Dynamic Study of Direct CO2 Capture from Indoor Air using Poly(ethylenimine)-Impregnated Fiber Sorbents

<table>
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<th>Journal:</th>
<th>Sustainable Energy &amp; Fuels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>SE-ART-05-2023-000618.R1</td>
</tr>
<tr>
<td>Article Type:</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>17-Jul-2023</td>
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Dynamic Study of Direct CO\textsubscript{2} Capture from Indoor Air using Poly(ethylenimine)-Impregnated Fiber Sorbents

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Abstract

Supported amine adsorbents are promising materials for direct air capture (DAC) of CO\textsubscript{2} due to their high CO\textsubscript{2} capacity and relatively low energy requirement for regeneration. For a DAC process, it is essential to properly define operating parameters to achieve high sorbent productivity (amount of CO\textsubscript{2} captured per unit quantity of sorbent material over unit time). It is furthermore essential to understand the kinetic behavior of the process under the influence of various operating conditions such as the inlet air velocity, sorbent composition, and humidity to select an effective range of operating conditions to maximize sorbent productivity. Here, the dynamic behavior of a DAC process is probed using a fixed fiber sorbent contactor containing poly(ethylenimine) (PEI)-impregnated composite silica/cellulose acetate (CA) fibers. Experiments are conducted using both simulated air (398 ppm CO\textsubscript{2} balanced by N\textsubscript{2}) and real indoor air (~400-500 ppm CO\textsubscript{2}). The experimental behavior of the fibers using simulated air and indoor air is compared, and the influence of the inlet air velocity on the breakthrough behavior is assessed. By changing operating conditions, the impact on the fiber sorbent productivity (mmol CO\textsubscript{2} \cdot g\textsubscript{fiber}\textsuperscript{-1} \cdot h\textsuperscript{-1}) is quantified to identify conditions that could favor high rates of CO\textsubscript{2} removal. The kinetics of steam-assisted CO\textsubscript{2} desorption are studied, identifying achievable desorption times. Productivities of 1.2 mmol CO\textsubscript{2} \cdot g\textsubscript{fiber}\textsuperscript{-1} \cdot h\textsuperscript{-1} are obtained using an inlet air velocity of 1.1 m/s. Performance trends show that further increasing the inlet air velocity will likely lead to even higher productivities.
1. Introduction

To effectively halt and reverse climate change, it is essential to develop methods that can directly remove CO₂ from the atmosphere, producing “negative emissions,” to achieve a net reduction in the atmospheric CO₂ concentration. Two classes of technologies exist that can lead to a net reduction in the atmospheric CO₂ concentration. The first is chemistry-based direct air capture technologies (DAC),¹–⁸ and the second is bio-based systems such as bioenergy with carbon capture and storage technologies (BECCS).⁹,¹⁰ The advantages of DAC over BECCS include less land use per unit amount of CO₂ captured¹¹–¹⁴ and potential to be deployed around the globe,¹⁵ including places unsuitable for plant growth or harvesting. The advantages of BECSS over DAC include the creation of a valuable co-product (energy). For DAC, multiple approaches have been proposed and studied, as summarized in the review papers by Sanz-Perez et al.¹⁶ and Zhu et al.¹⁷ Among the proposed DAC technologies,¹⁸–²⁷ amines supported on solid substrates have been shown to be particularly promising,²⁸–³³ and a variety of amine molecules³⁴–³⁸ and support materials³⁹–⁴² have been studied. Recently, additional research efforts have been devoted to DAC at cold temperatures to promote the application of DAC across a wider geographical expanse.¹⁵,⁴²–⁴⁴

In practical DAC units, it is essential to ensure a low pressure drop in the DAC unit to reduce the energy consumption in moving the ambient air and reduce the associated operating costs.⁴⁵–⁵¹ Therefore, it is crucial to select an appropriate contactor configuration that can lead to a minimal pressure drop. Sorbents in the shape of monoliths and fibers have been studied in the past and both are proven to be promising contactor structures with low pressure drops and relatively fast mass transfer.⁵²–⁵⁷ This study focuses on amine-impregnated fiber materials for DAC applications.⁵³,⁵⁸

In the past, a large number of studies have been conducted on fiber sorbents for CO₂ separation from flue gas.⁵⁹–⁶⁴ Recently, research efforts have shifted toward using these materials for DAC applications. Sujan et al.⁵³ studied the use of poly(ethylenimine) (PEI)-loaded silica fibers for CO₂ capture from simulated air and reached pseudoequilibrium CO₂ capacities of 0.59 and 1.6 mmol CO₂/g fiber from breakthrough experiments under dry and humid conditions, respectively. Wilfong et al.⁵⁴ studied directly spun epoxy-crosslinked PEI fiber sorbents and reached a CO₂ capacity of 0.2 mmol CO₂/g fiber during DAC cycling experiments in a ten-fiber module. Armstrong et al.⁶⁵ studied the system kinetics of DAC by sorbent-containing porous electro-spun fibers made with the solvothermal polymer additive removal technique, reaching a high cyclic capacity with an estimated productivity of 1.4 mmol CO₂ per gram-hour. Sekizkardes et al.⁶⁶ investigated fibers of
polymers of intrinsic microporosity (PIM) based on amidoxime and amine functionalities for DAC, and achieved a 0.8 mmol CO$_2$/g fiber uptake and a rapid CO$_2$ adsorption rate (5 minute adsorption cycle). Zhang et al.$^{67}$ studied tetraethylenepentamine-grafted polyacrylonitrile (TEPA@PAN) hollow fibers and achieved a CO$_2$ capacity of 2.03 mmol/g at ambient CO$_2$ concentration. Despite these above studies, to date, there is a dearth of research data published on CO$_2$ adsorption kinetics using real ambient air in a system setup mimicking realistic industrial DAC, especially on fibrous materials. Most kinetics studies have instead been focused on post-combustion CO$_2$ capture.$^{68,69}$ For the scale-up and commercialization of DAC technologies using fiber sorbents, it is essential to understand the fiber performance in ambient air, which may differ from simulated air due to the presence of varying humidity and several trace components. In addition, in industrial-scale DAC operations, air velocities as high as several meters per second may be applied to ensure rapid loading of the adsorbent. In contrast, breakthrough studies conducted so far in the laboratory have only reached air velocities on the magnitude of ~0.1 m/s.$^{53}$ Thus, there is a knowledge gap between the operating conditions of lab-scale tests and what is needed for commercial-scale applications of fiber sorbents.

The objective of this work is to analyze the dynamic performance of fiber sorbents using ambient indoor air. CO$_2$ breakthrough tests were conducted using both simulated air and real indoor air and the results are compared. The influence of operating conditions such as inlet air flowrates and PEI loadings on the system’s dynamic performance is analyzed. The operating conditions leading to maximum CO$_2$ productivity are identified. Moreover, the desorption phase was also studied via indirect contact steam heating as a preliminary verification of reasonably fast desorption kinetics.

2. Materials and Methods

2.1. Materials

Cellulose acetate (CA) (MW 50,000 Da) was purchased from Sigma-Aldrich Inc. Amorphous silica (C-803) was purchased from Grace Davison Inc. N-Methyl-2-pyrrolidone (NMP) (Reagent Plus, 99%) was purchased from Sigma-Aldrich and used as the solvent for polymer-dope preparation. Poly(vinylpyrrolidone) (PVP) (MW 55,000 Da) was purchased from Sigma-Aldrich and used as the pore-forming agent for the open-pore network in the polymer/silica fiber sorbents. Methanol (ACS Grade) and n-hexane (ACS Grade) were purchased from VWR. They were used in the solvent-exchange step to remove water and residual NMP in spun fibers. All solvents were used as received from the manufacturer with no purification or modification. Branched PEI (MW 800
Da) was purchased from Sigma-Aldrich and used as the amine source in post-spinning functionalization. Single-component gases and gas mixtures were purchased from Airgas as ultrahigh-purity (UHP) grade. A gas mixture of 398 ppm of CO$_2$/balance N$_2$ i.e. simulated air, was used for breakthrough experiments.

2.2. Preparation of Fiber Sorbents

CA-silica fibers were spun via the dry-jet, wet quench spinning technique using a custom-built fiber spinning line. The silica/CA ratio used for making the polymer dope was 60:40 wt%, which is close to the practical maximum. All polymers and silica were dried under 25 in Hg vacuum at 110 °C for 12 hours before being made into the polymer dope. More technical details on the silica fibers and the spinning procedure can be found in previous literatures.$^{53,58,64}$

After spinning, the fibers were impregnated with PEI via the following impregnation procedure: fibers were soaked in a vial containing 50 mL methanol. Then, PEI was added to the vial until reaching the desired concentration. Three types of fibers were prepared in separate vials with different PEI concentrations (10 wt%, 15 wt%, and 20 wt%). The amount of fiber in each vial was approximately 3 g. The vials were placed horizontally during the impregnation. The fibers stayed in the PEI solutions for 4 hours at 20 °C. Then, the impregnated fibers were solvent-exchanged with n-hexane. Finally, the impregnated fibers were dried at ambient temperature and pressure overnight.

2.3. Fiber Characterization

*Scanning electron microscopy (SEM)*

SEM was performed on a Hitachi SU8230 with a cold field emission gun at an accelerating voltage of 3 kV and an emission current of 10 μA.

*N$_2$ physisorption*

N$_2$ physisorption was conducted for pristine and impregnated fibers at 77 K on a surface area and porosity (SAP) system (autosorb iQ/Quantachrome). In each experiment, ~100 mg of fiber sample was activated at 110 °C for 6 h before the measurement. The BET surface area was estimated using the N$_2$ physisorption data in the P/P$_0$ range of 0.05 to 0.2.

*CO$_2$ adsorption*

The equilibrium CO$_2$ adsorption performance of PEI-CA-SiO$_2$ fibers was measured at 25 °C using an SAP system (autosorb iQ/Quantachrome). In each experiment, ~100 mg of fiber sample was
activated at 110 °C for 6 h before the measurement. An equilibration interval of 1 min was used, where the cell pressure was checked every 1 min and compared until the pressure in the cell was within the pressure tolerance (manufacturer tolerance setting 0). If the cell pressure dropped below the lower limit of the P/P₀ tolerance, the data point was stored.

**TGA combustion experiments**

The compositions of the pristine and impregnated fibers were estimated by TGA combustion experiments. The TGA equipment was a Q500 from TA instrument. In the experiment, the temperature was first increased from room temperature to 200 °C at 10 °C / min and kept at 200 °C for 1 hour under N₂ to remove all adsorbed CO₂ and H₂O. Then, the temperature was increased to 900 °C by 10 °C / min under simulated air (79% N₂ and 21% O₂, different from the simulated air mentioned elsewhere in this paper, which did not contain O₂) to burn off all organic components. The weight loss between 200 and 900 °C was the weight of organic component, i.e., CA and PEI, while the remaining weight at the end of the experiment was the weight of silica. From the results, the CA/silica weight ratio of the pristine fibers, as well as the PEI loading of impregnated fibers, were calculated.

2.4. Experimental System Setup

The system for the breakthrough experiments consisted of a simulated air injection system, an ambient air injection system, and a steam delivery system, as shown in Figure 1. In the ambient air injection system, three fans were placed in series to provide the required pressure to drive the air through the sorbent module. In this work, the maximum air velocity achieved by using three fans was 1.1 m/s.

A speed controller was installed to allow the fans to operate at lower power to provide lower air velocities when needed. This allowed the fans to provide an inlet air velocity as low as 0.17 m/s, a condition also tested in this work. The ambient air was propelled by the fans to flow through a flowmeter before entering the sample module to measure the air flowrate. The outlet gas was connected to a LI-850-3 LI-COR detector purchased from LI-COR Biosciences to measure the CO₂ and H₂O concentrations. Right before and after each adsorption test, the CO₂ concentrations in air were measured and the average of the two values was used in calculating the CO₂ uptake for that adsorption test. For all tests using indoor air conducted in this work, the CO₂ concentration in air was between 400 and 500 ppm.
The fiber module was a 20-cm long stainless-steel tube with an inner diameter of 0.43 cm. Inside, 40 PEI-CA-SiO$_2$ fibers filled the fiber module. The void fraction in the module was 63%.

Before the adsorption experiment, the fiber module was wrapped with a heating tape, which heated the fibers to 110 °C under flowing N$_2$ for 30 min to remove the adsorbed CO$_2$ and H$_2$O. Then, the heat was turned off and the fibers were allowed to cool down to room temperature (~25 °C) with the same N$_2$ flow. For the tests using simulated air, 398 ppm CO$_2$ balanced by N$_2$ was passed through the fixed bed; for the tests using ambient air, indoor air was propelled by the fans to pass through the fixed bed. For the tests using ambient air, the inlet ambient CO$_2$ concentration was measured right before and after each adsorption test, and the average of the two values was used as the ambient CO$_2$ concentration for that adsorption test. Both the inlet and outlet gas CO$_2$ and H$_2$O concentrations were measured by the LI-COR detector.

After the adsorption phase, the fibers were regenerated under N$_2$ flow at 110 °C for 10 min, and the modules were cooled following the same protocol before the next adsorption-desorption cycle.

For experiments involving humidity, a pre-humidification step was added after the post-desorption cooldown and before the next adsorption phase. N$_2$ was passed through a bubbler containing a saturated salt solution of KCl in deionized water before entering the fixed bed. The saturated KCl solution set the outlet gas RH at 85%. The vapor concentration of the outlet gas was monitored by the LI-COR detector to ensure that the fibers were fully saturated with H$_2$O before starting the adsorption. After reaching complete hydration of the sample, the inlet gas was switched to simulated air of 85% relative humidity (RH) reached by passing the gas through another bubbler containing KCl solution.
Figure 1. Schematic diagram of the experimental system used to perform both adsorption and desorption experiments. The system consists of a simulated air injection system, an ambient air injection system, and a steam delivery system for desorption by indirect heating.

The steam delivery system is also depicted in Figure 1. Water was converted into saturated steam in the steam generator. The saturated steam then flowed through a tube wrapped with heating tape to be further heated. The superheated steam then entered the heating jacket surrounding the fixed bed where the fiber sample was placed. The superheated steam exchanged heat with the sample via indirect contact heating. Finally, steam was condensed into water in the condenser.

The steam generation rate of the steam generator was 5.8 g/min. The temperature of the heating tape was set at 130 °C. Calculations showed that this provides a thermal input of 5.8 W into the sample module if only the sensible heat of the steam is used, and 224 W if the latent heat of condensation is also used.

During the test, the steam generator and the heating tape were turned on for at least one hour for thermal stabilization before starting the experiment. During this period, the steam generated flowed through the bypass line to directly reach the condenser. After achieving a stable steam flow, 500 sccm N\textsubscript{2} was flowed into the fixed bed to sweep out the O\textsubscript{2} from the bed, where fibers with CO\textsubscript{2} sorbed to pseudo-equilibrium conditions were present. Next, steam entered the heating jacket surrounding the fixed bed. This point was recorded as the starting point of the desorption phase. The outlet gas composition was measured by the LI-COR detector. The reason for re-
diluting the adsorbed CO\textsubscript{2} with N\textsubscript{2} was that the LI-COR detector could not accurately measure CO\textsubscript{2} concentrations above 2%, and hence a sufficiently high N\textsubscript{2} flow through the fixed bed was needed for the peak concentration of CO\textsubscript{2} in the outlet gas to be less than 2%. This allowed accurate measurements of the amount of CO\textsubscript{2} desorbed as well as the CO\textsubscript{2} desorption kinetics. This desorption study was more focused on CO\textsubscript{2} desorption kinetics, and the CO\textsubscript{2} purity of the desorbed gas would be the objective of future studies.

3. Results and Discussion

3.1. Characterization of Amine-Functionalized Sorbents

SEM images were taken of the as-spun fibers, as shown in Figure 2. The fibers have an average diameter of 410 microns. SiO\textsubscript{2} particles with an average size from 3 to 6 \( \mu \text{m} \) appear to be held in place by the surrounding polymer matrix and are uniformly embedded throughout the polymer matrix. No observable skin layer was noted on the outside of the fiber.

Figure 2. SEM images of as-spun fibers. (a) the entire cross-section of a fiber. (b) the cross-section of a fiber further magnified. (c) the cross-section of a fiber further magnified to show the SiO\textsubscript{2} particles held by the surrounding polymer matrix and the outer surface of the fiber sorbent.

The composition of pristine fibers was estimated by TGA combustion experiments. The silica to CA weight ratio was calculated using Equation 1:

\[
\frac{m_{\text{silica}}}{m_{\text{CA}}} = \frac{\text{sample wt after combustion}}{\text{initial sample wt} - \text{adsorbed CO}_2, \text{H}_2\text{O wt} - \text{sample wt after combustion}}
\]

The silica weight fraction of the pristine fibers was calculated to be 52%, which was slightly lower than the weight fraction in the dope (60%), indicating some silica loss during the fiber spinning. This observation is consistent with a previous study.\textsuperscript{53}
The PEI loading in the CA-SiO$_2$ fibers was also estimated by TGA combustion experiments. The PEI loading was quantified as grams of PEI per gram of silica in the fiber, as calculated using the Equation 2, where the weight of CA could be calculated using the silica/CA weight ratio calculated in the previous step:

$$\frac{m_{\text{PEI}}}{m_{\text{silica}}} = \frac{\text{initial sample wt} - \text{adsorbed CO}_2, \text{H}_2\text{O wt} - \text{sample wt after combustion} - \text{CA wt}}{\text{sample wt after combustion}}$$

The fibers impregnated with three different PEI concentrations were also combusted in the TGA to assess their PEI loadings, and the results are shown in Figure 3. As shown in the figure, the PEI loading increases with an increasing PEI concentration in the impregnation solution. The PEI loadings obtained using 10, 15 and 20% PEI solutions are 0.37, 0.68, and 1.04 g PEI/g SiO$_2$, respectively. These three fibers are denoted as 0.37PEI@SiO$_2$, 0.68PEI@SiO$_2$, and 1.04PEI@SiO$_2$, respectively. Compared to a previous study, the PEI loadings obtained in this work are lower when using the same PEI solution concentration. With a 10% PEI solution, the PEI loading in this work is 0.37 g PEI/g SiO$_2$, as compared to 0.7 g PEI/g SiO$_2$ in the previous work. In the previous work it was found that fibers impregnated in PEI concentrations above 10% became gel-like, with a noticeable degree of swelling, and could not be practically assembled into fiber modules. In this work, however, fibers impregnated in the 20% PEI solution still retained their physical integrity and could be assembled into sample modules. This difference suggests that the fibers used for this study might be more compact and less porous than those used previously, and the cause for such a difference is attributed to some nuanced differences in the spinning procedure.
Figure 3. PEI loading on the fibers with different PEI wt% in methanol during impregnation. Impregnation was performed at 20 °C for 4 h, with sample containers placed horizontally.

N₂ physisorption was conducted on pristine and impregnated fibers, and the results are shown in Figure 4. The results indicate that the amount of physisorbed N₂ decreases with an increasing PEI loading. The surface area and pore volume of each fiber sample were calculated and are shown in Table 1. With an increasing PEI loading, the surface area and pore volume decrease rapidly, suggesting that PEI has been successfully impregnated into the fibers. Compared to the previous study,⁵³ the pristine fibers in this study show higher surface areas but lower total pore volumes. Additionally, the surface areas and pore volumes after impregnation are much higher than those in the previous work using the same PEI concentration. This difference is likely due to nuanced differences in the spinning procedures, as both studies used the same batch of silica. This likely also caused the lower PEI loading seen in this work using the same PEI concentration for impregnation.
Figure 4. N\textsubscript{2} physisorption curves of pristine and impregnated fibers.

Table 1. BET surface areas and pore volumes of pristine and impregnated fibers

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<th>Sample</th>
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<th>Pore vol. (cm\textsuperscript{3}/g fiber)</th>
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<td>Pristine</td>
<td>183</td>
<td>0.76</td>
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<tr>
<td>0.37PEI@SiO\textsubscript{2}</td>
<td>133</td>
<td>0.54</td>
</tr>
<tr>
<td>0.74PEI@SiO\textsubscript{2}</td>
<td>68</td>
<td>0.28</td>
</tr>
<tr>
<td>1.04PEI@SiO\textsubscript{2}</td>
<td>31</td>
<td>0.10</td>
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CO\textsubscript{2} isotherms of pristine fibers, 0.37PEI@SiO\textsubscript{2} fibers, and 1.04PEI@SiO\textsubscript{2} fibers are shown in Figure 5. The impregnated fibers show much higher CO\textsubscript{2} uptakes than pristine fibers, and the 1.04PEI@SiO\textsubscript{2} fibers show higher CO\textsubscript{2} uptakes than 0.37PEI@SiO\textsubscript{2} fibers. Moreover, the advantage in CO\textsubscript{2} uptake of the impregnated fibers over pristine fibers, and the advantage in CO\textsubscript{2} uptake of the 1.04PEI@SiO\textsubscript{2} fibers over 0.37PEI@SiO\textsubscript{2} fibers, are more pronounced at lower pressures.
3.2. Comparison between Ambient and Simulated Air

Following the dry isotherm measurements, we explored CO\textsubscript{2} sorption using simulated and real indoor air. During the experiments, the ambient indoor air contained 45 ± 5% relative humidity (RH). This could lead to an increase in CO\textsubscript{2} uptake compared to dry simulated air cases, as moisture assists CO\textsubscript{2} uptake by supported amine sorbents.\textsuperscript{53} This influence of humidity on the system performance was studied by comparing the CO\textsubscript{2} uptakes using indoor air and simulated air. The 1.04PEI@SiO\textsubscript{2} fibers were used for this set of experiments. Three breakthrough tests were conducted at an inlet air velocity of 0.57 m/s, using (i) dry simulated air, (ii) indoor air with 45 ± 5% RH, and (iii) simulated air with 85% RH achieved by passing it through a saturated KCl solution, respectively. The pseudoequilibrium CO\textsubscript{2} uptakes of these three tests, defined as the CO\textsubscript{2} uptake when the outlet CO\textsubscript{2} concentration reached 95% of the inlet CO\textsubscript{2} concentration, are plotted in Figure 6. It is seen that the CO\textsubscript{2} uptake using ambient air lies between the CO\textsubscript{2} uptakes using simulated air of 0 and 85% RH. The CO\textsubscript{2} uptake at 0% RH is consistent with the CO\textsubscript{2} uptake...
measured by the SAP instrument. This result shows that humidity has a significant impact on improving the CO₂ uptake due to the co-adsorption of H₂O, which enhances CO₂ adsorption onto supported amine sorbents. Another cause for the higher CO₂ uptake using ambient air is the higher CO₂ concentration in ambient air (400-500 ppm) than simulated air (400 ppm). However, as indicated by the SAP CO₂ adsorption experiments, increasing CO₂ concentration by this extent has a relatively small effect on increasing CO₂ uptake. It is therefore presumed that compared to the effect of humidity, the variation in indoor ambient CO₂ concentration plays a relatively minor role.

Figure 6. Comparison of the pseudoequilibrium CO₂ uptakes using indoor air and simulated air. CO₂ concentration = 450 ± 50 ppm, T = 22 °C ± 2 °C, RH = 45 ± 5%.

3.3. Comparing the Kinetics of Fibers Impregnated in PEI Solutions of Different Concentrations

Breakthrough experiments were conducted using ambient air with 0.37PEI@SiO₂ and 1.04PEI@SiO₂ fibers to study the influence of PEI loading on adsorption kinetics using an inlet air velocity of 0.57 m/s. The breakthrough curves are shown in Figure 7 (a). The integrated CO₂ uptake curves are shown in Figure 7 (b). The integrated CO₂ uptake is defined as the accumulated CO₂ adsorption onto the fibers at a given moment. As the plot indicates, the
0.37PEI@SiO$_2$ fibers show an S-shaped breakthrough curve while the 1.04PEI@SiO$_2$ fibers show an immediate breakthrough at the beginning of the adsorption phase. The integrated CO$_2$ uptake curves also demonstrate a clear contrast between the two types of fibers. The 0.37PEI@SiO$_2$ fibers show a much greater slope and reach an elevated CO$_2$ (0.68 mmol/g) uptake much earlier (3000 s), as compared to the moderately higher CO$_2$ uptake (0.95 mmol/g) achieved in much longer time (6000 s) by the 1.04PEI@SiO$_2$ fibers. This suggests that the 0.37PEI@SiO$_2$ fibers have a significantly faster rate of mass transfer, likely due to differences in the extent of PEI pore blockage in the two samples. As shown in Table 1, the BET surface area of 0.37PEI@SiO$_2$ is four times greater than that of the 1.04PEI@SiO$_2$ fibers, and the pore volume of the 0.37PEI@SiO$_2$ fibers is five times greater than that of the 1.04PEI@SiO$_2$ fibers. The 0.37PEI@SiO$_2$ material has considerably greater contact area between CO$_2$ and PEI than the 1.04PEI@SiO$_2$ fibers, where PEI has likely blocked the pores and formed a layer on the surface of the fibers, making it difficult for CO$_2$ to access sorption sites. On the other hand, the CO$_2$ capacity of the 0.37PEI@SiO$_2$ fibers is 30% lower than that of the 1.04PEI@SiO$_2$ fibers. Considering that superior kinetics often outweighs the importance of a moderately higher CO$_2$ capacity, we elected to perform the following breakthrough studies using the 0.37PEI@SiO$_2$ fibers.

Figure 7. (a) breakthrough curves and (b) integrated CO$_2$ uptake curves on 0.37PEI@SiO$_2$ and 1.04PEI@SiO$_2$ fibers using ambient air at 0.57 m/s. CO$_2$ concentration = 450 ± 50 ppm, $T = 22^\circ$C ± 2$^\circ$C, RH = 45 ± 5%.
3.4. Fiber Durability

Ambient air was used to test the breakthrough behavior of the 0.37PEI@SiO$_2$ fibers over multiple cycles. In total, 12 adsorption-desorption consecutive cycles were performed with a relative humidity of 45 ± 5%. The inlet air flow rate was varied between 0.17 to 1.1 m/s in these tests. Tests 1, 3, 5, 8 and 12 were conducted at identical conditions with an inlet air velocity of 0.57 m/s to observe if any loss in capacity occurred throughout the tests. The other tests used different inlet air velocities to study the effects of gas velocity on the kinetic performance of the fibers, as discussed in the following sections. The pseudoequilibrium capacities of these five cycles are shown in Figure 8.

![Figure 8](image)

**Figure 8.** Pseudoequilibrium CO$_2$ capacities of cycles 1, 3, 5, 8 and 12 conducted at 0.57 m/s air velocity. CO$_2$ concentration = 450 ± 50 ppm, T = 22 °C ± 2 °C, RH = 45 ± 5%.

Figure 8 shows that the CO$_2$ capacity did not deteriorate significantly throughout the 12 cycles. The largest capacity loss occurred after cycle 1, where the capacity decreased by 22% from cycle 1 to cycle 3. Afterward, the CO$_2$ capacity stayed relatively stable. From cycle 3 to cycle 12, the CO$_2$ capacity only decreased by 3%.

The water content adsorbed by the fibers was also measured by the Li-Cor detector. The amount of water adsorbed at the pseudoequilibrium capacity is ~6 mmol/g fiber.
3.5. Influence of Varying Inlet Air Velocities

Inlet air velocity is an important parameter for practical deployment of DAC, since cycle times should be short and the feed is highly dilute. Higher air velocity leads to faster mass transfer (reduced external mass transfer resistance) and hence more favorable CO$_2$ adsorption kinetics, but also entails higher energy consumption by the fans that provide air movement. In this work, air velocity was varied between 0.17 to 1.1 m/s to explore its influence on CO$_2$ breakthrough performance. Figure 9 (a) shows the breakthrough curves of cycles 4, 5, 6, and 10, where the inlet air velocities were 0.17, 0.57, 0.35, and 1.1 m/s, respectively (note that the air velocities of cycles 5 and 6 are not in ascending order, as the other cycles are). These air velocities correspond to a contact time between air and fibers of 0.59, 0.18, 0.29, and 0.09 s, respectively. To compare the shapes of these curves on a normalized basis, Figure 9 (b) was plotted, where the x axis is normalized as the stoichiometric breakthrough time by multiplying the breakthrough time by the inlet air velocity. At the same x value, an equal amount of air will have passed through the reactor regardless of the air velocity. The plot indicates that the curves of cycles 4, 5, and 6 have similar shapes, where the CO$_2$ breakthrough occurs at the same CO$_2$ loading. For cycle 10, however, the breakthrough occurs at a lower CO$_2$ loading. This suggests that air velocity does not have significant influences on the breakthrough behavior when it is in the range of 0.17 to 0.57 m/s. This regime is suggestive of external mass transfer limitation. However, when air velocity is increased to 1.1 m/s, the breakthrough curve broadens as the breakthrough capacity decreases, which is a classic fingerprint of internal mass transfer limitations. It is noted that this reduction in the breakthrough capacity does not necessarily mean a decline in the overall performance using this high inlet air velocity, because in industrial DAC operations the optimal point to end the adsorption phase is usually well after the point of breakthrough to maximize the CO$_2$ productivity instead of the CO$_2$ uptake.

During the experiments, the pressure drop along the sorbent bed was less than 70 Pa across the range of inlet air velocities tested. At industrial scale, the pressure drop in the DAC system is not expected to vary significantly from this value, though $\Delta P$ will continue to increase as gas velocity increases. This suggests that the pressure drop will not be an obstacle to the implementation of the proposed fiber-based DAC system at larger scales.
Figure 9. (a) Breakthrough curves and (b) normalized breakthrough curves for cycles 4, 5, 6 and
10 with varying air velocities. CO2 concentration = 450 ± 50 ppm, T = 22 °C ± 2 °C, RH = 45 ± 5%.

3.6. Optimizing Productivity

The performance of practical DAC systems depends more on the CO2 productivity, i.e., the
amount of CO2 adsorbed per unit amount of fiber per unit time, as shown in Equation 3, than on
other commonly measured parameters like the breakthrough capacity.45,46,70 The productivity is
influenced by the shape of the breakthrough curve, the time of the adsorption phase, and the time
desorption phase and other procedures of the cycle, such as cooling. The productivity as a
function of the inlet air velocity and the duration of the adsorption phase is plotted in Figure 10
(a), where the duration of the rest of the cycle (desorption phase, cooling phase, etc.) is assumed
to be 15 minutes in this work. This estimate for the desorption time is chosen to be representative
of technically achievable desorption times using current materials and systems. The sensitivity of
the productivity estimates to the desorption times are shown in Figure 11, where the productivity
was calculated by assuming the desorption time to be 3, 30, and 60 min, respectively.

\[
\text{productivity} = \frac{\text{CO}_2 \text{ uptake (mmol)}}{\text{wt of fibers (g)} \times (\text{adsorption (h)} + \text{desorption and other phases of the cycle (h)})} \quad (3)
\]

As shown in Figure 10, for each inlet air velocity, there exists an optimal duration of the adsorption
phase that gives the maximum productivity achievable using this air velocity. The maximum
productivity achieved in these tests is 1.2 mmol of CO2 per gram of fiber per hour, and it is
achieved using an inlet air velocity of 1.1 m/s and an adsorption time of 11 min. Note that this productivity assumes nearly total recovery of CO₂ from the desorption phase, because in these experiments, each adsorption phase was preceded by a desorption phase of 10 min under N₂ flow at 110 °C. In the industrial setup, the CO₂ recovery from the desorption phase may not be as complete as in these tests, resulting in a lower swing capacity, and hence the productivities can potentially be lower.

**Figure 10** (b) plots the maximum productivity that can be achieved at each inlet air velocity. As the inlet air velocity increases, the maximum achievable productivity also increases. The shape of the graph indicates that the productivity has not yet reached a plateau at an inlet air velocity of 1.1 m/s, suggesting that further increasing the inlet air velocity should lead to higher productivities. Studies using higher inlet air velocities should be conducted in the future, as higher values could not be achieved with the current experimental set-up.

**Figure 10.** (a) Productivity as a function of the duration of adsorption phase and inlet air velocity (b) maximum productivity achievable at varying inlet air velocities. CO₂ concentration = 450 ± 50 ppm, T = 22 °C ± 2 °C, RH = 45 ± 5%.
Figure 11. Productivity as a function of duration of adsorption phase and inlet air velocity with a desorption phase duration of (a) 5 min (b) 30 min (c) 60 min. CO$_2$ concentration = 450 ± 50 ppm, $T = 22 \, ^\circ\text{C} \pm 2 \, ^\circ\text{C}$, RH = 45 ± 5%.

3.7. Kinetic Study of Steam Desorption

Steam desorption dynamics were studied using indirect contact heating to verify that the desorption phase is reasonably fast and that the assumption of a 15-minute desorption phase used above is valid. The steam desorption study conducted in this work is based on indirect contact heating, which differs from direct contact heating used in some industrial operations. However, it can be assumed that direct contact heating will lead to equivalent or faster desorption kinetics than indirect contact heating because of lower heat transfer resistance.

In this experiment, 0.3 g of 1.04PEI@SiO$_2$ fibers first underwent an adsorption phase using ambient air at a velocity of 0.57 m/s to reach their pseudoequilibrium capacity. After the adsorption, steam was passed through the heating jacket to indirectly exchange heat with the sample module. Steam flowed through the shell side of the reactor module, where heat was transferred to the stainless-steel reactor module and the fibers inside the module. Condensation was observed outside the sample module during the steam contact and the temperature of the sample module was measured to be constantly 100 °C during the desorption, meaning that the steam exchanging heat with the sample module was mostly saturated steam instead of highly superheated steam. After the desorption, another adsorption-desorption cycle was performed after the fibers had cooled. The CO$_2$ desorption curves and the accumulated CO$_2$ desorption from the two cycles are shown in Figure 12 a and b, respectively. As shown in the plots, the rate of CO$_2$ desorption...
increased rapidly during the first 30 s of the desorption. The rate of CO$_2$ desorption reached a maximum rapidly and then gradually decreased. After the initial 5 min, the outlet CO$_2$ concentration became negligible.

**Figure 12** shows the CO$_2$ uptakes during the two adsorption phases and the amounts of CO$_2$ desorbed during the first 5 min of the two desorption phases. The plot suggests that in the first cycle, 95% of the captured CO$_2$ was released within the first 5 min of the desorption phase. In the second cycle, this ratio became 98%. Compared to the experiments discussed earlier in this paper, where desorption was carried out for long periods using heating tape at 110 °C, using steam as the desorption agent results in a lower CO$_2$ swing capacity, but the difference is not significant. It has been shown by this set of experiments that the swing capacity obtained using steam is at least 95% of that using heating tapes. Assuming a desorption phase of 5 min followed by a cooling phase of 5 min with a swing capacity that is 95% of the maximum capacity, we can achieve a maximum productivity of 1.42 mmol of CO$_2$ per gram of fiber per hour. This validates the assumption of a 15-min desorption and cooling time used in the productivity calculation in the previous section.
Figure 12. (a) Rate of CO$_2$ desorption (b) integrated CO$_2$ desorption curves for two consecutive tests using 100 °C steam. The fibers first underwent an adsorption phase using ambient air at a velocity of 0.57 m/s to reach the pseudoequilibrium capacity (CO$_2$ concentration = 450 ± 50 ppm, $T = 22 \, ^\circ\text{C} \pm 2 \, ^\circ\text{C}, \, \text{RH} = 45 \pm 5\%$). (c) CO$_2$ uptakes reached in the two adsorption phases and the amounts of CO$_2$ desorbed in the first 5 min of the two desorption phases. Note: columns 2 and 4 depict the amount of CO$_2$ desorbed from the desorption phase, not the amount of CO$_2$ remaining on the fibers.

4. Conclusions

This work investigated the dynamics of adsorption and desorption of fiber DAC sorbents in a fixed bed reactor. Fibers containing 52 wt% silica and 48% CA were spun and impregnated with PEI of different loadings. The fibers were characterized by SEM, N$_2$ physisorption, CO$_2$ isotherms, and
TGA combustion. The dynamic behavior of CO₂ adsorption was studied in a custom-built fixed fiber contactor where simulated air, both dry and humid, and ambient indoor air were used for breakthrough studies. The desorption of CO₂ by indirect heating with steam was studied by flowing steam to the shell side of the fixed bed.

The results show that ambient air and dry simulated air can have considerably different CO₂ capacities. Due to the ~50% relative humidity present in ambient air, the pseudoequilibrium capacities using ambient air were ~80% greater than dry, simulated air. Although fibers impregnated in 10% PEI solution had a lower PEI loading than fibers impregnated in 20% PEI solution (0.37 g PEI/g silica as compared to 1.04 g PEI/g silica), leading to a lower pseudoequilibrium capacity (0.68 mmol/g as compared to 0.95 mmol/g), they had superior kinetics in CO₂ breakthrough experiments. The 0.37PEI@SiO₂ fibers demonstrated good stability over 12 adsorption-desorption cycles. The CO₂ breakthrough curves only changed shape when the inlet air velocity was increased from 0.57 to 1.1 m/s, indicating the onset of controlling internal mass transfer resistances. The maximum CO₂ productivity achieved so far, assuming a desorption phase of 15 min, is 1.2 mmol/g/h. This was achieved by using an inlet air velocity of 1.1 m/s on 0.37PEI@SiO₂ fibers. Desorption by indirect contact with steam showed promising kinetic behavior. The CO₂ outlet concentration reached the maximum rapidly in the first 30 s and >95% adsorbed CO₂ could be desorbed in the first 5 min of steam contact.

The key limitations of this study include the following. First, the inlet air velocities used in these experiments were still 3-10x lower than what would be expected for industrial operations. The key observations of this study, i.e. that a lower amine loading leads to better adsorption kinetics, and that the humidity in the air leads to better overall performance, may change when the air velocity is further increased. Second, only two PEI loadings were tested in detail, and it would be beneficial to test other loadings in the future to identify a potential optimum. Third, the tests were conducted at a relatively small scale using a sample tube with an inner diameter of 0.43 cm with 0.3 g fibers. Once the system is scaled up, the trends observed for adsorption and desorption dynamics may change. Therefore, experiments in larger sample tubes containing a larger quantity of fibers are recommended.

**Author contributions**

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Conflicts of Interest

The authors declare the following competing financial interest(s): C.W.J. has a financial interest in Global Thermostat, which seeks to commercialize CO\textsubscript{2} capture from air. This work is not affiliated with Global Thermostat. C.W.J. has a conflict-of-interest management plan in place at Georgia Tech.

Acknowledgements

The authors thank the Georgia Tech Direct Air Capture Center, DirACC, for fruitful discussions. The information, data, or work presented herein was funded in part by the Advanced Research Projects Agency-Energy (ARPA-E), U.S. Department of Energy, under Award Number DE-AR0001309. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

References


