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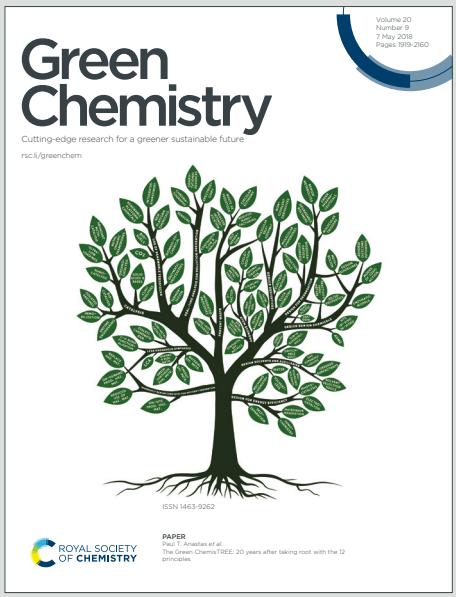

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1. This study, for the first time, demonstrates the successful conversion of volatile liquid amines into stable solid polymers via crosslinking reactions. These reactions are carried out under ambient conditions, generate no waste, and require no purification or separation steps, thereby aligning closely with green chemistry principles.
2. The resulting polymers are self-supporting and fundamentally distinct from conventional solid sorbents that rely on additional solid supports. They exhibit promising CO_2 uptake for direct air capture and, critically, enhanced stability that cannot be achieved by conventional supported amine sorbents.
3. This work introduces a new strategy for synthesising solid DAC sorbents without the use of porous materials. The approach is green and scalable, and the versatility of both crosslinkers and amines enables the development of a broad range of materials with potential applications extending beyond DAC.

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Transforming Volatile Amines into Stable Solid Sorbents via Crosslinking for Direct Air Capture of Carbon Dioxide

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Abstract

Supported amines are popular solid sorbents for direct air capture (DAC) of carbon dioxide (CO_2). However, those sorbents have several drawbacks such as leaching, volatility, oxidative degradation and corrosivity, among others. In this work, solid crosslinked (CL) polymers without the need of support were synthesised from several short chain amines that would be otherwise unviable for DAC due to their high volatility. This was achieved utilising an epoxide crosslinker N,N,N',N'-Tetrakis(2,3-epoxypropyl)-m-xylene-alpha,alpha'-diamine (TEP-MXDA), and small amines including ethylenediamine (EtDA), diaminobutane (DAB), hexamethylenediamine (HMD), diethylenetriamine (DET), triethylenetetramine (TETA) and m-xylylenediamine (mXDA) through a one-pot procedure at room temperature for 12 hours. The reaction yielded no wastes, no side products and required no separation and purification, adhering to 11 of the 12 principles of green chemistry overall. Under realistic DAC conditions, CO_2 absorption capacities up to 5.6 wt.% were achieved for CL-DET polymers. Additionally, the CL-TETA and CL-HMD polymers retained a greater CO_2 capacity compared to their silica supported counterparts after accelerated ageing tests conducted in air at 75℃ for 24 hours, corresponding to approximately 150 absorption/desorption cycles. Novel insight into the effect of amine chain length on resulting polymer mesh size and CO_2 absorption capacity is provided by positron annihilation lifetime spectroscopy (PALS) analysis, and reveals the beneficial role PEG plays in hydrogel-like amine-based crosslinked sorbents. This study demonstrates the viability of crosslinked short-chain amines as solid sorbents for DAC applications, and provides novel insight into the effects variables such as amine choice, amine chain length and crosslinking ratio have on the performance of the resulting materials in CO_2 absorption.

Keywords: Amine polymer; CO_2 removal; Direct air capture; Negative emission; Solid sorbent

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1. *Introduction*

Rising atmospheric carbon dioxide (CO_2) levels contribute greatly to climate change, resulting in an increase of global surface temperature by an estimated 0.8-1.2°C,[1] and thereby producing significant adverse effects on human livelihoods and ecosystem health.[2] The international panel on climate change recommends immediate drastic action be taken to reduce global CO_2 emissions by 2025 such that global warming is limited to no more than 1.5°C to mitigate or reduce most of these adverse consequences.[1] To achieve this goal, a multifaceted approach is required, of which one facet is direct air capture (DAC) of CO_2 .[3] With the potential to become a "carbon negative" process, DAC has become an area of significant research interest, leading to a wide variety of different materials and technologies being developed for DAC.[4, 5] DAC materials - which can be broadly categorised into liquid, solid and supported sorbents – ideally should feature simple and cheap syntheses, high CO_2 sorption capacity, rapid sorption kinetics, high recyclability and regenerability, and high scalability. Unfortunately, where some sorbents may excel in one or more of these aspects, there are often drawbacks to any type of DAC material.

One of the benchmark materials for solid sorbents is Mg-MOF-74, a metal organic framework (MOF) capable of achieving an impressive 32.5 wt.% CO_2 absorption capacity under a pure CO_2 stream at 25°C and 1 bar.[6] However, like many MOFs, Mg-MOF-74 is unstable under humid conditions[7] and displays reduced CO_2 absorption capacity as little as 0.18 wt.% under DAC conditions.[8] Conversely, Yaghi and co-workers recently reported the development of a covalent organic framework (COF), COF-999, capable of impressive CO_2 absorption capacities of up to 9.02 wt.% in high humidity DAC conditions with regenerative stability over 100 adsorption-desorption cycles.[9] While this represents a significant step forward, COF-999 may have limited scalability due to its costly and complex synthesis, a significant drawback considering the necessity for large scale production for DAC. Mass producible polymeric solid sorbents such as the Lewatit VP OC 1065 resin, capable of CO_2 absorption capacities of up to 8.14 wt.% ,[10] are similarly impressive in terms of their absorption capacity, but suffer from degradation due to their lack of chemical and thermal stability over many regeneration cycles.[11]

Supported sorbents are simply a liquid sorbent impregnated onto another solid material, which may itself also be a sorbent. Most commonly, viscous liquids containing amine/imine groups such as tetraethylenepentamine (TEPA) or polyethyleneimine (PEI) are supported on porous solid

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structures such as silica,[12] alumina,[13] activated carbon [14] or zeolites,[15] among others. Generally, supported sorbents feature issues with recyclability and regeneration, often as a result of evaporation, degradation or leaching of the impregnating liquid, leading to drastic decreases in absorption performance over relatively small amounts of regeneration cycles. For example, Kyselova *et al.* produced a PEI impregnated silica gel that achieved CO_2 absorption capacities of 10.26 wt.%, which was reduced to almost half after only 20 regeneration cycles.[12] Similarly, Sakwa-Novak *et al.* produced a PEI impregnated mesoporous silica capable of CO_2 absorption capacities of 7.48 wt.% which was reduced to only 2.9 wt.% after 24 hours of regeneration using steam treatment due to leaching of the PEI from the silica.[16]

Liquid sorbents are generally inexpensive and widely available with modest CO_2 absorption capacities, but often suffer from chemical degradation over many cycles, high regeneration temperatures, corrosivity, difficult handling, and low sorption kinetics due to the limited contact area between the liquid and air.[5] Aqueous alkaline solutions for example are cheap and readily available, but require regeneration temperatures up to 900°C.[17] Aqueous amino acid salts (AAS) are a potential alternative to aqueous alkaline solutions, featuring lower viscosity and lower regeneration temperatures than aqueous alkaline solutions, which are ideal qualities for liquid DAC sorbents.[18] In a recent study it was demonstrated potassium lysinate displayed the highest CO_2 absorption capacity compared to several other AAS's, achieving a CO_2 absorption capacity of approximately 6 wt.% .[19] Despite these promising results, AAS's may be limited for DAC by their economic costs and thermal stability over many cycles.[20]

Another type of popular liquid sorbent for capturing CO_2 is amines. Ostensibly any liquid amine can be used for CO_2 capture applications, due to their high affinity for CO_2, but amines often feature drawbacks similar to the aforementioned liquid sorbents. Aqueous ethanolamines for example, currently use in flue gas CO_2 capture applications,[21] are cheap and readily available but degrade over time via oxidation [22] and corrode the columns used to contain them.[23] Other amines such as ethylenediamine (EtDA), diethylenetriamine (DET) and triethylenetetramine (TETA) are cheap and widely available, and have some literature precedence for their ability to capture CO_2 under various non-DAC conditions.[24] However, in addition to the drawbacks of ethanolamines, all three of these amines suffer significant evaporative loss of sorbent due to their volatility and high vapour pressures.[24]

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In the present study, we investigate the utilisation of cheap, readily available short chain amines to produce solid, crosslinked polymers for DAC. The amines investigated include EtDA, 1,4-diaminobutane (DAB), hexamethylenediamine (HMD), DET, TETA and m-xylylenediamine (mXDA), which are unviable for DAC by themselves due to their high volatility and chemical instability. These amines were transformed into solid polymers via crosslinking with an epoxide, N,N,N',N'-Tetrakis(2,3-epoxypropyl)-m-xylene-alpha,alpha'-diamine (TEP-MXDA) as the crosslinker. To the best of the authors' knowledge, this is the first time the amines featured in this paper have been effectively used and assessed for DAC purposes. The synthesised materials were assessed for their CO_2 absorption capacities in DAC using an in-house apparatus and were assessed for their stability following an accelerated ageing procedure. Characterisation was conducted using Fourier transform infrared (FT-IR) spectroscopy before and after CO_2 absorption for both the pristine and aged materials. Further characterisation for a novel investigation into the effect of amine chain length on polymer network architecture is performed utilising a combination of positron annihilation lifetime spectroscopy (PALS) and differential scanning calorimetry (DSC) thermoporometry. Comparisons to silica supported versions of the same amines used in these materials are also made, showing improved stability and CO_2 absorption capacities in the crosslinked materials. Finally, the materials are assessed for their adherence to the 12 principles of green chemistry and compared literature materials to determine their viability in a broader context.

2. *Experimental*

2.1. Materials

Ethylenediamine (99%, EtDA), 1,4-diaminobutane (99%, DAB), hexamethylenediamine (98%, HMD), diethylenetriamine (99%, DET), triethylenetetramine (technical grade, TETA), m-xylylenediamine (99%, mXDA), polyethyleneglycol (PEG, m_W=200), trisodium phosphate (96%, Na_3PO_4), silica powder (SiO_2) and ethanol (absolute, EtOH) were all purchased from Sigma Aldrich used without further purification. The crosslinker, TEP-MXDA (99.7%), was purchased from Alfa Chemistry.

2.2. Synthesis of solid crosslinked polymer using small amines

In a typical procedure (Figure 1), 5.4 g of the crosslinker TEP-MXDA (15 mmol) Na_3PO_4 (0.5 wt.% of mass of amine) and PEG ($m_{PEG}=m_{crosslinker}+m_{amine}$) were mixed and stirred vigorously with a magnetic stirrer until homogenised. After that, the respective diamine (40 mmol) was added

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dropwise (DAB and HMD were melted at 75°C prior to synthesis) to the mixture with constant stirring, and the reaction was left to proceed overnight at room temperature. The crosslinker to amine molar ratio for the synthesised polymer was therefore 0.75:2. The following day the crosslinked polymer monolith was grinded into a white, snow-like powder with particle sizes between 200-800 µm for use in further experiments. Each polymer is henceforth referred to as CL-amine where CL stands for crosslinked and amine stands for the amine used for the polymer. Additional TETA-based polymers were made at higher crosslinker:amine molar ratios of 1:2, 1.25:2, 1.5:2 and 1:1 (2:2) by simply increasing the amount of crosslinker used in the procedure.

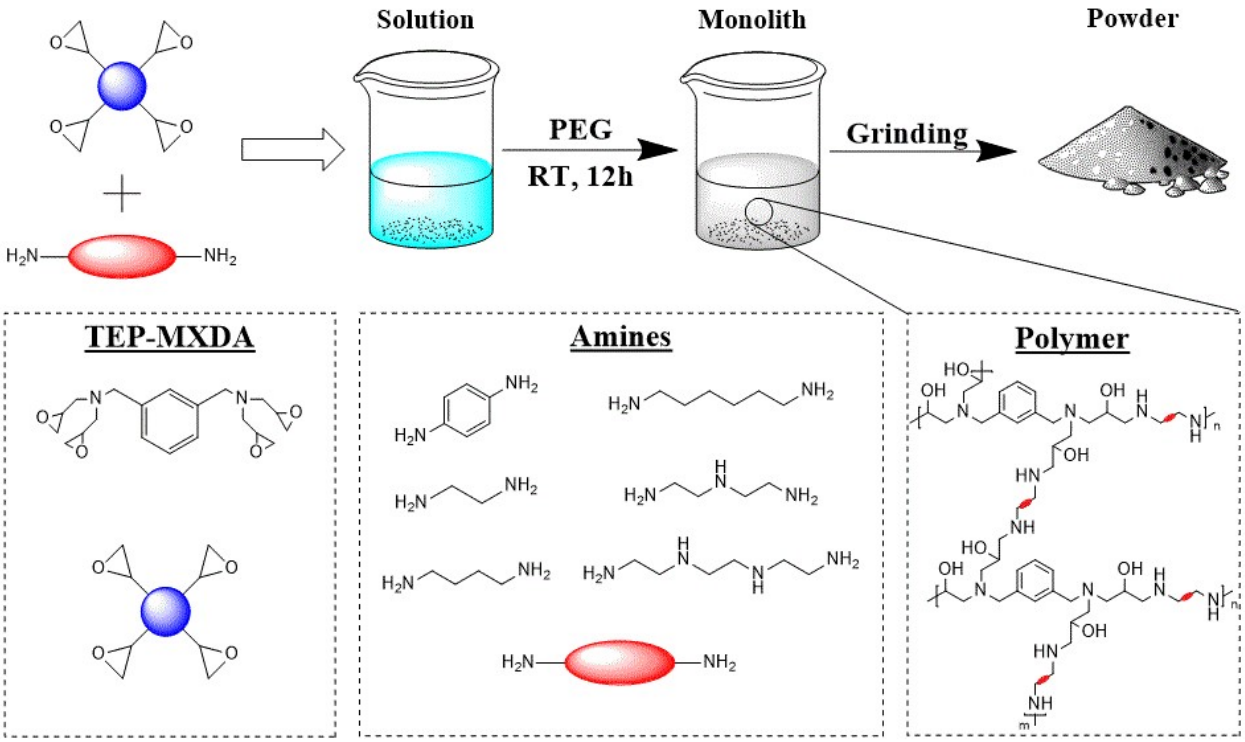

Figure 1 *– Graphical representation of the one-pot crosslinking reaction performed to produce the CL-amine materials, as well as the structures of the crosslinker (TEP-MXDA), amines and polymer materials.*

An additional CL-mXDA sample was synthesised at a 0.75:2 crosslinker:amine ratio following the same procedure as above. This sample was prepared for thermoporometry measurement using differential scanning calorimetry (DSC), so ethanol ($m_{EtOH}=m_{crosslinker}+m_{amine}$) was used as the solvent instead of PEG. After being ground into a powder this CL-mXDA was then dried under

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vacuum at 60°C overnight to remove ethanol, and then swelled with distilled water at a 1:1 polymer to water mass ratio before being used for the DSC experiments.

Silica supported TETA and HMD (referred to as TETA@SiO_2 and HMD@SiO_2) were made simply by mixing silica with the respective diamine at a 1:1 mass ratio of silica to diamine until the silica had completely imbibed the diamine. In the case of HMD, the HMD was melted at 75°C prior to mixing with the silica.

2.3. Characterisation

Fourier-transform infrared (FT-IR) spectroscopy characterisation was performed utilising a Thermo Scientific Nicolet Summit equipped with attenuated total reflectance (ATR) correction. Characterisations were performed before and after CO_2 absorption for the pristine and aged samples, in the wavelength range from 400-4000 cm^{-1} with a resolution of 4 cm^{-1} and a scan rate of 16 scans per second.

Thermogravimetric analysis-mass spectrometry (TGA-MS, Netzsch STA 449 F3 Jupiter with QMS 403 Quadro Aeolos) was utilised to determine the CO_2 desorption temperature of the sorbents and thus the appropriate temperature for ageing experiments. First, samples were exposed to air using the in-house DAC apparatus for 24 hours under an air flow of 500 mL min^{-1}. Then, approximately 10 mg of material was loaded into the alumina crucible and heated from 35 to 140°C at a rate of 1°C min^{-1} under nitrogen flow of 40 mL min^{-1}. The desorbed CO_2 was detected using a quadrupole mass spectrometer, and the temperature at which the CO_2 was detected was considered the CO_2 desorption temperature for future experiments.

2.4. Performance assessment of sorbents in DAC

The CO_2 absorption capacity of each of the materials in DAC, as well as their aged counterparts, was determined using an in-house DAC measurement apparatus as described in our previous work [11], with an in-house program recording air flow rate and inlet & outlet CO_2 & H_2O concentrations. All samples were degassed by simply being heated at 75°C (the desorption temperature determined with TGA) for 1.5 hours in a fan forced oven prior to absorption experiments.

2.5. Sorbent degradation investigation

Accelerated ageing to study sorbent stability was conducted by ageing the polymers at 75 °C in air for 24 hours, followed by absorption experiments to check the degradation in capture capacity.

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To elucidate the degradation mechanism, FT-IR spectra were obtained for the pristine CL-TETA and for CL-TETA after 24-hours of DAC; post-DAC regeneration; ageing at 75°C in air for 24 hours; ageing at 110°C in CO_2 for 24 hours; and post-ageing regenerations, with all regenerations conducted at 75°C for 1 hour. FT-IR spectra of the other polymers before and after accelerated ageing at 75°C in air for 24 hours were also obtained and can be found in Figure S3.

3. *Results and Discussion*

3.1. *Effect of amine*

As with our previous study,[25] the high reactivity between the amine groups in the diamines and the epoxide groups in the crosslinker led to the formation of a highly crosslinked polymer monolith after the one pot reaction was completed, presented graphically in **Figure 1**. In this present work, the synthesised polymers contained 15.3, 19.6, 21.4, 22.9, 24.8 and 25.7 % diamine by mass for the CL-EtDA, CL-DAB, CL-DET, CL-HMD, CL-mXDA and CL-TETA respectively. These monoliths were then easily ground into smaller particles to yield white, snow-like powders with no by-products, each of which, as shown in **Figure 2**, did not alter litmus paper, indicating they are non-corrosive on contact compared to the diamines used to synthesise them. The simplicity and effectiveness of this one pot reaction demonstrate the ease of large-scale production of these solid sorbents from otherwise unviable small amines. Furthermore, the use of PEG as opposed to the methyldiethanolamine used in our previous study further promotes the "green chemistry" of the synthesis process.

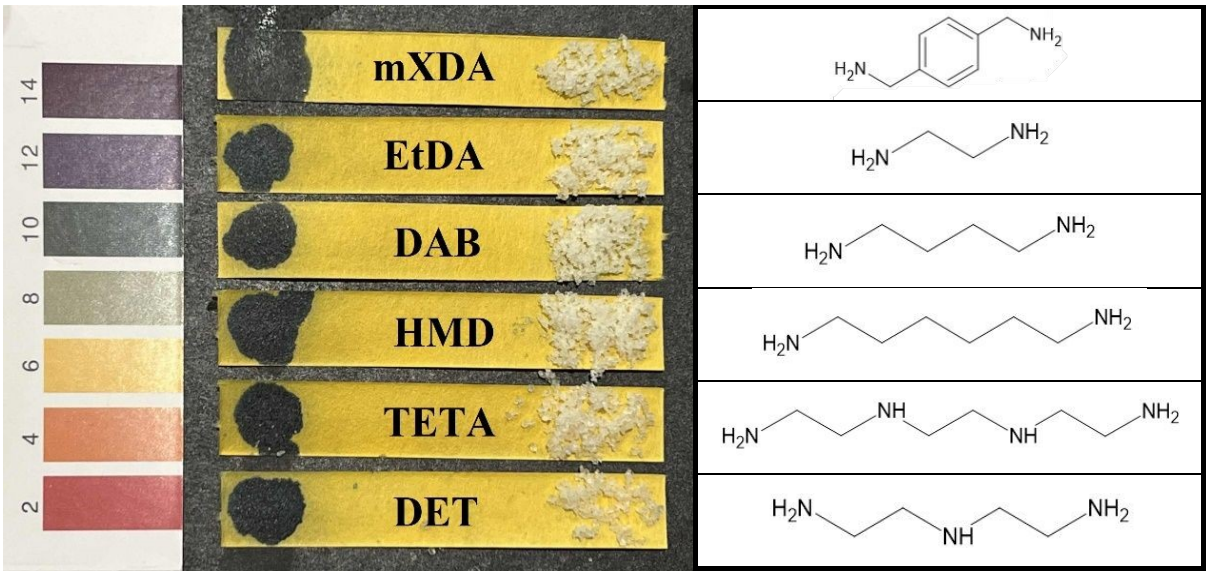

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Figure 2 - *The effect of each amine and their respective solid polymers on litmus paper, with the structure of each amine shown on the right.*

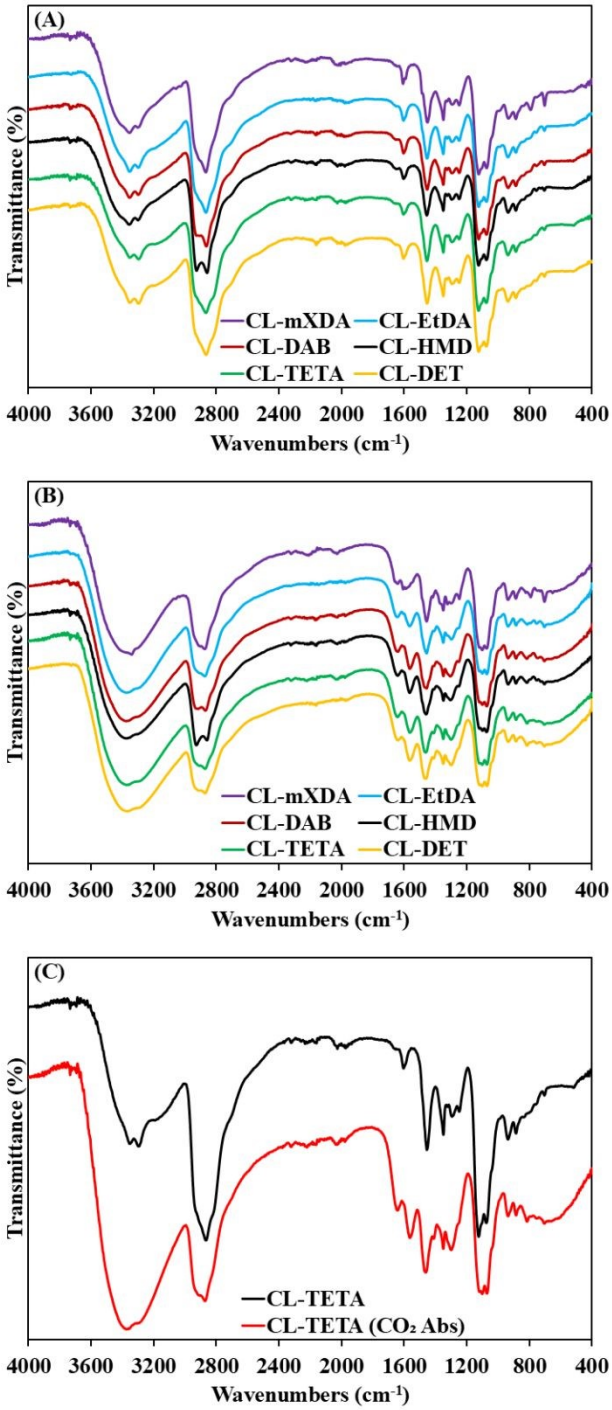

Figure 3 - *FT-IR spectra of the synthesised polymers before (A) and after (B) CO_2 absorption. In both 3A and 3B the spectra are ordered as follows from top to bottom according to the amine used*

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in polymer synthesis: CL-mXDA (purple), CL-EtDA (blue), CL-DAB (red), CL-HMD (black), CL-TETA (green) and CL-DET (yellow). (C) a direct comparison of the FT-IR spectra of the CL-TETA before (black) and after (red) CO_2 absorption.

FT-IR spectra shown in **Figure 3**A reveal peaks centred around 1450 cm^{-1}, which are attributed to O-H bending bands formed by opening of the epoxide ring during synthesis. The peaks in the range of 3000-3500 cm^{-1} are attributed to N-H and O-H stretching bands of the amines and epoxide ring opening, respectively, and 1130 cm^{-1} peak is attributed to C-O-C bands in the crosslinker.[25] For samples with CO_2 absorbed, shown in **Figure 3**B, the emergence of peaks at 1294 and 1636 cm^{-1} as well as an increase in intensity in the peak centred around 3400 cm^{-1} can be observed, which are attributed to the formation of carbamates as part of the absorption of CO_2 by amine groups and the absorption of water by the polymer respectively.[26]

CO_2 absorption capacities in DAC for each of the synthesised polymers are shown in **Figure 4**. From lowest to highest, CO_2 absorption capacities of 2.2, 2.5, 3.2, 3.9, 5.4 and 5.6 wt.% were achieved using CL-mXDA, CL-EtDA, CL-DAB, CL-HMD, CL-TETA and CL-DET polymers respectively. In all cases, the CO_2 absorption breakthrough curves (Figure S1A-F) for each material displays a sharp decrease in outlet CO_2 concentration at the beginning of measurement, which is attributed to the rapid absorption of CO_2 by the reactive amine groups in the materials. Generally, CO_2 absorption capacity correlates directly with the wt.% of diamine in each material, with the exceptions of the CL-mXDA and CL-DET.

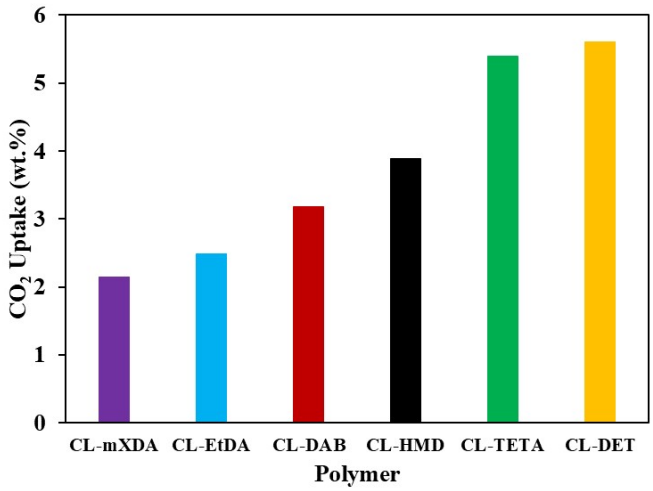

Figure 4 - *CO_2 absorption capacities for each of the synthesized polymers under DAC conditions.*

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In the case of the CL-DET, the increased CO_2 absorption capacity relative to its diamine wt.% is simply due to DET containing three amine groups as opposed to only two amine groups present in EtDA, DAB, HMD and mXDA. The superior performance of the CL-DET compared to CL-TETA (which contains four amine groups) is due to the use of technical-grade TETA. This grade includes isomers that are less reactive with CO_2, thereby slightly reducing the absorption capacity of CL-TETA. The aromatic benzene ring present in the CL-mXDA, which acts as an electron withdrawing group, may reduce the basicity of the amine groups in the polymer, thus reducing its reactivity in capturing CO_2 compared to other polymers. It is also possible that the aromatic ring has a hydrophobic effect and reduces water absorption of the polymer compared to the other polymer materials. Given the promoting effect of water on CO_2 absorption at low-moderate humidity acknowledged in the literature for amine-based sorbents,[27] this would then presumably also reduce CO_2 absorption capacity. For the CL-EtDA, CL-DAB and CL-HMD polymers, the increase in amine wt.% correlating with increased CO_2 capacity is contrary to what is expected, and is discussed further in depth in a later section.

3.2. Effect of amine chain length

For the CL-EtDA, CL-DAB and CL-HMD polymers increasing absorption capacity correlating with increasing diamine wt.% is contrary to what is expected, as an increase in wt.% of these diamines results in a decrease of effective amine groups per gram. Narku-Tetteh *et al.*'s study suggests that, ideally, an increase in alkyl chain length for alkanolamines should result in an increase in electron donating ability, and therefore higher CO_2 absorption.[28] In the same study however, it is noted that the effect of the increasing chain length is limited by differences in physical characteristics such as viscosity, density and interfacial tension.[28] This observation is supported by Singh *et al.*'s work where the CO_2 absorption capacity on a mol kg^{-1} basis (and thus a wt.% basis) for various alkanolamines as well as liquid EtDA, DAB and HMD decreases as alkyl chain length increases.[29] In the case of CL-EtDA, CL-DAB and CL-HMD, there is no liquid diamine present in the polymer structure and thus limiting factors such as viscosity and interfacial tension no longer apply, resulting in the observed increase in CO_2 absorption capacity due to increased electron donating ability from the longer alkyl chain lengths.

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In addition to greater electron donating ability, increased chain lengths for the amines could result in increased intermolecular spacing, facilitating CO_2 diffusion throughout the polymer matrix similar to the effect of water on PEI hydrogels as observed in Long *et al.*'s recent study.[30] Positron annihilation lifetime spectroscopy (PALS) results, presented in **Table 1**, reveal sub-nanometre free-volume regions (~0.5 nm) within the crosslinked polymer networks. These dynamic voids are partially solvated rather than dry pores, existing only in the swollen polymer mesh rather than as permanent cavities, and thus cannot be characterised by traditional porosity determinations such as BET. Liquids swell the polymer and are strongly hydrogen-bonded to the chains and immobilized, as evidenced by the absence of freezing transitions in DSC thermoporometry (Figure S2). Free-volume size is primarily governed by crosslinker properties (e.g. chain length), highlighting the role of network architecture in setting the characteristic spacing. The connectivity of these free-volume regions enables percolating diffusion of CO_2, which is defined here as transport through a connected network of dynamic free-volume regions, under operating conditions. This provides the relevant transport pathways for direct air capture, whereas conventional gas sorption on dried samples does not probe these pathways.

Table 1 - *Positron annihilation lifetime spectroscopy (PALS) results for CL-EtDA, CL-HMD and CL-mXDA for pore size determination.*

Polymer	**Intensity (I3)**	**Tau3 (ns)**	**Pore Diameter (nm)**
CL-EtDA	17.00 ± 0.16	2.255 ± 0.017	0.616 ± 0.003
CL-HMD	17.07 ± 0.12	2.330 ± 0.015	0.628 ± 0.002
CL-mXDA	15.15 ± 0.17	2.247 ± 0.017	0.614 ± 0.003

The PALS results further reveal the beneficial role of PEG within the polymer networks. Based on their diameters, PEG is unable to enter or block the "pores" of the polymers, similar to Himmelein *et al.*'s study wherein PEG is excluded from β-cyclodextrin pores of a similar size (~5.8 nm) .[31] Thus, rather than hindering, PEG likely compliments CO_2 absorption in these polymers, increasing amine efficiency by similar mechanisms previously observed for PEG containing amine sorbents.[32] Specifically, PEG intercalates the polymer chains spaces, swelling the polymer and granting increased CO_2 diffusion and amine distribution/access in the free volume "pore" network.[32] PEG may also assist in stabilisation of absorbed CO_2 species by ternary hydrogen-

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bonding interactions between amine groups, CO_2 and PEG, further promoting CO_2 absorption.[32] In cases where pore diameter is similar, amine reactivity dominates the absorption profile, as demonstrated by the CO_2 absorption differences between CL-EtDA and CL-mXDA observed previously.

3.3. Effect of crosslinker:amine ratio

To demonstrate the effect of the crosslinking ratio, additional materials were made by crosslinking TETA at 1:2, 1.25:2, 1.5:2 and 1:1 (2:2) crosslinker to amine ratios. As seen in **Figure 5**, there is a noticeable decrease in CO_2 capacity as the crosslinking ratio increases, with CO_2 absorption capacities of 3.2, 1.7, 1.0, and 0.3 wt.% achieved for the 1:2, 1.25:2, 1.5:2 and 1:1 ratio CL-TETA polymers respectively. This is due to the reduced amount of effective amine present per gram of material with higher crosslinker ratio, where increased TEP-MXDA during synthesis consumed more -NH and -NH_2 groups, reducing their presence in the resulting polymer and thus reducing CO_2 capacity. Increasing crosslinker ratio also resulted in physical differences, with higher crosslinker ratios producing polymers that were glassier, and sand like in nature after grinding, as opposed to the snow-like nature of the 0.75:2 ratio polymer. It is important to note, however, that while an increase in crosslinker ratio decreases absorption capacity, it also improves thermal stability. Also shown in **Figure 5**, the aged 1:2 ratio CL-TETA achieved a CO_2 absorption capacity of 2.9 wt.%, a reduction of only 8% compared to its pristine counterpart as opposed to the observed 25.6% reduction between the aged and pristine 0.75:2 CL-TETA in section 3.5 below.

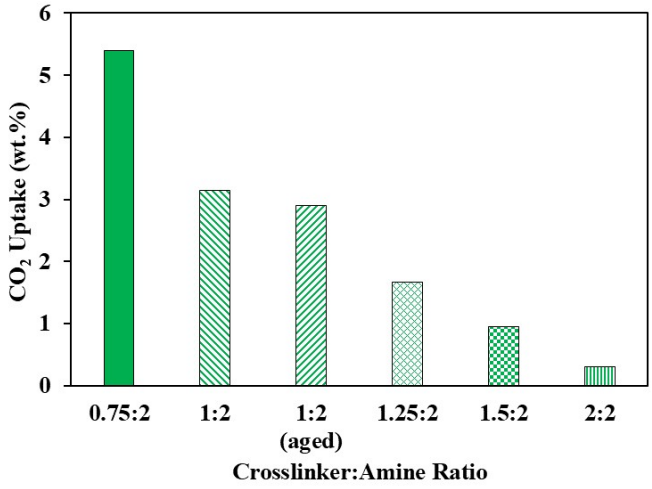

Figure 5 - *DAC CO_2 absorption capacities for different amine to crosslinker ratios of the CL-TETA polymers, as well as an aged counterpart of the 1:2 ratio CL-TETA polymer.*

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3.4. Effect of humidity on CO_2 absorption capacity

As previously mentioned, the absorption of water by polymers can have a beneficial synergistic effect on CO_2 absorption at low humidities. Therefore, amine-based polymers under moderately humid conditions display significantly greater absorption compared to dry conditions. To investigate the effect of humidity on the CO_2 absorption capacity of the polymers, DAC absorption experiments were performed on each of the pristine polymers using dry air without a humidifier column. Shown in **Figure 6**, dry CO_2 absorption capacities of 2.1, 0.9, 2.7, 3.1, 3.1 and 3.3 wt.% were achieved for the CL-mXDA, CL-EtDA, CL-DAB, CL-HMD, CL-TETA, and CL-DET polymers, respectively. As expected, most of the pristine polymers showed lower absorption capacities under dry conditions than under humid conditions, with reductions in capacity of 0.5, 62.3, 15.1, 20.3, 41.9 and 41.9 % for the CL-mXDA, CL-EtDA, CL-DAB, CL-HMD, CL-TETA, and CL-DET, respectively, compared to their absorption capacities with humidity. The CL-mXDA, however, achieved an increased CO_2 absorption capacity under dry conditions compared to humid conditions, indicating there is actually a negative effect of humidity on the capacity of CL-mXDA polymer absorbing CO_2. This can be understood by the hydrophobic nature of mXDA, which repels water to form clusters being confined within the polymer network, and thus limiting diffusion of CO_2 to the amine sites. Such confinement was observed by the depression of the freezing point of these water clusters to -19.4°C, , as revealed by the large exothermic peak in the DSC curves in Figure S2. [33]

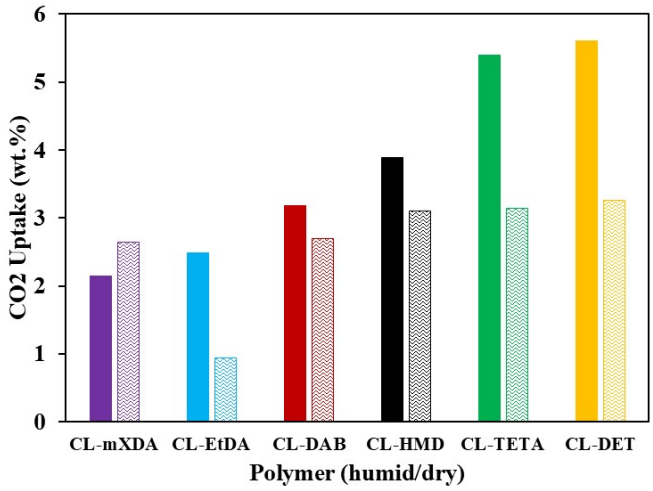

Figure 6 *- CO_2 absorption capacities of each of the polymers under humid (left/solid columns) and dry (right/striped columns) DAC conditions.*

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3.5. Sorbent performance under accelerated ageing conditions

As with most gas capture applications, recyclability of the sorbent is critical to ensuring viability of the sorbent performance under multiple, repeated, realistic sorption and desorption cycles. To investigate the stability of the sorbents, each polymer was subjected to an accelerated ageing process, which involved heating the sorbents to 75°C in air for 24 hours to "age" the polymer. Afterwards, they were tested for their CO_2 absorption capacity after ageing. **Figure 7** shows the aged polymers CO_2 absorption capacities, which were 1.6, 2.1, 2.6, 2.8, 4 and 2.9 wt.% for the CL-mXDA, CL-EtDA, CL-DAB, CL-HMD, CL-TETA and CL-DET, respectively. In all cases, the aged polymers display decreased absorption capacities compared to their pristine counterparts, with 26.5, 14.9, 18.2, 28.3, 25.6 and 48.1 % reductions in capacity observed for the CL-mXDA, CL-EtDA, CL-DAB, CL-HMD, CL-TETA and CL-DET aged polymers, respectively.

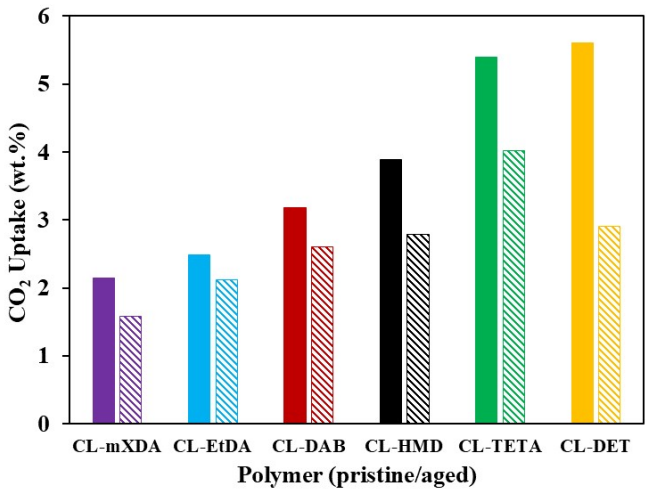

Figure 7 - *CO_2 absorption capacities for each of the pristine and aged polymers under DAC conditions. For each amine, the pristine polymer is shown on the left (solid columns) and the aged polymer is shown on the right (striped columns).*

To determine the cause of reduction in capture capacity post ageing, a series of FT-IR spectra, shown in Figure 8A, were obtained for CL-TETA before and after exposure to several conditions. Figure 8B displays the appearance of several new peaks at 1636, 1568 and 1294 cm^{-1} after DAC, and these peaks disappeared after regeneration. This suggests the formation of new species during DAC, which are reversible upon heating, consistent with the formation of carbamates and

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bicarbonates.[26, 34, 35] However, non-reversible species were generated during the ageing process as shown in Figure 8C. A new peak at 1662 cm^{-1} is observed for the aged CL-TETA, which remained after the same regeneration process. This peak corresponds to functional groups of C=O and/or C=N stretch, which are associated with oxidative species formed during ageing. As these species are formed at the expense of consuming amine groups and are irreversible, they cause permanent degradation in capture capacity to amine-based sorbents. [34, 35, 36] It should be noted the same peak is also observed for other aged samples as shown in Figure S3.

It is understood that urea formation can be another degradation pathway for amine-based sorbent. CL-TETA was thus aged at 110°C under CO_2 for 24 hours to investigate whether urea could form under such conditions. As shown in Figure 8D, new peaks at 1570 and 1294 cm^{-1} were observed after ageing, and these peaks subsequently disappeared after regenerating the CO_2-aged sample at 75°C for 1 hour in air. This indicates the newly formed species are thermally reversible, conforming with the species generated during DAC. Urea formation is unlikely even under CO_2-rich conditions, and thus would not occur during the DAC and ageing processes. Oxidation is therefore considered the primary degradation pathway of the polymer.

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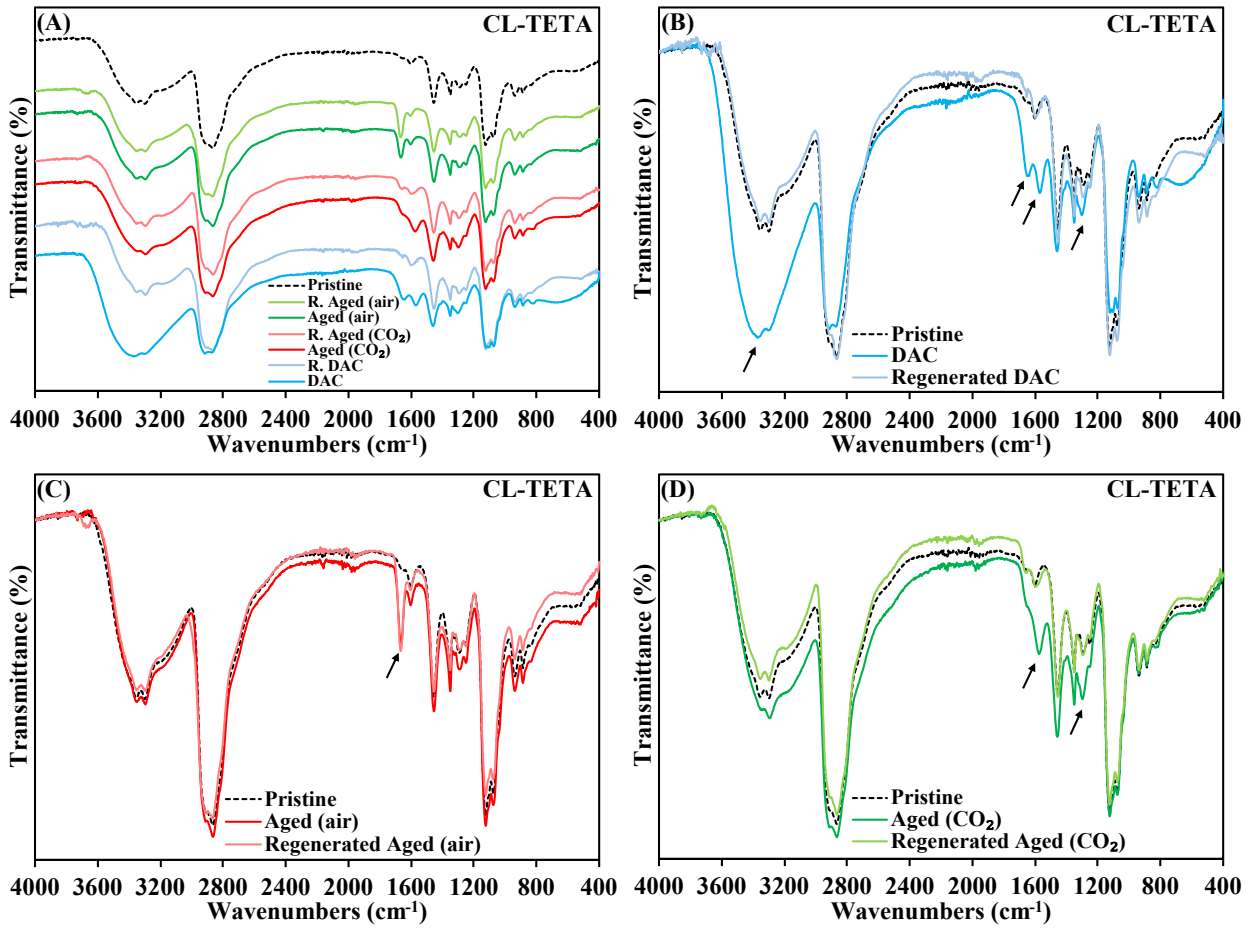

Figure 8 *– FT-IR spectra comparisons of (A) pristine CL-TETA before and after exposure to various conditions to elucidate the polymer degradation mechanism. Additional baseline normalised FT-IR spectra depict comparisons of pristine CL-TETA (black) to: (B) CL-TETA post-DAC (blue) and post-DAC regeneration (light blue); (C) CL-TETA post accelerated ageing in air at 75°C for 24 hours (red) and subsequent regeneration at 75°C in air (light red); and (D) CL-TETA post accelerated ageing in CO_2 at 110°C for 24 hours (green) and subsequent regeneration at 75°C in air (light green). Arrows indicate peaks pertinent to the degradation mechanism discussion above.*

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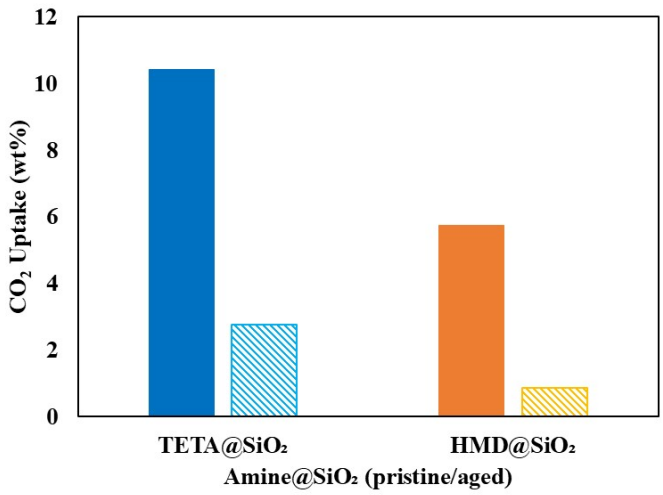

Figure 9 - *CO_2 absorption capacities for pristine and aged TETA (blue) and HMD (orange) supported on SiO_2 at a 1:1 amine:SiO_2 mass ratio under DAC conditions. The pristine materials are shown on the left (solid columns) and the aged materials shown on the right (striped columns).*

Under the accelerated ageing conditions, the polymers are subjected to 24 hours of high temperature heating in air which is approximately equivalent to 145 absorption/desorption cycles when performing 10-minute desorption cycles on a TGA (i.e. 10 min desorption x 145 cycles ≈ 24 hours). Although reductions in CO_2 capacity were observed for the aged polymers, it is important to note that the stability of these crosslinked polymers would be significantly improved if vacuum is applied for a practical temperature/vacuum swing absorption.

To further demonstrate the viability of small amine-based solid polymer sorbent, silica-supported composites TETA@SiO_2 and HMD@SiO_2 were made and analysed for their absorption capacities before and after ageing. As can be seen in **Figure 9**, CO_2 absorption capacities of 10.4 and 5.8 wt.% were achieved for TETA@SiO_2 and HMD@SiO_2, respectively, while absorption capacities of only 2.8 and 0.9 wt.% were achieved for their respective aged counterparts. This corresponds to a substantial reduction in absorption capacity of 73.5% and 84.9 % for supported TETA@SiO_2 and HMD@SiO_2, respectively, and is significantly greater than that of the crosslinked polymers (CL-TETA and CL-HMD were 25.6% and 28.3%, respectively).

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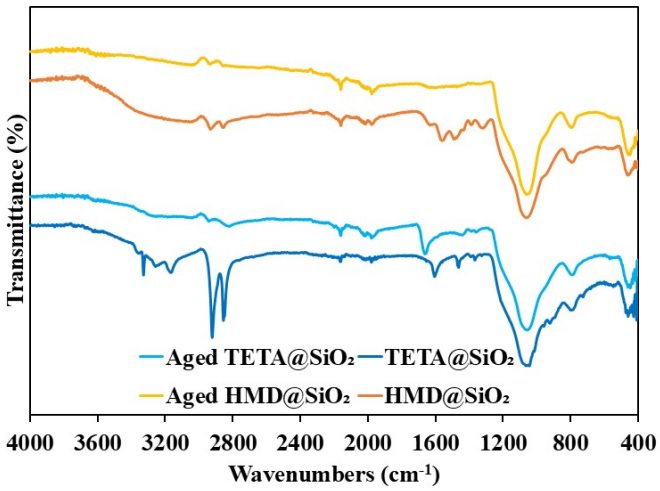

Figure 10 - *FT-IR spectra comparing the pristine and aged TETA@SiO_2 and HMD@SiO_2 materials. From top to bottom the respective spectra represent the aged HMD@SiO_2, pristine HMD@SiO_2, aged TETA@SiO_2 and pristine TETA@SiO_2.*

The large reductions in capacity for the silica-supported materials are due to the physical characteristics of the diamines. For TETA@SiO_2, the volatility of TETA causes it to evaporate during the ageing procedure and under air flow during the DAC absorption experiment. Additionally, the TETA that remains in the silica appears to oxidise, as evidenced by the emergence of a peak at 1656 cm^{-1}, which can be attributed to the formation of C=O and C=N. [34] In contrast, HMD is a solid a room temperature, and likely leaches or evaporates from the silica pores when heated, rendering it incapable of CO_2 absorption. This is reflected in the FT-IR spectra in **Figure 10**, where for both silica-supported amines, there is a complete disappearance of the peaks associated with the amines in the aged samples. Though not included here, it is reasonable to assume that the other amines would perform similarly when supported on silica. These results concretely demonstrate the improvements made to the usability of the volatile diamines by their conversion into crosslinked polymers. When also considering the relatively harsh conditions of the ageing process compared to lower temperature, lower duration vacuum swing desorption conditions used in industry, it is reasonable to claim that the crosslinked polymers would display a high degree of stability.

3.6. Determination of desorption temperature

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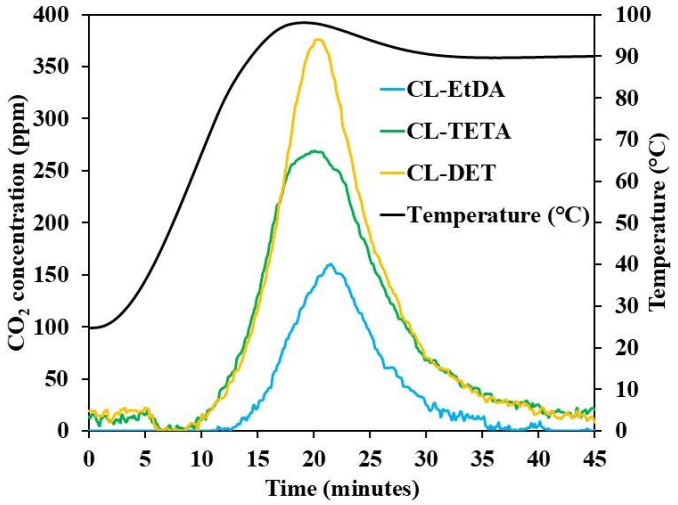

Figure 11 - *TGA-MS data showing desorption of CO_2 for the CL-EtDA (bottom, blue), CL-TETA (middle, green) and CL-DET (top, yellow) over a 45-minute duration and a temperature range (black curve) of 25 – 100°C.*

TGA-MS experiments were conducted to determine the temperature at which CO_2 was desorbed from the crosslinked materials. As shown in **Figure 11**, desorption of CO_2 for each of the materials began after 10 minutes at approximately 65℃, as indicated by the sharp increase in CO_2 concentration observed at that time and temperature. The CO_2 concentration peaked around 20-minute mark, suggesting most of the CO_2 can be released within 10 minutes. It should be noted that TGA desorption utilises milligrams of material and occurs under a stripping gas, however, 5 g of polymer samples were used for the actual DAC measurements, and thus the degassing was conducted at 75°C in air (no stripping gas) for 1.5 h to ensure complete CO_2 and moisture desorption prior to experiments. Importantly, the CO_2 desorption temperature of these materials is relatively low, especially compared to that of ethanolamines (120℃) and aqueous hydroxides (900℃), and thus requires a smaller energy investment for desorption of CO_2, which is ideal for DAC applications. However, the lower desorption temperature may be offset in large-scale processes by energetic requirements associated with stripping gasses/vacuum or downstream mechanical CO_2 compression for transport.[37] Traditional ethanolamine scrubbing processes perform desorption under high temperature and pressure to avoid such penalties,[37] and thus further comparative investigations are warranted to determine the actual energetic investment of desorption for these polymers in large-scale industrial deployment scenarios.

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3.7. Principles of green chemistry and comparisons to literature

Crosslinking amines to form solid CO_2 absorbents is a common practice, and discussions surrounding such materials primarily focus only on comparisons of absorption performance. For materials concerning environmental remediation applications, such as DAC of CO_2, adherence to the principles of green chemistry is imperative to ensure any negative environmental impacts from their synthesis, degradation or utilisation does not outweigh their benefit. In short, adherence to the twelve principles includes; 1) preventing waste, 2) maximising atomic efficiency, 3) reducing synthesis hazards, 4) ensuring safe products, 5) ensuring safe reaction conditions, 6) maximising energy efficiency, 7) utilising green feedstocks, 8) minimising derivatives, 9) utilising catalysts, 10) designing products with green degradation, 11) real time synthesis pollution monitoring and 12) minimising potential for accidents.[38]

For this study, in line with principles 1-6, 8, 11 and 12, the synthesis of the crosslinked polymers utilises a room temperature process wherein all reactants are incorporated into a minimally hazardous product. The incorporation of Na_3PO_4 is considered beneficial here as its presence in the polymers acts as a chelating agent to reduce potential metal-catalysed degradation reactions, increasing regenerability without impeding CO_2 absorption. Likewise, the use of PEG over MDEA improves upon the previous study[25] by minimising synthesis hazards while complimenting CO_2 absorption as discussed above. The short-chain amines utilised here are waste-, by- or co- products of other industrial processes.[39] Unlike TEPA or PEI in previous studies,[12-15] they are demonstrably unviable for DAC of CO_2 by vectors such as SiO_2 templating. Therefore, via the synthetic process utilised in this work, these amines are relatively "green" feedstocks for principle 7. Finally, in line with principle 9, the ring opening reaction from epoxy crosslinking is both catalysed by the -OH groups in PEG and auto-catalysed by the -OH groups generated by the reaction.[40] Thus, since the long-term degradative products (principle 10) are not explored in this study, the polymers and procedures in this study currently adhere to at least 11 of the 12 principles and can thus be considered "green" .[38]

Table 2 - *Comparison of CO_2 uptake performance, amine loading and experimental conditions of the CL-DET and CL-mXDA polymers from this study to similar materials from literature.*

Material	Amine Loading (wt.%)	Absorption conditions	CO_2 uptake (wt.%)	Source

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TEPA@G-10 Silica	30	TGA, 25°C, dry 400ppm CO_2 in N_2.	6.6	[41]
TEPA@SBA-15	25	TGA, 25°C, dry 400ppm CO_2 in N_2.	3.9	[42]
TEPA-MXDA	57	Break-through column, 25°C, 25% RH, 420ppm CO_2 in compressed air.	6.2	[25]
PEI@SBA-15	50	TGA, 25°C, dry 400ppm CO_2 in N_2.	4.6	[43]
PEI@SBA-15	25	TGA, 25°C, dry 400ppm CO_2 in N_2.	3.2	[42]
PEI Snow	30	G2201-i Isotopic Analyzer, pumped ambient laboratory air.	5.2	[44]
DET@HCP	11.6	3Flex volumetric analyzer, 25°C, dry 100% CO_2 (DAC measurement taken from absorption at P = 0.04 kPa).	1.9	[45]
COF-999	-	Break-through column, 25% RH, 400ppm CO_2 in bal. air.	7.4	[9]
Lewatit VP OC 1065 Resin	-	Break-through column, 25°C, 25% RH, 420ppm CO_2 in compressed air.	8.1	[11]
IRA-900-C Resin	-	Break-through column, 25°C, 20% RH, 420ppm CO_2 in compressed air.	8.4	[46]
CL-DET	21	Break-through column, 25°C, 25% RH, 420ppm CO_2 in compressed air.	5.6	This study.
CL-mXDA	25	Break-through column, 25°C, 25% RH, 420ppm CO_2 in compressed air.	2.2	This study.

Comparisons to literature are often difficult for DAC materials due to differences in amine loading, amine choice and experimental absorption conditions/equipment. Nonetheless, For this study, in line with principles 1-6, 8, 11 and 12, the synthesis of the crosslinked polymers utilises a room temperature process wherein all reactants are incorporated into a minimally hazardous product. The incorporation of Na3PO4 is considered beneficial here as its presence in the polymers acts as a chelating agent to reduce potential metal-catalysed degradation reactions, increasing regenerability without impeding CO2 absorption. Likewise, the use of PEG over MDEA improves upon the previous study25 by minimising synthesis hazards while complimenting CO2 absorption

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as discussed above. The short-chain amines utilised here are waste-, by- or co- products of other industrial processes.[39] Unlike TEPA or PEI in previous studies,[12-15] they are demonstrably unviable for DAC of CO2 by vectors such as SiO2 templating. Therefore, via the synthetic process utilised in this work, these amines are relatively "green" feedstocks for principle 7. Finally, in line with principle 9, the ring opening reaction from epoxy crosslinking is both catalysed by the -OH groups in PEG and auto-catalysed by the -OH groups generated by the reaction.[40] Thus, since the long-term degradative products (principle 10) are not explored in this study, the polymers and procedures in this study currently adhere to at least 11 of the 12 principles and can thus be considered "green" .[38]

Table 2 displays a comparison of CL-DET and CL-mXDA, the best and worst performing materials in this study respectively, to materials of a similar nature from the literature, with experimental conditions as close to those in this study as possible.[9, 11, 25, 41-46] Overall, CL-DET and CL-mXDA (and thus the other polymers) display competitive absorption capacities relative to other materials, particularly supported amines such as the silica supported PEI and TEPA which generally possess absorption capacities between 3.2-6.6 wt.% .[41-43] Notably, CL-DET outperforms the HCP supported DET significantly, though this could be attributed to differences in amine loading or experimental conditions.[45] Additionally, the exceptional "greenness" of the CL-DET and CL-mXDA (and other polymers) makes them attractive sorbents for DAC even in the context of higher performing materials such as COF-999 or the Lewatit VP OC 1095 and IRA-900-C resins.[9, 11, 46]

4. Conclusions

Short chain amines are cheap and commercially available but are underutilised for DAC of atmospheric CO_2, largely due to their corrosivity, volatility and instability over several regeneration cycles, among other drawbacks. In this work, we have provided an effective method for utilisation of the short chain amines mXDA, EtDA, DAB, HMD, TETA and DET via crosslinking with TEP-MXDA into solid polymer sorbents that can achieve plausible CO_2 absorption in DAC, with the highest being 5.6 wt.%.

Furthermore, this study provides valuable insights into the effect of amine chain length on CO_2 absorption capacity. For the CL-EtDA, CL-DAB and CL-HMD polymers, we observed an inverse

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relationship between CO_2 absorption capacity and the number of available amine sites. Because technical-grade TETA was used, a like-for-like comparison between CL-DET and CL-TETA is constrained. Nevertheless, our DAC results indicate it is likely worthwhile to investigate how amine chain length affects porosity and CO_2 absorption capacity in other solid crosslinked sorbents.

Importantly, the crosslinked reaction is from a simple procedure under ambient conditions and produces no by-products during synthesis. The resulting solid polymers are not corrosive and are ready for effective and immediate usage upon reaction completion. Additionally, the polymers display significantly higher stability compared to silica-supported versions of the TETA and HMD amines, which can be even further improved by optimisation of the crosslinker ratio as well as application of vacuum swing. Combined, these ideal "green" qualities indicate the promising potential for these crosslinked polymers as effective DAC sorbents, and their ability to utilise cheap, readily available short-chain amines that would be otherwise unviable for DAC applications.

Acknowledgements

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Authors contributions

Z. Wan and C.D. Wood conceived the research idea. E. Adam conducted the sorbents synthesis, carried out the performance assessment, collected and analysed data. D. Acharya conducted the PALS analysis and helped assisted data interpretation. W. Tian performed the thermoporometry and assisted data analysis. E. Adam prepared the initial draft with suggestions and revisions from Z. Wan, A. Arami-Niya and C.D. Wood, and finalised the manuscript with Z. Wan for submission.

Competing interests

The authors declare no competing interests.

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References

(1) Lee, H.; Calvin, K.; Dasgupta, D.; Krinner, G.; Mukherji, A.; Thorne, P. W.; Trisos, C.; Romero, J.; Aldunce, P.; Barrett, K.; et al. **2023**. DOI: 10.59327/ipcc/ar6-9789291691647.

(2) Armstrong McKay, D. I.; Staal, A.; Abrams, J. F.; Winkelmann, R.; Sakschewski, B.; Loriani, S.; Fetzer, I.; Cornell, S. E.; Rockström, J.; Lenton, T. M. Exceeding 1.5°C global warming could trigger multiple climate tipping points. *Science* **2022**, *377* (6611), eabn7950. DOI: doi:10.1126/science.abn7950.

(3) Lackner, K. S. The thermodynamics of direct air capture of carbon dioxide. *Energy* **2013**, *50*, 38-46. DOI: https://doi.org/10.1016/j.energy.2012.09.012.

(4) Bouaboula, H.; Chaouki, J.; Belmabkhout, Y.; Zaabout, A. Comparative review of Direct air capture technologies: From technical, commercial, economic, and environmental aspects. *Chemical Engineering Journal* **2024**, *484*, 149411. DOI: https://doi.org/10.1016/j.cej.2024.149411. Xu, H.; Yu, L.; Chong, C.; Wang, F. A comprehensive review on direct air carbon capture (DAC) technology by adsorption: From fundamentals to applications. *Energy Conversion and Management* **2024**, *322*, 119119. DOI: https://doi.org/10.1016/j.enconman.2024.119119.

(5) Sanz-Pérez, E. S.; Murdock, C. R.; Didas, S. A.; Jones, C. W. Direct Capture of CO2 from Ambient Air. *Chemical Reviews* **2016**, *116* (19), 11840-11876. DOI: 10.1021/acs.chemrev.6b00173.

(6) Ma, M.; Zhou, A.; Hong, T.; Jia, X.; Liu, M. Tailored porous structure and CO2 adsorption capacity of Mg-MOF-74 via solvent polarity regulation. *Chemical Engineering Journal* **2023**, *476*, 146845. DOI: https://doi.org/10.1016/j.cej.2023.146845.

(7) Zuluaga, S.; Fuentes-Fernandez, E. M. A.; Tan, K.; Xu, F.; Li, J.; Chabal, Y. J.; Thonhauser, T. Understanding and controlling water stability of MOF-74. *Journal of Materials Chemistry A* **2016**, *4* (14), 5176-5183, 10.1039/C5TA10416E. DOI: 10.1039/C5TA10416E. Tan, K.; Zuluaga, S.; Gong, Q.; Gao, Y.; Nijem, N.; Li, J.; Thonhauser, T.; Chabal, Y. J. Competitive Coadsorption of CO2 with H2O, NH3, SO2, NO, NO2, N2, O2, and CH4 in M-MOF-74 (M = Mg, Co, Ni): The Role of Hydrogen Bonding. *Chemistry of Materials* **2015**, *27* (6), 2203-2217. DOI: 10.1021/acs.chemmater.5b00315.

(8) Than-ardna, B.; Hiranphinyophat, S.; Matsumoto, M.; Meeyoo, V.; Kitiyanan, B. Synthesized structure of Mg-MOF-74 decorated on ZIF-8 as solid adsorbent for CO2 capture. *Resources Chemicals and Materials* **2025**, *4* (3), 100116. DOI: https://doi.org/10.1016/j.recm.2025.100116.

(9) Zhou, Z.; Ma, T.; Zhang, H.; Chheda, S.; Li, H.; Wang, K.; Ehrling, S.; Giovine, R.; Li, C.; Alawadhi, A. H.; et al. Carbon dioxide capture from open air using covalent organic frameworks. *Nature* **2024**, *635* (8037), 96-101. DOI: 10.1038/s41586-024-08080-x.

(10) Alesi, W. R., Jr.; Kitchin, J. R. Evaluation of a Primary Amine-Functionalized Ion-Exchange Resin for CO2 Capture. *Industrial & Engineering Chemistry Research* **2012**, *51* (19), 6907-6915. DOI: 10.1021/ie300452c.

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(11) Hunt, R.; Gillbanks, J.; Czapla, J.; Wan, Z.; Karmelich, C.; White, C.; Wood, C. Representative longevity testing of direct air capture materials. *Chemical Engineering Journal* **2024**, *481*, 148901. DOI: 10.1016/j.cej.2024.148901.

(12) Kyselová, V.; Havlín, J.; Ciahotný, K. Preparation and Testing of Polyethylenimine-Impregnated Silica Gel for CO2 Capture. In *Gels*, 2024; Vol. 10.

(13) Priyadarshini, P.; Rim, G.; Rosu, C.; Song, M.; Jones, C. W. Direct Air Capture of CO2 Using Amine/Alumina Sorbents at Cold Temperature. *ACS Environmental Au* **2023**, *3* (5), 295-307. DOI: 10.1021/acsenvironau.3c00010.

(14) Toh-ae, P.; Timasart, N.; Tumnantong, D.; Bovornratanaraks, T.; Poompradub, S. Utilization of waste tire derived activated carbon as CO2 capture and photocatalyst for CO2 conversion. *Scientific Reports* **2024**, *14* (1), 17100. DOI: 10.1038/s41598-024-67631-4.

(15) Kumar, R.; Ohtani, S.; Tsunoji, N. Direct air capture on amine-impregnated FAU zeolites: Exploring for high adsorption capacity and low-temperature regeneration. *Microporous and Mesoporous Materials* **2023**, *360*, 112714. DOI: https://doi.org/10.1016/j.micromeso.2023.112714.

(16) Sakwa-Novak, M. A.; Jones, C. W. Steam Induced Structural Changes of a Poly(ethylenimine) Impregnated γ-Alumina Sorbent for CO2 Extraction from Ambient Air. *ACS Applied Materials & Interfaces* **2014**, *6* (12), 9245-9255. DOI: 10.1021/am501500q.

(17) Keith, D. W.; Holmes, G.; St. Angelo, D.; Heidel, K. A Process for Capturing CO₂ from the Atmosphere. *Joule* **2018**, *2* (8), 1573-1594. DOI: 10.1016/j.joule.2018.05.006 (acccessed 2025/05/25).

(18) Khan, T.; Pervaiz, S.; Qadir, D.; Suleman, H.; Shamair, Z.; Ahmad, F. Alkaline salts of L-lysine as green solvents for direct air capture: Characterisation and performance analysis. *Journal of Environmental Chemical Engineering* **2025**, *13* (2), 115751. DOI: https://doi.org/10.1016/j.jece.2025.115751.

(19) Abdellah, M. H.; Kiani, A.; Conway, W.; Puxty, G.; Feron, P. The effects of counter ion on CO2 capture performance of amino acid salt solutions for direct air capture applications. *Separation and Purification Technology* **2025**, *358*, 130390. DOI: https://doi.org/10.1016/j.seppur.2024.130390.

(20) Huang, Q.; Thompson, J.; Lampe, L. M.; Selegue, J. P.; Liu, K. Thermal Degradation Comparison of Amino Acid Salts, Alkanolamines and Diamines in CO2 Capture. *Energy Procedia* **2014**, *63*, 1882-1889. DOI: https://doi.org/10.1016/j.egypro.2014.11.197.

(21) Rochelle, G. T. Amine Scrubbing for CO2 Capture. *Science* **2009**, *325* (5948), 1652-1654. DOI: 10.1126/science.1176731 (acccessed 2025/05/25). Kay, J. P.; Jensen, M. D.; Fiala, N. J. Pilot-scale Evaluations of Advanced Solvents for Postcombustion CO2 Capture. *Energy Procedia* **2014**, *63*, 1903-1910. DOI: https://doi.org/10.1016/j.egypro.2014.11.199.

(22) Mullen, D.; Braakhuis, L.; Knuutila, H. K.; Gibbins, J.; Lucquiaud, M. Monoethanolamine Degradation Rates in Post-combustion CO2 Capture Plants with the Capture of 100% of the Added CO2.

Green Chemistry Accepted Manuscript

View Article Online
DOI: 10.1039/D5GC06981E

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Industrial & Engineering Chemistry Research **2024**, *63* (31), 13677-13691. DOI: 10.1021/acs.iecr.4c01525.

(23) Mao, H.; Tang, J.; Day, G. S.; Peng, Y.; Wang, H.; Xiao, X.; Yang, Y.; Jiang, Y.; Chen, S.; Halat, D. M.; et al. A scalable solid-state nanoporous network with atomic-level interaction design for carbon dioxide capture. *Science Advances 8* (31), eabo6849. DOI: 10.1126/sciadv.abo6849 (acccessed 2025/05/25).

(24) Li, Y.; Gao, J.; Li, J.; Li, Y.; Bernards, M. T.; Tao, M.; He, Y.; Shi, Y. Screening and Performance Evaluation of Triethylenetetramine Nonaqueous Solutions for CO2 Capture with Microwave Regeneration. *Energy & Fuels* **2020**, *34* (9), 11270-11281. DOI: 10.1021/acs.energyfuels.0c02006. Tzirakis, F.; Papadopoulos, A. I.; Seferlis, P.; Tsivintzelis, I. CO2 Solubility in diethylenetriamine (DETA) and triethylenetetramine (TETA) aqueous mixtures: Experimental investigation and correlation using the CPA equation of state. *Chemical Thermodynamics and Thermal Analysis* **2021**, *3-4*, 100017. DOI: https://doi.org/10.1016/j.ctta.2021.100017. Liu, F.; Jing, G.; Zhou, X.; Lv, B.; Zhou, Z. Performance and Mechanisms of Triethylene Tetramine (TETA) and 2-Amino-2-methyl-1-propanol (AMP) in Aqueous and Nonaqueous Solutions for CO2 Capture. *ACS Sustainable Chemistry & Engineering* **2018**, *6* (1), 1352-1361. DOI: 10.1021/acssuschemeng.7b03717. Zhou, S.; Chen, X.; Nguyen, T.; Voice, A. K.; Rochelle, G. T. Aqueous Ethylenediamine for CO2 Capture. *ChemSusChem* **2010**, *3* (8), 913-918. DOI: https://doi.org/10.1002/cssc.200900293 (acccessed 2025/05/25).

(25) Wan, Z.; Hunt, R.; White, C.; Gillbanks, J.; Czapla, J.; Xiao, G.; Surin, S.; Wood, C. Facile Synthesis of Self-Supported Solid Amine Sorbents for Direct Air Capture. *ChemSusChem* **2024**, *17* (18), e202400212. DOI: https://doi.org/10.1002/cssc.202400212 (acccessed 2025/05/25).

(26) Yang, D.; Lv, M.; Chen, J. Efficient non-aqueous solvent formed by 2-piperidineethanol and ethylene glycol for CO2 absorption. *Chemical Communications* **2019**, *55* (83), 12483-12486, 10.1039/C9CC06320J. DOI: 10.1039/C9CC06320J.

(27) Hua, J.; Shen, X.; Jiao, X.; Lin, H.; Li, G.; Sun, X.; Yan, F.; Wu, H.; Zhang, Z. Direct air capture of CO2 by amine-impregnated resin: The effect of resin pore structure and humid conditions. *Carbon Capture Science & Technology* **2024**, *12*, 100237. DOI: https://doi.org/10.1016/j.ccst.2024.100237. Rim, G.; Song, M.; Proaño, L.; Ghaffari Nik, O.; Parker, S.; Lively, R. P.; Jones, C. W. Humidity Effects on Sub-Ambient Direct Air Capture of CO2 with Amine Functionalized Mg-Al LDHs and MMOs. *ACS ES&T Engineering* **2025**, *5* (1), 204-214. DOI: 10.1021/acsestengg.4c00503. Hou, C.; Chen, J.; Lai, Z.; Zhang, K.; Lv, H.; Ding, L. Study on the Roles of Water in Solid Amine-Based Direct Air Capture of CO2. *E3S Web of Conf.* **2023**, *406*, 10.1051/e3sconf/202340602042.

(28) Narku-Tetteh, J.; Muchan, P.; Idem, R. Effect of alkanol chain length of primary alkanolamines and alkyl chain length of secondary and tertiary alkanolamines on their CO2 capture activities. *Separation and Purification Technology* **2017**, *187*, 453-467. DOI: https://doi.org/10.1016/j.seppur.2017.07.004.

Green Chemistry Accepted Manuscript

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(29) Singh, P.; Niederer, J. P. M.; Versteeg, G. F. Structure and activity relationships for amine based CO2 absorbents—I. *International Journal of Greenhouse Gas Control* **2007**, *1* (1), 5-10. DOI: https://doi.org/10.1016/S1750-5836(07)00015-1.

(30) Long, Y.; Jiang, J.; Rohlfs, W.; Brilman, W.; Visser, C. W. Optimization of amine-based hydrogel sorbents for CO2 capture: The role of crosslinkers. *Polymer Testing* **2025**, *153*, 109017. DOI: https://doi.org/10.1016/j.polymertesting.2025.109017.

(31) Himmelein, S.; Sporenberg, N.; Schönhoff, M.; Ravoo, B. J. Size-Selective Permeation of Water-Soluble Polymers through the Bilayer Membrane of Cyclodextrin Vesicles Investigated by PFG-NMR. *Langmuir* **2014**, *30* (14), 3988-3995. DOI: 10.1021/la500226z.

(32) Moon, H. J.; Carrillo, J.-M. Y.; Song, M.; Rim, G.; Heller, W. T.; Leisen, J.; Proaño, L.; Short, G. N.; Banerjee, S.; Sumpter, B. G.; et al. Underlying Roles of Polyol Additives in Promoting CO2 Capture in PEI/Silica Adsorbents. *ChemSusChem* **2024**, *17* (22), e202400967. DOI: https://doi.org/10.1002/cssc.202400967 (acccessed 2026/05/26).

(33) Majda, D.; Makowski, W.; Mańko, M. Pore size distribution of micelle-templated silicas studied by thermoporosimetry using water and n-heptane. *Journal of Thermal Analysis and Calorimetry* **2012**, *109* (2), 663-669. DOI: 10.1007/s10973-012-2372-9.

(34) Srikanth, C. S.; Chuang, S. S. C. Spectroscopic Investigation into Oxidative Degradation of Silica-Supported Amine Sorbents for CO2 Capture. *ChemSusChem* **2012**, *5* (8), 1435-1442. DOI: https://doi.org/10.1002/cssc.201100662 (acccessed 2025/06/18). Vu, Q. T.; Yamada, H.; Yogo, K. Oxidative Degradation of Tetraethylenepentamine-Impregnated Silica Sorbents for CO2 Capture. *Energy & Fuels* **2019**, *33* (4), 3370-3379. DOI: 10.1021/acs.energyfuels.8b04307.

(35) Zhao, S.; Zhang, Y.; Li, L.; Feng, J.; Qiu, W.; Ning, Y.; Huang, Z.; Lin, H. Degradation of amine-functionalized adsorbents in carbon capture and direct air capture applications: Mechanism and solutions. *Separation and Purification Technology* **2025**, *354*, 129586. DOI: https://doi.org/10.1016/j.seppur.2024.129586.

(36) Sayari, A.; Belmabkhout, Y. Stabilization of Amine-Containing CO2 Adsorbents: Dramatic Effect of Water Vapor. *Journal of the American Chemical Society* **2010**, *132* (18), 6312-6314. DOI: 10.1021/ja1013773.

(37) Warudkar, S. S.; Cox, K. R.; Wong, M. S.; Hirasaki, G. J. Influence of stripper operating parameters on the performance of amine absorption systems for post-combustion carbon capture: Part I. High pressure strippers. *International Journal of Greenhouse Gas Control* **2013**, *16*, 342-350. DOI: https://doi.org/10.1016/j.ijggc.2013.01.050. Tatarczuk, A.; Tańczyk, M.; Więcław-Solny, L.; Zdeb, J. Pilot plant results of amine-based carbon capture with heat integrated stripper. *Applied Energy* **2024**, *367*, 123416. DOI: https://doi.org/10.1016/j.apenergy.2024.123416.

Green Chemistry Accepted Manuscript

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(38) Krasnodębski, M. The bumpy road to sustainability: Reassessing the history of the twelve principles of green chemistry. *Studies in History and Philosophy of Science* **2024**, *103*, 85-94. DOI: https://doi.org/10.1016/j.shpsa.2023.12.001.

(39) Eller, K.; Henkes, E.; Rossbacher, R.; Höke, H. Amines, Aliphatic. In *Ullmann's Encyclopedia of Industrial Chemistry*, 2000.

(40) Jayan, J. S.; Saritha, A.; Deeraj, B. D. S.; Joseph, K. Role of Polyethylene Glycol as a Catalyst and a Filler in Epoxy Systems. *Topics in Catalysis* **2024**, *67* (1), 218-231. DOI: 10.1007/s11244-023-01859-8.

(41) Ahmadian Hosseini, A.; Jahandar Lashaki, M. A comprehensive evaluation of amine-impregnated silica materials for direct air capture of carbon dioxide. *Separation and Purification Technology* **2023**, *325*, 124580. DOI: https://doi.org/10.1016/j.seppur.2023.124580.

(42) Miao, Y.; He, Z.; Zhu, X.; Izikowitz, D.; Li, J. Operating temperatures affect direct air capture of CO2 in polyamine-loaded mesoporous silica. *Chemical Engineering Journal* **2021**, *426*, 131875. DOI: 10.1016/j.cej.2021.131875.

(43) Miao, Y.; Wang, Y.; Zhu, X.; Chen, W.; He, Z.; Yu, L.; Li, J. Minimizing the effect of oxygen on supported polyamine for direct air capture. *Separation and Purification Technology* **2022**, *298*, 121583. DOI: https://doi.org/10.1016/j.seppur.2022.121583.

(44) Xu, X.; Myers, M. B.; Versteeg, F. G.; Pejcic, B.; Heath, C.; Wood, C. D. Direct air capture (DAC) of CO2 using polyethylenimine (PEI) "snow": a scalable strategy. *Chemical Communications* **2020**, *56* (52), 7151-7154, 10.1039/D0CC02572K. DOI: 10.1039/D0CC02572K.

(45) Spreng, T. L.; Danaci, D.; Ram, P. D.; Williams, D. R.; Pini, R.; Petit, C. Amine-Appended Hyper-Crosslinked Polymers for Direct Air Capture of CO2. *ACS Sustainable Chemistry & Engineering* **2026**, *14* (4), 1834-1846. DOI: 10.1021/acssuschemeng.5c08715.

(46) Wang, Y.; Kim, J.; Marreiros, J.; Rangnekar, N.; Yuan, Y.; Johnson, J. R.; McCool, B. A.; Realff, M. J.; Lively, R. P. Investigation of Moisture Swing Adsorbents for Direct Air Capture by Dynamic Breakthrough Studies. *ACS Sustainable Chemistry & Engineering* **2025**, *13* (18), 6554-6564. DOI: 10.1021/acssuschemeng.5c00227.

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Statement: Data for this article, including testing results, FTIR, TGA and DSC are available upon request from the corresponding authors.

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