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REVIEW

# Carbon Dioxide Capture by Polymers: Thermodynamics, Computer Modeling, Technology, and Applications

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## ABSTRACT

The process of capturing carbon dioxide ($CO_2$) emissions from the industrial sector or directly from the atmosphere is receiving substantial global attention. This is due to profound global alterations in the climate and ecosystems that are hazardous to human life and well-being. It is essential to understand the mechanisms and thermodynamics of carbon capture applications. Lower $CO_2$ emissions have been achieved through the application of $CO_2$ capture techniques. Herein, we review and compare the $CO_2$ sources, as well as the advantages and disadvantages of various options for $CO_2$ capture technology. This is done to aid the development of new technologies and opportunities to accelerate their scale-up. This review found that adsorption technology promises long-term protection against pollutants and moisture. This approach efficiently and dependably manages heat conditions using oxygen-containing compounds. Adsorption technology using polymer-based adsorbents employed in $CO_2$ capture is examined. Polymer-based materials are of particular interest due to their structural tunability, chemical functionality, and potential for cost-effective, scalable deployment. Additionally, the utilization of natural rubber for efficient carbon capture is reviewed. The last section provides an analysis indicating that adsorption technology is a promising technique for polymer-based adsorption suitable for further development in $CO_2$ capture.

## 1 | Introduction

The substantial rise in carbon dioxide ($CO_2$) levels in the atmosphere is the primary driver of climate change [1]. This phenomenon results in global warming. From the start of the Industrial Revolution in the 18th century to 2022, the concentration of atmospheric $CO_2$ increased from about 280 to 417 ppm [2]. The primary cause of climate change and the yearly 1–3 mm rise in sea levels is the unprecedented amount of atmospheric $CO_2$. Additionally, it is believed that animals and ecosystems are impacted by $CO_2$-driven ocean acidification [3, 4]. Due to economic expansion and population growth, global energy demand will continue rising. It is expected to increase to 800–1000 EJ (EJ = exajoule = $10^{18}$ J) by 2050 [5]. Climate change impacts social and environmental factors affecting everyone's health. These factors include the availability of unpolluted air, secure sources of drinking water, adequate food supplies, and appropriate housing. Climate change is

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**TABLE 1** | Global export value and quantity of polyamine and acyclic polyamines [39].

| **Polymer type** | | **Year** | | | | |
|---|---|---|---|---|---|---|
| | | **2018** | **2019** | **2020** | **2021** | **2022** |
| Polyamine | Value (USD thousands) | 464,891 | 269,658 | 237,605 | 69,915 | 95,383 |
| | Quantity (tonnes) | 174,190 | 153,065 | 112,892 | 64,381 | 26,867 |
| Acyclic polyamines | Value (USD thousand) | 889,714 | 829,272 | 779,663 | 1,049,779 | 1,385,934 |
| | Quantity (tonnes) | 274,504 | 269,637 | 241,719 | 274,205 | 285,260 |

forecast to result in approximately 250,000 deaths per year between 2030 and 2050, primarily due to factors such as famine, malaria, diarrheal diseases, and heat-related health issues [6]. Air pollution, an important global health issue, has a wide range of negative effects on both people and societal health [7]. The World Health Organization (WHO) has reported that air pollution annually accounts for almost 7 million premature deaths. These fatalities are a result of diverse health ailments that include heart failure, stroke, chronic bronchitis, lung cancer, and acute respiratory illnesses, such as pneumonia. Children in countries with low or middle incomes are disproportionately affected by the detrimental effects of air pollution [8]. Air pollution poses a significant risk to the global economy, resulting in healthcare costs that account for 6.1% of the global gross domestic product (approximately USD 8 trillion in 2019) [8]. Furthermore, a United Nations organization, the Intergovernmental Panel on Climate Change (IPCC), was founded to evaluate the scientific aspects of climate change and report on the subject. The IPCC's Sixth Assessment report, released in 2021, concluded that human activities have caused an approximate 1.1°C temperature increase in the Earth's climate from 1850 to 2005, primarily due to the release of heat-trapping gases [9]. In the coming decades, it is projected that this average global temperature increase will reach or exceed 1.5°C. This temperature increase will have a global influence [10].

However, in September 2015, the United Nations General Assembly endorsed their 2030 Agenda, which sets forth an ambitious plan for radical transformation by 2030 to attain a more sustainable future [11]. The 2030 Plan of Action for Environmental Sustainability is operationalized through the 17 global Sustainable Development Goals (SDGs). They signify a new age of collective endeavors by the international community to achieve this comprehensive strategy for the betterment of humanity, the environment, and economic well-being. Under the 17 SDGs, carbon capture is the emphasis of Goal 13; it is particularly important. Its objective is to actively combat climate change. SDG 13 aims to integrate environmental-friendly actions into national plans and policies, monitor advancements on climate funding pledges, and strengthen capabilities to address climate change. It also accounts for both adaptation and mitigation [12]. Raising awareness of $CO_2$ reduction or elimination is a crucial step in promoting sustainable development in the context of mitigating climate change.

Frequently, the terms $CO_2$ capture, utilization, and sequestration (CCUS) are used in the context of managing carbon emissions and combating climate change [13]. The main fields of research have been carbon capture and storage (CCS) or utilization (CCU) [14–17]. Geological storage of $CO_2$ is the goal of CCS [18]. In contrast, CCU refers to trapping $CO_2$ as a carbon source for chemical raw materials, such as fuels and fine chemicals [19]. These processes utilize captured $CO_2$ as a sustainable source of carbon, which is then transformed into useful goods [20, 21]. Methods of carbon capture in both the industrial and academic sectors include absorption-based $CO_2$ capture [22–25], membrane separation [26–29], $CO_2$ collection via adsorption [30, 31], chemical looping for $CO_2$ capture [32, 33], direct capture of $CO_2$ from air [34–36], and $CO_2$ capture by hybrid processes [37, 38]. Carbon capture products are now available on the market. However, as this is a new area of development involving considerable innovation, there is extensive new research on polymer capture of $CO_2$, but few commercially available products. Based on information from the International Trade Centre [39] two types of polymers can be utilized in $CO_2$ capture, polyamine and acyclic polyamines. Polymeric amines can aid in the adsorption of $CO_2$. Table 1 shows the decreased global export quantity and value for polyamine. However, the export quantity and value of acyclic polyamines remained high from 2018 to 2022.

In this review, we elucidate the potential mechanism and thermodynamics involved in $CO_2$ capture processes. Application of computer models to carbon capture is also discussed. We summarize and compare the major $CO_2$ capture technologies. This section covers the benefits and drawbacks of all carbon capture technologies. Finally, we conclude that utilization of polymer-based composite materials for $CO_2$ collection appears promising, highlighting remarkable polymers, their applications, and their carbon capture capabilities. Natural rubber and biomaterial polymers can capture carbon as well [39]. Hence, the objective of this review is to scrutinize and compare carbon capture technologies, as well as to discuss the challenges and future potential of using polymers to manage $CO_2$. This article summarizes the details of $CO_2$ capture and presents ideas for applications to reduce $CO_2$. Thus, this review is beneficial for individuals wanting to make informed decisions regarding the development of carbon capture.

## 2 | Mechanisms and Thermodynamics of $CO_2$ Capture

### 2.1 | Mechanism

Recently, there has been much effort in the development of polymer-based $CO_2$ capture [40]. The principal polymeric materials include porous organic and porous coordination

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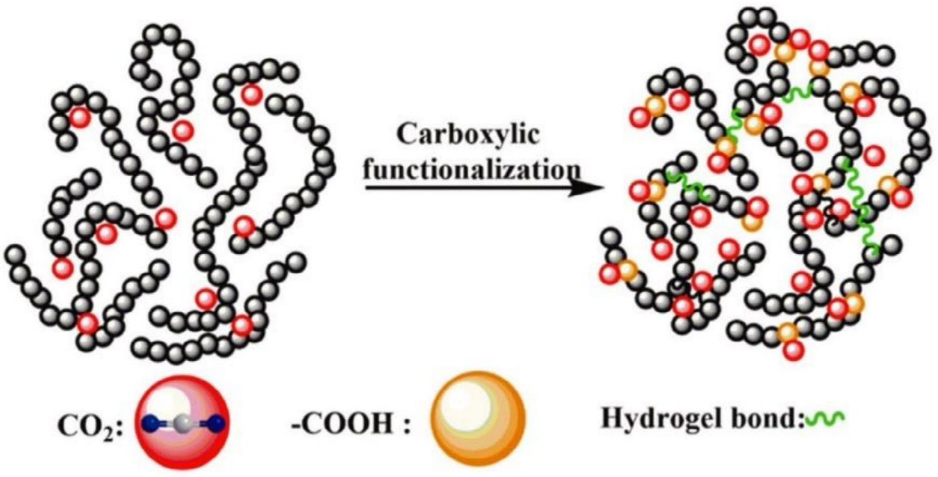

**FIGURE 1** | Mechanism by which hydrogel absorbs $CO_2$. Reproduced with permission [47]. Copyright 2021, Elsevier. [Color figure can be viewed at wileyonlinelibrary.com]

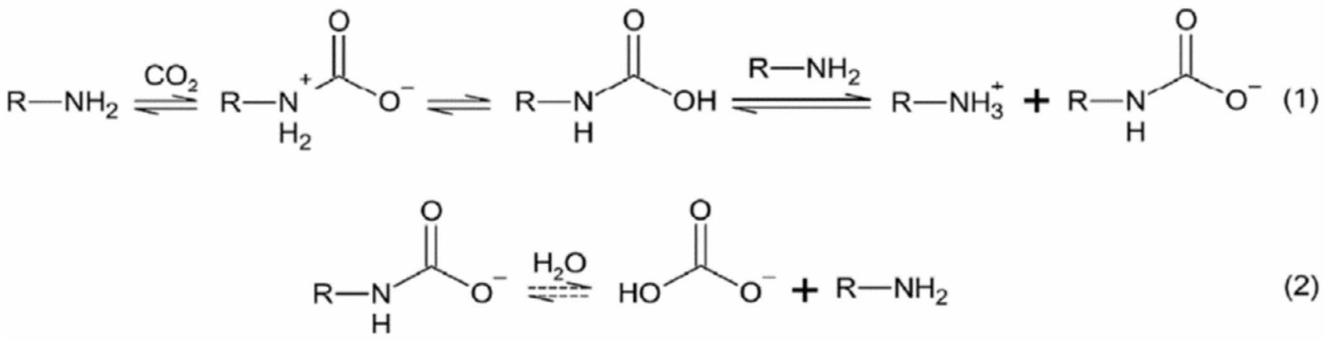

**FIGURE 2** | Interaction between $CO_2$ and primary/secondary amines through a zwitterion mechanism, while reaction between $CO_2$ and tertiary amines takes place via an acid–base reaction. Reproduced with permission [51]. Copyright 2018, Elsevier.

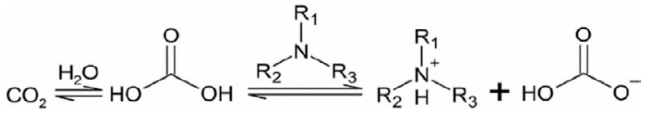

**FIGURE 3** | Interaction between $CO_2$ and a tertiary amine taking place via acid–base reaction. Reproduced with permission [51]. Copyright 2018, Elsevier.

polymers [41], microporous organic polymers [42], and amine-functionalized porous polymers [43, 44]. Polymeric amines have many derivatives, such as polyethylenimine (PEI), polypropylenimine (PPI), poly(acrylic acid) (PAA), polyaniline, amino dendrimers, and hyperbranched polyamines [45]. One illustrative example of polymeric amines utilized for $CO_2$ capture (which serves to elucidate its underlying mechanism) involves the utilization of a polyimide aerogel adsorbent that incorporates carboxyl groups inside the polymer backbone [46]. The polymer under consideration has the capability to absorb $CO_2$ due to the carboxyl groups and electron-rich heteroatoms inside its polyimide systems [47], as depicted in Figure 1. The efficacy of $CO_2$ capture is altered by factors such as microporosity, surface area, and the chemical composition of the aerogel. Addition of certain structural groups, such as amino, sulfonate [48], and hydroxyl groups [49] enhances the adsorption of $CO_2$.

The important functional group for $CO_2$ uptake is the amine group. The polymer backbone can also be varied, for example, changed to cellulose [50]. A mechanism for $CO_2$ capture by an amine group [51] is presented in Figure 2.

Amines containing a nitrogen atom with an unshared pair of electrons, both primary and secondary, have nucleophilic characteristics and function as Lewis bases. These amines engage in an attack on the electrophilic carbonyl group of $CO_2$, resulting in the formation of a zwitterion. This zwitterion undergoes quick deprotonation by another amine molecule, leading to the creation of a more stable carbamate ion. This reaction results in the formation of 2 mol of amine for each molecule of $CO_2$, as shown in Reaction (1) of Figure 2. Under acidic conditions, water molecules can undergo hydration with a carbamate species, leading to the creation of bicarbonate and the liberation of a free amine (Reaction (2) of Figure 2) [52]. The hydration reaction rate is reduced because of the inherent stability of the carbamate structure. Tertiary amines differ from primary and secondary amines in that they solely display Bronsted base characteristics. This means that they effectively counteract the formation of carbonic acid resulting from the reaction between $CO_2$ and water (as depicted in Figure 3). This chemical reaction entails the utilization of 1 mol of amine per mole of $CO_2$. The aforementioned reaction is sluggish because of the gradual generation of carbonic acid [53].

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The interaction mechanisms illustrated in Figures 1–3 are not universally applicable to all polymeric materials. These mechanisms primarily describe $CO_2$ capture in hydrophilic polymers and amine-functionalized systems, where chemical interactions such as zwitterion formation, carbamate formation, and acid–base reactions dominate the adsorption process [51–53]. In contrast, hydrophobic polymers or polymers lacking amine or other $CO_2$-philic functional groups generally capture $CO_2$ through physical adsorption mechanisms, mainly governed by van der Waals forces, pore confinement effects, and quadrupole–dipole interactions rather than chemical bonding [40, 41]. Furthermore, the polymer architecture, including crosslinking density, porosity, surface area, and pore size distribution (PSD), plays a crucial role in determining $CO_2$ diffusion, accessibility of active sites, and overall adsorption performance [42, 46, 47]. Highly crosslinked polymer networks may restrict gas transport, whereas enhanced microporosity and well-distributed functional groups can significantly improve $CO_2$ uptake [43–45]. Therefore, the mechanisms discussed herein are primarily applicable to hydrogels and amine-based polymers, while other polymeric systems may follow different $CO_2$ capture pathways depending on their chemical composition and structural characteristics.

## 2.2 | Thermodynamics of Carbon Dioxide Capture Polymers

Ideal gases provide a reasonable approximation for the composition and properties of air. The free energy of mixing of 1 mol each of two gases can be determined by referring to research work on the subject [54, 55].

$$G_{mix} = RT(x\ln x + (1 - x)\ln(1 - x)) \tag{1}$$

The variable $x$ represents the proportion of the main element in the mixture. It is notable that the free energy of mixing for the remaining air components, specifically nitrogen and oxygen, does not need integration. It can be assumed that these components are already blended. The computation of the Gibb's energy of mixing alone accounts for the additional free energy arising from combining $CO_2$ with an existing air mixture. Through a comprehensive assessment of the factors influencing the free energy of mixing in a multi-gas system, the incremental change in free energy resulting from the addition of another component is independent of the initial mixture's composition [56, 57].

The minimum work required to extract 1 mol of $CO_2$ from an unlimited source of an ideal gas mixture, characterized by a temperature T and pressure $P_0$, with a partial pressure of $CO_2$ represented as $P_1$, is:

$$W = RT\left[\ln\left(P_1 / P_0\right)\right] \tag{2}$$

Attaining the minimal free energy value is contingent upon the percentage of $CO_2$ collected being exceedingly minute. An alternative is to consider the entropy of mixing beginning with the required free energy for a sorbent process.

Let $\Delta G_0$ represent the change in free energy of a mixture under standard conditions of pressure ($P_0$) and temperature, and that $CO_2$ can be modeled as an ideal gas. Then, the change in the free energy of mixing is directly influenced by the pressure (P) of $CO_2$ [57].

$$\Delta G = \Delta G_0 - RT\ \ln\left(P / P_0\right) \tag{3}$$

In a system where the change in Gibbs free energy ($\Delta G$) is minimized, the sorbent reaction exhibits reversibility when the exit pressure of the separating chamber ($P_2$) is reached. By imposing this limitation, we achieve:

$$\Delta G_0 = RT\ \ln\left(P_2 / P_0\right) \tag{4}$$

Equation (4) represents the least amount of energy needed for the sorbent reaction to reach an exit pressure of $P_2$. When $P_2$ is equal to $P_1$, the absorption process does not result in a reduced $CO_2$ level in the stream. However, when the sorbent is loaded, the reaction can still take place irreversibly. If $P_2$ is less than $P_1$, the reaction is irreversible. Furthermore, the degree of irreversibility is directly proportional to the reduction in the ratio of $P_2$ to $P_1$. Consequently, the amount of energy required for adsorbent renewal will exceed the energy needed for the extraction procedure.

The concept of combined free energy provides a theoretical framework for determining the optimal conditions for separation of $CO_2$ from air. Nevertheless, incorporating the irreversibility of a practical sorbent process into the study of a sorbent-based system would typically result in a more accurate and realistic assessment of the process [58], as shown in Figure 4. Equation (4) is used to calculate the sorbent strength required to produce the desired decrease in $CO_2$ content of the gas, bringing it to the appropriate concentration at the end of a single operational stage. Sorbent-based systems can reduce the amount of free energy required per mole of $CO_2$ removed by utilizing different sorbent strengths throughout the various phases of the sorption process. One potential approach to partially reduce the $CO_2$ concentration of the input gas stream involves utilization of a sorbent that is partially saturated and has a lower free energy of sorption compared to an unused sorbent. To achieve a complete reduction in the partial pressure to $P_2$, it is necessary to utilize a fresh sorbent. This contrasts with a stable chemical sorbent exhibiting consistent chemical reactivity. The lowest amount of energy necessary for a specific sorbent is defined by the free energy of mixing, which sets a lower bound. The upper bound is determined by the single sorbent limit. As depicted in Figure 5A, in $CO_2$ capture from air, the disparity between the two limitations is negligible. The limit imposed on a single sorbent offers a fair approximation, even in cases when the ratio of ($P_1$–$P_2$) to $P_1$ is almost equal to 0.5 [57].

Considering a solid sorbent process with an activity that remains unaffected by its loading state can have advantages. This analysis offers significant insights into the inefficiencies in real-world implementations. Below, the phrase “single sorbent system” is employed to refer to a system of that nature. Within the realm of single sorbent systems, it is possible to determine a theoretical maximum level of effectiveness that cannot be exceeded within the limitations of these procedures. If the sorbent is regenerated under ideal conditions, the

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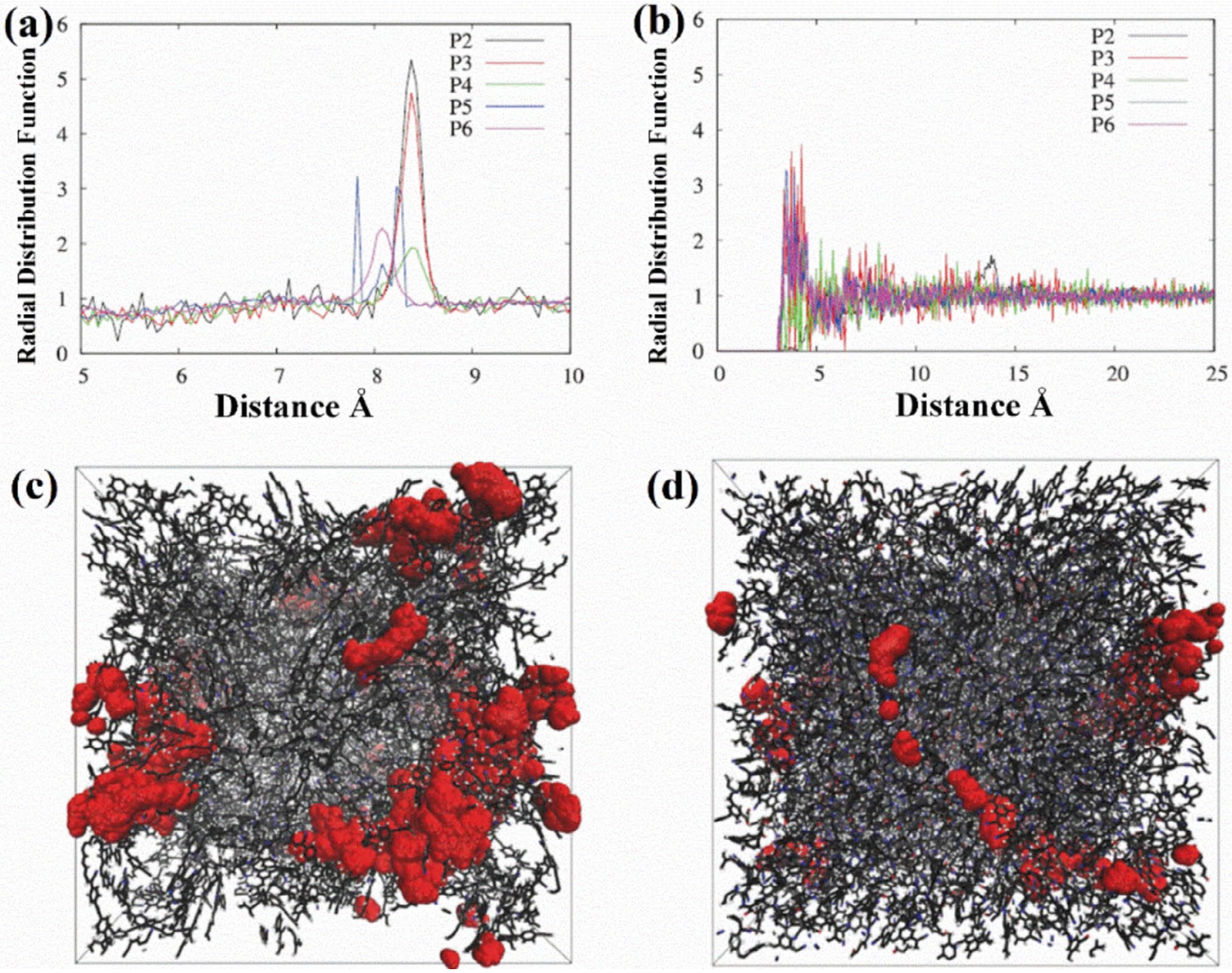

**FIGURE 4** | (a) Comparison of radial distribution of N atoms in polymers, (b) comparison of radial distribution of the C atom in $CO_2$ to the N atoms of polymers, (c) overlay of $CO_2$ diffusion in P2, and (d) $CO_2$ diffusion in P6. Reproduced with permission [58]. Copyright 2017, John Wiley and Sons. [Color figure can be viewed at wileyonlinelibrary.com]

extra energy added to the sorption cycle is equal to the energy required for sorption of the material at standard temperature and pressure.

There are several options available for measuring the energy efficiency of removing $CO_2$ from a gas stream by reducing its partial pressure from $P_1$ to $P_2$. This creates a $CO_2$ product stream at pressure $P_0$. One method involves comparing the actual amount of free energy used to extract $CO_2$ with the theoretically necessary amount at a partial pressure of $P_2$. This rationale is logical when $P_2$ remains constant, but it appears arbitrary in the context of $CO_2$ capture from air, as the selection of $P_2$ is influenced by cost or efficiency factors. An alternative approach could involve contemplating elimination of all $CO_2$ as a reference point, by comparing it to the threshold of $P_2 = 0$. Nevertheless, utilization of partial scrubbing systems could potentially result in efficiencies surpassing 100%, an undesirable condition. Therefore, the definition of efficiency involves comparing the least quantity of free energy required to capture 1 mol of $CO_2$ and the actual amount of free energy consumed in a process to capture the same amount of $CO_2$ [59]. Equation (1) provides the free energy associated with the sorbent, which is the most optimal choice for the process.

Based on other research, 21.86 kJ/mol $CO_2$ is the smallest amount of work necessary in a thermodynamic process for division of a stream containing 400 ppm of $CO_2$ into two separate streams. The resulting streams consist of one with a low $CO_2$ content and the other composed of $CO_2$ (99% purity). In contrast, when the initial feed contains a $CO_2$ concentration of 12%, the smallest amount of work needed in a thermodynamic process for separation is 7.58 kJ/mol $CO_2$. Based on the disparity in energy levels, it is more advantageous to extract $CO_2$ from a localized source than from the Earth's atmosphere. Figure 5B illustrates the lowest required thermodynamic work or the separation of $CO_2$ from three distinct sources: air, exhaust gases produced by a combined cycle power plant that runs on natural gas, and exhaust gas from pulverized coal combustion. These results are depicted as a function of both $CO_2$ recovery and purity [34]. The data indicate that the smallest amount of work necessary in a thermodynamic process for separation of $CO_2$ from air is higher compared to its division from an exhaust gas. These values exceed 20 kJ/mol $CO_2$, especially when aiming for higher $CO_2$ purities and recoveries. The minimum effort necessary for direct air capture (DAC) [60] is 8–10 kJ/mol $CO_2$, which is comparable to the energy needed for separating $CO_2$ from power plant exhaust gas with

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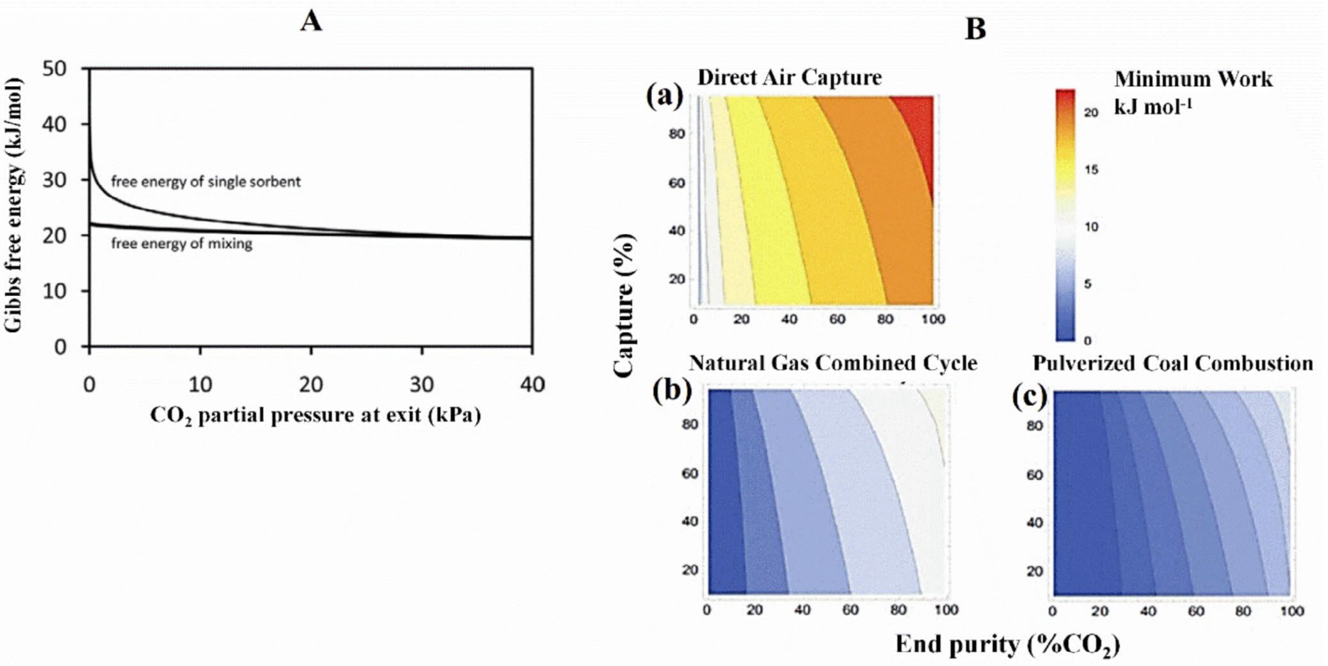

**FIGURE 5** | (A) The free energy required to separate $CO_2$ from air as a function of pressure at the system exit. Total pressure $P_0 = 100$ kPa, temperature $T = 300$ K. The bottom line in the plot corresponds to the free energy associated with a mixing process, while the upper line shows the free energy associated with a sorbent reaction that can reduce pressure to match the exit pressure. Sorbent energy deviates as the exit pressure approaches zero. Halfway, characterized by a 20 kPa exit pressure, there is a 4% disparity between the free energy of a single sorbent and the free energy resulting from a mixing process. When the ratio of $(P_1–P_2)$ to $P_1$ equals 0.5, the skimming limit from $P_2$ to $P_1$ can be considered a reliable approximation. Reproduced with permission [57]. Copyright 2013, Elsevier. (B) Minimum thermodynamic work of $CO_2$ separation from (a) air, (b) natural gas combined cycle flue gas and (c) pulverized coal combustion flue gas. Reproduced with permission [34]. Copyright 2022, MDPI. [Color figure can be viewed at wileyonlinelibrary.com]

a 90% recovery rate at 90% and 95% purities [61]. This applies specifically to cases where $CO_2$ purities and recoveries are below 10% and 60%, respectively. Additionally, $CO_2$ adsorption is influenced by temperature and pressure. $CO_2$ adsorption processes are enhanced by temperatures and pressures, especially for mesoporous polymers [62, 63].

Equations (1–4) are derived using ideal gas assumptions to define the theoretical minimum work and Gibbs free energy change for $CO_2$ separation, serving as a universal thermodynamic benchmark. While non-ideal effects such as humidity are not explicitly modeled, their practical impact is partially addressed through the reviewed experimental studies on waste-derived sorbents. For instance, modified cigarette filter (CF)-based adsorbents [64] were evaluated under realistic conditions and inherently reflect non-ideal gas–solid interactions. The results showed that the modified filter fibers show an excellent $CO_2$ adsorption capacity, 1.93 mmol/g. Therefore, the ideal gas-based results should be interpreted as lower-bound estimates, with explicit quantitative deviation or error analysis under non-ideal conditions identified as an important direction for future work.

## 3 | Computer Modeling

There are various approaches to computer modeling, depending on the desired scope. For example, at the microscopic scale, a density-functional theory (DFT) approach has been applied to investigate the chemical stability of atomic clusters and nanonization on the physical attraction of $CO_2$ [65]. The operating parameters for $CO_2$ capture, pressure, temperature, and particle size were experimentally explored using response surface methodology (RSM). Accordingly, analysis of isotherm modeling showed that the Hill model provided an excellent fit to the experimental data, as evidenced by its high $R^2$ value, close to unity. Furthermore, the kinetics model demonstrated that the process involved chemical adsorption and followed a second-order model. Thermodynamic analysis indicated that the adsorption of $CO_2$ was both spontaneous and exothermic. Molecular dynamics (MD) was used to study the potential of 6FDA/BPDA-DAM polymers [66, 67], which are membrane materials, for $CO_2$ separation and capture based on pyrolysis.

These polymers have outstanding specificity and the capability to dissolve $CO_2$ gas molecules because they have extremely small pores. An adapted Dreiding force-field coupled with MD yielded valuable data on the configuration of pores in a liquefied form. The $CO_2$ adsorption isotherm of the polymer matrix, considering the effects of matrix swelling, was determined by an isothermal isobaric molecular dynamics simulation. Consequently, the solvent-accessible surface area of different types of atoms, which comprise the pore interiors, showed that methyl carbon atoms and exposed oxygen have a stronger attraction to $CO_2$. Additionally, Monte Carlo (MC) techniques and MD can be combined to study the plasticization properties of polymers [68] for gas separation and capture. Considering polymer relaxation, the structural characteristics were significantly

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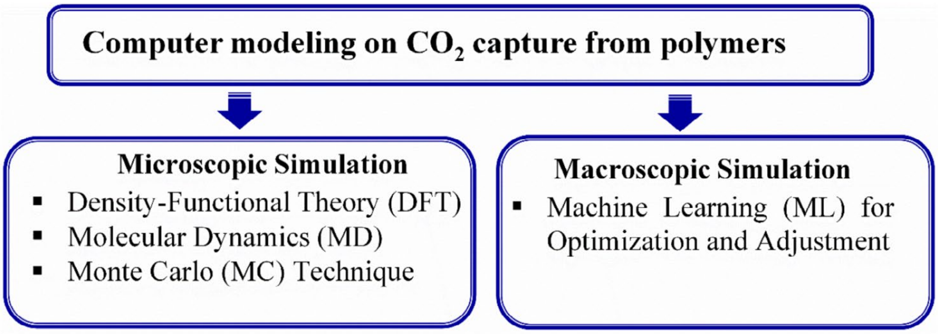

**FIGURE 6** | Computer modeling flowchart of microscopic and macroscopic simulations. [Color figure can be viewed at wileyonlinelibrary.com]

modified, particularly by $CO_2$ and $CH_4$. Microscopic simulation has paved the way for designing polymers that effectively capture $CO_2$ [69, 70], suggesting that enhancing the generated porous polymer by incorporating different functional groups onto its structure may enhance its effectiveness as an adsorbent for capturing $CO_2$ from the atmosphere. There are many functional monomers available for selecting and modifying polymer particles, which can enhance the affinity of composite nanostructures toward $CO_2$. Additionally, this research illustrated that utilizing DFT simulations helped to identify the optimal functionalization of composite materials for targeted $CO_2$ capture.

On the macroscopic scale, machine learning (ML) has played a role in developing and optimizing these materials. As previously reported [71], artificial intelligence (AI) and ML have promising applications in separation technologies and efficient carbon capture. This work reported the automated discovery of complex materials via inverse molecular design informed by process figures-of-merit and meso-scale target features lacking in existing computational frameworks. The current work provides a computational screening option before laboratory validation. Additionally, another study [72] used an ML algorithm, with a topological, path-based hash of the polymer repeating unit, to design exceptional gas-separation polymer membranes. This ML technique has been trained using limited experimental data, providing an innovative approach for investigating polymer membrane design that can be applied to $CO_2$ capture. Additionally, Basdogan et al. introduced a ML-based genetic approach to address the design challenge of polymer membranes for separating $CO_2$ from $N_2$ and $O_2$ [73]. Their approach generated numerous ML models using various fingerprinting featurization techniques. Through such ML models, the system could suggest novel polymer membranes that showed potential for separating $CO_2/N_2$ and $CO_2/O_2$. Computer modeling on $CO_2$ capture from polymers was summarized, as shown in Figure 6.

However, a comprehensive, critical overview of the technical considerations utilized ML-based methods for $CO_2$ capture [74]. The primary issues identified from the preceding discussions are (1) establishment of cohesive and unified databases, (2) prudent digitization of intrinsic material characteristics, and (3) verification of the precision of ML-generated outcomes in real-world situations. Another work [75], described a versatile, precise machine-learning approach for identifying novel polymers that exhibited optimal performance. Additionally, the gas permeabilities predicted by ML for the promising candidates were confirmed using high-fidelity molecular dynamics simulations, indicating that these predictions can be successfully applied in practice. Therefore, microscopic and macroscopic simulations can be integrated in multiple-scale models. However, DFT results provide the atomic and molecular properties at the quantum level and use them as the initial parameters of the MD method. The collective trajectories of MD simulation provide the interaction and dynamic information between molecules. Both these microscopic computations can be mapped onto ML's topological features and used to validate ML models. For example, Basdogan et al. provide a cross-scale validation [73].

Figure 7a illustrates the initial step of the model training process. It entails utilizing the SMILES string of the repeating unit of each polymer and its accompanying gas permeabilities. Figure 7b indicates the retrieval of pertinent substructures and molecular descriptors of each polymer, which are utilized as chemical inputs for training the ML model. In Figure 7c, the models of multitask ML and ensembles are trained to predict gas permeabilities. By utilizing the SHapley Additive exPlanations values of these models, it is possible to derive valuable physical insights. Figure 7d shows the models used to estimate the permeability of hypothetical polymers and known chemistries in an enlarged chemical space, with a focus on high-throughput analysis. Finally, Figure 7e shows high-fidelity molecular dynamics simulations conducted to validate the membrane permeabilities and selectivity of the most promising polymer choices [75]. In Figure 7, the training data source, model hyperparameters, and validation method are provided as a reference [76]. Reported prediction errors on the test data and MD confirmation indicate that this ML model is sufficiently robust and less prone to overfitting.

The permeability of polymer membranes is determined by the diffusivity and solubility of gas molecules. These properties can be assessed by analyzing the ML frameworks [77]. Permeability values are affected by electrostatic interactions and the presence of free-volume components. The findings support the growing trend in polymer research toward investigating non-planar structures to increase their microporosities. Such structures include kink, spiro, cardo, and pendant groups (such as $-CF_3$), as well as bulky and flexible groups (such as –O–), or multiple spatial linking arrangements employed in polyimides [78, 79]. ML models have demonstrated that SHAP value measurements indicate the presence of some substances, such as polyimides, ladder polymers, and poly (ethylene oxides). These moieties have a more significant detrimental effect on the permeability of $N_2$ and $CH_4$ compared to $O_2$ and $CO_2$ [80]. So, enhancing selectivity

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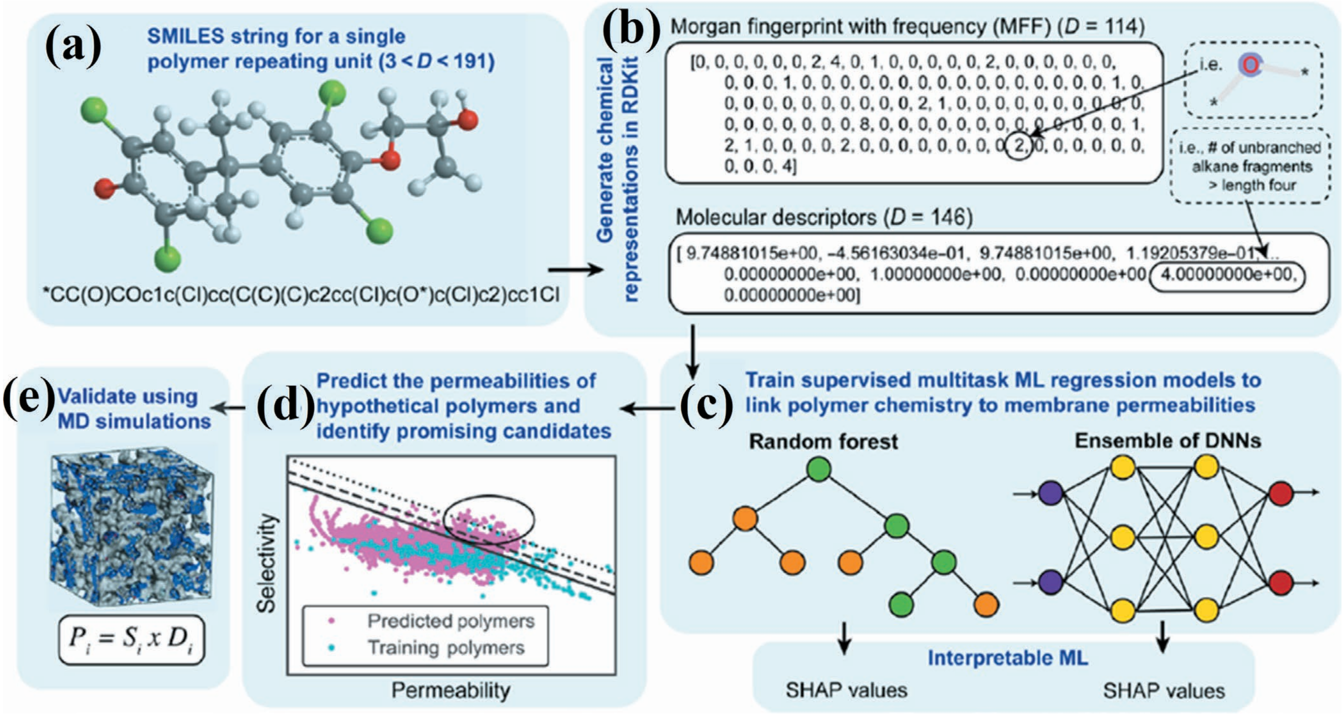

**FIGURE 7** | Workflow for utilizing ML to discover novel polymer membranes with optimal gas separation capabilities. Reproduced with permission [75]. Copyright 2022, AAAS. [Color figure can be viewed at wileyonlinelibrary.com]

can be achieved by expanding the permeability gap between specific gas pairs, which is advantageous in gas separation. This validates a well-established principle in membrane engineering, that the selectivity of membranes toward $CO_2$ can be improved by enhancing the solubility of $CO_2$ through integration of oxygen atoms into polymer membranes [80, 81].

Experimentally validated molecular dynamics simulations confirmed the predicted capabilities of the leading candidates. Several polymers in screening datasets have permeabilities anticipated to be higher than the Robeson upper bound. These polymers have the potential to be transformed into membranes with extraordinary separation properties. Applicable ML models can effectively identify polymers with great potential and superior performance. These models can identify thousands of potential candidates that surpass the upper limit established by the Robeson upper bound [82]. Furthermore, ultrahigh permeability polymers would enable unprecedented gas separation in industrial applications, achieving better throughput while preserving exceptional selectivity. With the ongoing progress of using machine-learning techniques coupled with growing computational capacity, it is anticipated that ML-assisted design frameworks will become more widely used, contributing to the discovery of materials for promising technologies.

## 4 | $CO_2$ Capture Technologies

Capture techniques to lower $CO_2$ emissions have advanced over the past few decades, although they are still in the preliminary stages of adoption. Currently, there are few operational carbon capture techniques [83]. However, several new techniques are being researched [84]. As technology progresses, carbon capture will assume a prominent role in the global transition to low-carbon activities. Carbon capture technology is part of the worldwide endeavor to alleviate the effects of global warming and meet climate commitments. Fossil fuels remain the predominant energy resource, although their utilization is detrimentally affecting the environment. Nonetheless, while the use of renewable energy has grown rapidly, it has not yet reached widespread adoption to reduce harmful environmental impacts. Carbon capture technology merits investigation as it can be employed to absorb carbon emissions before they reach the atmosphere. Figure 8 illustrates several carbon capture methods that have been extensively investigated in recent years and will be explained in the subsequent section.

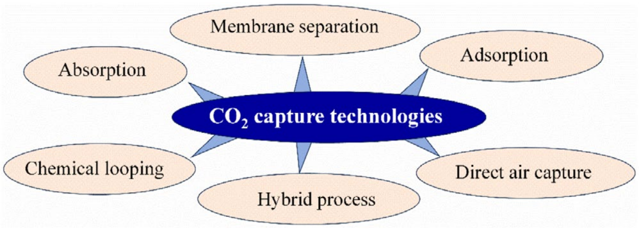

**FIGURE 8** | Summary of $CO_2$ capture technologies. [Color figure can be viewed at wileyonlinelibrary.com]

### 4.1 | Absorption

Absorption technology utilizes water solutions containing hydroxide sorbents with a strong affinity for $CO_2$. These sorbents are strong bases, including sodium hydroxide (NaOH)

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[22], potassium hydroxide (KOH) [23], and calcium hydroxide ($Ca(OH)_2$) [24, 85]. However, the oil and chemical industries use absorption as the most advanced method of separation, employing chemical or physical solvents [47]. Absorption processes consist of both physical and chemical processes. In the context of physical processes, absorption refers to the phenomenon by which a substance or material assimilates another substance or energy. This corresponds to Henry's Law [31] when $CO_2$ is sequestered in an absorption process. This phenomenon happens when the gas is exposed to high-pressure and low-temperature conditions. Conversely, desorption, the release of $CO_2$, occurs when the pressure is reduced and the temperature is increased [31]. This method has been extensively utilized in several industrial processes, such as the production of natural gas, synthesis gas, and hydrogen, which often have high $CO_2$ levels [86]. Additionally, traditional chemical absorption processes comprise an absorber and a stripper, wherein the absorbent undergoes heat regeneration. In a chemical absorption process, a flue gas containing $CO_2$ is introduced into a packed bed absorber. Within the absorber, the flue gas encounters a $CO_2$-lean absorbent in a counter-current manner. After the absorption process, the absorbent enriched with $CO_2$ is moved toward a stripper unit for thermal regeneration [31]. Following a regeneration process, the absorbent with reduced $CO_2$ levels is subsequently returned to the absorber for reuse in a cyclic process. Chemical absorption technology is a well-established and mature method for $CO_2$ capture. This technology has been successfully implemented in several industries for decades. However, it has not yet been extensively utilized for $CO_2$ capture from electricity generation facilities. One additional benefit of this technology is its ease of retrofitting to pre-existing power facilities. Table 2 provides a complete summary of absorption technologies that have been intensively researched in both corporate and educational organizations.

## 4.2 | Membrane Applications

Membrane-based $CO_2$ separation is often conducted in a continuous and steady-state manner. The permeation process is driven by a pressure difference across the membrane. This technology has been implemented in several commercial contexts, such as air separation for the acquisition of nitrogen or oxygen-enriched air of technical quality, extraction of $CO_2$ from $CH_4$ in natural gas, and separation of gas in well operations [26, 28, 97]. Additionally, various studies investigated the application of membrane separation techniques to remove $CO_2$ from flue gas streams of power plants [27, 98–101]. Utilization of membrane technology for $CO_2$ capture presents major challenges. Recently, bipolar membranes have been of considerable interest [102–104]. This involves a novel type of ion exchange membrane that can separate water into $OH^-$ and $H^+$ during electrolysis [105]. The biopolymer membrane (BPM) comprises an anion exchange layer, a cation exchange layer, and a catalytic layer (such as $Al(OH)_3$) sandwiched between them [106]. Upon charging, the water molecules in the BPM undergo dissociation at the active sites of the catalytic layer, resulting in the formation of $H^+$ and $OH^-$ ions. A strong electric field propels the $H^+$ ions toward the cathode via the cation exchange layer, while the $OH^-$ ions are directed toward the anode through the anion exchange layer. Recently, thin-film composite membranes, including polypropylene (PP) [107, 108], polyamide (PA) [109, 110], poly(ethylene glycol) (PEG) [111], polyvinylidene fluoride (PVDF) [108], polytetrafluoroethylene (PTFE) [112], polydimethylsiloxane (PDMS) [113], polyether sulfone (PES) [113], and polyacrylonitrile (PAN) [114] have attracted research attention. Their popularity is due to the cost-effective approach applied in the design of thin-film composite membrane structures. Multilayer composites weighing only 1–2 g/m$^2$ are employed, which is in contrast to typical asymmetric membranes weighing 50 g/m$^2$ [115].

Gas is transferred through a membrane by the process of solution-diffusion, which is driven by a differential in the pressure between the feed and permeating sides of the membrane. Then, gas molecules undergo an adsorption process onto a membrane surface, followed by dissolution into the interior of the membrane, and subsequent diffusion through the membrane. Finally, the gas molecules are desorbed from the opposite side of the membrane [115].

## 4.3 | Adsorption

Adsorption processes rely on the chemical or physical attachment of $CO_2$ using specialized sorbents, such as amine-functionalized sorbents, metal–organic frameworks, zeolites, and other materials [30, 31]. Polymers or solid-based polymers are appealing sorbents. Several researchers have attempted to apply organic and inorganic polymers for $CO_2$ capture [116–119]. Shao et al. described the synthesis of N-enriched porous carbons (NPCs) from inexpensive, triazine-based, porous organic polymers, utilizing KOH as an activating agent in the presence of nitrogen gas ($N_2$), as shown in Figure 9a [120]. Sorbents with ultra-micropores, having diameters $\leq 0.8$ nm, have been very effective in $CO_2$ capture. Therefore, $CO_2$ absorption was analyzed in relation to cumulative ultra-micropore volume ($V_{ultra}$). It is noteworthy that $CO_2$ absorption had a similar trend to that of $V_{ultra}$ (Figure 9b). Specifically, NPC-4-600, having the highest $V_{ultra}$ value, 0.20 cm$^3$/g, also had the highest $CO_2$ absorption (207 mg/g). Conversely, NPC-1-500, with the lowest $V_{ultra}$ value, 0.10 cm$^3$/g, had the lowest $CO_2$ uptake, 120 mg/g. The $R^2$ value was 0.9118 (Figure 9c), providing further evidence of the key role played by $V_{ultra}$ in $CO_2$ adsorption. Additionally, Patel et al. introduced covalent organic polymers (COPs) for adsorption, which are a novel group of porous polymers with a high $CO_2$ capturing capacity [117]. Their findings indicated that the COPs had $CO_2$ adsorption capacities of up to 5616 mg/g, measured at a 200-bar pressure.

Additionally, these COPs could operate at industrially useful temperatures, as high as 65°C [117]. The stability of COPs in boiling water was maintained for a minimum of 1 week, and they exhibited extremely high selectivity for $CO_2/H_2$ [117]. Similarly, the COP-2 material (i.e., polymer synthesis from the monomers tris(4-bromophenyl) amine) had an $H_2$ uptake of 1.74 wt% at 77 K and 1 bar. This level of uptake is one of the highest reported among microporous organic polymers under comparable conditions. Additionally, the material had $CO_2$ and methane ($CH_4$) adsorption capabilities of 594 and 78 mg/g, respectively, at 298 K and 18 bar [116]. This adsorption technique is suitable for $CO_2$ capture owing to its reversible nature, high adsorption capacity, low-cost materials, easy regeneration, and low production cost [121].

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**TABLE 2** | Absorption technologies reported in various studies for $CO_2$ capture.

| Absorption technology | Highlights | References |
|---|---|---|
| Amine based | | |
| Synthesis of amine hybrid silsesquioxane aerogel (AHSA) was achieved using a sol–gel technique followed by supercritical drying in a single step. | $CO_2$ adsorption capabilities of AHSA in a 1% $CO_2$ environment are significantly greater than those of other porous adsorbents based on amines, which have been generated utilizing a gas mixture with a 1% or greater level of $CO_2$ gas. | [87] |
| This process involves incorporation of commercially available hydrogels into organic amine solutions, resulting in formation of amine-infused hydrogels. | This novel material has a significantly enhanced capacity for $CO_2$ capture, surpassing that of conventional aqueous amine solutions when subjected to comparable experimental conditions. | [88] |
| Alkaline solutions | | |
| NaOH and KOH were used at 30 wt% in $H_2O$ to capture $CO_2$ in the presence of potassium ($K^+$), sodium ($Na^+$), and calcium ($Ca^{2+}$) ions. | A highly alkaline solution can decrease the concentration of $CO_2$ by facilitating the formation of carbonates, specifically sodium bicarbonate ($NaHCO_3$), sodium carbonate ($Na_2CO_3$), and potassium carbonate ($K_2CO_3$). | [89] |
| Use of NaOH water solutions for $CO_2$ capture. | Initially, $CO_2$ is collected using NaOH within an absorber, resulting in the production of $Na_2CO_3$. This mechanism occurs via an exothermic reaction under typical temperature and pressure conditions. In a second cycle, known as the regrowth cycle, the regeneration process for NaOH takes place in a causticizer/precipitator. This involves a reaction between $Na_2CO_3$ and $Ca(OH)_2$, resulting in the production of NaOH and $CaCO_3$. | [90] |
| KOH can be used to capture $CO_2$. | This results in formation of potassium carbonate ($K_2CO_3$) and/or bicarbonate ($KHCO_3$). These compounds are used extensively as cleaning agents and emulsifiers as well as in various other applications. | [91] |
| Ionic liquids | | |
| A study examined $CO_2$ absorption in various imidazolium-based ionic liquids (ILs), pyridinium-based ionic liquids, and a tetraalkylammonium-based poly(ionic liquid) (PIL), specifically poly[(p-vinylbenzyl) trimethylammonium hexafluorophosphate] P[VBTMA][$PF_6$]. | The poly(ionic liquid) P[[VBTMA][$PF_6$]] exhibited significant $CO_2$ absorption, surpassing other ionic liquids. Additionally, the monomer showed a greater $CO_2$ capacity compared to alternative ionic liquids. | [92] |
| Polyurethane-based poly(ionic liquid)s (PILs) are being investigated as promising materials for $CO_2$ collection. | Polyol (polycarbonate) with phosphonium (PILPC-TBP) showed a superior capacity for $CO_2$ sorption (21.4 mg $CO_2$/g at 303.15 K and 0.08 MPa) compared to PILs. | [93] |
| Ammonia | | |
| Examination and economic evaluation of a new carbon capture technology that uses ammonia to produce ammonium bicarbonate. | Modeling results suggest that the existing system has significant efficiency in capturing carbon, 95.5%. | [94] |
| Enhancement of $CO_2$ absorption can be improved through the combination of poly(ethylene glycol) dimethyl ether and ammonium-based ionic liquids. | The absorption rate of $CO_2$ is positively correlated with the mole fraction of the polymer in the liquid mixture. | [95] |
| Physical absorption | | |
| Examination and comparison of the solubility of $CO_2$ in 14 different physical solvents and two commonly utilized solvents in industrial applications, namely Selexol and sulfolane. | Polyethylene glycol dimethyl ethers, as well as mixtures containing these solvents, are highly effective solvents for $CO_2$ removal. | [96] |

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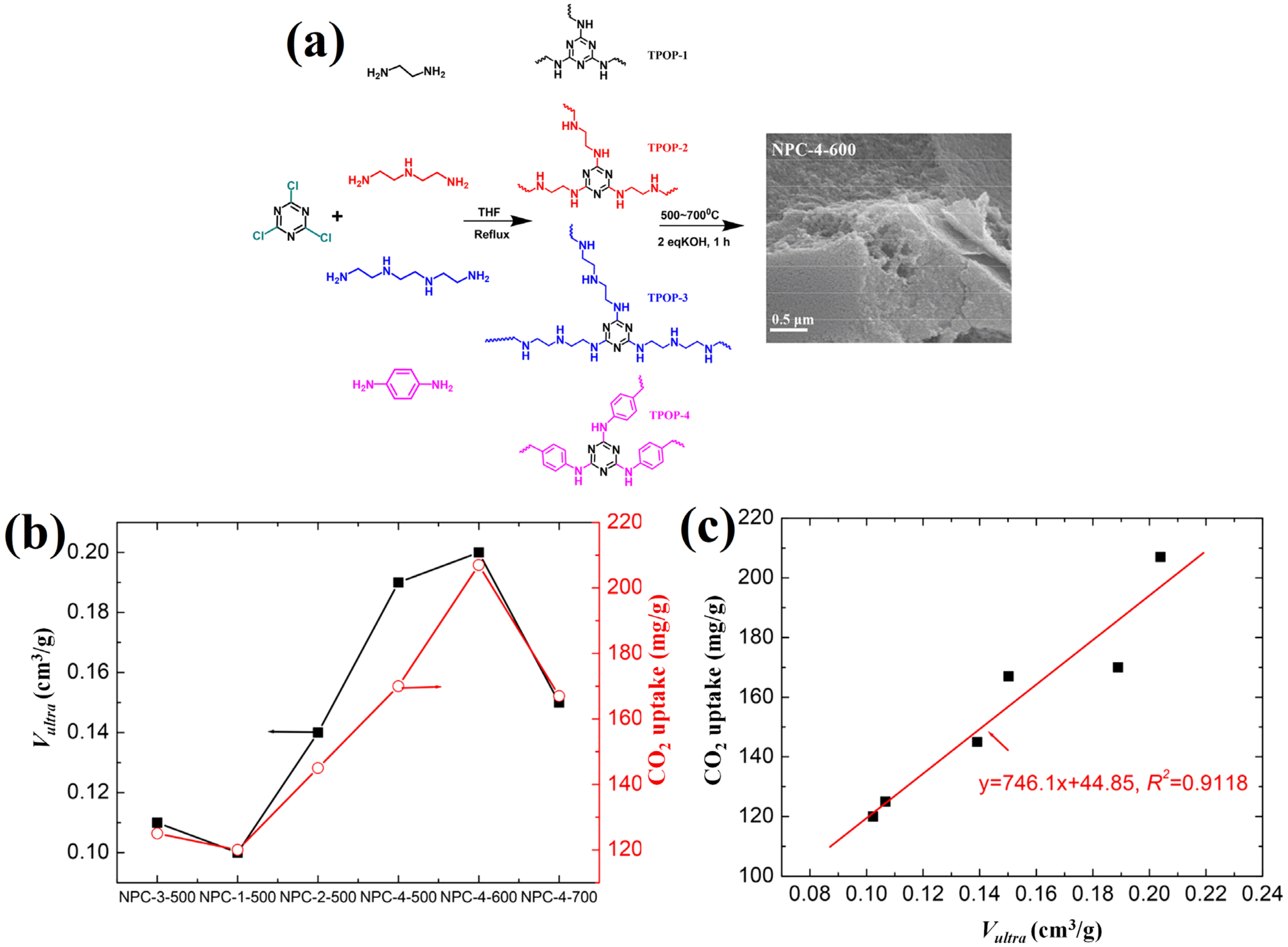

**FIGURE 9** | Method for producing triazine-based porous polymers and non-reacting species (a), a correlation between $CO_2$ uptake by non-reacting species at 273 K and 1.0 bar using $V_{\text{ultra}}$ (b), and $CO_2$ uptake on N-enriched porous carbons materials as a function of $V_{\text{ultra}}$ (c). Reproduced with permission [120]. Copyright 2018, ACS. [Color figure can be viewed at wileyonlinelibrary.com]

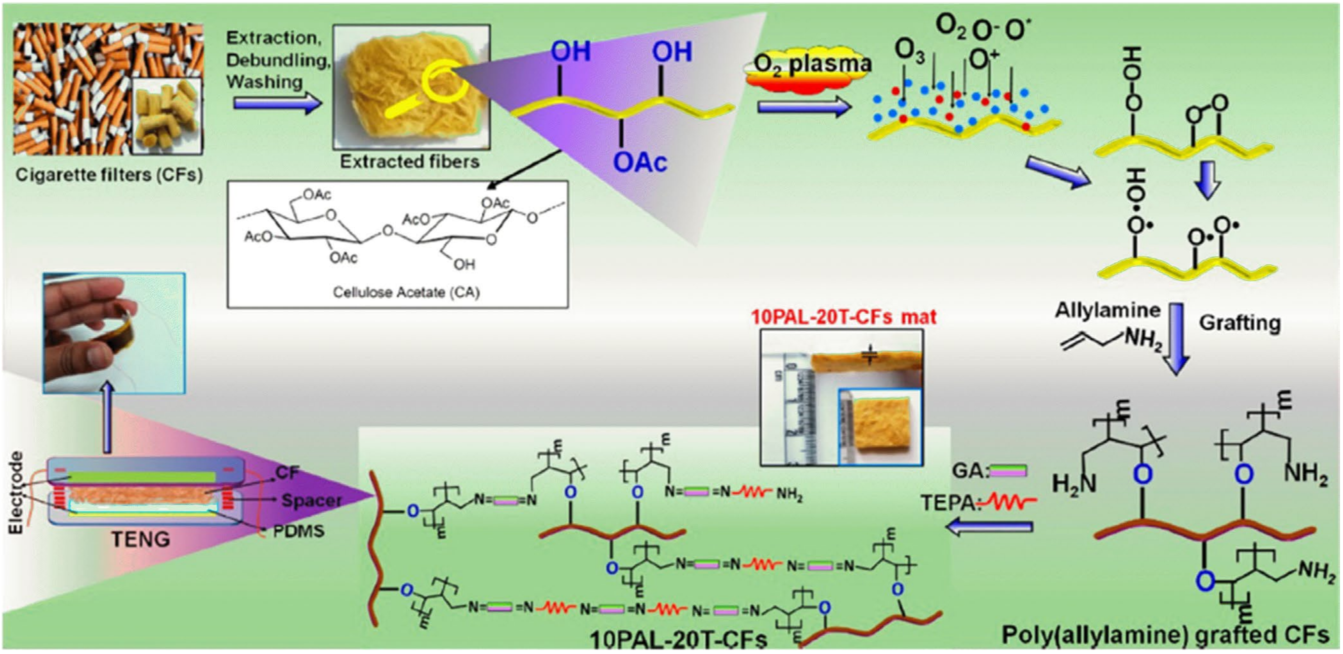

**FIGURE 10** | Synthesis of the modified fibers (10PAL-20T-CFs), potential chemical processes involved, and resulting 10PAL-20T-CFs/PDMS TENG. Reproduced with permission [64]. Copyright 2022, ACS. [Color figure can be viewed at wileyonlinelibrary.com]

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Waste has been utilized as a raw material for manufacturing carbon capture compounds [64, 122–125]. In a recent study, an innovative method was presented for conversion of waste CFs, one of the primary ocean pollutants. The objective of this technique was to transform CFs into high-efficiency triboelectric nanogenerators (TENGs) and effective $CO_2$ adsorbents. Targeted modification was applied to discarded CFs to create $CO_2$ adsorbents [64], as depicted in Figure 10. The empirical findings revealed that an adsorbent consisting of modified fibers exhibited a significantly enhanced $CO_2$ absorption, 1.93 mmol/g. This is approximately 9.2 times greater than the $CO_2$ uptake of the unmodified fibers (0.21 mmol/g) [64], as shown in Figure 11. The study demonstrated a methodology for achieving a sustainable ecosystem by implementing intelligent recycling techniques for the management of waste CFs. Study findings suggested that this approach holds promise for addressing challenges related to $CO_2$ mitigation and global warming, especially in geographical regions near the ocean [64]. Furthermore, utilization of waste eggshells has been explored as a primary resource for manufacturing calcium oxide-based sorbents [122]. This is an alternative to commercially available calcium carbonate. A calcined eggshell (CES) sorbent had a greater capacity for $CO_2$ capture than the commercially available $CaCO_3$ sorbents [122]. This discovery suggests that the CES had favorable qualities as a $CO_2$ sorbent, primarily due to its relatively low cost, environmentally friendly characteristics, and its capacity for $CO_2$ capture.

In absorption processes, a solvent can be presented in concentrations of up to 30% by weight, which constrains the extent of interactions with $CO_2$ [126]. Conversely, in adsorption, a base is introduced to the sorbent, which is a more restricted state. This allows for a higher weight percentage of the base to be loaded, thereby enhancing interaction with $CO_2$.

## 4.4 | Chemical Looping

Chemical-looping combustion and chemical-looping reforming are potentially cost-effective techniques for capturing $CO_2$ while minimizing energy losses. This is because these procedures intrinsically separate both $CO_2$ and $H_2O$ from flue gas [32, 33]. This obviates the necessity for energy-intensive separation procedures and supplementary apparatus. Such technology utilizes a metal oxide (Fe, Cu, Co, Mo, Mn, Cr, or Ce) as an oxygen carrier. It is used to move oxygen from the combustion air to the fuel, thereby avoiding direct contact with the ambient air and fuel [32]. Figure 12 displays a diagram illustrating the fundamental chemical looping reforming (CLR) process [127]. Introduction of compressed air into the oxidation reactor enables a reaction with a metallic oxygen carrier, resulting in the production of an oxidized metallic oxygen carrier and an air stream depleted of oxygen ($N_2$-rich stream). The oxidized metallic oxygen carrier reacts with natural gas in the fuel reactor, in the presence of steam, to produce syngas. The oxygen-depleted transporter gas is brought back to the oxidation reactor. A mixture of FeO and $Fe_3O_4$ was hypothesized as an oxygen transporter in the analysis. The excess oxygen carrier is circulated between two interconnected reactors to improve the heat transfer from the oxidation reactor to the fuel reactor for endothermic reactions. The entire process is self-sustaining and does not require heating. The CLR often operates at pressures higher than atmospheric levels. The understanding of high-pressure circulating reactor operation has been acquired by operating a power plant that employs a pressurized fluidized combustion bed at Värtan, Sweden [128].

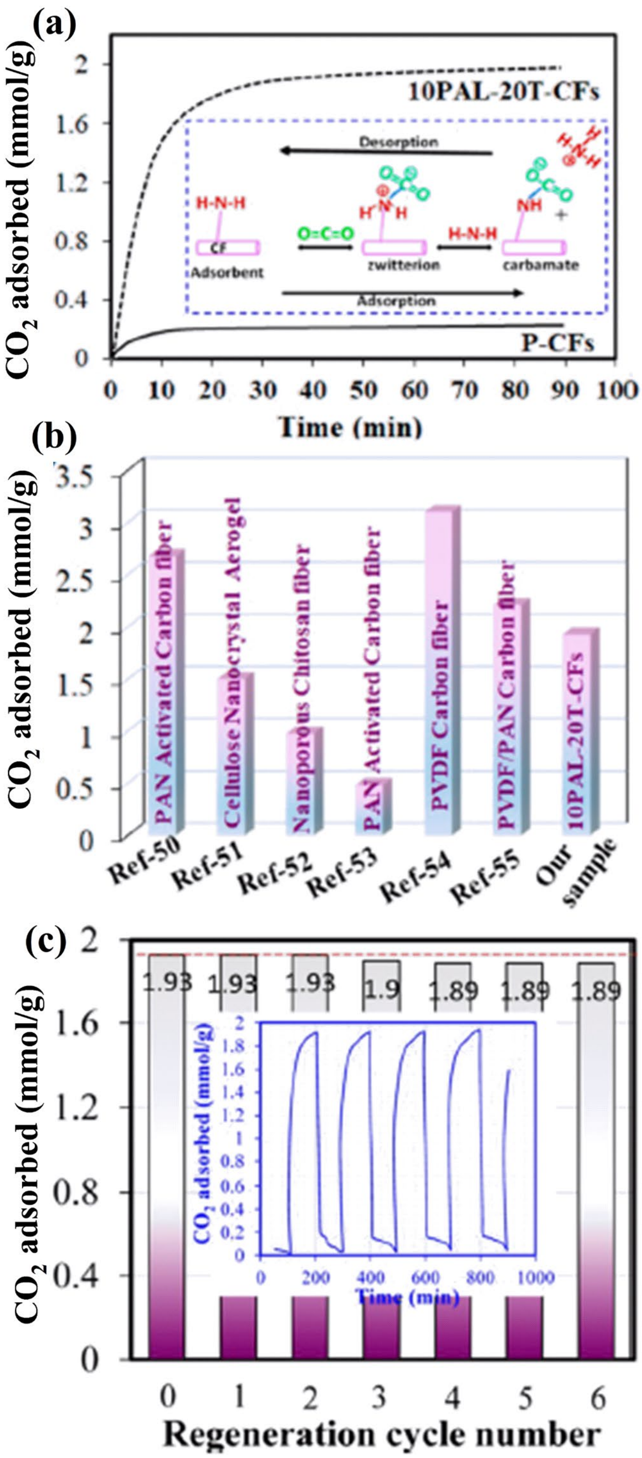

**FIGURE 11** | (a) Weight gain from $CO_2$ adsorption for pristine CFs and 10PAL-20T-CF adsorbents based on thermogravimetric analysis (TGA) results. This diagram depicts a chemisorption process involved in adsorption of $CO_2$, (b) comparison of $CO_2$ adsorption capacity of several adsorbents, (c) study on reusability and cyclic stability of 10PAL-20T-CF adsorbent. The inset displays adsorption–desorption cycles. Reproduced with permission [64]. Copyright 2022, ACS. [Color figure can be viewed at wileyonlinelibrary.com]

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### 4.5 | Direct Air Capture

Direct air capture captures $CO_2$ from air. This approach encompasses various technologies, including absorption, adsorption, ion transfer resins, substance carbonation, membranes, photosynthesis, frozen segregation, electronics, and electricity. Absorption, adsorption, and membrane processes are discussed above. DAC offers several additional benefits. Specifically, the location of the $CO_2$ source does not affect the DAC process as $CO_2$ is evenly distributed throughout the atmosphere. Consequently, if the capture plant is situated close to a consumption or storage site, the transportation costs for $CO_2$ are either negligible or non-existent [129]. Startups invest heavily in DAC due to its substantial cost reduction potential and superior overall efficiency in capturing $CO_2$ [35, 36].

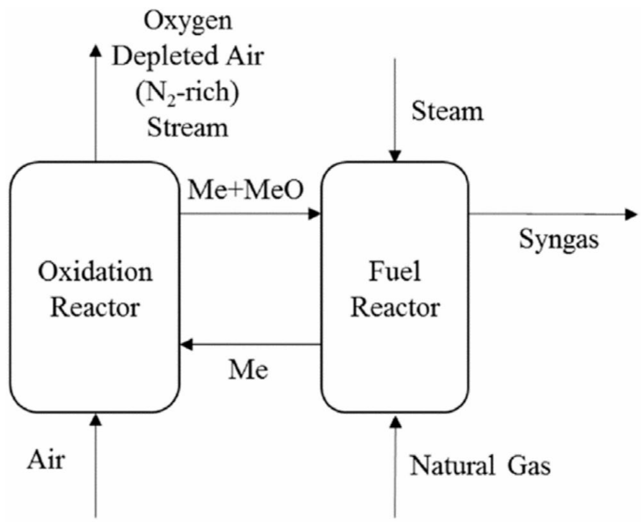

**FIGURE 12** | Diagram depicting a chemical looping reforming process. Reproduced with permission [127]. Copyright 2018, MDPI.

### 4.6 | Hybrid Processes

Hybrid separation processes are promising for capturing $CO_2$. They are cost-effective, energy-efficient, and scalable using hybrid separation consisting of multiple capture subsystems. A single process for $CO_2$ capture either uses excessive energy or is more expensive. Hybrid technology integrates diverse approaches to mitigate the specific drawbacks [130, 131]. Zeng et al. reported an enhanced efficiency of capturing and separating $CO_2$ when membranes were used in conjunction with ionic liquids. This improvement is due to the use of carbonate and bicarbonate, which can be easily regenerated [132]. In their study, Scholes et al. used hybrid hollow fiber membrane-MEA technology for post-combustion $CO_2$ capture [133]. This technique offered significant advantages in terms of $CO_2$ capture, energy consumption, and cost. A new hybrid system was developed by American Air Liquide. This system has the potential to save energy and involves capturing $CO_2$ at sub-ambient temperatures, between 20°C and 50°C, using a combination of a membrane and cryogenic distillation [37].

**TABLE 3** | Comparison of the advantages and disadvantages of various technologies.

| Polymer—Technology | Source of $CO_2$ | Advantages | Disadvantages |
|---|---|---|---|
| PILs—Absorption | Industrial processes, such as the production of natural gas, synthesis gas, and hydrogen | Very efficient separation method that is mature and well-established, with a high capture efficiency | A considerably elevated energy penalty is incurred, mostly due to the substantial energy demands associated with solvent regeneration |
| PP—Membrane | Flue gas, Power plants | Utilization of membranes in gas-separation applications is a potential avenue with enhanced energy efficiency and environmental sustainability compared to alternative separation methods | Increased costs due to challenges associated with the aging and plasticization of membrane materials |
| COPs—Adsorption | Gas streams in various industries | Ensuring stability against contaminants and moisture over an extended period,<br>Endures heat conditions | Corrosion of equipment<br>Environmental impact |
| Chemical looping | Flue gas | Highly effective and reliable oxygen-carrying substances | Complex reactor design |
| AHSA—Direct air capture | Flue gas, Power plants | Independent of $CO_2$ source location | Energy intensive |
| Hybrid | Flue gas, Power plants | Improved collaboration and streamlining of processes,<br>Energy and capital costs of the capture process decrease | Complicated process |

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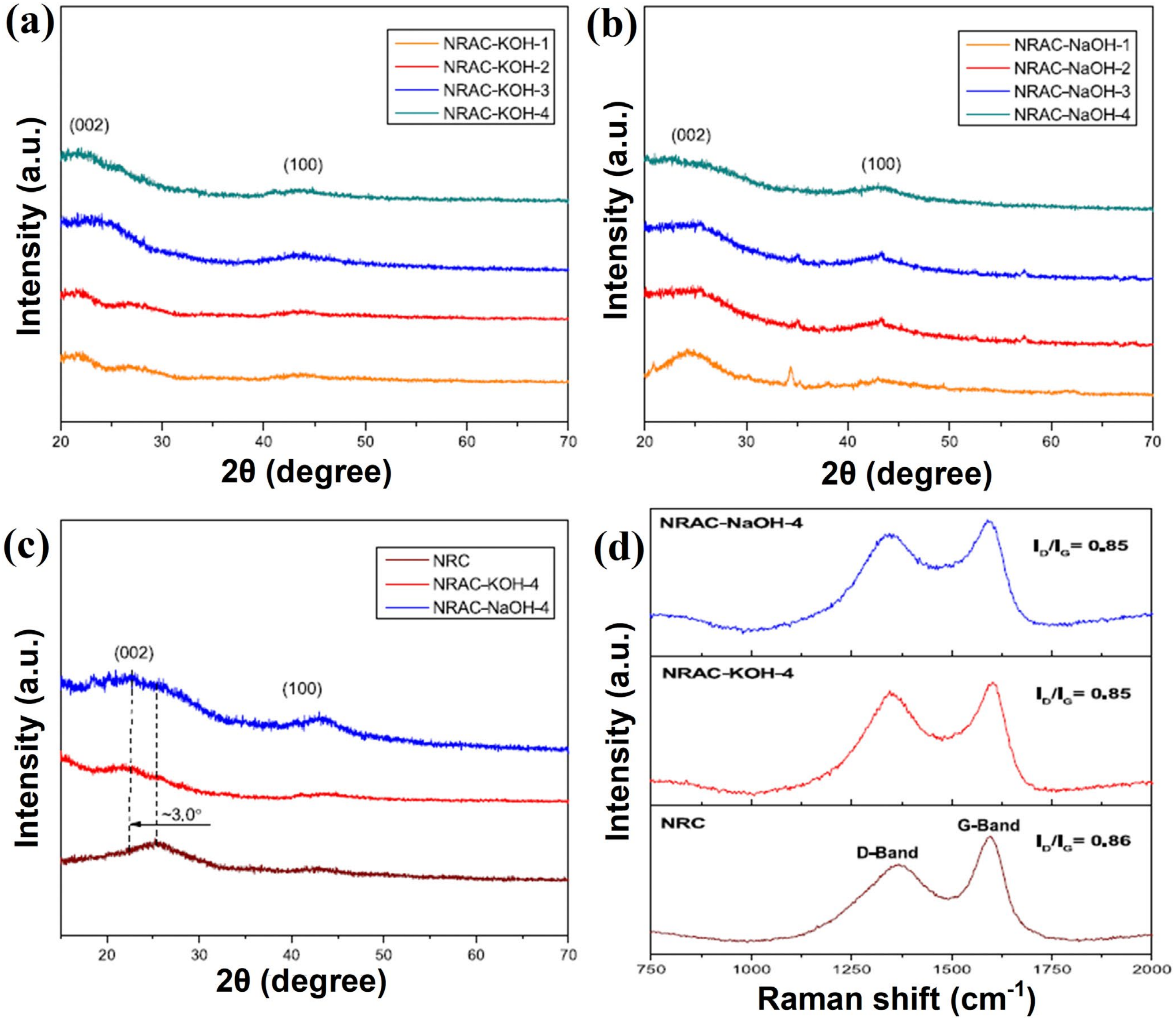

**FIGURE 13** | X-ray diffraction (XRD) patterns of (a) NRAC-KOH-*x*, (b) NRAC-NaOH-*x* (where $x = 1, 2, 3, 4$) are related to the relative mass ratio of activators, (c) correlation of XRD patterns between NRC, NRAC-KOH-4, and NRAC-NaOH-4, and (d) Raman spectra of NRC, NRAC-KOH-4, and NRAC-NaOH-4. Reproduced with permission [141]. Copyright 2023, Elsevier. [Color figure can be viewed at wileyonlinelibrary.com]

Additionally, Dai et al. created hybrid membranes by combining Nafion and PEG dimethyl ether (PEGDME) [38]. The membranes demonstrated a significant degree of permeability and the capability to dissolve $CO_2$ in PEGDME, resulting in enhanced $CO_2$ permeability compared to membranes employing a PEG supplement. The presence of water vapor in the gaseous streams further enhances the $CO_2$ permeability and $CO_2/N_2$ selectivity, reaching a value of 446 Barrer and 37, respectively [38]. Future research should prioritize hybrid methods that either incorporate $CO_2$-capture subsystems or apply simultaneous collection and utilization methodologies. Thermodynamic evaluations of these systems have proven their high energy performance and efficiency in terms of cost, suggesting decreased capital and operational expenses.

The advantages and disadvantages of all $CO_2$ capture techniques, including adsorption, membrane separation, absorption, DAC, chemical looping, and hybrid processes were summarized in Table 3.

## 5 | Utilization of Polymer-Based Adsorbents for $CO_2$ Capture

### 5.1 | Adsorption Technology Is an Intriguing Area of Study

This can be attributed to its capability to significantly decrease the overall rate of $CO_2$ emissions arising from its low energy demand, cost efficiency, substantial $CO_2$ adsorption capability, straightforward regeneration process, and adaptability to various temperature and pressure conditions [121, 134]. There has been extensive study of the adsorption efficiency of polymers, such as natural rubber (NR), polyurethane (PU), polyethylenimine

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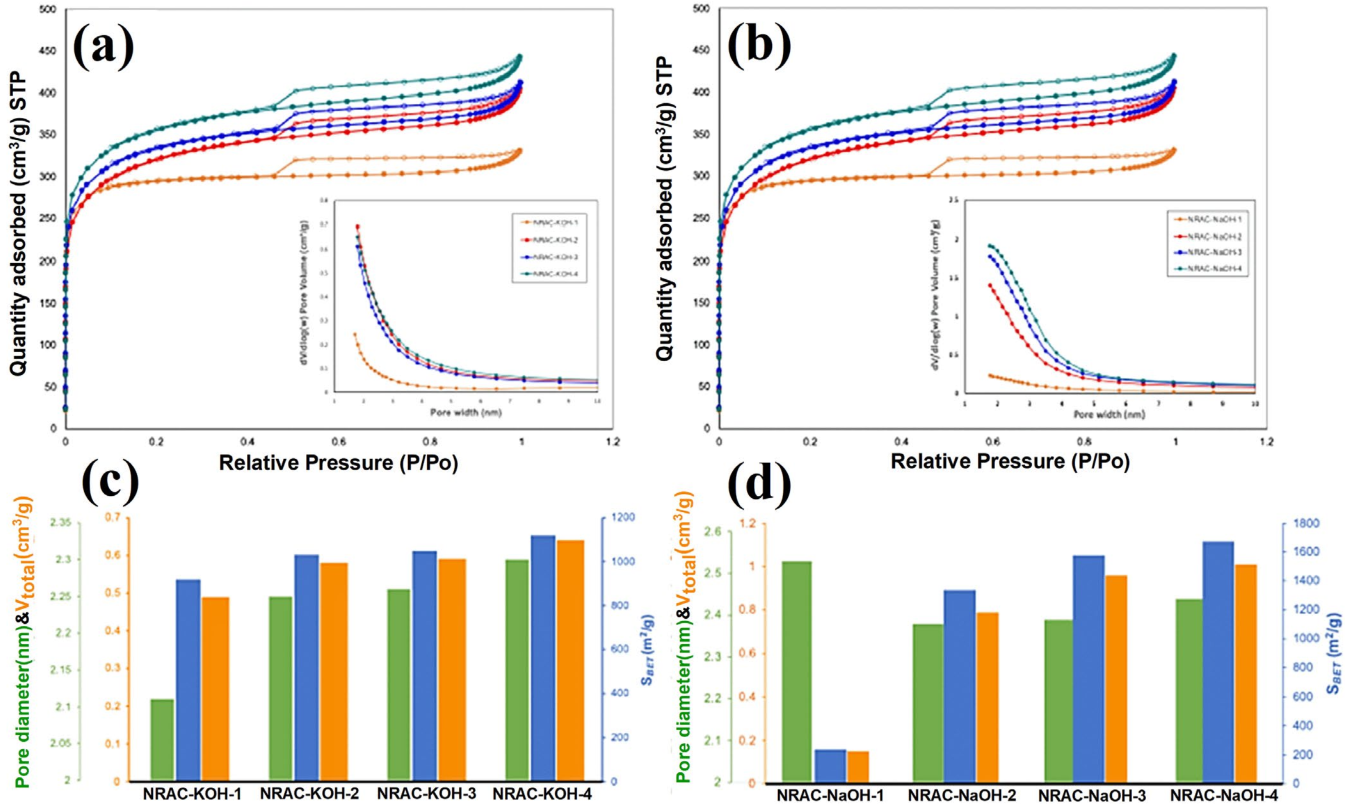

**FIGURE 14** | $N_2$ adsorption–desorption isotherms and PSD derived using a Barett-Joyner-Helenda method for (a) NRAC-KOH-*x* and (b) NRAC-NaOH-*x* ($x=1$, 2, 3, and 4, related to the mass ratio of activator) and pore characteristics of (c) NRAC-KOH-*x* and (d) NRAC-NaOH-*x*. Reproduced with permission [141]. Copyright 2023, Elsevier. [Color figure can be viewed at wileyonlinelibrary.com]

(PEI), polyamide (PA), polypropylene (PP), and poly-ethylene glycol (PEG) [50, 63, 84, 93, 121]. Polymers have been studied and applied in many different applications [135–140]. Utilization of polymer-based materials with diverse sizes, shapes, and morphologies has been done in several biological and industrial contexts. Recently, porous carbon was synthesized from NR. The resulting material, referred to as NR derived-activated carbon (NRAC), was produced through chemical stimulation involving potassium hydroxide (KOH) and sodium hydroxide (NaOH). The objective of this process was to enhance the efficacy of $CO_2$ capture. X-ray diffraction results for the crystalline phase of NRC, as well as all alkaline-treated NRACs (NRAC-KOH-1, NRAC-KOH-2, NRAC-KOH-3, NRAC-KOH-4, NRAC-NaOH-1, NRAC-NaOH-2, NRAC-NaOH-3, and NRAC-NaOH-4) are visually presented in Figure 13a–c. Experimental findings revealed the presence of two distinct diffraction peaks at 22° (002) and 43° (100), which can be attributed to the amorphous nature of the carbon materials [142]. There was no change in peaks as the concentration of KOH and NaOH increased. It is noteworthy to mention that alkaline treatment of NRACs resulted in the shift of the amorphous carbon peak from $2\theta$:22° to $2\theta$:25° (Figure 13c). The findings presented in this study were consistent with the outcomes reported [143], which investigated the production of activated carbon from camellia pollen grains. Raman spectral analysis was used to determine the graphitization degree of the carbon structure before activation (NRC) and following activation (NRAC-KOH-4 and NRAC-NaOH-4), as depicted in Figure 13d. The carbon samples displayed two identifiable peaks at 1348 and 1584 $\mathrm{cm}^{-1}$ related to the D- and G-bands, respectively. These findings indicated the presence of a characteristic amorphous carbon structure. The D-band is associated with carbon structures that lack order, whereas the G-band indicates the presence of $sp^2$ stretching vibrations in graphitic carbon layers [142].

The demand for porous materials as prospective adsorbents has greatly increased because of their substantial surface area, porosity, remarkable heat and chemical resistance, and cost-efficient manufacturing methods [144, 145]. Nurfarhana et al. [141] found that the precise measurement of the surface areas, total pore volume, and basicity linearly increased with the NRAC-to-activator mass ratio. $N_2$ adsorption–desorption isotherms were used to examine the surface area and pores of the carbons. The PSD of the NRACs was determined using a Barett-Joyner-Helenda (BJH) method. These results are given in Figure 14a,b. The adsorbed volume of $N_2$ (measured in $\mathrm{cm}^3/\mathrm{g}$) for all NRACs treated with alkali increased as the relative pressure ($P/P_0$) approached 0.1, suggesting the presence of microporosity. Figure 14c,d display specific surface areas ($S_{BET}$), total pore volume (VT), and average pore diameter (Da). The findings indicate a direct correlation between $S_{BET}$ and the concentration of KOH used in the experiment. The specific surface area increased when an excessive amount of activator was used. This is because the activation agent penetrated the NRC. Such penetration led to creation of pores and linked channels within the carbon matrix [146]. NRAC-NaOH-4 had the highest $CO_2$ adsorption capacity, up to 2.98 mmol/g under a pressure of less than 1 bar at 25°C.

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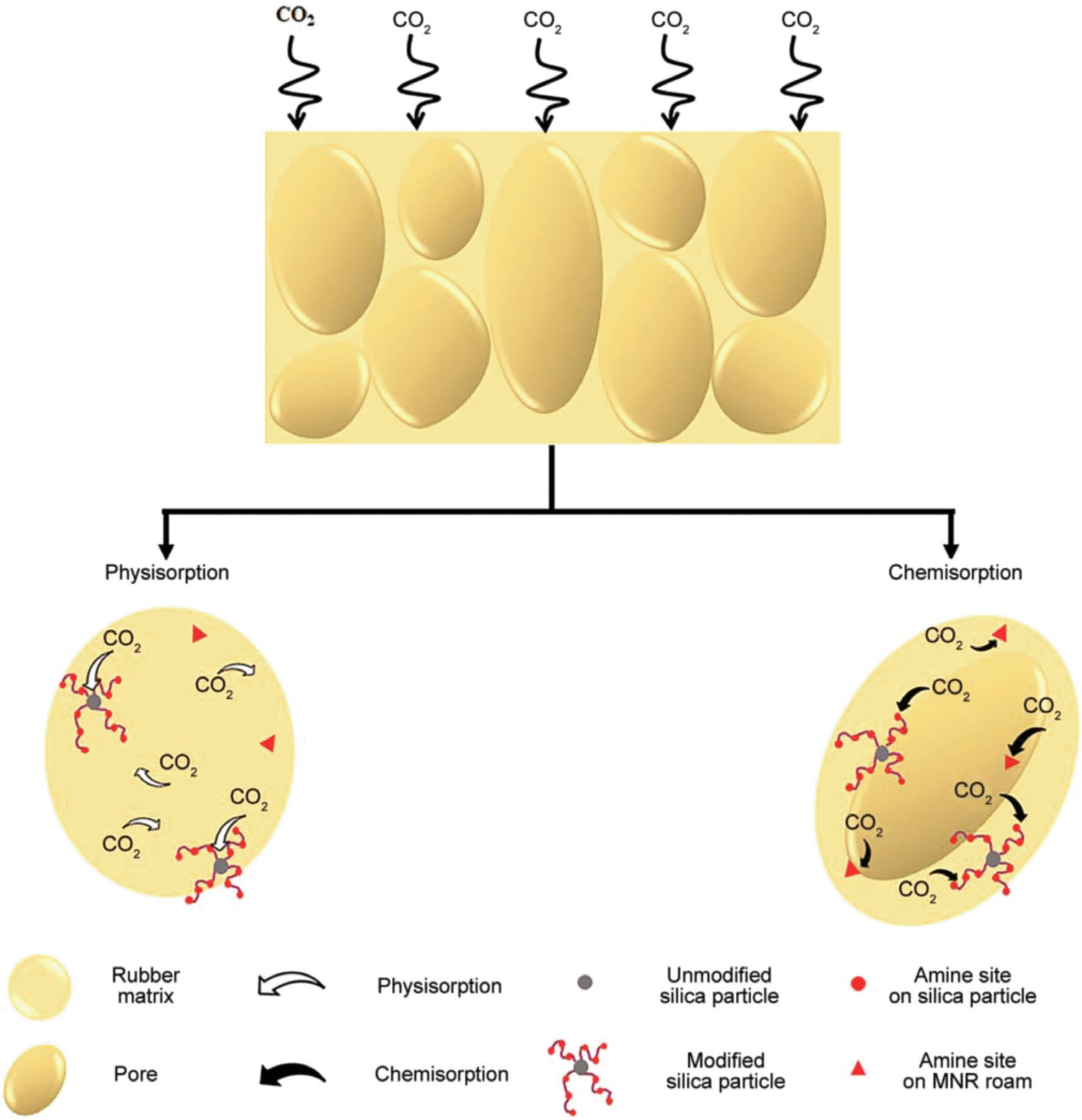

**FIGURE 15** | Schematic diagram showing $CO_2$ adsorption mechanism of MNR foam composites. Reproduced with permission [84]. Copyright 2021, BME-PT Hungary. [Color figure can be viewed at wileyonlinelibrary.com]

NR has been extensively studied [147–150]. NR foam and NR/silica foam composites have been used as adsorbents for $CO_2$ capture [84, 151]. The chemical makeup of NR latex was modified by adding diallylamine. Silica particles underwent modification using (3-aminopropyl)trimethoxysilane, N-[(3 trimethoxysilyl)propyl]ethylenediamine, or N-[(3-trimethoxysilyl)propyl]diethylenetriamine (mono-, di-, and tri-amines) to enhance the $CO_2$ capture capability of a modified natural rubber (MNR) material. NR foam had an adsorption capacity of 0.79 mg/g of adsorbent, while MNR foam exhibited a 1.6-fold higher value (1.26 mg/g of adsorbent) compared to other samples. This was attributed to more amine groups within the MNR structure that enhanced the selectivity for $CO_2$ [84]. The $CO_2$ adsorption mechanism reported in the MNR foam composite involved a synergistic combination of physisorption and chemisorption, as depicted in Figure 15. Physisorption occurs in the pores of the MNR foam or modified silica particles. Chemisorption resulted from reactions between $CO_2$ molecules and amine groups inside the MNR structure or on the surface of the modified silica particles. Inclusion of silica particles treated with 3-aminopropyltrimethoxysilane in the composite material, consisting of NR/silica foam, resulted in notably increased $CO_2$ adsorption capacity, from 1.81 to 6.71 mg/g [151].

It may be possible to reuse the NR/silica foam composite. For commercial applications, the importance of the adsorbent material lies in its high adsorption capacity and in its ability to be effectively reused in cyclical adsorption–desorption processes. Figure 16 illustrates the $CO_2$ adsorption capacity of the NR/silica foam composites over many adsorption–desorption cycles. The initial adsorption cycles have a substantial capacity for $CO_2$ adsorption due to the uniform distribution of solid sorbent loaded during its manufacture. Due to the notable decrease in $CO_2$ adsorption capacities, the NR foam could be reused for a maximum of seven cycles, whereas the NR/silica foam composite containing unaltered or altered silica particles could be

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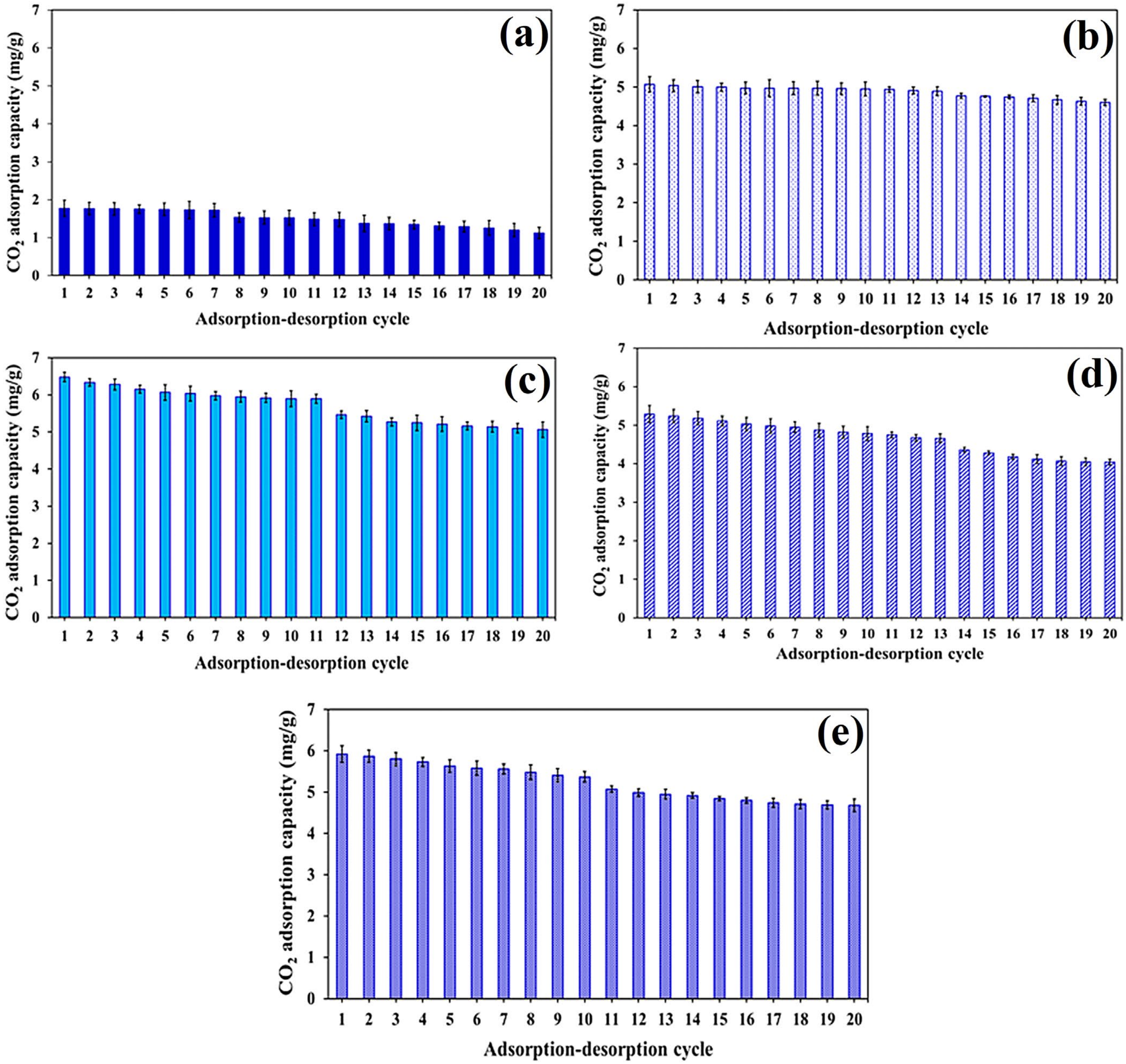

**FIGURE 16** | The capacity of NR and NR/silica foam composites to adsorb $CO_2$ on (a) NR, (b) NR-USi, (c) NR-NSi, (d) NR-2NSi, and (e) NR-3NSi, across 20 consecutive adsorption–desorption cycles. Reproduced with permission [151]. Copyright 2020, Elsevier. [Color figure can be viewed at wileyonlinelibrary.com]

reused for over 10 cycles. The increased reusability of the NR/silica foam composites can be attributed to inclusion of unmodified or modified silica particles. These particles enhance the thermal and mechanical properties of the NR foam composite, leading to increased stability [152, 153].

The adsorption experiments were conducted at moderate temperatures (approximately 25°C–50°C) at a 1 bar pressure. In terms of sorbent stability, the adsorption–desorption cycling results (Figure 16) indicate a gradual decrease in $CO_2$ adsorption capacity, which can be attributed to thermally induced structural changes in the NR-based composites. As $CO_2$ adsorption is an exothermic process, repeated heat generation and dissipation during cyclic operation may affect polymer chain mobility and filler–matrix interactions. Incorporation of silica fillers, particularly modified silica (NSi), enhances the thermal stability of the NR matrix, as reflected by the upward shift of the degradation temperature by approximately 15°C–20°C compared to neat NR [151]. This is due to the improved heat absorption and transfer capability of the silica phase [153]. At elevated temperatures, the organic modifier chains grafted onto the NSi surface become more flexible, leading to reduced chain entanglement and chain expansion, which increases the accessibility of active amine groups for $CO_2$ capture [154]. While this mechanism contributes to improved adsorption capacity at higher temperatures, repeated thermal cycling may progressively induce structural rearrangements and partial deactivation of active sites, resulting in the observed performance degradation. Although the present study provides

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**TABLE 4** | Summary of highlights, applications, and their performance for $CO_2$ capture.

| Polymer | Highlights | Applications | Performance | References |
|---|---|---|---|---|
| Natural rubber (NR) | NR/silica foam composite material, containing silica particles that have been altered to have a short chain structure, exhibited a greater capacity for adsorbing $CO_2$ compared to those modified with longer chain structures. | Air purification filter designed to reduce the concentration of $CO_2$ in a building or room that experiences periodic occupancy | $CO_2$ adsorption capacity of the NR/silica foam experienced a significant boost, rising from 1.81 to 6.71 mg/g following the introduction of modified silica. | [151] |
| | Modified NR foam composites demonstrated a 3 to 5 times increased $CO_2$ adsorption capacity upon being filled with either unmodified or tri-amine-modified silica particles. | Sorbent material to reduce $CO_2$ greenhouse gas emissions into the atmosphere | Addition of tri-amine-modified silica particles resulted in a maximum $CO_2$ adsorption capacity for an MNR foam composite (10.35 mg/g of adsorbent) at 100°C. | [84] |
| Polyurethane (PU) | PUF-based carbon demonstrated good selectivity for $CO_2$ capture from $CO_2$ and $N_2$ mixtures, high recyclability, and low preparation costs. | $CO_2$ capture from flue gases | Samples generated under optimal conditions had $CO_2$ adsorption capabilities of 6.67 and 4.33 mmol/g at 0°C and 25°C, respectively, at 1 bar. | [155] |
| Polyethylenimine (PEI) | Meso-13X-PEI exhibited much greater selectivity for capturing $CO_2$ compared to $N_2$, along with a higher capacity for capturing $CO_2$ at elevated temperatures (100°C) and low $CO_2$ concentrations, which are relevant to post-combustion settings. | Post-combustion $CO_2$ capture | Meso-13X-PEI exhibited a range of 11–58 $mg/g_{adsorbent}$ with temperature from 25°C to 125°C, reaching a maximum value of 80 $mg/g_{adsorbent}$ at 100°C. | [156] |
| | PCN-777s loaded with PEI and PS were excellent in adsorbing $CO_2$, and PEI@PCN-777s were very good at capturing $CO_2$ due to the basic sites on PEI (smaller pores). | Selective capture of $CO_2$ from gas in industrial plants | PEI (20%)@P777 exhibited approximately 2.3-times and 5.7-times higher adsorption capacity (at 0.15 atm) and selectivity ($CO_2/N_2$). | [157] |
| | PEI supported on pore-expanded MCM-41 was a more efficient $CO_2$ adsorbent than PEI supported on calcined silica. | Efficient extraction of carbon dioxide from the exhaust emissions of industrial facilities | The presence of pure $CO_2$ at 25°C the uptake for PMEPEI (50) after 180 min of exposure did not exceed 6.5% versus 18% under the same conditions at 75°C. | [158] |
| Poly(methyl methacrylate)-graft-Polyoxyethylene(methacrylate) (PMMA-g-PPOEM) | PMMA-g-PPOEM hyperbranched polymers showed preferential $CO_2$ selectivity that was increased by elevating the POE fraction. | $CO_2$ capture from power plants | Selectivity of $CO_2$ was significantly boosted to 350 barrer when the PAMAM level reached 50 wt%. | [159] |

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temperature-dependent adsorption behavior that offers mechanistic insight into sorbent stability, extended long-term cycling tests and post-cycling physicochemical characterization are required to fully elucidate the long-term durability of the modified NR sorbents under industrially relevant operating conditions.

All the results reviewed herein indicate that NR has the potential as an effective adsorbent for $CO_2$ in porous materials. An overview of polymer-based adsorbents that have been investigated is provided in Table 4.

## 6 | Conclusions and Outlook

This brief overview presents an analysis and discussion of $CO_2$ capture, which is essential due to increased pollution. The initial section of this review provided a concise summary of the genesis of carbon capture, specifically addressing the issues and consequences of climate change, SDGs, and current advancements in $CO_2$ management, utilizing carbon capture products available in the market. The 2022 export data for carbon-absorbent materials revealed the importance of polyamines in $CO_2$ adsorption. The mechanisms and thermodynamics of $CO_2$ capture were reviewed to show that the effectiveness of $CO_2$ capture is impacted by microporosity, surface area, and the chemical composition of an aerogel. Adding specific functional groups, such as amino, sulfonate, and hydroxyl groups, increases $CO_2$ adsorption capability. The reviewed data demonstrated that the minimal thermodynamic work necessary for $CO_2$ extraction from the atmosphere was greater compared to exhaust gas. Furthermore, the adsorption isotherm of $CO_2$ in the polyimide polymer, which considers the cause of polymer swelling, was determined using isothermal isobaric molecular dynamics modeling. That study showed that the solvent-accessible surface area of various atom types inside the pores, indicating that methyl carbon atoms and exposed oxygen had a higher affinity for binding $CO_2$. Additionally, $CO_2$ capture techniques have been developed that involve adsorption, membrane separation, absorption, DAC, chemical looping, and hybrid processes. This paper outlines the benefits and drawbacks of different carbon capture systems. The review highlighted that adsorption technology shows promise for providing prolonged defense against contaminants and moisture. This method effectively and reliably regulates thermal conditions by utilizing oxygen-carrying substances.

An assessment was conducted on the application of adsorption technology for $CO_2$ capture using polymer-based adsorbents. The use and carbon capture effectiveness of natural rubber were specifically examined, given its remarkable properties as a biologically generated product. NR can function as a reliable adsorbent for $CO_2$. The chemical makeup of NR latex was modified by introducing diallylamine. Additionally, the silica particles underwent modification using (3-aminopropyl)trimethoxysilane, N-[(3-trimethoxysilyl)propyl]ethylenediamine, or N-[(3-trimethoxysilyl)propyl]diethylenetriamine (mono-, di-, and tri-amines) to enhance the $CO_2$ adsorption capability of the MNR material. The natural rubber foam's adsorption capacity was 0.79 mg/g of adsorbent. Concurrently, MNR foam demonstrated a 1.6-fold adsorption increase (1.26 mg/g) compared to other samples. The increased abundance of amine groups in the MNR structure was responsible for enhancing its selectivity for $CO_2$. Polymer-based adsorption is a very effective technique that is well-suited for advancing carbon capture technology.

Future research on $CO_2$ capture should focus on developing advanced adsorbent materials. These materials should have higher efficiency, stability, and regeneration capacity. Researchers should also explore hybrid technologies that combine adsorption with other methods. Such methods include membrane separation or chemical looping. The goal is to reduce overall energy demands.

### Author Contributions

**Hassarutai Yangthong:** data curation (lead), investigation (lead), visualization (lead), writing – original draft (lead). **Phakamat Lim-arun:** data curation (supporting), investigation (supporting). **Siriwan Jansinak:** data curation (supporting). **Supitta Suethao:** investigation (supporting), visualization (supporting). **Jirasak Wong-ekkabut:** writing – original draft (supporting). **Sutee Boonchui:** writing – original draft (supporting). **Pornsiri Kaewpradit:** writing – review and editing (equal). **Pairote Jittham:** writing – review and editing (equal). **Sedthawatt Sucharitpwatskul:** writing – review and editing (equal). **Karine Mougin:** supervision (equal), writing – review and editing (equal). **Arnaud Spangenberg:** supervision (equal), writing – review and editing (equal). **Antoine Le Duigou:** supervision (equal), writing – review and editing (equal). **Wirasak Smitthipong:** conceptualization (lead), supervision (lead), writing – review and editing (lead).

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### Conflicts of Interest

The authors declare no conflicts of interest.

### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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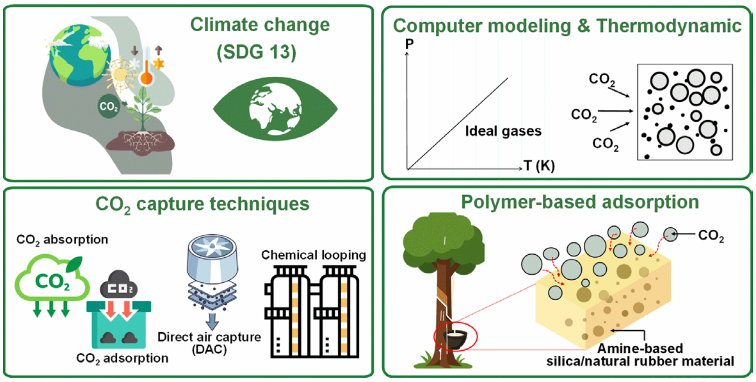

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