolites has not been confirmed experimentally, however, there are speculations that the CO_2 uptake of some zeolite structures is expected to rise under moist conditions [12]. For porous adsorbents such as zeolites, CO_2 storage is predominately seen to be caused by adsorbate-adsorbate interactions [159], which is in contrast to the case of selective CO_2 sequestration that is largely influenced by adsorbent-adsorbate interactions or their chemical affinity for CO_2 at low pressures [160].

No doubt, zeolites are potential adsorbents for CO_2 capture; however, their adsorption efficiencies are usually influenced by their chemical constituents/composition, charge density, and pore size. Highly crystalline zeolites with three-dimensional pores and high surface areas can be obtained by controlling the Si/Al ratio in the zeolite matrix. The notable influence of the presence of alkali/alkaline earth cations in zeolite matrices is another subject yet to be fully explored; thus, optimizing the composition of a sample zeolite may somewhat alter its CO_2 adsorption capacity, which is also justified by the work of Balashankar and Rajendran [161], who optimized a zeolite screening process for postcombustion trapping of CO_2 under vacuum swing adsorption in order to determine the optimal conditions for high efficiency. In lieu of the myriad of approaches adopted for increasing the CO_2 adsorptive capacities of zeolites, they still present some shortcomings which include their relatively low CO_2/N_2 selectivity when compared with their CO_2 adsorption potentials/high hydrophilicity, especially in feed mixtures containing both gases. Nonetheless, the CO_2 absorptive capacities of zeolites may likely decrease especially in situations where the CO_2/N_2 mixtures are entrained with moisture. Also, upon adsorption, zeolite regeneration is only achievable at temperatures (>300 °C) [162].

The CO_2 capture potential of zeolites has been widely discussed owing to their molecular sieving abilities and strong dipole-quadrupole/electrostatic interactions that exist between CO_2 and the alkali/alkali-earth-metal cations (Li, Na, and Al) in the zeolite matrices [163]. These cations influence the heat of adsorption of CO_2, such that it increases with a corresponding increase in the monovalent charge density of the inherent negative charges in the material [164, 165]. Zeolites 13X and 5A have been reported to give high CO_2 retention/performances in the range of 3–25 wt.% at room temperature and a CO_2 pressure of 100% [3, 166–168]; they also recorded a CO_2 capture of 2–12 wt.% at room temperature and a CO_2 partial pressure of 15% [169–171]. Cavenati et al. [172] demonstrated the ability of zeolite 13X as a suitable adsorbent for CO_2; they recorded a CO_2 capture of 28.7 wt.% and CO_2/N_2 separation capacity of 3.65 at 298 K and 10 bar. The work of Jadhav et al. [173] bothers on the modification of zeolite 13X using monoethanolamine (MEA) impregnation in order to improve its CO_2 trapping capacity. The CO_2 adsorption capacity of the modified zeolite 13X was seen to be better than that of the pristine zeolite by a factor of about 1.6 at 303 K, while at a temperature of 393 K, the efficiency was seen to improve by a factor of 3.5. However, in lieu of the reduction in pore volume and surface area that ensued from the MEA impregnation, they asserted that the improved capacity of the modified zeolite 13X was due to the chemical interactions between CO_2 and the infused amine groups. Zeolites 13X and 5A impregnated with LiOH (LEZ-13X and LEZ-5A) were used to trap CO_2 under ambient conditions. Based on the BET analysis, the surface areas of the LiOH-doped sorbents were much smaller than those of the undoped zeolite. Also, the LiOH-doped zeolites gave higher CO_2 adsorption relative to the bare zeolite when in contact with air/oxygen. An optimization of the optimum moisture content for maximum CO_2 removal was carried out by correlating the measured relative humidity (RH) with CO_2 uptake [174].

Some recent advances in the use of graphene have also shown its potential as a suitable adsorbent for GHGs/CO_2. Graphene is a 2D super carbon-based allotrope with Sp^2

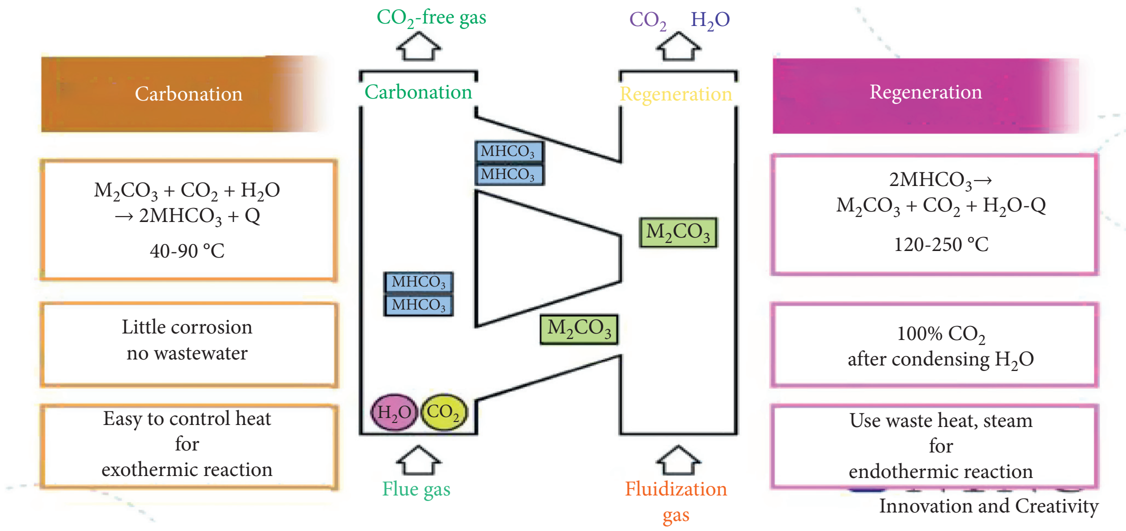

Figure 6: Dry sorbent CO_2 capture with fluidized beds and adsorbent regeneration (adopted from Bolland [44]).

hybridized atomic layers [175]. Graphene and its derivatives are potential materials for effective CO_2 capture [176–181]. According to Kemp et al. [182], this happens by reason of the grafting of compatible functional groups onto graphene layers, thus giving rise to highly stable N-doped graphene composites with surface areas in the region of 1336 m^2/g and reversible CO_2 capacity of 2.7 mmol/g at 298 K and 1 atm for repeated adsorption cycles. Oh et al. [183] studied the performance of borane-modified graphene; they reported a CO_2 uptake of 1.82 mmol/g at 1 atm and 298 K. New hybrid systems such as mesoporous graphene oxide (mGO)-ZnO nanocomposite [184], mesoporous TiO_2-graphene oxide nanocomposites [185], Mg-Al layered double hydroxide (LDH) graphene oxide [186], MOF-5-aminated graphite oxide (aGO) [187], UiO-66-graphene oxide composites [188], as well as MIL-53(Al)-graphene nanoplates (GNP) [189] have shown improved CO_2 adsorptive properties over their nonhybrid counterparts. Table 3 gives a summary of the advances made in different categories of carbon sequestration technologies.

The certification of materials as good adsorbents for CO_2 separation from flue gas depends on the following criteria:

(i) Adsorptive capacity: this gives information on the quantity of CO_2 that can be trapped on the surface of the solid adsorbent. It is defined as the gravimetric or volumetric uptake of CO_2 per unit mass of adsorbent (i.e., grams or volume of CO_2/grams of adsorbent). This dictates the amount of sorbent as well as the size of the adsorbent/packed bed required for a particular operation. The adsorptive capacity of a solid adsorbent determines the energy required during the adsorbent regeneration step.

(ii) Selectivity: this is defined as the CO_2 uptake ratio with respect to another gas (i.e., N_2 during post-combustion CO_2 capture or CH_4 in CO_2 sequestration from natural gas). The adsorbent selectivity for carbon-based compounds has a resultant effect on the purity of the adsorbed gas [190]. The simplest approach for estimating the selectivity of a solid adsorbent is to evaluate its adsorption profile based on the single-component adsorption isotherms of CO_2 and N_2.

(iii) Enthalpy of adsorption: this is the amount of energy required to regenerate the solid sorbent, which in turn impacts the cost of the regeneration process. It also measures the affinity of the material for CO_2/target-substance in relation to the strength of the adsorbate-adsorbent interactions.

(iv) Chemical, physical, and thermal stabilities: excellent solid adsorbents must be able to demonstrate high stability when in contact with the contaminated streams, especially during the adsorption-regeneration cycle [191].

(v) Hydrostability: essentially, hydrosorbent stability is a necessary requirement for the sustainable performance of solid adsorbents in contact with water vapour. Furthermore, the thermal capacity and conductivity of the adsorbent are also essential properties for solid adsorbents during mass transfer operations.

(vi) Adsorption-desorption kinetics: the time taken for adsorption and adsorbent regeneration greatly relies on the profile of the adsorbate adsorption-desorption kinetics, which is determined by breakthrough curves. Adsorbents that adsorb and give off adsorbates with ease upon regeneration are more often preferred, owing to the fact that these can be achieved within shorter cycle times for small quantities of adsorbents, which in turn influences the overall cost of trapping the adsorbate.

(vii) Cost of adsorbent: since several adsorbents that exhibit excellent sorption attributes are readily available at low costs, they are rather deemed the most ideal candidates for CO_2 capture. In lieu of the advantages gained from the cheap nature of these

Table 3: Summary of advances made in the categories of carbon sequestration technologies.

S. no.	Categories of carbon sequestration technologies	Process type/solvent	Trapped carbonaceous gas	Refs.
1	Physiochemical absorption	*Physical absorption*		
		Selexol: ethers of polyethylene glycol	CO_2	[36]
			CO_2	[44]
		Rectisol: (CH_3OH)	CO_2	[34]
		Fluorinated solvents: ($C_4H_6O_3$)	CH_4	[53]
		Purisol ionic liquids	CO_2/CH_4	[27, 53]
		Chemical absorption		
		Monoethanolamine (MEA)	CO_2	[55]
		Diethanolamine (DEA)	CO_2	[27]
		Methyl diethanolamine (MDEA)	CO_2	[56, 57]
		$Ca(OH)_2$+DEA	CO_2	[27]
2	Cryogenic separation	*Air separation system*	CO_2	[60, 61]
3	Membrane separation	*Adsorption*		
		MOP: (BOP-1) functionalized with Cl and NH_2 moieties	CO_2/CH_4	[66, 67]
		MOFs: (i) With open metal sites	CO_2	[70, 71, 81, 82]
		(ii) With presynthetic modification of organic ligands	CO_2	[91–93]
			CO_2	[99, 102, 107]
		(iii) Postsynthetic functionalization of MOF-metal matrices	CO_2 and CH_4	[107]
4	Microbial and algal seed coats	*Regenerative agriculture* (MECC)	CO_2 and CH4	[151]
5	Adsorption	Zeolite/activated carbon	CO_2	[44, 152, 153]
		Graphene		
		(i) Pristine graphene	CO_2/GHGs	[181]
		(ii) N-doped	CO_2	[182]
		(iii) Borane-modified graphene	CO_2	[183]
		(iv) Mesoporous graphene oxide (mGO)-ZnO nanocomposite	CO_2	[184]
		(v) Mesoporous TiO_2-graphene oxide	CO_2	[185]
		(vi) Mg-Al layered double hydroxide (LDH) graphene oxide	CO_2	[186]
		(vii) MOF-5-aminated graphite oxide (aGO)	CO_2	[187]
		(viii) UiO-66-graphene oxide composites	CO_2	[188]
		(ix) MIL-53(Al)-graphene nanoplates	CO_2	[189]

materials, the environmental impact of their synthetic routes is a major hurdle that needs to be overcome. As previously mentioned, some solid adsorbents that have been adopted for the trapping of carbonaceous substances/CO_2 include activated carbon (AC), single/multiwalled carbon nanotubes (CNTs), and graphenes. ACs are inexpensive, porous-amorphous structures, which possess high specific surface areas that serve as gas traps for greenhouse gas (GHG)/CO_2-uptake [192–194]. Unlike zeolites, one of the basic ills associated with the use of ACs for CO_2 adsorption is that there are no active sites for the gas to bond with the adsorbate as orchestrated by the presence of cations in zeolite. Weak interactions result in low enthalpies of adsorption and sorbent regeneration. ACs give very low CO_2 uptake at reduced pressures due to the absence of electric fields on the surfaces of ACs. Kacem et al. [195] carried out a study to test the capacity of ACs and zeolite for CO_2 separation from N_2 and CH_4 based on their regeneration potential, reusability, and adsorptivity. They observed that the CO_2 uptake for ACs was far higher than that of zeolites at pressures above 4 bar. The amount of CO_2 recovered at the AC regeneration stage was purer compared to that recovered from the zeolite samples. In addition, the ACs were found to be more stable in the presence of water vapor, thus resisting any framework collapse [196].

To improve the performance of ACs for CO_2 adsorption, amines have been found to be very effective [197–200]. Maria et al. [201] modified the surface of a microporous AC of 80% active surface via the simultaneous grafting of amine and an amide onto its surface. The work of Gibson et al. [202] bothers on the impregnation of polyamine within the pores of carbon, where the CO_2 adsorption was seen to be 12 times that of the undoped carbon. CO_2 -uptake by AC has been enhanced by direct impregnation with chitosan and triethylenetetramine onto AC surface, where about 60 and

90% increment in CO_2 uptake were recorded at 298 K and 40 bar. The performance of NH_3-modified ACs have been investigated at 1 atm and within a temperature range of 303 to 333 K [203]; reports from the investigation showed that the calculated enthalpies of CO_2 adsorption for the modified AC and the piristine AC are 70.5 $kJmol^{-1}$ and 25.5 $kJmol^{-1}$, respectively, thus indicating that the adsorption process is largely due to chemisorption. At 303 K and 1 bar, the recorded selectivity and adsorption capacity of the NH_3-modified AC gave corresponding CO_2 uptake of 3.22 mmol/g for the NH_3-modified AC and 2.9 mmol/g for the un-modified AC [203]. CNTs are very friendly with amine solvents, such that when combined, they are very efficient in the trapping of CO_2 [204–208]. Liu et al. [204] synthesized industry-grade CNTs that were functionalized with tetraethylenepentamine (TEPA). The effect of the amine loading on CO_2 uptake, enthalpy of adsorption, and adsorbent regeneration was investigated. The TEPA-impregnated CNTs gave a CO_2 adsorption rate of 3.09 mmol/g adsorbent at 343 K. A similar investigation was conducted using 3-aminopropyl triethoxy silane (APTES) [209], polyethylenimine (PEI) [206], and di-/tri-ethanolamines [210].

2. Future Considerations for Carbon Capture Systems

No doubt, in the near future, greenhouse gas emissions will continue to constitute a global menace to the earth's climate, her populace, and the ecosystem. However, over decades, the literature reveals that concerted efforts were channeled towards abating/controlling CO_2 emissions owing to the large volume of CO_2 released from fossil fuels. On a unit basis, the amount of other gaseous constituents can be somewhat significant, hence the need to look into trying out some of the methods developed for CO_2 capture for their likelihood of being compatible with other greenhouse gases. This then suggests that new methods or modified versions of some existing methods may become necessary in order to achieve this expectation. In addition, there is a need to have a clear understanding of the chemical structure of these gaseous constituents (HCl_3, CCl_4, H_2Cl_2, CH_4, etc.) and how porous materials can be engineered to ensure their entrapment. The framework of some choice MOFs can be tuned to make them have high selectivity with respect to a target component relative to other gases. For instance, if CH_4 is the target gas to be trapped, the matrix of a choice MOF has to be tuned to ensure its selectivity for CH_4; the same goes for membranes where high functionalities can be achieved via doping the membranes with nanoparticles or activating them with ionic liquids. This hybrid approach helps to combat the ills associated with using one type of approach per operation because a hybrid system offers the combined abilities of different blends to trap these gaseous constituents. Some of the challenges associated with CO_2 capture during post-combustion capture have also been pointed out to include low CO_2 partial pressure, high flue gas temperature, and high CO_2 concentration in the gas. Also, as already discussed, aqueous amines are suitable for acid gas absorption, but their shortcomings (high costs of solvent regeneration, low CO_2/H_2S selectivity, corrosivity, and solvent volatility), these have spiked up a revolution in technological advances, where ionic liquids can be used alongside membranes or MOFs for improved adsorption of not just CO_2 but other greenhouse gases.

3. Conclusion

Carbon capture systems have proven to be very helpful in reducing the global carbon footprint of the earth. Based on the recent advances recorded in the use of membranes of high thermal, hydrological, and chemical stability, as well as ionic liquids, MOFs, and other solid adsorbents, it is clear that no one adsorbent is an all-time solution to all the greenhouse gas emissions. It then suffices to say that the best solution still lies in creating optimized hybrid capture systems comprising of one or more combinations of MOFs with methyl functionalized ligands [119] + inorganic/ionic liquids; bionanocomposite membranes comprising of rGO + DEA or $K_2CO_3/Ca(OH)_2$ + DEA; and zeolite + ionic liquids, etc., for efficient trapping of greenhouse gases.

Despite the potential of each material as a stand-alone technology, the recommendation of the novel hybrid solvents often drifts towards lower energy costs, low solvent loss, low fouling tendencies, and regeneration requirements compared to those associated with conventional amine solvents and this is due to the inherent phase changes that are usually associated with ionic liquids/nonaqueous solvents and enzyme-activation systems which are all promising technologies. For mixtures of low carbon dioxide contents, chemical solvents are usually preferred to physical solvents because physical solvents give better performances at high CO_2 partial pressures.

Also, since the presence of fluorine and chlorine functional groups in polymer-/MOF-based membranes help in the adsorption of CO_2 [121], the functional groups of the adsorbents can also be tweaked in favour of their adsorptive capacities for CH_4 and other carbonaceous gases when polymers/MOFs such as polyhedral metal-organic (PMO) frameworks are being fabricated using supermolecular building blocks functionalized with halogenated solvents of chlorine and fluorine in order to boost their abilities to trap CO_2 and some light hydrocarbons including CH_4 and C_3H_8. Since a large majority of these systems have been adopted in capturing CO_2, a good insight of the underlying mechanisms that help to ensure carbon seizure in these systems or their modified forms will help tailor the properties of these adsorbents to suit their applications to other gases. Based on the findings of this review, better CO_2 adsorption is often recorded at lower temperatures and higher pressures. Furthermore, as a result of the high solubilities of some of these gases in some ionic liquids, these liquids can be selected, functionalized, and integrated into some choice adsorbents for the basic purpose of trapping any greenhouse gas of interest. This will not only help to reduce cost but will in turn maximize the effectiveness and efficiencies of modern-day greenhouse capture systems.

Data Availability

All data used to support the findings of this study are available within the article.

Conflicts of Interest

The authors are sure that there are no known conflicts of interest as regards the publication of this manuscript.

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