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# CO$_2$ Capture by Dry Alkanolamines and an Efficient Microwave Regeneration Process

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Removal of acidic gases such as H$_2$S and CO$_2$ is performed during the purification of raw natural gas, most commonly using amine gas treatment. However, this industrially entrenched method is limited by significant shortcomings including low operational capture efficiency, amine pipeline corrosion and a large energy penalty due to the sorbent regeneration process. To address these shortcomings, we have studied the use of perfluorinated silica-stabilized dry alkanolamines (DA$_f$) for CO$_2$ capture. Due to their micronized liquid domains, DA$_f$ display high operational CO$_2$ capture efficiency. Further, to minimize energy requirements for sorbent regeneration, microwave-assisted regeneration of the spent DA$_f$ sorbent was also studied and shown to decrease the energy requirements by about ten times. In contrast to very recent work, our results show that the use of DA$_f$ exhibits extraordinary recyclability, with negligible decrease in absorption capacity over at least ten absorption-regeneration cycles, indicating the potential of this material for gas treatment applications.

## 1 Introduction

2 Carbon dioxide capture is crucial not only for mitigating
3 greenhouse gas emissions but also for natural gas processing.
4 The recent United States shale gas boom has precipitated a rise
5 in the production of natural gas, making the need for effective
6 CO$_2$ capture technologies more pressing than ever.[5] Examples
7 of solid sorbents for CO$_2$ capture include metal-organic
8 frameworks,[6-8] porous polymers[9-12] and zeolites.[13] Such
9 sorbents have the advantage of a high surface area to accelerate
10 CO$_2$ uptake.[14] Nevertheless, liquid sorbents, which often
11 require agitation to achieve high gas-liquid interfacial areas, are
12 still predominant in industrial processes. In fact, amongst
13 various CO$_2$ capture technologies, the most established is amine
14 gas treatment, which relies on the use of alkanolamines to
15 separate acidic gases such as H$_2$S and CO$_2$ from raw natural
16 gas.[15]

17 Despite amine-based gas sweetening being an already well-
18 established industrial process, it faces multiple shortcomings
19 including low operational CO$_2$ capture efficiency, amine
20 corrosivity and a significant energy penalty due to the sorbent
21 regeneration process.[1,16] Although primary and secondary
22 alkanolamines react with CO$_2$ in a 2:1 mole ratio to form their
23 corresponding carbamates with a theoretical CO$_2$ absorption
24 capacity of 50 mol% (Scheme 1),[17-19] industrial systems
25 utilizing alkanolamines typically only operate at 15 to 30 mol%
26 capture efficiency.[20] In addition, the high viscosity and
27 corrosivity of alkanolamines necessitate their dilution with
28 water to approximately 30 wt.% of amines.[15] This leads to an
29 associated energy penalty during sorbent regeneration, whereby
30 CO$_2$-loaded alkanolamine sorbents are heated to regenerate the
31 amines, since the additional water content increases the overall

32 heat capacity of the sorbent. To address this problem,
33 researchers have turned to utilizing ionic liquid-alkanolamine
34 blends[21] or to amine-functionalized porous solids for CO$_2$
35 capture.[22-24]

36 Dawson *et al.* recently reported an alternative approach
37 whereby they used hydrophobic silica-stabilized dry
38 alkanolamines (DA$_h$) for CO$_2$ capture.[25] However, the DA$_h$
39 exhibited low recyclability and substantial sorbent loss during
40 regeneration, as well as significantly decreased CO$_2$ uptake
41 after the first cycle. Nevertheless, this approach circumvents the
42 need for dilution of the sorbent with water, thereby decreasing
43 the energy penalty incurred during sorbent regeneration.
44 Amine-related corrosion problems are also potentially reduced
45 because the amine is isolated by the silica particles from
46 pipelines.
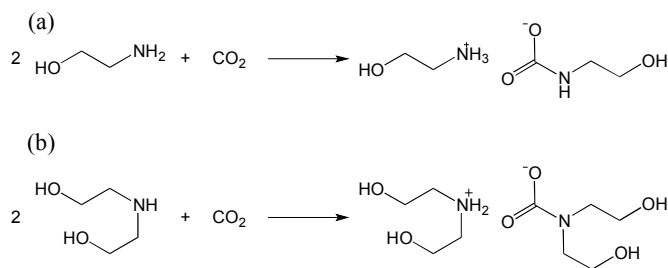
**Scheme 1.** Reaction of (a) monoethanolamine (MEA) and (b) diethanolamine (DEA) with CO$_2$ to form the corresponding carbamate salts.

We herein report the use of dry, undiluted alkanolamines for CO$_2$ capture whereby instead of hydrocarbon-functionalized,

hydrophobic fumed silica, perfluoroalkyl-functionalized oleophobic fumed silica was utilized for dry alkanolamine, DA, formation. These findings were previously outlined in our patent filed in May 2013, prior to the work being reported by Dawson *et al.*[26] We refer to this DA as DA$_f$. In contrast to the findings by Dawson *et al.*,[25] we found that DA$_f$ shows excellent recyclability and stability. Studies were conducted on monoethanolamine (MEA) and diethanolamine (DEA) due to their widespread industrial usage. Furthermore, a novel method using microwave-assisted heating for DA$_f$ regeneration was also investigated as an energy-efficient alternative to the conventional (convective and conductive heating) regeneration method.

DA are powdered materials and can be thought of as inverted foams, *i.e.* liquid droplets dispersed in air, whereby microscopic liquid droplets stabilized by nanoparticles form the dispersed phase and air is the continuous matrix (Figure 1). They appear as a free-flowing powder and are analogous in form to dry water (DW) which has received significant attention in recent years.[27-31]
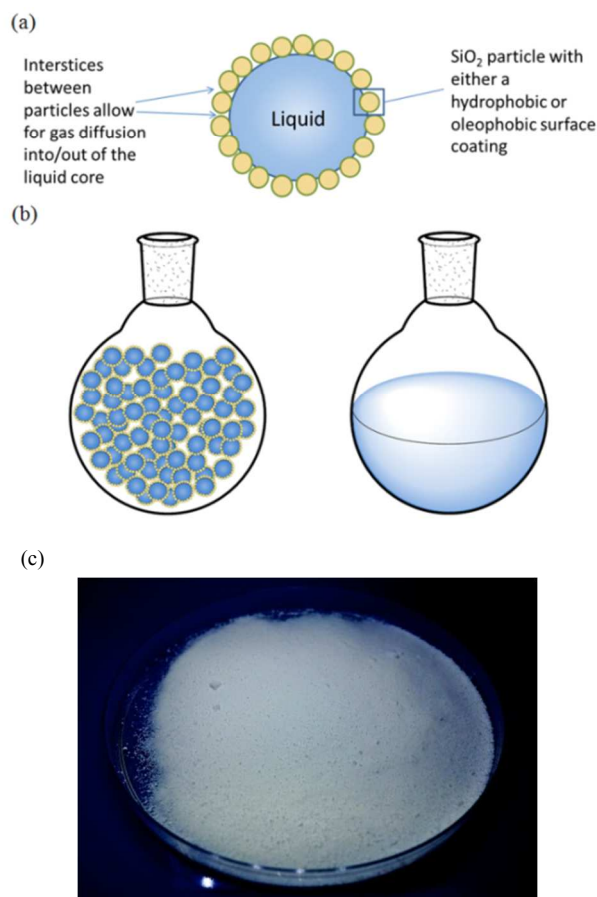


**Figure 1.** (a) Sketch of a liquid droplet in air encapsulated by particles of low surface energy. Since the particles form a porous shell on the surface of the liquid, there is rapid diffusion of gases into and out of the liquid through the particle interstices. (b) Sketch of a dry liquid (left) and bulk liquid (right) in round-bottomed flasks. (c) Photograph of DA$_f$ powder containing DEA.

For dry liquid formation to occur, the stabilizing particles must be hygrophobic towards the encapsulated liquid, otherwise a foam or paste may ensue.[18] Generally, for a flat surface to be hygrophobic towards a liquid (contact angle > 90°), the solid surface tension $\gamma_S$ must be $\gamma_S \ll \gamma_L/4$, where $\gamma_L$ is the surface tension of the liquid.[32] It has recently been demonstrated that the formation of dry oils with liquids of decreasing surface tension requires the use of nanoparticles with increasing degrees of fluorination on their surfaces.[33] Based on the surface tensions of MEA and DEA (Table S1), it can be deduced that oleophobic perfluoroalkyl-functionalized nanoparticles are preferable over oleophilic hydrocarbon-functionalized nanoparticles for stabilization of DA (Figure S1).

## Experimental

### Materials

All materials were purchased from commercial sources and used as received. *1H,1H,2H,2H*-perfluorooctyltriethoxysilane (purity 97%) was purchased from Fluorochem. Ethanolamine (purity 98%), diethanolamine (purity 98%) and fumed silica powder with an average particle size (aggregate) of 0.2-0.3 μm (product number S5505) were purchased from Sigma Aldrich. Ethanol (purity 99%) was purchased from International Scientific. Aqueous ammonia (28%) was purchased from Malayan Acid Works. Compressed $CO_2$ (purity 99.8%) was purchased from Singapore Oxygen Air Liquide.

### Methods

#### Synthesis of perfluoroalkyl-functionalized oleophobic SiO$_2$ nanoparticles

10 g of fumed $SiO_2$ was added to a well-mixed solution of 220 mL ethanol, 11 mL 28% aqueous $NH_3$ and 0.5 mL of *1H,1H,2H,2H*-perfluorooctyltriethoxysilane, which was then homogenized (using an IKA T18 basic Ultra Turrax digital homogenizer) for 30 min until a homogeneous suspension was obtained. The resulting dispersion was stirred at 400 ± 50 rpm at room temperature overnight, after which the dispersion was heated on a hot plate to evaporate the solvents and subsequently dried in an oven at 80 °C for 1-2 days to collect the dry perfluorinated silica powder. Thermogravimetric analysis (TGA) was performed using a TGA Q500 v6.7 Build 203 instrument, from room temperature to 800 °C at a rate of 20 °C/min with 40 mL/min of nitrogen gas as balance gas and 60 mL/min of air as sample gas. TGA of perfluorinated silica *versus* unmodified fumed silica particles showed that the perfluorocarbon groups comprised approximately 35 wt.% of the functionalized silica (Figure S2). Dynamic Light Scattering (DLS) studies were performed with a Brookhaven ZetaPlus Zeta Potential Analyzer, to determine the size distribution of

137  unmodified fumed silica particles *versus* perfluorinated fumed
138  silica particles after dispersing them in ethanol. DLS studies
139  showed that the average aggregate size of perfluorinated silica
140  particles was smaller than that of unmodified fumed silica
141  particles (282 nm *vs* 367 nm, see Table S2).

142

143  **Preparation of dry alkanolamines**

144  5 g of perfluorinated $SiO_2$ nanoparticles was placed in a plastic
145  beaker while 5 mL of the selected alkanolamine (pre-heated for
146  1 hr. at 100 °C to minimize the water content) was slowly
147  added into the beaker and blended with the particles using a
148  simple coffee whisk (Figure S3a) at a rate of 500–1800 rpm for
149  1 min or until formation of a free-flowing powder.

150  **Absorption of $CO_2$ into bulk or dry alkanolamines**

151  The reaction was performed at room temperature and pressure.
152  5 mL of alkanolamine or approximately 10 g of $DA_f$ powder
153  (containing 5 mL of alkanolamine) was put into a round-
154  bottomed flask placed in a water bath to modulate the heating
155  effects arising from the exothermic nature of the reaction. $CO_2$
156  gas was bubbled at a flow rate of 500 ± 50 mL/min through the
157  flask with the outlet connected to a gas bubbler until the
158  absorption profile plateaued. At short time intervals of 30 sec or
159  1 min, the flask was taken out of the water bath, dried and
160  weighed on a weighing balance to record the increase in mass.
161  The maximum $CO_2$ uptake by alkanolamines (in the absence of
162  water) was calculated by assuming a reaction mole ratio of 2:1
163  alkanolamine to $CO_2$.

164

165  **Regeneration of sorbents by conventional hotplate heating**

166  The $CO_2$-loaded alkanolamine or $DA_f$ powder was regenerated
167  by bubbling argon gas at a flow rate of 500 ± 50 mL/min
168  through the sorbent while the flask was heated in an oil bath at
169  120 °C to release the absorbed $CO_2$. The flask was equipped
170  with a reflux condenser maintained at 15 °C to minimize the
171  evaporative loss of the sorbents and the outlet was connected to
172  a gas bubbler.

173  **Regeneration of sorbents by dielectric heating**

174  The $CO_2$-loaded $DA_f$ powder was put in an open Teflon cup.
175  The cup was placed in a holder and subsequently placed in a
176  programmable microwave synthesizer at 2.45 GHz. The
177  maximum power of the synthesizer was set at 500 W. No purge
178  gas was used. To maintain the stripping temperature of 120 °C,
179  a thermocouple was inserted into a separate Teflon cup
180  containing unloaded-sorbent which provided feedback to the
181  software to control the microwave power. In addition, stirring
182  of the sample within the cup was carried out as part of the
183  microwave heating process. The microwave synthesizer was
184  used to heat the $CO_2$-loaded sorbent at 120 °C for
185  approximately 1 hr until no further mass loss occurred, after
186  which time the cup was removed and weighed. The decrease in
187  weight was attributed to $CO_2$ loss (typical mass decrease for
188  diethanolamine: 0.08-0.1 g/g $DA_f$ or 0.16-0.2 g/g bulk DEA).

## Results and discussion

Brunauer-Emmett-Teller (BET) analysis performed on
perfluorinated $SiO_2$ particles showed that $CO_2$ adsorption on
these particles at room temperature was negligible (Figure 2),
because 1 g of perfluorinated $SiO_2$ nanoparticles absorbed
approximately 6 mg of $CO_2$ at atmospheric pressure while 1 g
of the $DA_f$ (containing 0.48 g of perfluorinated silica) absorbed
approximately 100 mg of $CO_2$. Of this 100 mg, about 3% is
attributed to adsorption by silica. Hence, the mass increase is
largely due to $CO_2$ uptake by the alkanolamine.

Carbon dioxide absorption results for both $DA_f$ and bulk
liquid are shown in Figure 3. The theoretical maximum
alkanolamine $CO_2$ uptake (in the absence of water) was
calculated by assuming a reaction mole ratio of 2:1
alkanolamine to $CO_2$. Hence, 1 g MEA theoretically absorbs
about 0.36 g $CO_2$ at maximum, and 1 g DEA theoretically
absorbs 0.21 g $CO_2$. Based on Figure 3, $CO_2$ absorption by dry
and bulk MEA in the first 10 min of $CO_2$ exposure reached 98
and 60 wt% of the theoretical maximum absorption
respectively. Similarly, dry and bulk DEA achieved about 90
and 35 wt% of the theoretical maximum within 20 min. Mass
changes due to replacement of air in the reaction vessel
headspace with $CO_2$ were taken into account in the calculations.
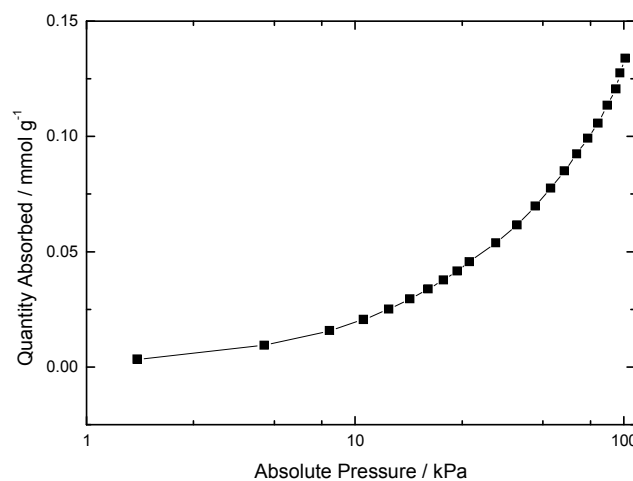


**Figure 2.** Isothermal $CO_2$ adsorption at 22 °C by perfluorinated
$SiO_2$ nanoparticles showing negligible $CO_2$ uptake (0.135 mmol
$g^{-1}$ at 100 kPa).

For both amines, the $DA_f$ showed significantly higher $CO_2$
absorption than their corresponding bulk liquid counterparts
(Figure 3). The lower absolute absorption of the bulk amines is
due to mass transport effects arising from the large increase in
the liquid viscosity caused by carbamate salt formation, which
was verified by measuring the viscosities of the alkanolamine
liquids before and after $CO_2$ absorption (Table S3). The effect
of viscosity of a liquid on the mass transfer kinetics is described
by the Stokes-Einstein equation:[34]

228

$$D_{ij} = \frac{kT}{n_{SE}\,\pi\,\eta_j\,R_i}\left[\frac{R_j}{R_i}\right] \qquad (1)$$

(a)



(b)
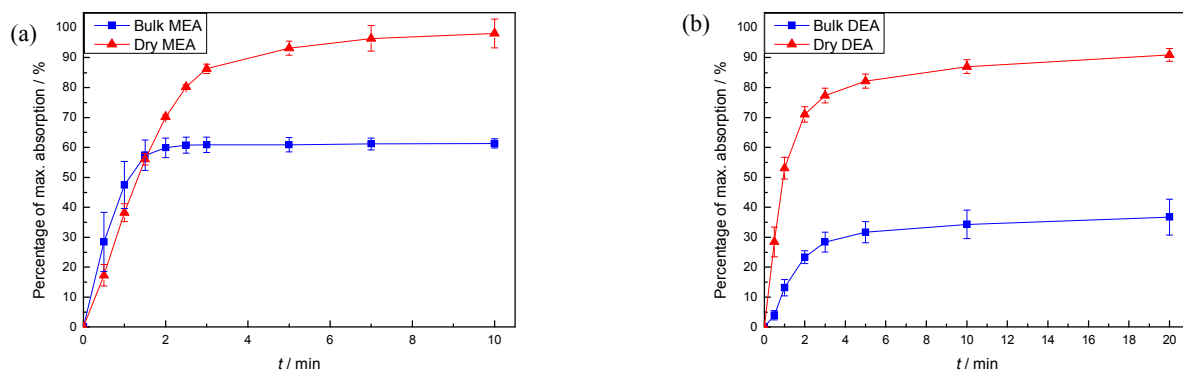


**Figure 3.** Results of the absorption profile of $CO_2$ into bulk alkanolamine or $DA_f$ for (a) MEA (b) DEA at room temperature and pressure.

(a)



(b)



(c)



(d)
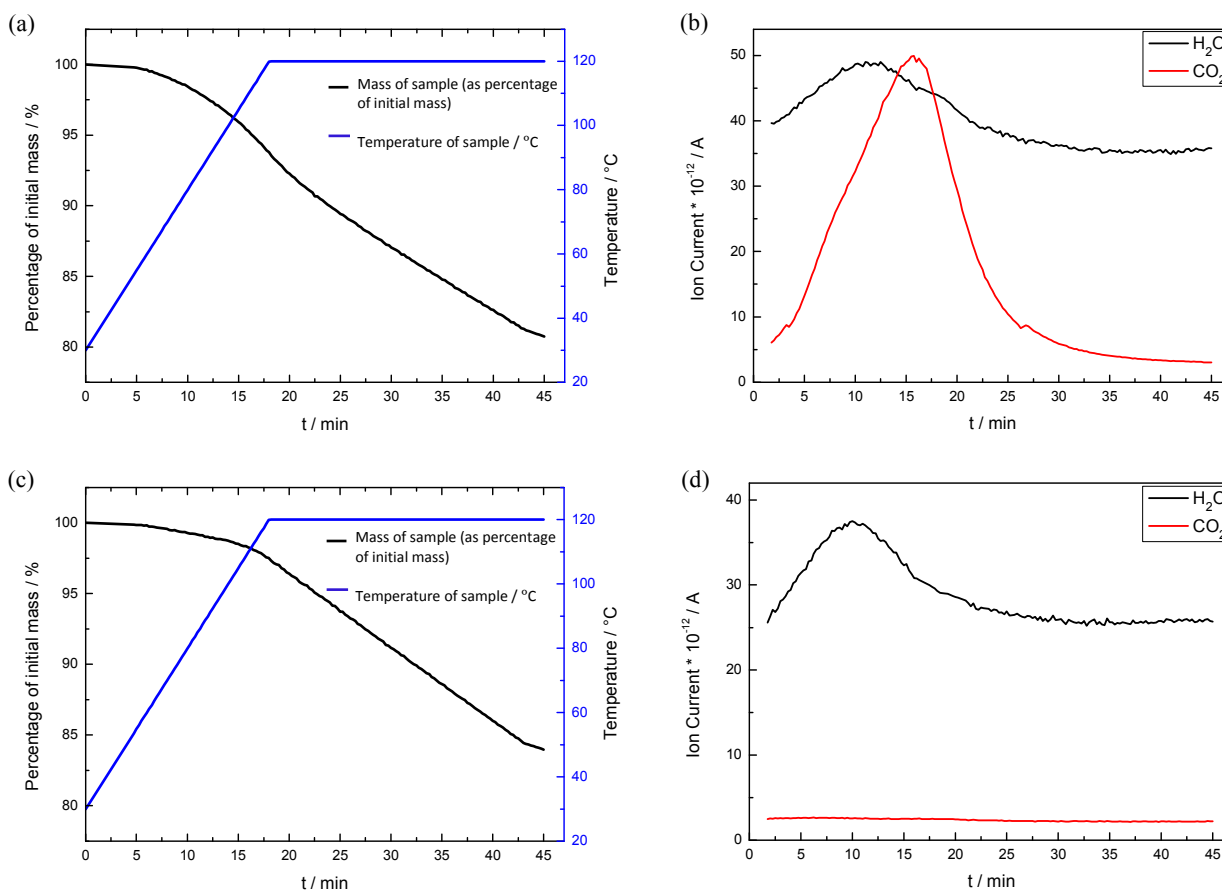


**Figure 4**. (a) and (b) TG-MS graphs of $CO_2$-loaded bulk DEA, (c) and (d) TG-MS graphs of bulk DEA without $CO_2$ loading. (a) The black line shows a decrease of 18.92% of the initial sample mass for $CO_2$-loaded bulk DEA with a concomitant increase in sample temperature from 30 to 120 ºC as depicted by the blue line, (b) graph corresponding to (a), depicting ion current detection of both $CO_2$ and $H_2O$. (c) The black line shows a decrease of 16.03% of the initial sample mass for bulk DEA, (d) graph corresponding to (c) depicting detection of only $H_2O$ but not $CO_2$.

In this equation, $D_{ij}$ is the diffusion coefficient of solute $i$ in pure solvent $j$, $k$ is the Boltzmann constant, $T$ is the temperature, $n_{SE}$ is the Stokes-Einstein number, $\eta_j$ is the solvent viscosity, $R_i$ is the radius of the solute molecule and $R_j$ is the radius of the solvent molecule. According to Equation (1), the diffusion coefficient of $CO_2$ gas in the amine sorbent decreases with increasing solvent viscosity. Further, given that the system studied is stationary and unagitated, increased

viscosity also significantly affects the replenishing of unreacted amine near the gas-liquid interface, which is dependent upon movement of alkanolamine molecules towards the interface *via* convection currents or diffusion.

However, due to the small domain sizes within $DA_f$ (approximate diameter of a microscopic liquid marble is $80 \pm 30$ μm, as measured by cryo-SEM), the required distance of $CO_2$ diffusion within the droplets to contact unreacted alkanolamine is significantly less than for the bulk liquid. This helps to explain why the $DA_f$ achieve a much larger gas absorption relative to the theoretical capacity within the timeframe of the experiment than do the bulk amines. In addition, the reason for the slightly higher absorption capacity for dry MEA compared to dry DEA is due to the inherently lower viscosity of the former compared to the latter.

Based on the work of Wang *et al.*,[31] who postulated that the higher methane gas hydrate formation rate in dry *versus* bulk water was due to the higher surface area to volume ratio in dry water, and taking the view that the rate of gas uptake is dependent upon the gas-liquid interfacial area, we expect that the $CO_2$ absorption rate by $DA_f$ would follow a similar trend (estimated surface area to volume ratio in $DA_f$ is 75,000 $m^{-1}$ based on volume of alkanolamine present). Nevertheless, the gas-liquid interfacial area for the microscopic liquid droplets is reduced by the presence of the silica shell around each droplet; $CO_2$ must diffuse across this porous shell to react with the encapsulated alkanolamines.

Our $CO_2$ uptake studies showed that for MEA, the absorption rate by the bulk liquid in the first minute was faster than that by dry MEA (Figure S4). This is presumably because the lower liquid viscosity of MEA compared with DEA means that $CO_2$ mass transfer effects do not outweigh the effect of the silica barrier initially. However, as carbamate formation proceeds, the viscosity of the liquid mixture increases (Table S3), and mass transfer effects become more important. The rate of $CO_2$ uptake therefore becomes faster for dry over bulk MEA. For DEA, dry DEA exhibits faster $CO_2$ absorption than bulk DEA throughout the entire absorption cycle (Figure S4), because the mass transfer rate in the more viscous DEA liquid was much slower and hence the effect of higher surface area to volume ratio of dry DEA was more prominent.

Since the carbamate salts decompose in the temperature range of 100-150 °C,[35,36] the $CO_2$-loaded bulk alkanolamines were heated to 120 °C to release the absorbed $CO_2$ gas and regenerate the alkanolamines. The decrease in mass was attributed to both $CO_2$ and $H_2O$ release, which was verified by thermogravimetric mass spectroscopy (TG-MS) analysis (see Figure 4).

For each sample of bulk alkanolamine and $DA_f$, three cycles of absorption and desorption of $CO_2$ were performed (Figure 5). Based on Figure 5, DEA appears to be more recyclable than MEA, with negligible change in $CO_2$ uptake capacity over three cycles. This is because secondary amines like DEA form weaker bonds with $CO_2$ than primary amines like MEA, allowing for easier regeneration of the free amines.[37] This is supported in the findings of McCann *et al.*, where the enthalpy

of carbamate formation for MEA and DEA was found to be $-29.7$ kJ/mol and $-23.7$ kJ/mol respectively.[38] Moreover, MEA has a lower boiling point than DEA (170 °C *vs* 271 °C) and a much higher vapour pressure, leading to a greater degree of sorbent loss per cycle.

As heating is essential for the sorbent regeneration process, it is imperative to maximize the heat transfer efficiency within the amine sorbents. This is dependent on the three main mechanisms of heat transfer, namely conduction, convection and radiation. In the case of $DA_f$, these three mechanisms happen to be hindered by the silica shell encasing the micronized alkanolamine droplets and the air pockets throughout the dry liquids. For heat transfer *via* conduction, fumed silica particles exhibit low thermal conductivity due to the nanoscale pores among them in their fractal arrangement,[39,40] causing the silica shell to block effective heat conduction from the heat source to the droplets. Importantly, the many air pockets between the microscopic particle-coated liquid marbles in $DA_f$ also limit heat conductivity. With regards to convection, the liquid in $DA_f$ exists as dispersed microscopic droplets, thereby limiting convective heat transfer. As for radiative heat transfer, Taylan and Berberoglu have shown that the silica shell in dry water greatly attenuates infrared radiative heat transfer due to its high single-scattering albedo, *i.e.* a significantly larger proportion of heat radiation is scattered compared to that absorbed by the silica shell,[41] thus preventing infrared radiative heat transfer from the heat source to the droplets.

(a)
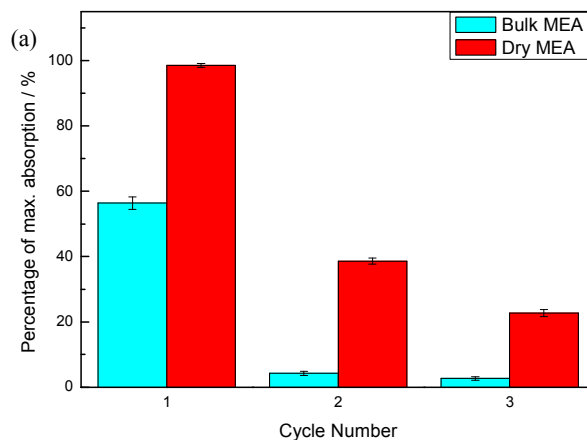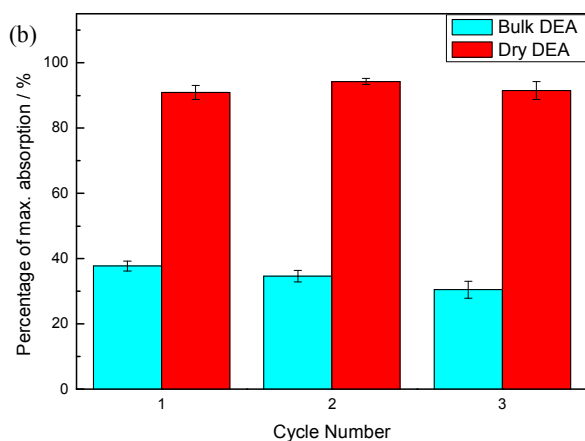
**Figure 5.** Comparison of solvent recyclability for (a) bulk MEA *versus* dry MEA, whereby heating lasts for 2 hr. for each cycle of regeneration and (b) bulk DEA *versus* dry DEA, whereby heating lasts for 1 hr. for each cycle of regeneration.

Since the three major forms of heat transfer are significantly inhibited for $DA_f$, we turned to microwave heating as an alternative method to improve the efficiency of heat transfer during the regeneration process. This method is dependent on the ability of the irradiated material, *e.g.* a solvent, to absorb microwave energy and convert it to heat, which is quantified by a dielectric parameter called the loss factor *tan δ*. This loss factor is expressed as:[42]

$$tan\,\delta = \frac{\varepsilon''}{\varepsilon'} \tag{2}$$

where $\varepsilon''$ is the dielectric loss, which is indicative of the efficiency with which electromagnetic radiation is converted into heat, and $\varepsilon'$ is the dielectric constant describing the ability of molecules to be polarized by the electric field. A solvent with a high *tan δ* value of more than 0.5 is required for efficient microwave absorption. DEA, with a high *tan δ* value of ~ 0.6 at 2.45 GHz at 278 K can be rapidly heated to temperatures >100 °C within a minute when irradiated under microwave conditions.[42,43]
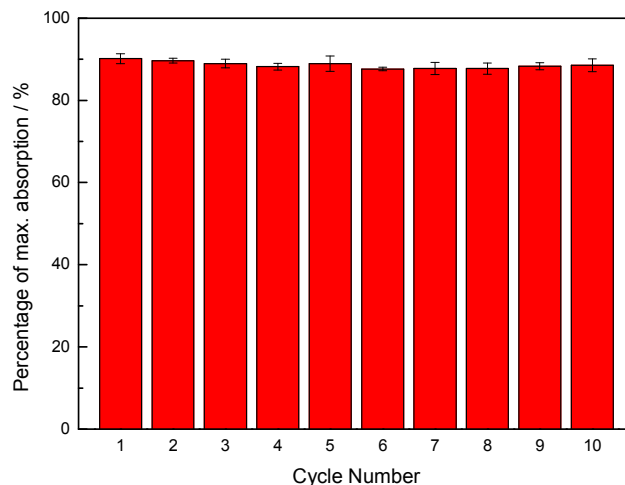


**Figure 6.** Sorbent recyclability for dry DEA using dielectric heating (1 hr. per cycle) for regeneration, showing negligible drop in absorption capacity over 10 cycles.

Owing to the higher recyclability of DEA over MEA, we chose to study DEA for microwave heating-based regeneration. Samples of approximately 10 g of dry DEA containing 5 mL of liquid DEA were loaded with $CO_2$ until the absorption plateaued, and the $CO_2$-loaded samples were subsequently heated in a programmable microwave synthesizer at 120 °C for approximately 1 hr. until no further mass loss occurred. To test the recyclability of the sorbent and confirm that the observed mass loss was correctly attributed to $CO_2$ loss, 10 repeated cycles of $CO_2$ absorption and removal were carried out, as shown in Figure 6. The level of $CO_2$ uptake by dry DEA was found to be stable over at least 10 cycles, showing excellent recyclability of dry DEA. Similar regeneration results were obtained using a simple household microwave instrument, although the heating periods were limited to 10-20 sec in order to avoid overheating.

Regeneration of $DA_f$ *via* microwave heating was found to be more efficient than conventional hotplate heating under the same conditions (whereby no purge gas was used). Conventional hotplate heating took more than 3 hr and consumed about 0.38 kWh per cycle on average. Microwave heating on the other hand took about 1 hr and consumed about 0.034 kWh per cycle on average, which is less than 10% of the energy consumption by conventional hotplate heating.

Finally, the recyclability of the perfluorinated silica particles was investigated. Alkanolamines typically undergo degradation over multiple absorption and regeneration cycles after which they must be replaced.[44] Nevertheless, the perfluorinated silica particles could be separated from the amines by dispersion of $DA_f$ in ethanol and then centrifuged, and re-used in at least three subsequent batches of $DA_f$. This leads to significant cost-savings since only the alkanolamines need to be replaced.

## Conclusions

In conclusion, the dry alkanolamines described herein demonstrate significantly enhanced performance with regards to $CO_2$ absorption capacity and sorbent recyclability. Furthermore, the novel dielectric heating technique for sorbent regeneration proposed here has proven to possess the benefits of reduced energy consumption and minimal use of purge gas. The perfluorinated silica particles can also be recycled and re-used to prepare $DA_f$ with negligible change in their wettability and overall quality for at least three cycles. Moreover, as suggested by the recent work of Dawson *et al.*,[25] the amine component of the $DA_f$ is also isolated by the silica particles from pipelines and other corrosion sensitive materials, leading to further reduction in maintenance costs associated with adding corrosion inhibitors and repairing damage to pipelines. Last but not least, this novel method of using $DA_f$ is not restricted to MEA and DEA; in principle any dry liquid can be formed provided that nanoparticles of the appropriate surface energy are selected.[33] The implications are that this idea can be extended to other liquid $CO_2$ sorbents, possibly leading to a similar improvement in absorption rate and capacity. However, there still exist several challenges for the application of $DA_f$ industrially. Firstly, the powdery nature of $DA_f$ will likely require significant changes in the current process technology and facilities specialized in handling liquid amine sorbents. Secondly, due to the nanoscale primary particle size of fumed silica, careful confinement of the powder needs to be put in place to prevent contamination in the outlet gas stream. Thirdly, stripper columns need to be modified to incorporate dielectric heating capabilities. Nevertheless, given the multiple advantages of utilizing $DA_f$ for $CO_2$ absorption and desorption, we believe that they should still be considered promising candidates for practical applications in $CO_2$ capture.

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## Notes and references

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Electronic Supplementary Information (ESI) available: detailed experimental procedures, SI Figures S1-S4 and SI Tables S1-S3. See DOI: 10.1039/c000000x/

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Dry alkanolamines are shown here to be highly efficient $CO_2$ sorbents, recyclable via microwave regeneration.