

Evaluation of Moderately Grafted Primary, Diamine, and Triamine Sorbents for CO₂ Adsorption from Ambient Air: Balancing Kinetics and Capacity Under Humid Conditions

Basil Wadi, Ayub Golmakani, Vasilije Manovic, Seyed Ali Nabavi*

Centre for Climate and Environmental Protection, Cranfield University, Bedford, Bedfordshire MK43 0AL, UK.

*Corresponding author: Seyed Ali Nabavi (s.nabavi@cranfield.ac.uk)

ABSTRACT

Successful deployment of direct air capture (DAC) to mitigate the consequences of climate change depends on many factors, one of which is the development of kinetically efficient CO₂ sorbents with a high sorption capacity, at ultra-low CO₂ concentrations. This work evaluated CO₂ adsorption performance of primary-, diamine-, and triamine-grafted SBA-15 at pressures below 5 kPa for DAC applications, measured through volumetric sorption, followed by humid air (23% RH) adsorption by gravimetric analysis. Under humid air flow, triamines at an amine loading of 4.6 mmol/g showed the highest enhancement in adsorption, with an uptake of 26 mg/g, but the slowest average adsorption rate of 216 µg/g/min. Diamine at an amine loading of 2.78 mmol/g had an adsorption rate of 295 µg/g/min, but demonstrated the lowest uptake of 13 mg/g. In comparison, primary amines at a loading of 2.6 mmol/g reached an equilibrium uptake of 22 mg/g, with a higher adsorption rate of 354 µg/g/min. Triamine grafted at 3.5 mmol/g had the fastest kinetics of all samples, reaching 525 µg/g/min. Results indicated that primary amines and moderate-to-high density triamine reagents incorporated into mesoporous media can offer a superior adsorption rate that can make up for lower adsorption capacities, by optimising cyclic performance, and should be considered when designing for continuous DAC processes.

Keywords: Carbon capture; direct air capture; grafted amines; primary amine; secondary amine; amine-functionalised sorbent

1. Introduction

The intergovernmental panel on climate change (IPCC) recently reported that even if immediate action is taken to decrease CO₂ emissions down to zero, additional negative emission technologies (NETs) are necessary to limit global warming to 1.5°C by 2100. As a result, direct air capture (DAC) has become a promising technology for atmospheric CO₂ capture, targeting distributed sources, such as transport or agricultural or commercial businesses, that makeup about 50% of emissions [1–3]. Lime-based materials have been shown to be effective in adsorbing CO₂ from air at atmospheric conditions without any required equipment, but require large areas for high-efficiency thin-film applications and weeks to months for this process to take place [4]. This makes DAC applications that utilise cyclic adsorption processes that modulate pressure or temperature for adsorption-desorption steps feasible alternatives for long-term and large-scale applications, with recent successful applications of integrated as well as stand-alone temperature-vacuum swing arrangements [5–8]. However, ambient air conditions have significant implications on the use of current benchmark adsorbents. Kumar et al. [9] investigated a number of physisorbents and one chemisorbent under DAC conditions. They found that Zeolite 13x and Mg-MOF-74, which in a variety of applications provide exceptional performance, led to low CO₂ uptakes of 1.5 and 6.3 mg/g, respectively, under ambient air conditions. This was a direct result of a low selectivity of CO₂ with respect to H₂O. Moreover, Mg-MOF-74 also showed structural degradation in the presence of moisture. In comparison, a variety of amine functionalised adsorbents have already been shown to have a high CO₂:N₂ selectivity[10–12], and in the work presented by Kumar et al. [9], tetraethylenepentaamine (TEPA)-impregnated SBA-15 preformed significantly better, achieving a CO₂ uptake of 158 mg/g when exposed to an air stream at 49% relative humidity (RH) and 23°C for 12 h. This is in agreement with a number of studies that incorporated

polyethylenimine (PEI) in sorbents for DAC conditions, reporting similar CO₂ adsorption and selectivity [13–16]. Sayari et al. [17] showed that under certain adsorbent synthesis conditions, an amine efficiency of ~308 mg of CO₂/g_{PEI} can be achieved for an air stream at 49% RH.

These studies show that high amine densities, commonly a quality of impregnated materials, provide exceptional adsorption capacity. However, the superior adsorption awarded often results in slow adsorption kinetics and significantly high regeneration energy demands [18,19]. Brilman et al. [20] illustrated this in a study by impregnating TEPA from 26 to 45% on silica and measuring the CO₂ uptake of a dry N₂ stream with 400 ppm of CO₂. They showed a large variation in kinetics, with the adsorption rates varying from 300 min up to 900 min to achieve CO₂ loadings of 60 to 110 mg/g. For amine-grafted materials under similar conditions, Belmabkhout et al. [21] investigated the feasibility of using triamine-grafted silica for CO₂ capture in simulated air. An uptake of 40 mg/g was achievable at an adsorption time of 328 min, comparable to low-density TEPA materials by [20] In both cases, only dry conditions were studied, and RH was not accounted for. In a study that accounted for humidity, Gebald et al. [22] prepared a novel adsorbent by freeze-drying amines on nanofibrillated cellulose. Diamine-functionalised materials achieved an adsorption capacity of 30 mg/g of CO₂ after 2 h under air flow at 40% RH, a superior adsorption rate compared to the PEI-impregnated silicas.

When using amine functionalised silicas for CO₂ adsorption under ambient air conditions that include moisture content, the overall uptake is mainly associated with CO₂ chemisorption, but H₂O can also be physically adsorbed on the surface or react with amines to facilitate CO₂ adsorption. However, in a recent study by Jung et al. [23], it was shown that within the limits of a maximum CO₂ vapour fraction of 0.05, and up to a P_{H₂O} of 4 kPa, amine sites tend to favour CO₂ adsorption over H₂O on PEI impregnated silicas, a behaviour similarly seen by TEPA-impregnated

mesoporous silicas in the adsorption of CO₂ from ambient air, presented by Kumar et al. [9]. This is similarly demonstrated by Belmabkhout et al. [21,24] in studies on the competitive adsorption of CO₂ and H₂O in triamine-grafted silicas. Additionally, Didas et al.[25] presented CO₂ adsorption and water adsorption studies on silica functionalised with secondary amines and varying levels of primary amines, and showed that the degree of water adsorbed has a very small variation at partial pressures present in ambient air at partial pressures <0.01 bar. This makes amine functionalised silicas very effective adsorbent materials for CO₂ adsorption from ambient air, at relatively low humidity.

In designing long-term DAC processes that can be scaled up, it is important to optimise the energy efficiency of each adsorption-desorption cycle. Although there have been investigations on the performance of amines for DAC applications, they either focus on densely impregnated materials, one amine type, or dismiss the effect of humidity, making it difficult to attribute amine-specific capture efficiencies in ambient air conditions. This work classifies and compares adsorption rates and capacities of different amines with distinct amine loadings per gram of adsorbent. This is essential in guiding the future development, aiding in the identification of which adsorbent compositions are best suited for a particular DAC configuration or operating mode; carried out through an assessment of the overall CO₂ uptake, adsorption kinetics, and implied desorption energy requirements. Herein, primary amine, diamine, and triamine were grafted on SBA-15 to provide a range of surface densities to evaluate their CO₂ adsorption from ambient air. The effects of humidity in ambient air on CO₂ uptake, the adsorption rates, and the associated implied desorption demands were then assessed. Additionally, the selectivity of CO₂/N₂ is quantified for a comparison of the separation efficiency of each amine type. The results were then discussed in

relation to the chemisorbed species formed in the presence of moisture, and their feasibility for DAC applications elucidated through a comparison with benchmark adsorbents.

2. Materials and Methods

2.1 Materials and synthesis

(3-aminopropyl)triethoxysilane (APTES), 3-(2-aminoethylamino)propyltri-methoxysilane (AEAPT), 3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane (TAEPT), toluene (99.8%), and methanol (HPLC grade) were supplied by Sigma-Aldrich, UK. SBA-15 mesoporous silica adsorbent (in the form of fine powder) was purchased from XFNANO. Nitrogen and carbon dioxide were supplied by BOC, UK, with a purity above 99.99%. Air was supplied from the outside atmosphere via a compressor supply line at a dew point of 3°C.

Grafting of SBA-15 followed the inert reflux procedure for grafting of SBA-15. The desired quantity of amine was added to 1 g of SBA-15 and placed under inert reflux with toluene as a solvent for 18 h at 70°C. The samples were then filtered and dried in air and were denoted as S-x-y, with x referring to the amine type (P-primary, D-diamine, T-triamine) and y the amine density grafted in mmol/g, **Table 1**. The amine loading for primary and diamine were chosen as the minimum content comparable to triamine, which corresponds to the maximum surface coverage of SBA-15.

2.2 Material characterisation

The amine density was estimated by thermogravimetric analysis (TGA 8000, PerkinElmer) and elemental analysis (EA, vario EL III, Elementar). For TGA, an 8-10 mg sample was placed under a nitrogen flow of 60 mL/min and the temperature incrementally increased at a rate of 20°C/min

from 30°C to 800°C. This was followed by a five-minute hold at 800°C under air flow. EA measurements utilised combustion analysis to provide the nitrogen content present in each sample.

The structural morphology of the functionalised materials was determined based on nitrogen physisorption analysis at -196°C by a 3P Meso 222 sorption analyser (3P Instruments). A sample weight of 0.2-0.3 g was used for each measurement and degassed for 2 h at 90°C under vacuum suction. The Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods were used to calculate surface area (p/p^0 of 0.05 to 0.2) and pore volume ($p/p^0 = .95$), respectively [26,27]. The reported pore size distribution (PSD) was calculated by the Broekhoff-de Boer (BdB) method simplified by the Frenkel-Halsey-Hill (FHH) approximation [28].

2.3 Adsorption measurements

CO₂ and N₂ equilibrium adsorption were measured using the 3P meso analyser mentioned previously. Each measurement used 0.25-0.3 g of sample, degassed under the same conditions described for nitrogen physisorption, and measured at a temperature of 25°C, which was maintained by an antifreeze bath (3P Instruments). The CO₂ isotherms were fitted using a modified form of the Toth equation [29,30] and the N₂ data by the Henry isotherm, details of which can be found elsewhere [26]. Selectivity ($\hat{S}$) from adsorption isotherms was calculated by Eq (1):

$$\hat{S} = \frac{q_i/P_i}{q_j/P_j} \quad (1)$$

in which q (mmol/g) is each component's adsorption capacity and P (kPa) is each component's partial pressure.

Ambient air adsorption measurements were conducted by TGA (TGA 8000, Perkin Elmer). A 7.5 mg sample was used for the moderately grafted primary, diamine, and triamine SBA-15, while a 10 mg sample was used for the heavily loaded triamine sample(S-T-4.5); this was chosen since at

this weight, an approximately equal amount of adsorbent occupies the same volume within the sample pan. The sample temperature was then stabilised at 25°C and exposed to a flow of 60 mL/min of air at 100 kPa for a period of 150 to 250 min, depending on the material. The air was extracted from the ambient air (located at Cranfield, UK) using a compressor at a measured dew point of 3°C equivalent to a 24% RH at the measurement temperature of 25°C. The uptake measured by TGA was considered representative of equilibrium when the rate of change of the sample weight was lower than 10⁻⁴ mg/min.

3. Results and Discussion

Table 1. Structural properties of raw SBA-15 and functionalised materials.

Sample	Amine type	Amine added (mmol/g)	Amine density (mmol/g)	S _{BET} (m ² /g)	V _p (cm ³ /g)	D _p (nm)
Raw SBA	-	-	-	490	1.2	7.0
S-P-2.6	Primary	8	2.60	267	0.63	5.7
S-D-2.8	Diamine	2	2.78	288	0.74	6.2
S-T-3.5	Triamine	2	3.52	274	0.66	6.3
S-T-4.6	Triamine	8	4.66	115	0.26	5.8

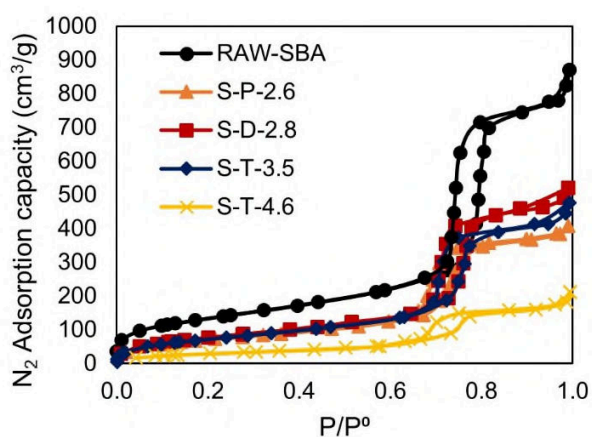


Figure 1. N₂ isotherms at -196°C for primary-, secondary-, and triamine-functionalised SBA-15

3.1 Material characterisation

The structural characteristics of functionalised material samples are provided in **Table 1** and **Figure 1**. The nitrogen isotherms of S-P-2.6, S-D-2.8, and S-T-3.5 are type IV with a hysteresis loop typical of the mesoporous pores of SBA-15 [26]. S-T-4.6 was grafted with the highest density of amine, and the measured effective surface area decreased to 115 m²/g, a 76% change from the unfunctionalised SBA-15. This degree of pore filling is more often seen in impregnated mesoporous silicas [31–33]. However, the change in surface area and pore volume does align with the literature when a high enough density of triamine is grafted on SBA-15 of similar structural characteristics [34]. The molecular length and level of grafted density of triamine lead to excessive pore filling, and this is reflected in the nitrogen isotherm for this specific sample.

3.2 CO₂ and N₂ volumetric adsorption

The adsorption isotherms for CO₂ and N₂ at 25°C are presented in **Figure 2**. Up to 20 kPa, the CO₂ adsorption capacity is identical for S-P-2.6 and S-D-2.8, reaching ~0.95 mmol/g. Compared to S-P-2.6, S-D-2.8 has a lower loss of pore volume and surface area post functionalisation, and an overall smaller degree of chemisorption as shown by us in a previous study [30,35]. Both these characteristics contribute to the increase in adsorption uptake above 20 kPa, with physisorption facilitated by the chemisorbed species becoming the principal adsorption mechanism. Distinguishing this is important as the larger contribution from physisorption plays an important part in the low-pressure adsorption of CO₂ from air of the diamine sample. S-T-3.5 showed a larger CO₂ uptake compared to other samples for CO₂ partial pressure > 0.17 kPa. At 2 kPa, S-T-3.5 adsorbed 32 mg/g compared to 26 mg/g in both S-P-2.6 and S-D-2.8, indicating the presence of more sterically accessible sites for chemisorption. S-T-4.6 has an amine density of 4.66 mmol/g, the highest of all functionalities, yet achieves the lowest capacity as pressure increases. This is likely caused by pore plugging from high amine density, as previously discussed. The saturation

of the pores with long TAEPT chains leads to diffusion limitations that hinder access to active sites, for both chemisorption and physisorption. Consequently, there is an initially high degree of CO₂ chemisorption, measured by the 14.5 mg/g at 0.04 kPa that sharply increases up to 32 mg/g at 2.5 kPa before leveling off (**Figure 2**), and comprising 61% of the total uptake measured at 100 kPa. Once these sites are occupied, there is little pore space left for further adsorption and the capacity increases at a much slower rate. This means that the distribution of TAEPT in this sample becomes significant at much lower pressures, a necessary quality for CO₂ capture from air.

All the materials exhibited almost negligible N₂ uptake compared to CO₂. The highest uptake of N₂ was ~0.75 mg/g by S-T-3.4 at 100 kPa N₂ partial pressure, followed by S-P-2.6 at 0.5 mg/g, and lowest for S-T-4.6 at 0.2 mg/g. The CO₂/N₂ selectivity calculated from the fitted isotherms is presented in **Table 2**. In a 50:50 binary mixture of CO₂:N₂ at a total pressure of 100 kPa, the selectivity of S-T-4.6 reaches 392 followed by 197 in S-P-2.6 and 159 in S-D-2.8. These values align with other works on triamine-grafted MCM-41 and exceed zeolite, carbons, and MOF selectivity under similar conditions [36–38]. Although presenting a high selectivity, a more representative mixture of CO₂ and N₂ for DAC would comprise a ratio of 0.04:99.96 as presented in **Table 2**. This selectivity might not consider the presence of O₂ in air, but it has been shown in the literature that the trends of selectivity for CO₂/N₂ and CO₂/O₂ in a variety of zeolitic imidazolate framework (ZIF) materials and commercial BPL carbon (Calgon Corp) are similar[38]. Additionally, Belmabkhout et al.[39] investigated the breakthrough of a gas mixture representative of air (0.03:79.98:19.99 for CO₂:N₂:O₂) in triamine-grafted MCM-41 at 25°C and 100 kPa. The breakthrough curves of O₂ and N₂ were almost identical. At a CO₂ partial pressure of 0.04 kPa, the selectivity of S-P-2.6 and S-D-2.8 approach infinity, exceeding 25,000 with the highly grafted S-T-4.6 reaching over 140,000. The primary contribution to the differences in selectivity for S-P-2.6

and S-T-4.6 is thus a result of the exceptionally low N_2 adsorption capacity, caused by the high surface coverage of the amine moieties grafted, and thus lower S_{BET} and pore volume compared to S-D-2.8 and S-T-3.5. This is expected due to the nature of CO_2 adsorption by amines (selective chemisorption), but also by the very low uptake of N_2 by the studied materials.

Table 2. Selectivity of functionalised materials in a mixture of CO_2 and N_2 at a total pressure of 101.3 kPa and 25°C

Sample	$\hat{S}$ (50:50 binary mixture)	$\hat{S}$ (0.04:99.96 mixture)
S-P-2.6	206	72552
S-D-2.8	167	51000
S-T-3.5	131	24963
S-T-4.6	399	174453

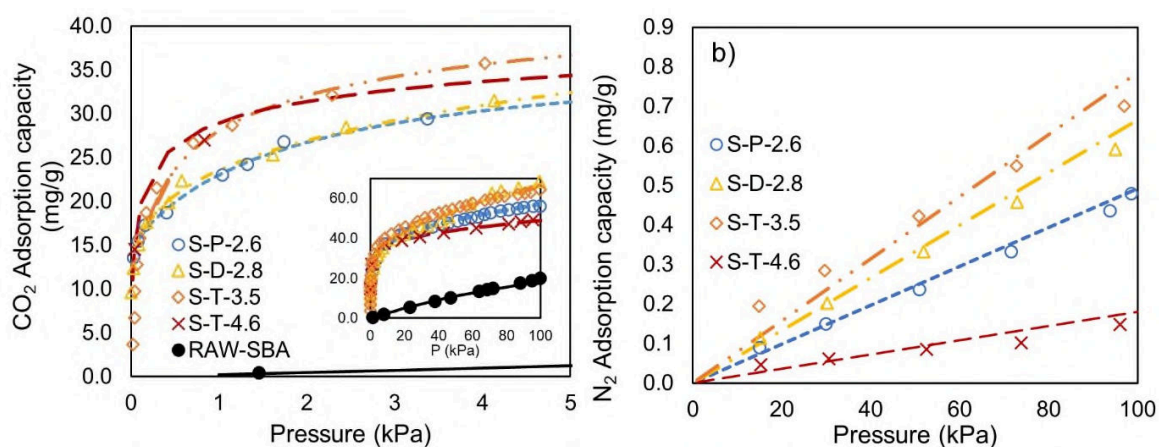


Figure 2. Equilibrium adsorption isotherms of functionalised materials at 25°C of (a) CO_2 , and (b) N_2 . The markers represent the experimental data, while the following lines represent the respective isotherm model: (—) RAW-SBA, (---) S-P-2.6, (-.-) S-D-2.8, (— —) S-T-3.5, (— —) S-T-4.6.

Table 3. Comparison of the gravimetric uptake under humid air flow and equilibrium volumetric adsorption of pure CO₂ at P_{CO2} of 0.04 kPa. The ambient air flow is at 24% RH.

Sample	Ambient air (mg/g)	Pure CO ₂ (mg/g)
S-P-2.6	22.3	14.2
S-D-2.8	13.5	13.6
S-T-3.5	21.3	8.0
S-T-4.6	26.3	14.5

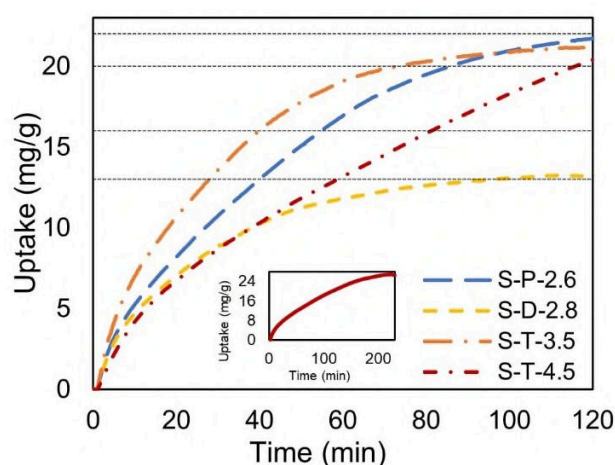


Figure 3. Gravimetric uptake of functionalised materials under ambient air flow at 24% RH up to 120 min of adsorption time. The dashed lines represent specific points of CO₂ loading at 13, 16, 20, 22 mg/g. S-T-4.5 takes up to 200 min to reach equilibrium, and the full adsorption loading is included as a miniture graphic for reference.

3.3 Ambient air gravimetric measurements

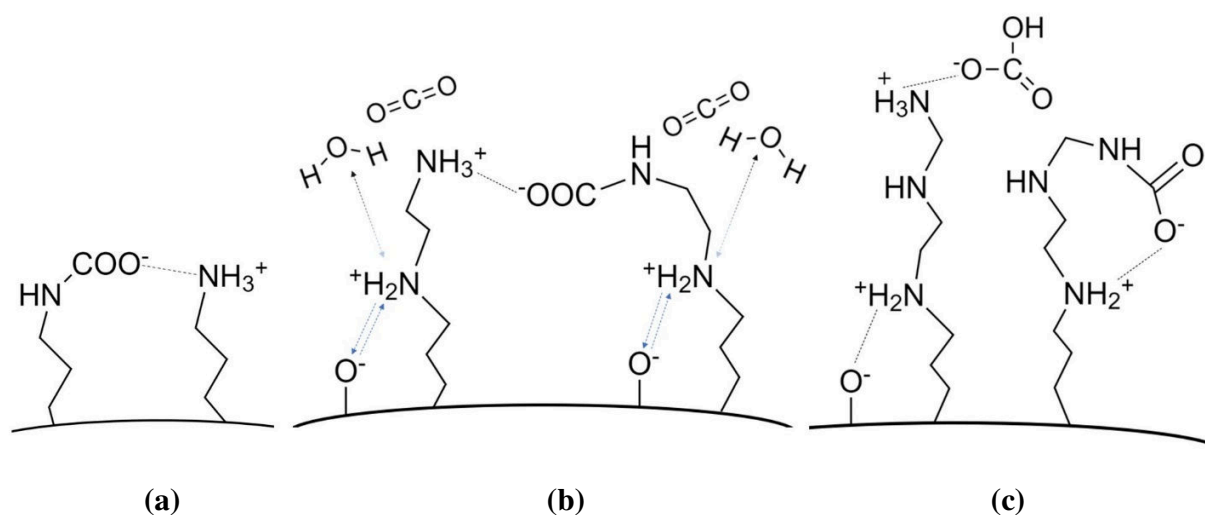
The gravimetric CO₂ adsorption of the functionalised materials under air flow with 24% RH is presented in **Figure 3** and **Table 3**. Considering the purpose of this work is to assess the differences in capacity and kinetics by different amine types and the negligible quantity of CO₂ adsorbed by the raw SBA-15 material at CO₂ partial pressures of 0.04 kPa presented in **Figure 2**, only the functionalised materials were studied under air adsorption conditions. The highest adsorption was

achieved for S-T-4.6 (26.3 mg/g) followed by S-P-2.6 (22.9 mg/g), S-T-3.5 (21.9 mg/g), and S-D-2.8 (13.5 mg/g). A comparison of the differences between the dry gas volumetric adsorption and humid dynamic adsorption uptake at P_{CO_2} of 0.04 kPa can provide insight on the changes in the observed performance (**Table 3**). The equilibrium adsorption capacity at 0.04 kPa in dry conditions is highest for primary amine and decreases in the order of primary>diamine>triamine. Comparatively, for ambient air adsorption, there is a considerable enhancement in triamine-grafted materials, followed by primary amines, and close to none for diamine. It has been previously shown that the differences observed may be caused by a combination of total RH, adsorbent pore structure, and the measurement method [40]. However, referring to previously discussed preferential adsorption of CO_2 by various amine functionalised silicas, and the 24% RH in the ambient air stream, it can be inferred that the adsorbed quantity of H_2O contributing to the calculated uptake is relatively inconsequential under the conditions studied.

With primary amine (S-P-2.6), the minor enhancement from 14.2 mg/g to 22.3 mg/g in capacity from dry to humid conditions agrees with previous studies under similar conditions [41]. The enhancement observed is likely a combination of RH and pore accessibility. It has been proposed that the presence of water may enhance amine adsorption by the formation of surface-bound carbamate species, but at this level of amine density there is a small number of available surface silanols, making it a low contributor [42,43]. The most prominent species formed are likely ammonium carbamate ion pairs, illustrated in **Scheme 1a**, shown to readily form on primary amine-functionalised silicas at similar surface coverage, in both dry and wet conditions [43–45]. Additionally, it has been suggested by Mebane et al. [46] that the presence of water vapour can enhance the total formation of ammonium carbamate through the formation of intermediates that support the diffusion of CO_2 into internal pores. Under this study's conditions, the observed

enhancement in uptake at the rate of adsorption measured is likely a result of a higher quantity of ammonium carbamate formation facilitated by the diffusion of CO₂ [45,47,48]. This agrees with previous studies showing that the slow-forming bicarbonate through CO₂ chemisorption does not occur on primary amines [43,45,47,49].

Scheme 1. Schematic of possible formed species and interactions from the chemisorption of CO₂ in the presence of moisture of (a) primary amine, (b) diamine, and (c) triamine functionalised SBA-15.



The diamine sample (S-D-2.8) under ambient air flow had the lowest uptake, with no discernable enhancement from water vapour. The secondary amine moiety in diamine has been shown to form hydrogen bonds with surface silanols, leaving only primary amine moieties to interact with CO₂ [50]. Furthermore, Li et al. [51] showed that secondary amines in PEI can form hydronium carbamate in humid conditions, but that ammonium carbamate is more energetically favourable. In contrast, Didas et al.[52] showed that secondary amines in single amine reagents are more hydrophobic compared to primary amines. The uptake in S-D-2.8 may be a result of the initial formation of carbamate by easily accessible primary amines, aided by water vapour, **Scheme 1b**.

In the next period, and considering that this material contains 1.4 mmol/g of each primary amine and diamine, it can be surmised that any further chemisorption is sterically limited due to a combination of chemisorbed species and amine clustering, or unavailable amine moieties forming surface hydrogen bond.

The largest difference in uptake was seen specifically in the triamine samples, and may be due to a combination of adsorption mechanisms previously discussed, with an additional possibility of the formation of bicarbonate through CO₂ adsorption in humid conditions [53]. In agreement with pure CO₂ studies on amine-impregnated silica by Hahn et al. [42], the triamine-grafted samples seem to have a propensity to adsorb H₂O, either to form bicarbonate or to act as a base for the deprotonation of a carbamate zwitterion in place of an amine, **Scheme 1c**. The densely grafted S-T-4.6 adsorbs CO₂ in humid conditions in a mechanism like that of impregnated amines such as diethylenetriamine (DETA), evidenced by the difference between dry and humid adsorption and the slower adsorption time in this specific material. In comparison, S-T-3.5 resulted in a fast-initial adsorption rate, signifying a large quantity of fast-forming chemisorbed species, such as ammonium carbamate, likely promoted by the water vapour present.

The adsorption time of S-T-3.5 and S-T-4.6 for 16 mg/g was 40 and 81 min, respectively. The faster adsorption rate in S-T-3.5 can be a result of facilitated pore diffusion by the adsorbed H₂O film and larger pore volume. In S-T-4.6, the pore filling causes an accumulation of triamine closer to the surface of adsorbent pores and along the pore surface, slowing internal diffusion. Unlike diamine, triamine contains two secondary amines that adsorb in a manner similar to impregnated amine reagents such as DETA; that is, even if one secondary amine forms hydrogen bonds with the surface such as seen in diamines, the second one when accessible, can provide a site for ammonium carbamate, hydronium carbamate, or even bicarbonate formation.

Comparing the adsorption rates of the different amines, S-T-4.6 reached 26 mg/g after 200 min of air exposure, a significant trade-off in adsorption time for a ~4 mg/g increase from 22 mg/g. Consequently, the adsorption times for 13, 16, 20 and 22 mg/g uptake are considered optimal targets and have been compared amongst the different amines. As S-P-2.6 approaches equilibrium, the adsorption rate is equivalent to S-T-4.6, taking >130 min to reach 22 mg/g, but at lower loadings such as 16 mg/g, it takes only 55 min (26 min faster), and for 20 mg/g only 86 min (30 min faster). Although S-P-2.6 demonstrates good rates of adsorption, S-T-3.5 outperforms them all, achieving uptakes of 16 mg/g and 20 mg/g at 40 and 73 min, respectively.

From the variations seen in adsorption by the different amines studied, primary amines and triamines grafted at densities seen in S-P-2.6 and S-T-3.5, that provide ample pore volume, can be the most efficient for ambient air adsorption. In this case, targeting an uptake ahead of the slower rates seen near equilibrium, such as 20 mg/g at an adsorption half time of 37 and 42 min, respectively, for S-T-3.5 and S-P-2.6, would be an optimal usage of these types of amine-grafted materials.

3.4 Feasibility for DAC

The majority of DAC processes are still in the initial stages of development, but an important factor to consider for continuous operation is the balanced performance of an adsorbent, specifically in terms of the adsorption kinetics and corresponding uptake in humid air adsorption [54]. **Figure 4** summarises selected works reporting the adsorption performance of amine functionalised adsorbents relevant to DAC applications, by tabulating the average adsorption times

based on the adsorption half time, defined as the time to reach 50% of the maximum CO₂ adsorption. The impregnation of an adsorbent with TEPA has shown to achieve high CO₂ loading at low partial pressures; In work by Brilman et al. [20], an impregnated silica with 38% TEPA reached an uptake of 110 mg/g after 16 h exposure to dry N₂ at 400 ppm CO₂. Although this is superior to many adsorbents, this work did not account for the effects of humidity on adsorption and desorption rates. In their study, the total time for adsorption was relatively long, but did show an approximate adsorption half time of 250 min, which averages to an adsorption rate of 202 µg/g/min. Nonetheless, Azarabadi et al.[55] demonstrated that the cyclability and low cycle times of an adsorbent are crucial in minimising DAC costs, with respect to these two parameters, the CO₂ capacity of amine impregnated silicas have been shown to deteriorate faster than amine grafted silicas, making them less suitable for long-term DAC processes.

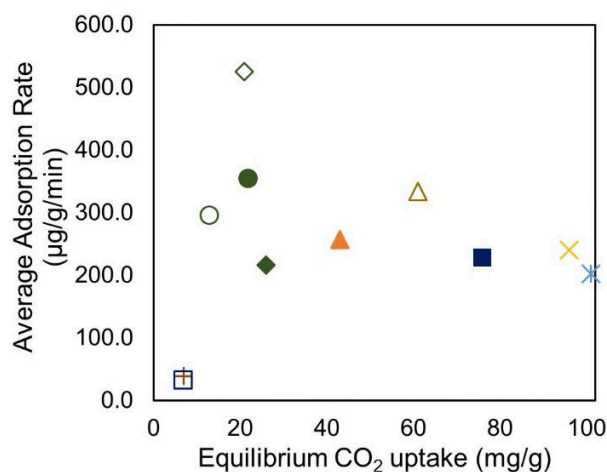


Figure 4. Comparison of adsorption performance of amine functionalised adsorbents from literature in DAC conditions with this work. (+) AEAPTMS grafted silica Gel (2.48 N mmol/g) [56], (Δ) AEAPDMS-NFC-FD (4.9 N mmol/g) [22], (▲) Triamine grafted MCM-41 (7 N mmol/g) [21], (x) 38% TEPA impregnated silica (10 N mmol/g) [20], (x) Stabilized PEI impregnated on

Silica T-PEI/CARiACT G10 HPV (10.5 N mmol/g) [19], (□) Hyberbranched aminosilica (2.3 N mmol/g) [57], (■) Hyberbranched aminosilica (9.9 N mmol/g) [57], (●) S-P-2.6 (2.6 N mmol/g), (○) S-D-2.8 (2.8 N mmol/g), (◇) S-T-3.5 (3.5 N mmol/g), (◆) S-T-4.6 (4.6 N mmol/g). Detailed summary of the data and adsorption conditions can be found in the Supplementary Information, Table S1.

Densely grafted triamine (>5 mmol/g) on pore-expanded MCM-41 has also been studied under DAC conditions, reaching 43 mg/g after 167 min through breakthrough experiments and averaging an adsorption rate of 257 $\mu\text{g/g/min}$, a slightly better performance compared to the 38% TEPA silica[21]. Hyperbranched aminosilica (HAS) adsorbents developed by Choi et al.[58] have also shown high uptake at amine densities >8 mmol/g under DAC conditions, reaching 75 mg/g, but at a slower rate, with a an averaged adsorption rate of 228 $\mu\text{g/g/min}$. All these studies show that elevated amine densities result in high uptake, but also cause a decreasing trend in the rates of adsorption, due to diffusion limitations from pore filling. These findings are in agreement with higher partial pressure CO_2 adsorption studies on amine functionalised adsorbents previously carried by our group and within literature, with higher amine loadings (>20% by weight) leading to noticeably slower CO_2 uptake[59–61].

Despite the low equilibrium uptake of primary amines and triamines in this study, the adsorption rate to reach 75% of equilibrium uptake in ambient air was superior to densely grafted triamine- and diamine-functionalised SBA-15. The average adsorption rate of S-P-2.6 was 354 $\mu\text{g/g/min}$, while S-T-3.5 reached a value of 525 $\mu\text{g/g/min}$. Both are indicative of superior kinetic performance and potential for cyclic DAC applications. Additionally, S-T-3.5 shows no indication of bicarbonate formation due to the fast adsorption rate, but material S-T-4.6 may have. Bicarbonate

formation can heavily affect performance as it has been shown to limit desorption efficiency or incur additional regeneration energy requirements in ethylmonoethanolamine (EMEA) solution [62].

Other factors affecting regeneration were demonstrated in a study by Wagner et al. [63] on DAC by densely grafted triamine (7.3 mmol/g) on MCM-41, there was a rapid deterioration in uptake due to the presence of moisture in the desorption gas, which was maintained at 75°C for 2 h. The reason for such behaviour was unclear, but it was suggested that it can potentially due to the extended two-hour desorption period used in wet conditions. Under ideal conditions, benchmark low temperature solid-sorbent applications of DAC have already been shown to require higher regeneration energy demands compared to liquid-based applications, but the costs are comparable if low grade heat is used to meet a sorbent's regeneration energy requirements [64]. In a study by Kulkarni et al.[65], they use low-grade steam for desorption and showed that the energy required for a TSA CO₂ capture process of dry air, employing triamine grafted pore expanded MCM-41, is ~5962 MJ/t CO₂ and is dominated by parasitic losses from the heating step. They suggested that the energy could be reduced by up to ~20% if higher capacity adsorbents are employed. However, there was no investigation into the energy implications of maximising the number of adsorption-desorption cycles per 24-hour period. For this reason, further work should be carried out concentrating on the desorption demands of different amines, and the effect of cycle times on the overall process energy requirements to better understand the benefit of fast cycle times in DAC initiatives.

With respect to cyclability, recent work from our group on triamine grafted SBA-15 pellets showed no reduction in capacity over several adsorption-desorption cycles at desorption conditions of 90°C, under nitrogen flow following CO₂ adsorption[60]. There is also extensive literature

showing the cyclability of amine grafted ordered mesoporous silicas (MCM-41, SBA-15, etc.), following adsorption of ultra-low CO₂ partial pressures present in air, low partial pressures from post-combustion gas mixtures, and pure CO₂ gas adsorption [2,18,24,32,56,66,67]. It has also been shown that amine grafted adsorbents are preferable to amine impregnated adsorbents, as impregnation shows comparatively lower cyclic stability[59,61]. For triamine grafted mesoporous silica, Wagner et al.[63] did demonstrate that their cyclability for DAC can vary widely depending on the conditions used for desorption, with humid desorption conditions sharply dropping the cyclic capacity compared to dry desorption gas, which had no effect. Under dry desorption conditions, a few studies, including work from our group, have shown the effective regenerable quality of this class of adsorbent, in which, primary amine functionalities show higher heats of adsorption at lower uptakes compared to diamine and triamine grafted silicas[30,50,68]. Future studies will concentrate on probing a range of dry desorption conditions to elucidate the ideal desorption temperature and time of these adsorbents, while gauging the effect of different moisture content and temperature of the ambient air, thus encompassing a wide range of conditions.

4. Conclusion

In this work, there is a strong indication that primary amines and moderate-to-high triamine loadings on SBA-15 perform well in CO₂ adsorptions from ambient air, achieving acceptable capture capacities with fast kinetics for CO₂ adsorption at ultra-low partial pressures and in the presence of moisture. Under equilibrium volumetric sorption of dry CO₂, at a CO₂ partial pressure of 0.04 kPa, adsorption was highest for primary amine followed by diamine and last triamines. In comparison, for CO₂ adsorption under air flow at 24% RH, the order is altered, CO₂ loading is enhanced more so for triamine, followed by primary amine and finally diamine. The change in CO₂ loading in DAC conditions indicate that triamine is subject to the largest enhancement from

moisture, affecting both the total uptake and adsorption rate, in a manner dependent on the amount of loaded amine. When comparing CO₂ loading at below equilibrium for faster cyclic processes, the Triamine grafted sample at a loading of 3.5 mmol/g under airflow adsorbed the highest quantity in the shortest time, ~16 mg/g in only 40 minutes. This sample was followed by primary amine at a loading of 2.6 mmol/g, presenting a balanced uptake and adsorption rate of ~16 mg/g in 55 minutes. For both S-P-2.6, and S-T-3.5, the average adsorption rate for two consecutive cycles targeting the adsorption capacity at half-time are 354 and 525 $\mu\text{g/g/min}$, which are promising results for rapid cyclic applications. In comparison, densely grafted triamine at 4.6 resulted in the lowest adsorption rate of 216 $\mu\text{g/g/min}$.

In conclusion, primary amines, and moderate-to-high densities of triamine result in a balance of capacity and kinetics that can potentially be better utilised for continuous DAC processes, demonstrating potentially superior adsorption rates for continuous cycle arrangements. This behaviour opens the possibility of utilisation in novel process configurations for DAC, that rely on fast-cycle modulation to maximise total CO₂ adsorbed, while maintaining operation at atmospheric pressures. Future studies should concentrate on the fixed bed employment of these materials to further scrutinise the expected adsorption rates accounting for fixed-bed mass transfer contributions. Additionally, in pellet form, the desorption energy demands of these materials in DAC conditions should be further studied, across a wide range of ambient air conditions. This will also facilitate an estimation of the change in energy requirements and operating cost per ton of CO₂ captured, as the adsorption-desorption cycle time changes in a TSA process configuration.

AUTHOR INFORMATION

Corresponding Author

Seyed Ali Nabavi (s.nabavi@cranfield.ac.uk)

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Supporting Information

Additional data of adsorption performance in DAC conditions of amine functionalised adsorbents from literature. This information is available free of charge via the Internet at <https://pubs.acs.org/>.

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ABBREVIATIONS

AEAPT	3-(2-aminoethylamino)propyltri-methoxysilane
APTES	(3-aminopropyl)triethoxysilane
BdB-FHH	Broekhoff-de Boer - Frenkel-Halsey-Hill
BJH	Barrett-Joyner-Halenda
EA	Elemental analysis
RH	Relative humidity
TAEPT	3-[2-(2-aminoethylamino) ethylamino]propyltrimethoxysilane
TGA	Thermogravimetric analysis
PEI	Polyethylenimine
ZIF	Zeolite imidazolate framework

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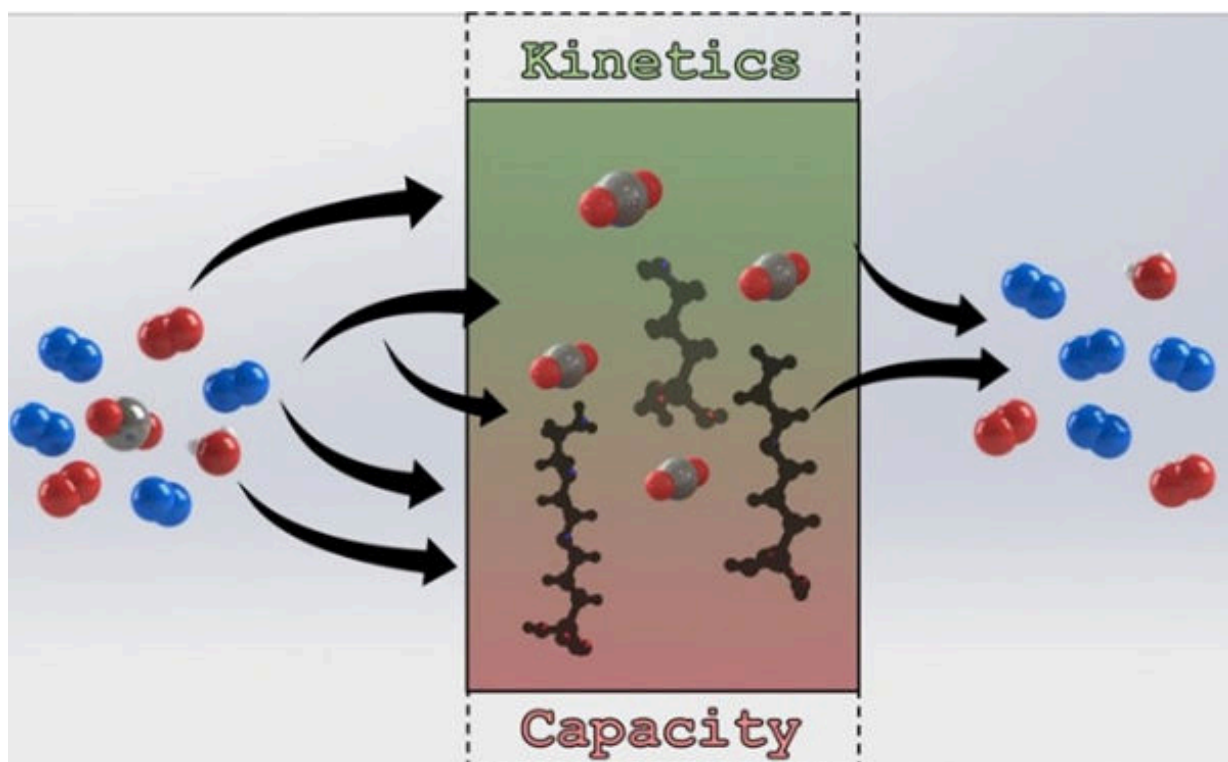
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Evaluation of moderately grafted primary, diamine, and triamine sorbents for CO₂ adsorption from ambient air: balancing kinetics and capacity under humid conditions

Wadi, Basil; Golmakani, Ayub; Manovic, Vasilije; Nabavi, Seyed Ali

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