Malaysian Journal of Analytical Sciences (MJAS)
Published by Malaysian Analytical Sciences Society

A REVIEW OF THE CURRENT TREND IN THE SYNTHESIS OF NITROGEN-RICH FUNCTIONAL POLYMERS FOR CARBON DIOXIDE ADSORPTION

(Sorotan Terhadap Trend Semasa Dalam Sintesis Polimer Fungsional Kaya Nitrogen Untuk Penjerapan Karbon Dioksida)

Noorhidayah Ishak[1], Azalina Mohamed Nasir[2], Chow Wen Shyang[3], Dai Viet N. Vo[4], Bassim H. Hameed[5], Mohd Azmier Ahmad[1], and Azam Taufik Mohd Din[1*]

[1] *School of Chemical Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia*
[2] *Faculty of Chemical Engineering and Technology, Kompleks Pusat Pengajian Jejawi 3, Kawasan Perindustrian Jejawi, Universiti Malaysia Perlis (UniMAP) 02600 Arau, Perlis, Malaysia*
[3] *School of Materials and Mining Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia*
[4] *Institute of Environmental Technology and Sustainable Development, Nguyen Tat Thanh University, 298-300A Nguyen Tat Thanh, District 4, Ho Chi Minh City, 755414, Viet Nam.*
[5] *Department of Chemical Engineering, College of Engineering, Qatar University, P.O. Box: 2713, Doha, Qatar*

[*] *Corresponding author chazam@usm.my*

Received: 1January 2024; Accepted: 19 March 2024; Published: 29 April 2024

Abstract

The consumption of fossil fuels (oil, coal, and natural gas) has increased due to the increasing demand for energy from various industries. The International Energy Agency, in its World Energy Outlook 2022, has noted a steady increase in global energy demand from fossil fuels from 350 EJ in 2000 to over 500 EJ in 2030. This increase has contributed significantly to the emission of greenhouse gases, mainly carbon dioxide (CO_2), leading to global warming and climate change. Carbon capture by adsorption on polymeric adsorbents is a strategic approach to mitigate climate change by reducing CO_2 concentration in the atmosphere. This review focuses on the preparation of various nitrogen-rich functional polymers, mainly polyamine, polyamide/polyimide, and covalent triazine framework. This article provides important information on improving the functionality of nitrogen-rich functional polymers for CO_2 adsorption. Brief insights into the CO_2 adsorption mechanism and molecular modeling using density functional theory are also included. The challenges and future recommendations are also addressed in this review.

Keywords: carbon capture, adsorbent, climate change, density functional theory

Abstrak

Penggunaan bahan api (minyak, arang, dan gas asli) telah meningkat kerana pertambahan permintaan untuk tenaga dalam pelbagai sektor industri. Agensi Tenaga Antarabangsa (IEA) dalam Tinjauan Tenaga Dunia 2022 telah mencatatkan pertambahan yang mantap dalam permintaan global tenaga daripada bahan api fosil dari 350 EJ pada tahun 2000 hingga melebihi 500 EJ pada tahun 2030. Peningkatan ini telah menyumbang kesan yang ketara pada pembebasan gas hijau terutamanya karbon dioksida (CO_2) yang

membawa kepada pemanasan global dan perubahan iklim. Penangkapan karbon menggunakan kaedah penjerapan ke atas bahan penjerap daripada polimer ialah satu strategi bagi mengatasi perubahan iklim dengan cara mengurangkan kepekatan CO_2 dalam atmosfera. Sorotan ini memfokuskan kepada penyediaan beberapa jenis polimer fungsional kaya nitrogen, antaranya poliamina, poliamida/poliimida, dan kerangka kovalen triazina. Artikel ini menyediakan maklumat penting bagi menambah baik kefungsian polimer kaya nitrogen bagi tujuan penjerapan CO_2. Pemahaman ringkas mengenai mekanisma penjerapan CO_2 serta pemodelan molekul menggunakan teori ketumpatan berfungsi turut disertakan. Cabaran dan cadangan masa hadapan turut disampaikan dalam sorotan ini.

Kata kunci: penangkapan karbon, bahan penjerap, perubahan iklim, teori ketumpatan berfungsi

Introduction

The increasing demand for energy due to population growth has led many countries to explore their natural resources to strengthen their economy. The increase in greenhouse gas emissions is mainly contributed by carbon dioxide (CO_2) generated from the combustion of fossil fuels and natural resources, impacting the environment, and causing global warming and climate change [1]. To address this issue, the Paris Agreement was adopted on 12th December 2015 by 196 parties at the United Nations Climate Change Conference 21 in Paris. It aims to reduce global warming to below 2 °C, if possible, to 1.5 °C compared to the pre-industrial level [2]. Carbon capture, utilization, and storage is considered one of the strategic climate mitigation options to meet this international goal. It refers to technologies that capture CO_2 emissions from main contributors, such as energy production and manufacturing facilities that utilize either non-renewable or renewable energy sources (e.g., biomass) [3]. If the captured CO_2 is not consumed, it is compressed and transported through pipelines, ships, rails, or trucks for use in various applications, or injected into deep geological formations, such as a gas reservoir or saline formation that traps CO_2 for permanent storage [4].

An increasing number of publications have reported on carbon capture using various methods, including absorption, adsorption, membrane separation, and cryogenic distillation [5]. However, the conventional CO_2 capture technology using liquid amine systems has some drawbacks. For instance, the regeneration and desorption of captured CO_2 from aqueous amine scrubbing systems can be energy-inefficient due to the high regeneration temperature. The significantly inefficient energy consumption requirements can lead to economic inefficiency. Other shortcomings, such as equipment corrosion and concerns about amine leakage into the environment, are frequently encountered in these conventional aqueous amine schemes [6]. If a system experiences amine leakage and is exposed to atmospheric oxidants, it can lead to a degradation reaction, producing toxic compounds (e.g., nitrosamines, nitramines, and amides) that pose a threat to human health and environmental safety [7]. Adsorption using solid materials is a practical technology that can be applied for CO_2 capture. Adsorption offers low energy requirements and low operating costs, including controlled waste generation, high CO_2 adsorption uptake in ambient conditions, high specific surface area, high mechanical durability, adequate pore size distribution, and accessibility for regeneration [8].

Adsorption is a sorption process of CO_2 molecules onto the surface of a solid adsorbent that has residual surface energy due to unbalanced forces. These unbalanced forces will attract CO_2 molecules colliding with the solid surface, causing them to remain on the solid surface. The attraction that forms between gaseous CO_2 and the adsorbent can be classified as a weak physical interaction (i.e., physical adsorption) and a stronger chemical bond (i.e., chemical adsorption) [9]. Several solid materials, such as zeolites and silica, have been reported for CO_2 capture. These materials possess high CO_2 capture capacity and high selectivity of CO_2 over nitrogen (N_2) under atmospheric conditions. Nevertheless, the adsorption capacity of zeolites can be affected by the presence of water. Hence, dehumidification would be necessary in such conditions prior to CO_2 capture. This additional step would significantly increase the investment cost, total energy consumption, and the difficulty of the operation [10].

Mesoporous carbon-based materials offer promising potential for CO_2 capture due to their widely available resources, high chemical and thermal stability, and inexpensive and tunable porous structure [11].

On the other hand, polymeric materials are great adsorbents for CO_2 adsorption due to the presence of different functional groups on their backbone. The adsorption capacity and selectivity of a polymeric adsorbent can be improved when these functional groups form specific interactions with CO_2. Surface morphology and tunable porosity can enhance the intraparticle transport of CO_2 toward the active sites of the adsorbent, thereby increasing its performance [12]. Recently, porous polymeric adsorbents have been receiving attention due to the increasing number of publications on the functionalization of polymers with various functional groups to improve the performance of adsorbents. A previous study reported the introduction of nitrogen- and oxygen-based functional groups that could enhance the CO_2 adsorption capacity of the adsorbent [13]. The functionalization of polymers has also led to the development of various combinations of porous support materials, such as zeolite and mesoporous silica, with functional polymeric materials. The functionalized polymeric solid sorbent can overcome the issue of low stability caused by the leaching of amines over repeated capture/regeneration cycles and the limited transportation of CO_2 to the active sites in an amine-impregnated CO_2 sorbent system [13]. Hassan et al. [14] also synthesized triptycene-based nitrogen-rich hyper-cross-linked polymer (HCP). Their results indicated a higher adsorption capacity of 160 mg/g at 273 K and 1 bar, and a lower specific surface area of 848 m^2/g. The specific surface area decreased as a result of the functionalization with the nitrogen functional group; however, this modification did not affect the performance of CO_2 adsorption. The inclusion of a nitrogen heteroatom in HCP has increased the affinity of the material toward CO_2 due to their dipole-quadrupole interaction [14].

Tremendous efforts have been dedicated to designing porous materials with different channel geometries, pore sizes, and chemical compositions to improve the effectiveness of sorbents. These design variations have considered several criteria, such as high adsorption capacity, cost-effectiveness, fast kinetics, energy efficiency, and long-term stability [15,16]. This review presents a comprehensive discussion of the current trends in the development of polymeric adsorbents for CO_2 adsorption. The introduction is presented in the first section, elaborating on the background study on CO_2 adsorption. This includes the main sources of CO_2 production, the current policies being applied, and carbon capture methods. In the second section, the preparation of nitrogen-functional polymers for CO_2 adsorption is discussed. The structure of CO_2 and the mechanisms of interaction with CO_2 are elaborated in the subsequent section. This review ends with conclusions and recommendations for future studies.

Preparation of nitrogen-rich functional polymer

Nitrogen-rich porous solid adsorbents have been widely explored for their CO_2 chemisorption ability under low CO_2 concentrations. Figure 1 shows nitrogen moieties like amine, amide, imide, triazine, melamine, imidazole, and hydrazine, which are often used to produce nitrogen-rich functional polymers in CO_2 capture applications [17–20]. This section presents a brief discussion on the preparation of nitrogen-rich polymers, mainly focusing on polyamine, polyamide/polyimide, and covalent triazine frameworks.

Preparation of amine-functionalized polymer

Polyethyleneimine (PEI) or polyaziridine is a polymer composed of an amino group and two carbon aliphatic CH_2CH_2 spacers, and it is widely applied as an adsorbent in CO_2 adsorption [21, 22]. This amine-bearing polymer is well known for its highly positive charge, and it can exist in a linear and branched chain with different properties. Linear PEIs are composed of secondary amines, whereas branched PEIs are composed of primary, secondary, and tertiary amino groups that can be found on the polymeric backbone [23]. For CO_2 adsorbent application, PEIs are commonly combined with different porous inorganic supports to achieve cost-effectiveness and high amine content through chemical grafting of amine reagent, physical impregnation, and impregnation-cross-linked method [24–26].

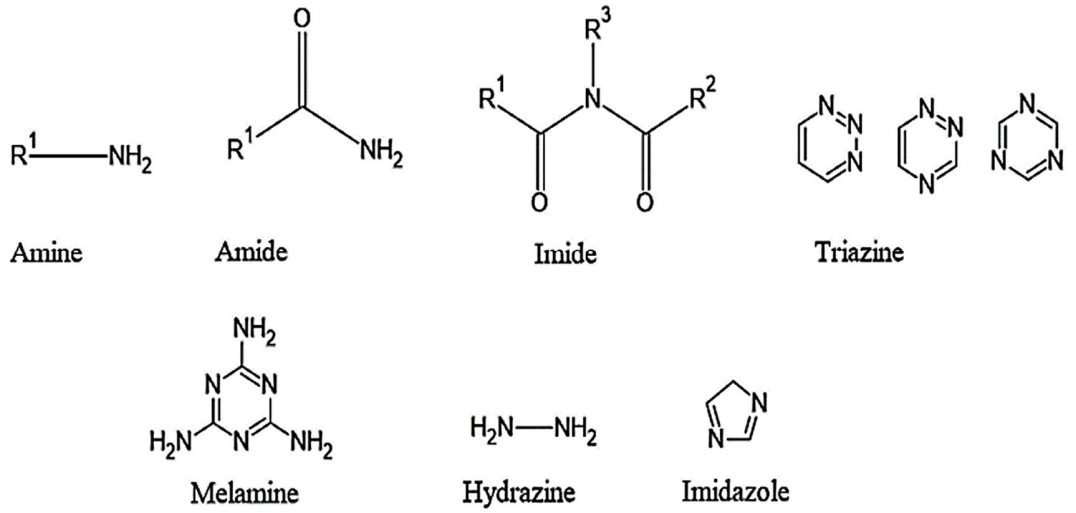

Figure 1. Nitrogen functional groups are commonly used in nitrogen-rich functional polymers

Physical impregnation onto porous materials

Physical impregnation of low vapor pressure amine polymers onto porous support materials is an easy and more scalable method [54, 60]. Li et al. [30] used the wet impregnation method by dissolving PEI in the solvent to obtain a homogeneous solution. Then, the porous material (Al_2O_3) was added to the solution, and the mixture was stirred until the solvent evaporated. The obtained material was dried in a vacuum oven overnight. The synthesized 50%PEI@Al_2O_3 adsorbent exhibited high adsorption stability for up to ten cycles with an adsorption capacity of 136 mg/g. The high operating temperature increased the kinetic effect, reduced the viscosity of PEI molecules, and increased the diffusion of CO_2 molecules, thereby increasing the likelihood of molecular collisions between CO_2 and PEI molecules. Nonetheless, this method also suffered from several drawbacks, such as amine leaching during the capture and regeneration cycles, and low active site accessibility after impregnation, which reduced the performance of the adsorbent [31]. Li et al. [32] reported a simplified and environmentally friendly method to prepare amine-modified amorphous silica to overcome the issue of particle agglomeration between PEI and silica by introducing a solventless mechanical grinding method. The CO_2 adsorption capacity of 70% PEI/SiO_2 was approximately 2.47 mmol/g at 70 °C and 1.5 bar. These results show that the absorbents have a remarkable CO_2 adsorption capacity at high temperatures.

In addition to infusion into porous solid supports, porous polymer supports are also used to enhance CO_2 performance. This approach will increase CO_2 adsorption performance with low mass transfer limitation caused by clogged pores by maximizing amine loading and improving the accessibility of gas through the sorbent [24]. Choi et al. [33] prepared metal-organic frameworks (MOFs) and immobilized polyacrylonitrile (PAN) fiber mats with PEI impregnation for CO_2 capture. The PEI was impregnated into the PAN-MOF electrospun mats using the wet impregnation method. They selected two types of MOFs, namely ZIF-8 and HKSUT-1, to prepare the PAN/MOF electrospun mats. The impregnation of PEI into the PAN/ZIF-8 electrospun mats enhanced their adsorption capacity by 45% and improved the CO_2/N_2 sorption selectivity due to the strong intermolecular interactions between the amine group in PEI and CO_2 molecules. However, a further increase in PEI loading reduced the adsorption capacity due to the reduction of surface area and pore volume.

Chemical grafting

A functional adsorbent with specific amine group and functional group densities suitable for investigating the

CO_2 adsorption mechanism can be obtained using the surface grafting method. However, this method is expensive and involves a complex procedure. Yin et al. [34] successfully synthesized PEI-modified poly(melamine)-polyacrylamide (MF/PAM-g-PEI), which demonstrated higher CO_2 adsorption of 2.8 mmol/g (10% CO_2 and 90% N_2; 30 mL/min) at 273 K compared to non-modified MF and PAM polymer networks. The polymer network was synthesized by interpenetrating PAM between the molecular chains of MF and functionalizing it with PEI to attain a solid amine adsorbent, as shown in Figure 2. The interpenetration of PAM into the porous amino resin improved its swelling capacity and provided amine grafting sites for the amine agents. Consequently, the adsorption capacity and the regeneration performance of the adsorbents increased.

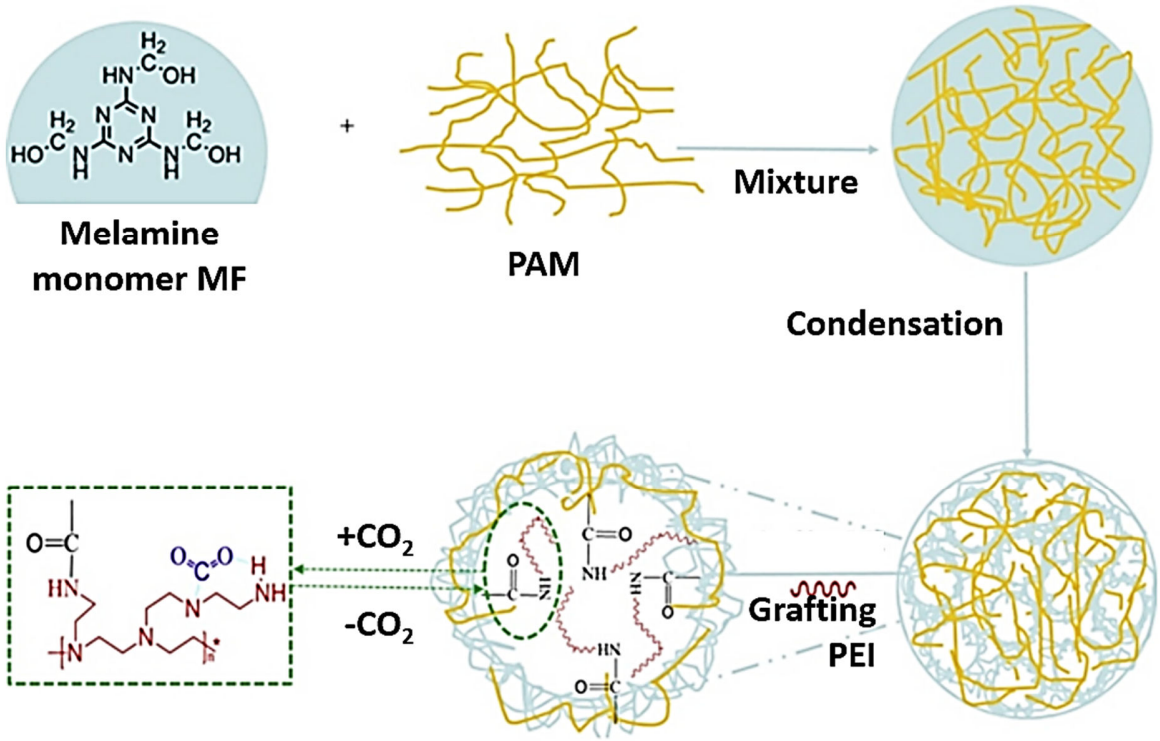

Figure 2. Schematic diagram of the synthesis of MF/PAM polymer network [34]

The grafting method was applied by Wang et al. [35] using nucleophilic substitution reaction without a catalyst to prepare the precursor for PEI-based polymers. The surface of the precursor was evenly coated with amine groups, while its internal side has a dual role of a pore-forming agent through self-decomposition and in creating nitrogen sites that can enhance surface polarity. The formation of narrowly distributed ultramicropores (d = ~0.6 nm) can attract CO_2 by relying on the van der Waals force as affinity attraction. This material achieved a CO_2 uptake of 4.92 mmol/g. The polymers exhibited the typical adsorption-desorption patterns of Type-I isotherms. Alongside the distribution of pore sizes, the polymers exhibited a recognizable microstructural feature, with ultramicropore sizes ranging from 0.6 to 0.9 nm [35]. Yang et al. [36] also synthesized an amine-functionalized polymer for CO_2 adsorption from flue gas under the pressure swing adsorption operating mode. Linear pentaethylenehexamine (PEHA) was functionalized on the open-cell foams of low-density and high-porosity polypropylene/polyolefin elastomer (PP/POE), which served as a support material.

Impregnation-cross-linking method

Porous poly(divinylbenzene) (PDVB) was synthesized using the high internal phase emulsion (HIPE) template. The porous structure was further tailored by adding a pore-forming agent and applying the post-cross-linking method. The adsorption capacity of meso-PDVB increased with the introduction of PEHA to 4.52 and 4.99 mmol/g at a 10% CO_2 concentration, with higher N efficiency observed under wet conditions [25]. The same group also reported the preparation of porous polyHIPE with silica hydroxyl groups that act as a silane coupling agent via the copolymerization of styrene, divinylbenzene, triethoxyvinylsilane (VTEO), and tetraethyl orthosilicate (TEOS), as illustrated in Figure 3. The surface morphology of polyHIPE in Figure 3 shows the formation of a thin layer of TEOS and VTEO compared to the surface morphology of polyHIPE without the presence of both silane groups. The material can be easily functionalized with aziridine via the Friedel-Crafts cross-linking reaction through the silanol group of polyHIPE, as shown in Figure 3, thus increasing the specific surface area and enriching the CO_2 chemical adsorption sites [37]. This group also synthesized a novel amine-functionalized adsorbent with an interconnected porous structure. The adsorbent was prepared using HIPE polymerization of styrene and divinylbenzene, and then functionalized with PEI in a one-step synthesis. The 4.0PEI70k@polyHIPE adsorbent showed a maximum adsorption capacity of 4.18 mmol CO_2 per gram of adsorbent at 20 °C (CO_2:N_2 = 1:9; volume ratio of 30 mL/min) under humid conditions. The monolithic structure produced from the HIPE template on a macroscopic scale of the materials offers a better advantage in industrial applications compared to powder adsorbent [38]. This is also supported by Haorui, who synthesized cross-linked polyHIPE with PEI, producing a sponge-like PEI-based solid amine adsorbent that exhibited a record high CO_2 adsorption capacity of 14.22 mmol/g with stable regeneration performance; hence, the adsorbent holds great potential in CO_2 adsorption and separation [39].

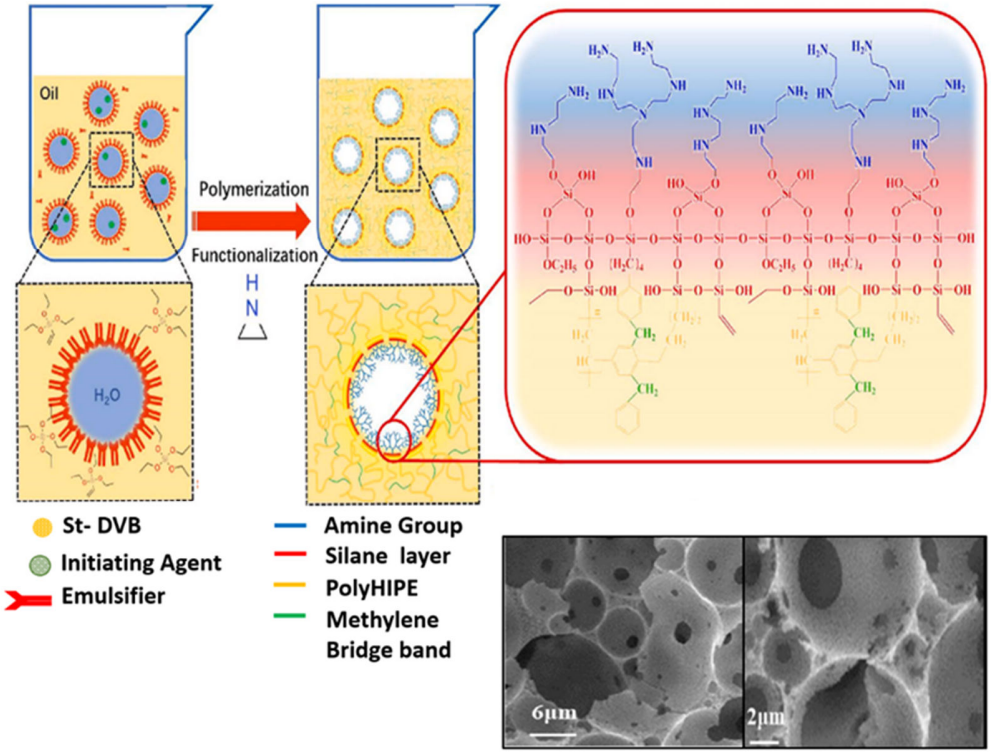

Figure 3. Synthesis of the hierarchically porous solid amine adsorbent and scanning electron microscopy images of cross-linked polyHIPE [37]

Table 1. Summary of different methods used for introducing amine group in polymer

No.	Polymer	Amine Introduction Method	Support	Adsorption Capacity	Advantages	Disadvantage	Ref
1	Polyethyleneimine/ tetraethylenepentamine (PEI/TEPA)	Physical impregnation	Macroporous silica	TEPA/SIO: 5.36 mmol/g PEI-1200: 3.75 mmol/g	• A simple, effective, and inexpensive method	• Low accessibility toward active sites after impregnation • The use of organic solvent during impregnation increases production cost • High amine loading can lead to agglomeration	[40]
2	PEI	Physical impregnation	Colloidal silica and ceramic fiber honeycomb monolith	PEI-SS (50%): 1.79 mmol/g			[41]
3	PEI	Physical impregnation	Silica support	2.3 mmol/g			[22]
4	TEPA grafted on polyethylene/ polypropylene (PE/PP) grafted with poly(glycidyl methacrylate) (PGMA)	Chemical grafting	PGMA-grafted fiber	117 mg/g	• Improved swelling capacity • Improved regeneration performance • The functionalization method can be tailored and the functional group on the surface porous material can be controlled	• Require complex sample preparation	[42]
5	Poly(aminoethyl methacrylate)	Chemical grafting	N/A	2.4 mmol/g			[43]
6	PEI	Chemical grafting	Poly(acrylic acid) foam	5.91 mmol/g			[44]
7	Molecular imprinted polymer (PEI and glycol diglycidyl ether)	Impregnation cross-linked	Molecular imprinted polymer	MIP: 6.58 mmol/g; NIP: 5.87 mmol/g.	• Improved regeneration stability • The monolithic structure of polyHIPE offers a greater advantage in industrial applications • Avoid high resistance to mass transfer during adsorption	• Complex synthesis processes	[45]
8	PolyHIPE-PEI	Impregnation-cross-linking method	PolyHIPE	6.22 mmol/g			[46]

Preparation of amide- and imide-functionalized polymers

Both amide- and imide-based polymers, which are commonly synthesized for CO_2 capture applications, consist of a carbonyl group and nitrogen atoms. These polymers can be prepared for CO_2 capture using several methods, such as polycondensation, polymerization, and radical copolymerization.

Radical copolymerization of polyacrylamide

Polyacrylamide is a polymer obtained from the radical copolymerization of acrylamide (AAm) or methacrylamide (MAAM), which demonstrated great potential in CO_2 adsorption and separation [45, 47, 48]. Yoo et al. [49] synthesized an MOF (MIL-101) loaded with polymethacrylate (PM). This polymer was synthesized using radical copolymerization in the presence of azobisisobutyronitrile as an initiator, while ethylene glycol dimethacrylate (EGDMA) and MAAM were used as monomers to produce PM@MOF, which was further reduced to R-PM@MOF to introduce free –NH_2 group. The CO_2 adsorption capacity and selectivity performance of this adsorbent increased under optimum PM loading and the reduction of PM to R-PM due to the introduction of an amine functional group [49].

In another work, Fayemiwo et al. [50] synthesized three different HCPs using radical bulk polymerization, whereby EGDMA was used as the monomer cross-linker, while MAAM, AAm, and triallylamine (TAAm) were used as the functional monomers. The results showed that the maximum CO_2 uptake was obtained by HCPMAAM-2 (1.45 mmol/g), followed by HCP-AAm and HCP-TAAm at 273 K. The highest CO_2/N_2 selectivity (15/85) was achieved by HCPMAAM. Meanwhile, HCP-TAAm showed low adsorption performance and selectivity, possibly attributed to the weak attraction between tertiary amine and CO_2. In comparison, HCP-MAAM-2 and HCP-Aam have NH_2 functional groups that can form strong interactions with CO_2 molecules. The same group also reported the life cycle assessment of HCP-MAAM as an adsorbent. The results indicated that this adsorbent has lower environmental impacts compared to molecularly imprinted polymers, as the latter used solvents sourced from fossil fuels [50]. Su et al. [51] reported an improved molecular imprinting polymerization method using the surface imprinting technique to produce CO_2 molecular imprinting polymer (CO_2-MIP). As shown in Figure 4, the porous polymer was prepared using surface radical polymerization with continuous stirring using acrylamide as a monomer, EGDMA as a cross-linker, and activated carbon (AC) synthesized from sunflower heads (biomass waste) acted as a carrier. The MIP was polymerized onto the surface of the AC. The results showed that the macropores of the carrier decreased after molecularly imprinted polymerization, whereas its micropores and mesopores increased, leading to a decrease in the average pore size. The results obtained indicated better performance than other CO_2-MIP samples prepared using suspension polymerization [51].

Polycondensation polymerization of polyimide

Polycondensation is a polymerization method that produces a long-chain polymer from single or multiple monomers by releasing water or any related by-products. Aromatic polyimide has gained attention in CO_2 capture applications as this microporous material has outstanding thermal stability, excellent chemical resistance, and abundant heteroatoms [52]. The polycondensation of an aromatic dianhydride and tridimensional geometry amine can produce microporous polyimide with a high specific surface area for excellent CO_2 adsorption.

Ning et al. [53] introduced a new composite adsorbent named PI-UiO/GO-1, which was synthesized using a chemical in situ knitting method involving the reaction among 4,4'-oxydiphthalic anhydride, 2,4,6-trimethyl-1,3-phenylenediamine, UiO-66-NH_2, and graphene oxide (GO). Compared to pristine UiO-66-NH_2, the PI-UiO/GO-1 adsorbent exhibited superior performance, including higher CO_2 capacity, higher CO_2/N_2 selectivity (64.71 compared to 15.43), and significantly improved acid-base resistance stability. Interestingly, grafting polyimide onto UiO-66-NH_2 had no impact on the microporous structure. However, the introduction of C-N covalent bonds and secondary amines in PI-UiO/GOs enhanced the selective adsorption of CO_2. This enhancement was achieved through the interaction between the negative charge of N and O atoms in polyimide and the electrophilic C in CO_2, thereby

enhancing the selectivity and CO_2 adsorption capacity of the adsorbent [53].

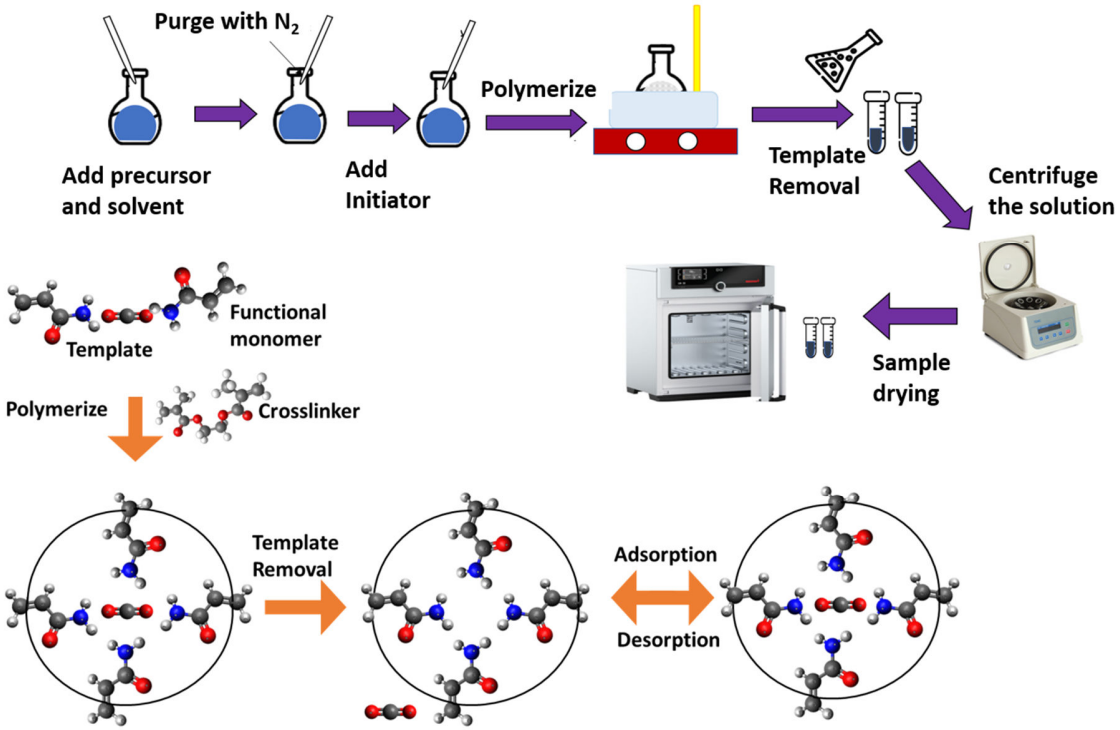

Figure 4. Schematic diagram of the steps in MIP preparation for CO_2 adsorption

Song et al. [54] reported a more simplified and economical method for preparing cross-linkable hyperbranched polyimide for CO_2 capture using polycondensation and thermal cross-linking. The cross-linked structure served as a scaffold that restricted the movement of polyimide chains, thus preventing the polymer skeleton from collapsing and facilitating the formation of micropores [54, 55].

Earlier research described the synthesis of two cross-linked microporous polyimides (i.e., TAPM-PEPA-CL and TAPA-PEPA-CL) using aromatic alkynyl monomers through thermal cross-linking polymerization in diphenyl sulfone [56]. The former exhibited a higher Brunauer-Emmett-Teller (BET) surface area and microporous volume (736 m^2/g and 0.175 cm^3/g, respectively) compared to the latter (351 m^2/g and 0.018 cm^3/g, respectively). Additionally, the adsorption capacity of TAPM-PEPA-CL was significantly enhanced. These results indicate that adjusting the topological structure of cross-linked microporous polyimides can influence their microporosity and CO_2 adsorption performance [56]. Wang et al. [57] also introduced cross-links to linear polyimide by synthesizing linear cross-linked polyimides with porous structures. This adsorbent showed higher porosity with improved CO_2 adsorption (5.7–9.3 wt.%) and good CO_2/N_2 selectivity (34.4–58.5) at 273 K compared to the other linear polyimide [57].

Preparation of covalent triazine framework

A covalent triazine framework (CTF) is often classified as a type of covalent organic framework (COF). It is synthesized through the classical ionothermal cyclotrimerization of a precursor containing carbonitrile groups. Covalent triazine frameworks possess distinctive attributes, including exceptional stability and robustness due to the presence of conjugated aromatic

C=N linkages, making them suitable for various adsorption applications [58, 59]. The design of CTFs allows for controlling the textural, structural, and physicochemical characteristics of the framework by manipulating the geometry, dimensions, and functionalities of the organic building units [60, 61]. Chen et al. [62] reported the preparation of four pyrene-based CTF materials using one-pot ionothermal polymerization. Pyrene units were chosen as the building blocks for forming CTFs due to their strong π–π interactions, which contribute to the dense structure of COFs. Additionally, the π-conjugated system derived from the pyrene group contributed to the overall structural rigidity of the CTFs. These newly developed materials exhibited remarkably high BET surface areas ranging from 1,415 to 1,753 m^2/g, along with notable CO_2 uptake capacities. The triazine-based frameworks have garnered significant interest in CO_2 adsorption research because their carbon backbones contain higher nitrogen content than other frameworks, leading to higher porosity characterized by both micropores and mesopores [62]. Liu et al. [17] prepared triazole-functionalized triazine-based porous organic polymer using copper-catalyzed azide-alkyne cycloaddition (Cu-AAC) polymerization, as shown in Figure 5. The presence of triazine and triazole rings in the CTF chain enriched the nitrogen content, thus enhancing the interaction between CO_2 and this porous material. A triazine ring with a pre-decorated azide functional group was used as the key building block for the synthesis of CTF. The Cu-AAC reaction led to the formation of 1,4-triazole, which showed a considerable CO_2 adsorption capacity of 52.0 cm^3/g at 273 K and 1 bar. They also reported a lower adsorption capacity due to the lower permanent porosity [17]. The CTF can also be prepared through the polycondensation of formamide and triazine-based amine to produce nitrogen-rich microporous polyaminals [63, 64]. The outcome of this reaction yielded various geometric configurations and functionalities, depending on the initial monomers used. As a result, it allowed for the tuning of BET surface areas and pore sizes within a range of 842–1,227 m^2/g and 0.53–3.82 nm, respectively [63]. The adsorption capacity of CO_2 can also be influenced by the pore size and BET surface area [63].

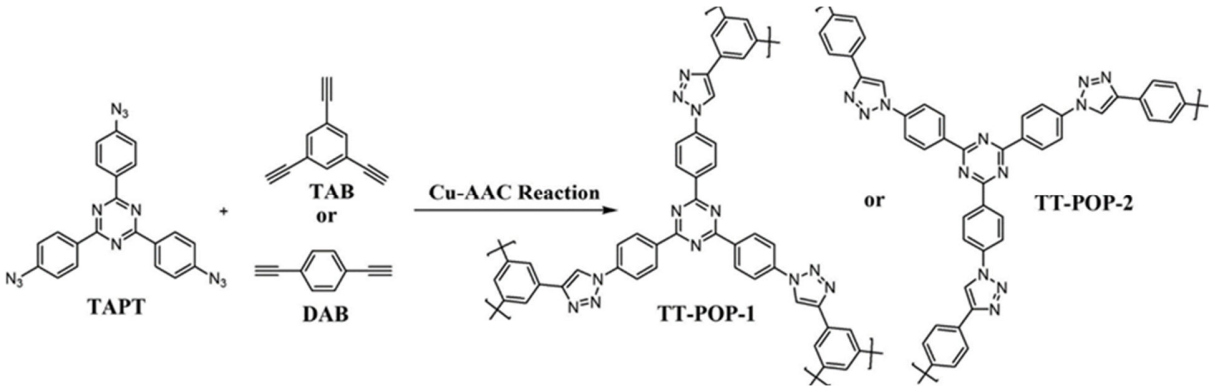

Figure 5. Schematic diagram of the synthesis of triazine-based porous organic polymer [17]

Carbon dioxide adsorption mechanism

Carbon dioxide has two oxygen atoms bonded to a central carbon atom through a covalent double bond. Its linear geometry causes the net molecular dipole moment to be zero, making it a non-polar molecule. Quadrupole interaction, or London dispersion interaction, can form between CO_2 molecules, where the middle carbon carries a partial positive charge and both terminal oxygens carry partial negative charges. The opposite charge that comes into contact forms the quadrupole interaction or electrostatic interaction (+/−). Figure 6 shows the electrostatic potential surfaces of CO_2, illustrating the distribution of charges on the molecular surface. The surfaces plotted in pink indicate the negative potential regions, while the surface in green indicate the most positive region. The surface potential site of CO_2 shows the carbon atom with a positive charge (poor electron) and the oxygen atoms at both ends with

a negative potential (rich electron). The potentials of the positive and negative regions can form electrostatic interactions with electrophilic and nucleophilic regions of other molecules [65, 66].

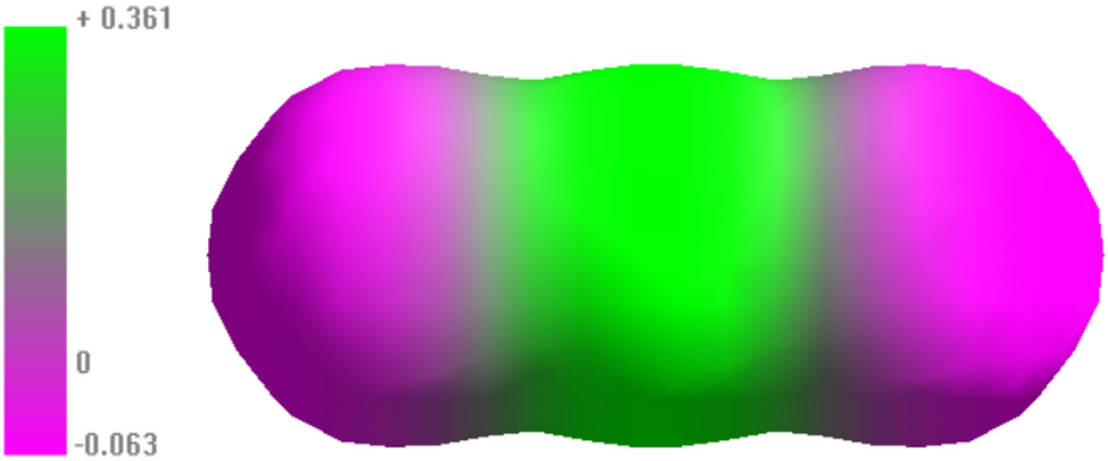

Figure 6. Electrostatic potential surfaces generated for two molecules.

The interaction between CO_2 and an amine (primary or secondary) functional group can lead to the formation of a zwitterion. Faisal et al. [67] reported the mechanism of the reaction between the primary amine of ethylenediamine (RNH_2), which was functionalized onto the surface of mesoporous carbon and reacted with CO_2 to form carbamate ions, as shown in Equation (1). Meanwhile, mesoporous carbon triethylenetetramine, which contains both primary and secondary amines (RNH_2 and R_2NH, respectively), reacted with CO_2, as illustrated in Equation (1) and (2) [67].

$$CO_2 + 2RNH_2 \rightarrow RNH_3^+ + RNHCOO^- \quad (1)$$

$$CO_2 + 2R_1R_2NH \rightarrow R_1R_2NH_2^+ + R_1R_2NCOO^- \quad (2)$$

$$CO_2 + RNH_2 + H_2O \rightarrow HCO_3^- + RNH_3^+ \quad (3)$$

$$RNH_3^+RNHCOO^- + H_2O \rightarrow RNH_2 + HCO_3^-RNH_3^+ \quad (4)$$

$$CO_2 + RN_3 + H_2O \rightarrow HCO_3^- + R_3NH^+ \quad (5)$$

This mechanism is supported by another study that used a different support-free cross-linked PEI sorbent [68]. They reported that primary and secondary amines reacted rapidly with CO_2 to form carbamates, as shown in Equations (1) and (2). This mechanism, which was proposed by Caplow et al. [69], is initiated by the nucleophilic attack of an amine that acts as a Lewis base to form a zwitterion. Later, this zwitterion is deprotonated by another amine acting as a Bronsted base, resulting in the formation of an ammonium carbamate ion [69]. The reaction between an amine and CO_2 in the presence of water can lead to the formation of ammonium bicarbonate, as shown in Equation (3). This reaction involves the interaction between zwitterion and water molecules, whereby only one amino group is needed to interact with one CO_2 molecule instead of two amino groups, as shown in Equations (1) and (2) [68]. The formation of ammonium carbonate can also occur through the hydrolysis of ammonium carbonate, as presented in Equation 4 [70]. In the case of tertiary amines, which possess no hydrogen atom or any weak amine nucleophiles, such as sterically hindered amines, this group of amines does not directly react with CO_2. Hence, water or other strong nucleophiles will attack the electrophilic CO_2 and generate bicarbonate/carbonate, as shown in Equation

(5) [68–71]. The reaction mechanism between CO_2 and amine, whether in a solution or solid adsorbent under dry or humid conditions, depends on the type of nucleophile, the Bronsted base, and the stabilizing component. The strong, stable interaction that forms between CO_2 and amine is the main reason why amine polymer is widely used. Numerous studies have reported the use of amine polymers combined with other porous materials, highlighting their remarkable potential as CO_2 adsorbents. However, extensive research must be done to modify the adsorbents so that they can fulfill this application. Suresh et al. [72] reported that based on an electron density difference map analysis, CO_2 was capable of interacting with oxygen molecules in amide carbonyl via Lewis acid-base reaction. They also reported weak H bonds with phenyl C−H and π–π interactions with the aromatic phenyl group [72]. An intermolecular interaction can form between CTF and CO_2 through the nitrogen-based functional group. Lee et al. [73] and Tan et al. [74] each reported a theoretical study of the intermolecular interaction between melamine and CO_2. The nitrogen atoms in the melamine molecule and the C in the CO_2 molecule (N-C) can interact, including the hydrogen bonds between the H-amine and the O-CO_2 molecule [73,74]. Tumnantong et al. [75] suggested that the adsorption mechanism of the synthesized modified natural rubber (MNR) composite was a combination of physisorption and chemisorption. This was further proven by the kinetic study conducted by the group, where Avrami's kinetic model fitted well with the adsorption kinetics data, showing a high R^2 value (>0.95). The Avrami exponent, n_a reflects the changes in the mechanism during adsorption. In the MNR foam composites, the values ranged from 1.0535 to 1.2469, indicating a complex reaction mechanism.

Application of molecular modeling in adsorption mechanisms

The Hohenberg-Kohn principle is the foundation of the density functional theory (DFT) approach. The electron density function is utilized in molecular simulation. This approach has low computing complexity and can determine the chemical bond energy, forecast the structures of compounds, and predict reaction processes. Table 2 presents a summary of DFT applications in studying the interaction between CO_2 and the polymer. Schukraft et al. [76] conducted a study on the interaction of adsorption sites in triazine-biphenyl HCP with CO_2 adsorption using DFT and in situ diffuse reflectance infrared Fourier transform spectroscopy. The study indicated that the strong intermolecular interaction between HCP and CO_2 was confirmed and compared using experimental infrared spectra and theoretical vibrational bands during CO_2 adsorption.

A study by Dash [66] involved the calculation of binding energy (BE) to study the interaction between a COF polymer containing a triazine group building block and CO_2 using DFT simulation. The results indicate that the BE between the triazine benzene and CO_2 complex is higher than the BE of the triazine benzene and N_2 complex, with approximately 18.1 kJ/mol and 13.47 kJ/mol, respectively. These differences are due to electrostatic interactions. These electrostatic interactions can be classified as dipole-quadrupole and dipole-induced dipole interactions. Moreover, the formation of hydrogen bonds can be explained by the interaction between the hydrogen atom of the aromatic ring and the oxygen atom of CO_2. The strength of the hydrogen bond increases with a greater number of aromatic rings [66]. Xu et al. [77] described the interaction between CO_2 and a polyimide matrix through molecular dynamic simulations. Their analysis through the radial distribution function revealed that CO_2 has greater intermolecular affinity with the polyimide chain; in addition, O and N atoms in the imide groups are identified as the preferred sorption sites for CO_2 molecules [77]. Zhang et al. [78] used four organic amines with different properties to prepare amine-functionalized X-5 adsorbents using the impregnation method. The study involved the strategy of matching mechanisms between different organic amines and porous resins for CO_2 adsorption using DFT calculations to investigate the interaction between the amine and CO_2.

Table 2 Summary of DFT applications in investigating CO_2 interaction mechanism.

Polymer	Purpose	Approach	Software	Ref
Amide-functionalized microporous organic polymer	To analyze CO_2 molecule interactions with amide functional groups via Lewis acid-base type interactions	DFT, geometry optimization by M06-2X/cc-pVTZ level of theory	Gaussian 09 program	[72]
Poly(1-vinylimidazole)	To study how CO_2 interacts with oligomers of n-VIm, where 'n' represents the number of monomers (from 1 to 4)	DFT, geometry optimization by B3LYP–D3/6–311++G* (d, p) level	Gaussian 03 program	[79]
α- and β-Polyvinylidene fluoride (PVDF)-supported imidazolium and pyridinium	To investigate the interaction of PVDF/ionic liquid (IL)-based system with binary mixtures of CO_2, CO, CH_4, and H_2 gases (the gas adsorption interactions involving PVDF tetramers, ILs, and the combinations of PVDF/IL complexes are elucidated by considering various quantum chemical descriptors)	DFT, geometry optimization by B3LYP, along with triple zeta basis set 6-311+G (d, p)	Gaussian 16 program and Gaussview 6.0	[80]
Polyvinyl chloride (PVC)/ polyvinyl imidazole (PVIm)	To analyze the interaction of CO_2 and methane gases with PVC and PVIm	DFT, geometry optimization by B3LYP–D3/6–311++G* (d, p) level	Gaussian 03 program	[81]
Graphene oxide/ polymer composite	To analyze the interaction of CO_2 and nitrogen gases with GO/polymer composite complex	Geometry optimization by DFT using the long-range corrected ωB97XD functional 39 together with the 6–31+G(d) basis set	Gaussian 16 package	[82]

Conclusion and future direction

This review discusses the preparation methods for three types of nitrogen-rich polymers, namely amine-functionalized polymer, amide- and imide-functionalized polymer, and covalent triazine framework. Several limitations, as well as advantages, have been identified in the implementation of these methods. Impregnating silica with high amine loading can cause agglomeration of the adsorbent, which may impact its adsorption capacity. This impregnation method can also suffer from leaching and degradation of amine during the regeneration cycle, which can affect the stability of the adsorbent. Despite these drawbacks, the sample preparation is easy and uses inexpensive chemicals (silica and PEI) compared to other methods. On the other hand, surface grafting is quite costly and requires complex preparation procedures. Nonetheless, this technique can overcome amine leaching, dissolution, and deactivation of the adsorbent. In-depth modification and cross-linking of amine can improve the stability of the adsorbent, even after ten regeneration cycles. Meanwhile, the use of HIPE template during polymerization can produce excellent, stable porous solid amine adsorbents with a three-dimensional interpenetrating network. The monolithic polymer produced from the HIPE template has a greater potential for industrial applications compared to powder adsorbent. This polymer also possesses a high pore

volume and specific surface area. However, the abundance of specific surface area will not benefit CO_2 adsorption as mesopore structures are favored for CO_2 adsorption. Free radical polymerization in the preparation of molecularly imprinted polymer can produce simple and highly selective tailor-made polymers. However, the use of solvents during the washing step can have an impact on the environment. This issue can be addressed by using a greener solvent or reducing the consumption of fresh solvent through recycling or using tools that can assist in the washing step. The use of imide-functionalized polymers in the polycondensation method can produce highly porous polymers with improved adsorption capacity and stability. The disadvantage of this method is that the chemical used is quite expensive and the preparation is complex. In the future, more research related to the formulation and design of materials on a large scale should be emphasized. In-depth analysis should also be considered to determine the cost of preparing the materials and the process involved during the adsorption of CO_2 onto adsorbents. The long-term stability and life-cycle assessment of adsorbents should be studied to determine their environmental impact before undergoing scalable production. Molecular modeling has proven to be a valuable approach for studying CO_2 adsorption and its interaction with various functional materials. The findings reveal that investigations at the molecular level can enhance the understanding of CO_2 interaction mechanisms. This study can greatly contribute to designing and optimizing functional polymers for carbon adsorption and storage purposes.

Acknowledgment

This work was co-supported by the Ministry of Higher Education Malaysia through the Fundamental Research Grant Scheme (FRGS/1/2023/TK05/USM/02/4), with financial support under the SLAB scholarship, and Universiti Sains Malaysia through the Bridging Grant (304/PJKIMIA/6315719). The authors are also thankful to Universiti Malaysia Perlis for providing laboratory facilities.

References

1. Martins, T., Barreto, A.C., Souza, F.M. and Souza, A.M. (2021). Fossil fuels consumption and carbon dioxide emissions in G7 countries: Empirical evidence from ARDL bounds testing approach. *Environmental Pollution*, 291:118093.
2. Nations, U. (2015) Paris Agreement. Paris.
3. Vannak, H., Osaka, Y., Tsujiguchi, T. and Kodama, A. (2024). The efficacy of carbon molecular sieve and solid amine for CO_2 separation from a simulated wet flue gas by an internally heated/cooled temperature swing adsorption process. *Applied Thermal Engineering*, 239: 122145.
4. Energy Technology Perspectives 2020 - Special report on carbon capture utilisation and storage. *Energy Technology Perspectives 2020 - Special Report on Carbon Capture Utilisation and Storage*.
5. Ma, C., Bai, J., Hu, X., Jiang, Z. and Wang, L. (2023). Nitrogen-doped porous carbons from polyacrylonitrile fiber as effective CO_2 adsorbents. *Journal of Environmental Sciences (China)*, 125: 533-543.
6. Wang, X. and Song, C. (2020). Carbon capture from flue gas and the atmosphere: A perspective. *Frontiers in Energy Research*, 2020: 560849.
7. Gelles, T., Lawson, S., Rownaghi, A.A. and Rezaei, F. (2020). Recent advances in development of amine functionalized adsorbents for CO_2 capture. *Adsorption*, 2020: 151.
8. Borhan, A., Yusup, S., Lim, J.W. and Show, P.L. (2019) Characterization and modelling studies of activated carbon produced from rubber-seed shell using KOH for CO_2 Adsorption. *Processes*, 7: 110855.
9. Hu, H. and Xu, K. (2020). Physicochemical technologies for HRPs and risk control. *High-Risk Pollutants in Wastewater*, Elsevier: pp. 169-207.
10. Kwon, D. il, Kim, J.C., Lee, H., Lee, W. and Jo, C. (2022). Engineering micropore walls of beta zeolites by post-functionalization for CO_2 adsorption performance screening under humid conditions. *Chemical Engineering Journal*, 427: 131461.
11. Mochizuki, Y., Bud, J., Byambajav, E. and Tsubouchi, N. (2022). Influence of ammonia treatment on the CO_2 adsorption of activated carbon. *Journal of Environmental Chemical Engineering*, 10: 107273.

12. Ansari, K.B., Gaikar, V.G., Trinh, Q.T., Khan, M.S., Banerjee, A., Kanchan, D.R., Mesfer, M.K. and Danish, M. (2022). Carbon dioxide capture over amine functionalized styrene divinylbenzene copolymer: An experimental batch and continuous studies. *Journal of Environmental Chemical Engineering*, 10: 106910.
13. Varghese, A.M. and Karanikolos, G.N. (2020). CO_2 capture adsorbents functionalized by amine – bearing polymers: A review. *International Journal of Greenhouse Gas Control*, Elsevier, 96: 103005.
14. Hassan, A., Goswami, S., Alam, A., Bera, R. and Das, N. (2021). Triptycene based and nitrogen rich hyper cross linked polymers (TNHCPs) as efficient CO_2 and iodine adsorbent. *Separation and Purification Technology*, 257: 117923.
15. Chen, J., Jiang, L., Wang, W., Shen, Z., Liu, S., Li, X. and Wang, Y. (2022). Constructing highly porous carbon materials from porous organic polymers for superior CO_2 adsorption and separation. *Journal of Colloid and Interface Science*, 609: 775–784.
16. Barbarin, I., Politakos, N., Serrano-Cantador, L., Cecilia, J.A., Sanz, O. and Tomovska, R. (2022). Towards functionalized graphene/polymer monolithic structures for selective CO_2 capture. *Microporous and Mesoporous Materials*, 337: 111907.
17. Liu, X., Du, J., Ye, Y., Liu, Y., Wang, S., Meng, X., Song, X., Liang, Z. and Yan, W. (2022). Boosting selective C_2H_2/CH_4, C_2H_4/CH_4 and CO_2/CH_4 adsorption performance via 1,2,3-triazole functionalized triazine-based porous organic polymers. *Chinese Journal of Chemical Engineering*, 42: 64-72.
18. Shang, Q., Cheng, Y., Gong, Z., Yan, Y., Han, B., Liao, G. and Wang, D. (2022). Constructing novel hyper-crosslinked conjugated polymers through molecular expansion for enhanced gas adsorption performance. *Journal of Hazardous Materials*, 426: 127850.
19. Li, L., Luo, Z., Zou, W., Liang, S., Wang, H. and Zhang, C. (2024). Physicochemical synergistic adsorption of CO_2 by PEI-impregnated hierarchical porous polymers. *Greenhouse Gases: Science and Technology*, 2024: 2263.
20. Liu, Y., Li, S., Pudukudy, M., Lin, L., Yang, H., Li, M., Shan, S., Hu, T. and Zhi, Y. (2024). Melamine-based nitrogen-heterocyclic polymer networks as efficient platforms for CO_2 adsorption and conversion. *Separation and Purification Technology*, 331: 125645.
21. HaiyanYang, Wang, X., Liu, J., Liu, W., Gong, Y. and Sun, Y. (2022). Amine-impregnated polymeric resin with high CO_2 adsorption capacity for biogas upgrading. *Chemical Engineering Journal*, 430: 132899.
22. Liu, L., Jin, S., Park, Y., Kim, K.M. and Lee, C.H. (2021). Sorption equilibria, kinetics, and temperature-swing adsorption performance of polyethyleneimine-impregnated silica for post-combustion carbon dioxide capture. *Separation and Purification Technology*, 266: 118582.
23. Chen, Z., Lv, Z., Sun, Y., Chi, Z. and Qing, G. (2020). Recent advancements in polyethyleneimine-based materials and their biomedical, biotechnology, and biomaterial applications. *Journal of Materials Chemistry B*. 8(15): 2951-2973.
24. Rosu, C., Narayanan, P., Leisen, J.E. and Jones, C.W. (2022). Sequential polymer infusion into solid substrates (SPISS): Impact of processing on sorbent CO_2 adsorption properties. *Separation and Purification Technology*, 292: 121042.
25. Wang, S., Liu, H. and Chen, S. (2022). A strategy to synthesis amine-functional poly(divinylbenzene)HIPEs with controllable porous structure for effective CO_2 adsorption. *Fuel*, 322: 124120.
26. Chen, X., Quan, H., Yu, J., Hu, Y. and Huang, Z. (2024). Development of composite amine functionalized polyester microspheres for efficient CO_2 capture. *Environmental Science and Pollution Research*, 31: 7027–7042.
27. Meng, Y., Ju, T., Meng, F., Han, S., Song, M. and Jiang, J. (2021). Insights into the critical role of abundant-porosity supports in polyethylenimine functionalization as efficient and stable CO_2 adsorbents. *ACS Applied Materials & Interfaces*, 13: 54018–54031.
28. Hack, J., Frazzetto, S., Evers, L., Maeda, N. and Meier, D.M. (2022). Branched versus linear

structure: Lowering the CO_2 desorption temperature of polyethylenimine-functionalized silica adsorbents. *Energies*, 15: 31075.

29. Mohamad, N.A., Nasef, M.M., Nia, P.M., Zubair, N.A., Ahmad, A., Abdullah, T.A.T. and Ali, R.R. (2021). Tetraethylenepentamine-containing adsorbent with optimized amination efficiency based on grafted polyolefin microfibrous substrate for CO_2 adsorption. *Arabian Journal of Chemistry*, 14: 103067.
30. Li, C., Yan, F., Shen, X., Qu, F., Wang, Y. and Zhang, Z. (2021). Highly efficient and stable PEI@Al_2O_3 adsorbents derived from coal fly ash for biogas upgrading. *Chemical Engineering Journal*, 409: 128117.
31. Irani, V., Khosh, A.G. and Tavasoli, A. (2020). Polyethyleneimine (PEI) functionalized metal oxide nanoparticles recovered from the catalytic converters of spent automotive exhaust systems and application for CO_2 adsorption. *Frontiers in Energy Research*, 8: 196.
32. Li, C., Wang, X., Yang, A., Chen, P., Zhao, T. and Liu, F. (2021). Polyethyleneimine-modified amorphous silica for the selective adsorption of CO_2/N_2 at high temperatures. *ACS Omega*, 6: 35389-35397.
33. Choi, C., Kadam, R.L., Gaikwad, S., Hwang, K.S. and Han, S. (2020). Metal organic frameworks immobilized polyacrylonitrile fiber mats with polyethyleneimine impregnation for CO_2 capture. *Microporous and Mesoporous Materials*, 296: 110006.
34. Yin, F., Zhuang, L., Luo, X. and Chen, S. (2018). Simple synthesis of nitrogen-rich polymer network and its further amination with PEI for CO_2 adsorption. *Applied Surface Science*, 434: 514-521.
35. Wang, H., Chen, C., Chen, Y., Wan, H., Dong, L. and Guan, G. (2021). Construction of ultramicropore-enriched N-doped carbons for CO_2 capture: Self-decomposition of polyethyleneimine-based precursor to promote pore formation and surface polarity. *Journal of Environmental Chemical Engineering*, 9: 105046.
36. Yang, C., Xiong, Y., Chen, J., Jin, J. and Mi, J. (2021) Amine-functionalized micron-porous polymer foams with high CO_2 adsorption efficiency and exceptional stability in PSA process. *Chemical Engineering Journal*, Elsevier, 420: 129555.
37. Wang, S., Qiu, X., Chen, Y. and Chen, S. (2022). Preparation and structure tuning of CO_2 adsorbent based on in-situ amine-functionalized hierarchical porous polymer. *Microporous and Mesoporous Materials*, 330: 111585.
38. Wang, S., Wu, J., Ma, N. and Chen, S. (2021). High molecular weight polyethylenimine encapsulated into a porous polymer monolithic by one-step polymerization for CO_2 capture. *New Journal of Chemistry,* 45: 12538-12548.
39. Liu, H., Wang, X., Chen, S. and Chen, S. (2024). Sponge-like polyethyleneimine adsorbents with interconnected open channels enabling ultra-high CO_2 adsorption and separation capacity. *Separation and Purification Technology*, 330: 125528.
40. Choi, W., Park, J., Kim, C. and Choi, M. (2021). Structural effects of amine polymers on stability and energy efficiency of adsorbents in post-combustion CO_2 capture. *Chemical Engineering Journal*, 408: 127289.
41. Wu, J., Zhu, X., Yang, F., Ge, T. and Wang, R. (2021). Easily-synthesized and low-cost amine-functionalized silica sol-coated structured adsorbents for CO_2 capture. *Chemical Engineering Journal*, 425: 131409.
42. Mohamad, N.A., Nasef, M.M., Nia, P.M., Zubair, N.A., Ahmad, A., Abdullah, T.A.T. and Ali, R.R. (2021). Tetraethylenepentamine-containing adsorbent with optimized amination efficiency based on grafted polyolefin microfibrous substrate for CO_2 adsorption. *Arabian Journal of Chemistry*, 14: 103067.
43. Tiainen, T., Mannisto, J.K., Tenhu, H. and Hietala, S. (2022). CO_2 capture and low-temperature release by poly(aminoethyl methacrylate) and derivatives. *Langmuir*, 38: 5197-5208.
44. Deng, J., Liu, Z., Du, Z., Zou, W. and Zhang, C. (2019). Fabrication of PEI-grafted porous polymer foam for CO_2 capture. *Journal of Applied Polymer Science*, 136: 2-8.
45. Liu, F., Kuang, Y., Wang, S., Chen, S. and Fu, W. (2018). Preparation and characterization of molecularly imprinted solid amine adsorbent for

CO_2 adsorption. *New Journal of Chemistry*, 42: 10016-10023.

46. Liu, H., Wang, S., Wang, X., Feng, X.J. and Chen, S. (2022). A stable solid amine adsorbent with interconnected open-cell structure for rapid CO_2 adsorption and CO_2/CH_4 separation. *Energy*, 258: 124899.
47. Nabavi, S.A., Vladisavljević, G.T., Wicaksono, A., Georgiadou, S. and Manović, V. (2017). Production of molecularly imprinted polymer particles with amide-decorated cavities for CO_2 capture using membrane emulsification/suspension polymerisation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 521: 231-238.
48. Nabavi, S.A., Vladisavljević, G.T., Wicaksono, A., Georgiadou, S. and Manović, V. (2017). Production of molecularly imprinted polymer particles with amide-decorated cavities for CO_2 capture using membrane emulsification/suspension polymerisation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 521, 231-238.
49. Yoo, D.K., Yoon, T.U., Bae, Y.S. and Jhung, S.H. (2020). Metal-Organic Framework MIL-101 loaded with polymethacrylamide with or without further reduction: Effective and selective CO_2 adsorption with amino or amide functionality. *Chemical Engineering Journal*, 380: 122496.
50. Fayemiwo, K.A., Chiarasumran, N., Nabavi, S.A., Manović, V., Benyahia, B. and Vladisavljević, G.T. (2020). CO_2 capture performance and environmental impact of copolymers of ethylene glycol dimethacrylate with acrylamide, methacrylamide and triallylamine. *Journal of Environmental Chemical Engineering*, 103536.
51. Su, W., Wang, R. and Zhao, T. (2020). CO_2-imprinted sustainable carbon derived from sunflower heads for highly effective capture of CO_2 from flue gas. *Aerosol and Air Quality Research*, 20: 180-192.
52. Liu, Y., Zhao, X.-Y., Sun, Y.-G., Li, W.-Z., Zhang, X.-S. and Luan, J. (2023). Synthesis and applications of low dielectric polyimide. *Resources Chemicals and Materials*, 2: 49-62.
53. Ning, H., Yang, Z., Yin, Z., Wang, D., Meng, Z., Wang, C., Zhang, Y. and Chen, Z. (2021). A novel strategy to enhance the performance of CO_2 adsorption separation: grafting hyper-cross-linked polyimide onto composites of UiO-66-NH_2 and GO. *ACS Applied Materials & Interfaces*, 13: 17781-17790.
54. Song, N., Ma, T., Wang, T., Li, Z., Yao, H. and Guan, S. (2020). Microporous polyimides with high surface area and CO_2 selectivity fabricated from cross-linkable linear polyimides. *Journal of Colloid and Interface Science*, 573: 328-335.
55. Song, N., Wang, T., Ma, T., Li, J., Yao, H. and Guan, S. (2022). Microporous polyimide networks with tunable micropore size constructed through side-chain engineering of linear precursors. *Polymer*, 255: 125161.
56. Wang, T., Yang, Y., Song, N., Zhu, S., Yao, H., Zhang, Y. and Guan, S. (2021). Thermal crosslinking polymerization of aromatic alkynyl monomers to microporous polyimides in diphenyl sulfone. *Microporous and Mesoporous Materials*, 328: 111447.
57. Wang, T., Yao, H., Song, N., Yang, Y., Shi, K. and Guan, S. (2021). Microporous polymer networks constructed from cross-linkable linear polyimides for CO_2 adsorption. *Microporous and Mesoporous Materials*, 311: 110708.
58. Huang, Q., Zhan, Z., Sun, R., Mu, J., Tan, B. and Wu, C. (2023). Light triggered pore size tuning in photoswitching covalent triazine frameworks for low energy CO_2 capture. *Angewandte Chemie - International Edition*, 62: 5500.
59. Ping, R., Ma, C., Shen, Z., Zhang, G., Wang, D., Liu, F. and Liu, M. (2023). Metalloporphyrin and triazine integrated nitrogen-rich frameworks as high-performance platform for CO_2 adsorption and conversion under ambient pressure. *Separation and Purification Technology*, 310: 123151.
60. Pourebrahimi, S. and Pirooz, M. (2022). Functionalized covalent triazine frameworks as promising platforms for environmental remediation: A review. *Cleaner Chemical Engineering*, 2: 100012.
61. Ngo, H.M., Pal, U., Kang, Y.S. and Ok, K.M. (2023). DFT-based study for the enhancement of

CO_2 adsorption on metal-doped nitrogen-enriched polytriazines. *ACS Omega*, 8: 8876-8884.

62. Chen, Y., Hu, X., Guo, J., Guo, Z., Zhan, H. and Du, S. (2022). Optimizing CO_2 capture and separation in pyrene derived covalent triazine frameworks. *European Polymer Journal*, 171: 111215.
63. Li, G., Zhou, X. and Wang, Z. (2020). Highly nitrogen-rich microporous polyaminals using n, n-dimethylformamide and formamide as the starting monomers for CO_2 adsorption and separation. *Journal of Physical Chemistry C*, 124: 3087-3094.
64. Zhang, B., Yan, J., Li, G. and Wang, Z. (2019). Cost-effective preparation of microporous polymers from formamide derivatives and adsorption of CO_2 under dry and humid conditions. *Polymer Chemistry*, 10: 3371-3379.
65. Alkorta, I. and Legon, A.C. (2018) An ab initio investigation of the geometries and binding strengths of tetrel-, pnictogen-, and chalcogen-bonded complexes of CO_2, N_2O, and CS_2 with simple Lewis bases: some generalizations. *Molecules*, 23: 92250.
66. Dash, B. (2018). Carbon dioxide capture using covalent organic frameworks (COFs) type material-a theoretical investigation. *Journal of Molecular Modeling*, 24: 3646.
67. Faisal, M., Pamungkas, A.Z. and Krisnandi, Y.K. (2021). Study of amine functionalized mesoporous carbon as CO_2 storage materials. *Processes*, 9: 1-13.
68. Wang, F., Yu, L., Li, Y. and Huang, D. (2021). CO_2 adsorption capacity of organic alkali sorbent CPEI from polyethyleneimine. Adsorption Science and Technology, 2021: 6629365.
69. Caplow, M. (2002). Kinetics of carbamate formation and breakdown. *Journal of the American Chemical Society*, 90: 6795-6803.
70. Said, R. ben, Kolle, J.M., Essalah, K., Tangour, B. and Sayari, A. (2020). A unified approach to CO_2 −amine reaction mechanisms. *ACS Omega*, 5: 44.
71. v. Kortunov, P., Siskin, M., Saunders Baugh, L. and C. Calabro, D. (2015). In situ nuclear magnetic resonance mechanistic studies of carbon dioxide reactions with liquid amines in aqueous systems: New insights on carbon capture reaction pathways. *Energy & Fuels*, 29: 5919-5939.
72. Suresh, V. M., Bonakala, S., Atreya, H. S., Balasubramanian, S., and Maji, T. K. (2014). Amide functionalized microporous organic polymer (Am-MOP) for selective CO_2 sorption and catalysis. *ACS Applied Materials & Interfaces,* 6(7): 4630-4637.
73. Lee, H.M., Youn, I.S., Saleh, M., Lee, J.W. and Kim, K.S. (2015). Interactions of CO_2 with various functional molecules. *Physical Chemistry Chemical Physics*, 17: 673.
74. Tan, M.X., Zhang, Y. and Ying, J.Y. (2013). Mesoporous poly(melamine-formaldehyde) solid sorbent for carbon dioxide capture. *ChemSusChem*, 6: 107.
75. Tumnantong, D., Panploo, K., Chalermsinsuwan, B., Prasassarakich, P. and Poompradub, S. (2021). Carbon dioxide adsorption of diallylamine-modified natural rubber with modified silica particles. *Express Polymer Letters*, 15: 899-909.
76. Schukraft, G.E.M., Itskou, I., Woodward, R.T., Van Der Linden, B., Petit, C. and Urakawa, A. (2022). Evaluation of CO_2 and H_2O adsorption on a porous polymer using DFT and in situ DRIFT spectroscopy. *Journal of Physical Chemistry B*, 126: 3912.
77. Xu, Y., Zhou, Z., Guo, Y., Liu, L., Xu, Y., Qiao, C. and Jia, Y. (2022). Carbon dioxide detection using polymer-coated fiber bragg grating based on volume dilation mechanism and molecular dynamics simulation. *Applied Surface Science*, 584: 152616.
78. Zang, P., Tang, J., Zhang, H., Wang, X., Zhao, P., Cui, L., Chen, J., Zhao, P. and Dong, Y. (2024). Insights into amine-resin matching strategy for CO_2 capture: Adsorption performance tests and mechanistic investigation. *Separation and Purification Technology*, 331: 125622.
79. Mehrdad, A. and Noorani, N. (2019). Study of co_2 adsorption onto poly(1–vinylimidazole) using quartz crystal microbalance and density functional theory methods. *Journal of Molecular Liquids*, 291:111288.
80. Sarkar, R. and Kundu, T.K. (2021). Density Functional theory-based analyses on selective gas separation by β-PVDF-supported ionic liquid

membranes. *Journal of Molecular Graphics and Modelling*, 108: 108004.

81. Noorani, N. and Mehrdad, A. (2019). Adsorption, permeation, and DFT studies of PVC/PVIm blends for separation of CO_2/CH_4. *Journal of Molecular Liquids*, 292: 111410.
82. Stankovic, B., Barbarin, I., Sanz, O. and Tomovska, R. (2022). Experimental and theoretical study of the effect of different functionalities of graphene oxide / polymer composites on selective CO_2 capture. *Scientific Reports*, 2022: 1-13.