Electrical swing adsorption on functionalized hollow fibers

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Abstract

Temperature swing adsorption (TSA) is a favorable adsorption technique when applied for capturing CO₂ but limited by long cycle times and low concentrations of the recovered adsorbate. Direct heating of the adsorbent can mitigate these drawbacks. Combined with the beneficial mass transfer of a hollow fiber geometry it offers a powerful sorption process. In this study, we combine the advantages of direct heating and the benefits of the hollow fiber geometry in electrically conducting hybrid hollow fibers. Two different solid sorbents are manufactured and characterized: polyethylenimine-impregnated silicon carbide fibers (SiC-PEI) and fibers consisting of a carbon nanotube matrix with dispersed zeolite particles (CNT-zeolite). Both fibers exhibit Joule heating properties and high adsorption capacities. The CO₂ uptake, CO₂ isotherms, and the kinetic behavior are examined. The maximum CO₂ uptakes at 30 °C and 15 vol % CO₂ are 8.3 mg/g_{fiber} for SiC-PEI and 102.2 mg/g_{fiber} for CNT-zeolite. A lab-scale module is designed and used to determine the CO₂ capacity of a fiber bundle. The energy requirement to heat such a fiber bundle from ambient temperature to 80 °C is 3.1 J/(g_{Fiber}K) (SiC-PEI) and 15.8 J/(g_{Fiber}K) (CNT-zeolite). To investigate the suitability of the fibers for real process applicability, a mathematical model is established

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and simulation results are presented and discussed. The two different approaches prove to be viable options for CO₂ separation. They are not limited to CO₂ capture but can be expanded to other gas separation tasks.

Keywords: Electrical swing adsorption, heatable hollow fiber, PEI, zeolite, CO₂ capture

1. Introduction

Temperature swing adsorption (TSA) is a well-established technology for the separation and purification of different gas streams [1]. In particular, when large streams or dilute systems are separated, TSA processes offer benefits over pressure swing adsorption (PSA) processes, for instance when purifying natural gas [2] or for direct air capture of CO₂ [3]. Temperature swing adsorption processes are also favorable for capturing CO₂ from flue gases to reduce anthropogenic greenhouse gas emissions [4, 5]. CO₂ removal is an imperative measure if global warming is to be limited to 1.5 °C [6]. In common TSA applications, a stream of hot steam or gas passes the adsorption column to heat the adsorbent [7] and thus reduce its adsorption capacity for regeneration. The main limitations of TSA are long cycle times usually in the range of several hours [8], thermal aging of the adsorbent [9], and low concentrations of the recovered adsorbate depending on the volume of the required gas stream for heating [1].

Direct heating methods of the adsorbent can efficiently overcome these main limitations making TSA a process that can potentially outperform other separation techniques. Among the methods for alternative heating of the adsorbent are electrical heating (Joule heating) [10], induction heating [11], and microwave heating [12, 13]. Electrical regeneration uses the Joule effect of an electrically conductive adsorbent under applied electric voltage, which means the

conversion of the electric power at the electrical resistance to thermal heat that dissipates from the adsorbent. Sullivan et al. [14] state that electrical heating is the most promising regeneration method among the new heating concepts due to even heating of the adsorbent and low energy losses from the power source to the adsorbent.

The main advantage of electric swing adsorption (ESA) is the higher heating efficiency resulting from the direct local heat input at the adsorbent. Local heating enables much faster cycle times, as the heating rate does not depend on the heat capacity of the heat source and thus the rate of heat transfer between the adsorbent, and the heat source disappears as a limiting factor [14, 15]. Additionally, the control of gas flow is independent of the heat flow. This independent control allows designing smaller systems with a lower purge gas flow [16] avoiding dilution of the product. The adsorbate can, therefore, be captured with higher purities. ESA further promises to be superior to other forms of TSA from the energy point of view [8, 10].

To capture CO₂ using an ESA approach appropriate sorbents have to be identified. According to Grande et al. [2], suitable materials are zeolites and amine impregnated solid sorbents. Other sorbents for CO₂ capture with ESA include activated carbon fibers [15, 17, 18], carbon monoliths [3, 19, 20], monoliths composed of carbon and zeolites [21, 22], and graphene-based sorbents [23]. Polymeric amines are considered favorable for CO₂ separation processes [24] as they absorb CO₂ remarkably well compared to other gases. Amine impregnated solid sorbents offer high chemical stability and can be applied under humid conditions [25] while some studies even report increasing adsorption capacities in the presence of water [26–28]. Zeolites also have a number of advantages when used for CO₂ capture. They exhibit high CO₂ uptake at low partial pressures as well as high selectivities of CO₂

Figure 1: Schematic representation of the adsorption and electrically induced desorption step in a hollow fiber bundle.

over N_2 [29, 30], their adsorption kinetics are very fast, filling most of the total capacity within seconds, while their regenerability is seldom prone to degeneration yielding stable CO_2 uptake capacities over many cycles [31].

Generally, adsorption columns use packed beds with inherent limitations such as a high mass transfer resistance [32], a high heat transfer resistance as well as undefined flow conditions. Fibrous sorbents promise to overcome fundamental shortcomings of TSA processes [33–35]. Feng et al. [33] were the first to introduce a hollow fiber geometry which resulted in a lower pressure drop and a lower mass transfer resistance. Controlled flow conditions in the laminar regime led to sharper breakthrough curves and thus higher recoveries [33].

In this study, we perform ESA on a hollow fiber geometry, schematically illustrated in Figure 1. Highly adsorptive, electrically conductive fibers serve as electrical resistances for direct heating of the adsorbent regeneration combined with the improved mass transfer of the hollow fiber geometry. We compare two different adsorbent-fiber composites: silicon carbide (SiC) fibers impregnated with polyethyleneimine (PEI) and zeolites incorporated into a carbon nanotube (CNT) matrix. Previous work proved the applicability of PEI-impregnation on

hollow fibers and the suitability of CNT-based solid sorbents for CO₂ capture [36, 37]. Both CNT and SiC feature excellent thermal and chemical stability, and low thermal expansion coefficients. They provide a stable framework, are electrically conductive, and have a high surface-to-volume ratio. PEI and zeolites increase the CO₂ adsorption capacity of the fibers. Adsorption isotherms and kinetics of the fibers are presented and their electrical heatability is shown. Arranged in fiber bundles, the fibers are used in a prototype module to prove the promising performance of hollow fibers as ESA bundles.

2. Experimental

2.1. Materials

The following chemicals were used without further purification: Polyethyleneimine (branched, molecular weight: 800 Da, Sigma Aldrich), Triton X-100 (Sigma Aldrich), carbon nanotubes (multi-walled, $\geq 98\%$ carbon basis, outer diameter: $10\text{ nm} \pm 1\text{ nm}$, inner diameter: $4.5\text{ nm} \pm 0.5\text{ nm}$, length: $3\text{-}6\text{ }\mu\text{m}$, Sigma-Aldrich), zeolite (NaY zeolite, SiO₂/Al₂O₃-mole ratio: 5.1, Zeolyst CBV100), polyurethane glue PU1000 (Polytec), silver conductive paste (Sigma Aldrich), ethanol (purity: $> 98.8\%$ vol %, Overlack), isopropyl alcohol (98% purity, Applichem), CO₂ (purity: 4.5, Westfalen AG), gas mixture 15 vol % CO₂, 85 vol % N₂ (purity: CO₂: 3.0, N₂: 4.8, Westfalen AG).

2.2. Fiber preparation and characterization

SiC fibers were synthesized according to de Wit et al. [38] by sintering at 1000 °C. A short description can be found in the Supporting Information. Two methods were applied for impregnating SiC fibers with PEI. A solution of 5 wt % PEI in ethanol was used in both

approaches. Following a common wet impregnation method [39], the fiber was suspended in a stirred PEI solution for 6 h with subsequent drying overnight under vacuum (30 °C, 90 mbar). For the second impregnation method, the lower end of the fiber was sealed with glue while PEI solution was filtered inside-out through the fiber into the stirred PEI bath with a flux of $100 \text{ L m}^{-2} \text{ h}^{-1}$. A total volume of 40 mL was filtered through one fiber. The subsequent drying was carried out according to the stirring approach. The sealed end of the fiber was removed. The total amount of immobilized PEI m_{PEI} was calculated by the weight difference before and after the immobilization: $m_{PEI} = m_{coated} - m_{uncoated}$ and the specific load of the fiber m_{PEI}'' amounts to $m_{PEI}'' = \frac{m_{coated} - m_{uncoated}}{m_{coated}}$, where $m_{uncoated}$ is the mass of the pure SiC fiber and m_{coated} the mass of the fiber impregnated with PEI.

A detailed description of the synthesis of the CNT fibers can be found in Gendel et al. [40]. To incorporate the zeolite particles, 4 g L^{-1} zeolite were added to the aqueous suspension (deionized water, $18 \Omega \text{ cm}$) with 1 vol % surfactant (Triton X-100), 1 g L^{-1} CNT powder used for the fiber preparation. Thus, a ratio of CNT to zeolite of 20/80 wt % was achieved. The synthesis is described in short in the Supporting Information.

Electron micrographs were taken with a scanning electron microscope S4800 of Hitachi. The samples were dried under vacuum overnight (30 °C and 90 mbar) and sputtered with 6 nm gold/palladium (60:40, w:w) before analysis.

2.3. Specific CO_2 uptake and sorption kinetics

Adsorption capacities and kinetics of the fibers were determined by thermogravimetric analysis (TGA) with a PerkinElmer Thermal Analyzer 6000. The fibers were measured with a constant gas flux of 150 mL min^{-1} of N_2 , CO_2 or a gas mixture (15 vol % CO_2 in N_2), re-

spectively. The temperature program of SiC-PEI fibers consisted of desorbing any impurities and adsorbed CO_2 at 110°C under N_2 for 90 min. The desorption temperature was chosen such that as many impurities as possible would be removed while there was still a reasonable distance to the temperature at which PEI volatilizes and/or decomposes (135°C) [41]. Temperature was then decreased to 30°C under CO_2 or the gas mixture for 60 min. The sample was again desorbed at 110°C under N_2 for 90 min, before a second adsorption step at 80°C for 60 min under CO_2 or the gas mixture was conducted. Staying under CO_2 , the temperature was increased to 110°C and then held for 60 min. The temperature program for CNT-zeolite fibers started with a heating step under N_2 (300°C for 120 min). Temperature was decreased every 45 min to 120°C , 100°C , 80°C , 60°C , 40°C , and 30°C under CO_2 or the gas mixture. To determine the sorption kinetics of the CNT-zeolite fibers additional measurements were necessary with the gas mixture of 15 vol %. Three separate measurements with different fibers were conducted. First, a degassing step under N_2 was performed at 250°C for 120 min. Subsequently, an adsorption steps followed at 30°C , 50°C , or 80°C .

Adsorption capacities c_{CO_2} were calculated by

$$c_{\text{CO}_2} = \frac{m_i - m_0}{m_0} \quad (1)$$

where m_0 is the reference mass of the sample after desorption under N_2 , while m_i is the mass after adsorption with CO_2 at the respective temperature i .

2.4. Sorption isotherms

Pure CO_2 sorption isotherms were measured at ambient temperature using pycnometry (ASAP 2020, Micromeritics) for pressures ranging from 0.004 to 1.1 bar. Degassing for pycnometry measurements was conducted under vacuum ($1.3\text{ }\mu\text{bar}$) at 110°C for 6 h for the

PEI-impregnated SiC fibers. CNT-zeolite fibers were degassed under vacuum (1.3 μ bar) at 250 °C for 6 h. The equilibrium criterion was $\frac{p_n - p_{n+1}}{p_n} \frac{1}{\Delta t} < 4.5 \cdot 10^{-7} \frac{1}{s}$ which led to a variable equilibrium time for each pressure and each sample.

2.5. Procedure for experiments with fiber bundles inside a module

A bundle of 15 fibers with a length of 10 cm for each fiber type was tested in the module. The fibers were glued to bundles at their endings with electrically conductive glue. SiC-PEI was glued with Polytec PU1000 while CNT-zeolite was glued with silver conductive paste due to different wetting properties of the fiber materials. Copper wire was twined around both ends of the fibers for electrical connections.

To test the performance of the bundle in the module, we compared external heating tests to internal heating (Joule heating). For external heating, the sealed module with the bundle inside was flushed with pure CO₂ for 30 min. Inlet and outlet valves were then closed and a gas bag was connected to the outlet. The set-up was placed in an oven, heated to 80 °C and held for 60 min with the outlet valve open to the gas bag which collected the desorbed CO₂. Upon removal from the oven the valve of the bag was closed, the module was cooled to room temperature and the captured volume was measured by water displacement (see Figure S1). To correct for thermal expansion of the gas, the empty module was heated and the same procedure as described above was followed. The measured gas volume was then subtracted from the result of the external heating test.

The gas bag analysis was repeated with electrical heating meaning that instead of using an oven for heating, the fibers were heated with Joule heating by an applied voltage. The fibers were heated to 80 °C and kept at this temperature for 15 min. The desorbed volume

was measured by water displacement analog to the oven heating procedure. This measured volume captured by the bag was corrected against the thermal expansion of the gas inside the module using the ideal gas law.

2.6. Mathematical modelling

A mathematical model was implemented to investigate breakthrough times, evaluate cycle times and estimate the energy requirement of an ESA process using the fibers presented in this work. High thermal conductivity and low mass transfer resistance of the hollow fiber sorbents [33–35] allow model simplifications to decrease mathematical complexity. Since all fibers are assumed to be equal and evenly distributed, the description of a single fiber is sufficient [42]. Further, the following assumptions were made:

- all gases are ideal gases,
- radial gradients for transfer of mass, heat, and momentum are neglected,
- only CO₂ is adsorbed,
- the flow within the fiber is laminar and fully developed,
- the heat of adsorption is constant.

All relevant equations are stated in the Supporting Information.

Boundary conditions and performance criteria

A basic electric swing adsorption process comprises three steps namely an adsorption, a desorption and a regeneration step per cycle (see Figure 2). First, the open column is fed with gas containing 15 vol % CO₂ in N₂ which corresponds to concentrations found in flue

Figure 2: Three-step electric swing adsorption process including an adsorption step at ambient conditions, a desorption step including electric heating as well as partial vacuum, and a regeneration step for the column to reach ambient conditions, which includes cooling and optional pressurization.

gases [43]. The column is loaded to its full capacity to evaluate the maximum performance of our novel adsorption materials in terms of minimum energy requirement, recovery, and purity. Once the column is fully loaded, its outlet is closed and the system is electrically heated until the desired desorption temperature is reached. Simultaneously, a partial vacuum is generated at the inlet to enhance the desorption performance. Once the adsorbent is regenerated, the column is cooled and pressurized to ambient conditions (regeneration step). Mathematical boundary conditions are shown in the Supporting Information (Table S1).

Adsorption processes are often characterized by their minimum energy requirements (MER) per mass of recovered CO_2 to compare different operating points [44]. For an ESA process, the MER is calculated by

$$MER = \frac{\Delta E_{tot}}{\Delta M_{\text{CO}_2}} \quad (2)$$

where ΔE_{total} is the total energy requirement per cycle and ΔM_{CO_2} the amount of CO_2 produced in this cycle. The corresponding equations for ΔE_{tot} can be found in the Supporting

Information. Additional process parameters such as the CO₂ product stream purity and overall recovery are calculated by

$$purity = \frac{\int_{t_{des}}^{t_{reg}} M_{productCO_2}}{\int_{t_{des}}^{t_{reg}} M_{product}} \quad (3)$$

$$recovery = \frac{\int_{t_{des}}^{t_{reg}} M_{productCO_2}}{\int_{t_{ads}}^{t_{reg}} M_{feedCO_2} + M_{regCO_2}} \quad (4)$$

where t_{ads} , t_{des} and t_{reg} are the starting times of the adsorption, desorption and regeneration steps, respectively. $M_{product}$ is the molar product stream and $M_{productCO_2}$ the molar CO₂ product stream. For the recovery, the amount of CO₂ fed in the adsorption step M_{feedCO_2} and in the regeneration step M_{regCO_2} are calculated. To compare different operating points in terms of desorption temperatures and pressures a reference case was established according to the experimental procedures presented before. Detailed operating conditions can be found in Table S2.

3. Results and Discussion

3.1. Fiber characterization

Two features are relevant for fibers used in an electrical swing adsorption process: high adsorption capacities and good electrical properties for fast Joule heating during desorption. The SiC-PEI fiber consists of an electrically conductive silicon carbide (SiC) support that is impregnated with polyethylenimine (PEI), a polymeric amine known for high adsorption capacities of CO₂ also under humid conditions [30]. The CNT-zeolite fibers contain a high load of zeolites for a high adsorption capacity while the supporting carbon matrix provides

electric conductivity. Different properties of the fibers such as the conductivity are displayed in Table 1. Figure 3 shows electron micrographs of the outer surface of both composite fibers and their cross section. The geometrical dimensions of the fibers are comparable to each other (see Table 1) where SiC-PEI has an outer diameter of 1.8 mm and an inner diameter of 0.8 mm while CNT-zeolite provides an outer diameter of 1.5 mm and an inner diameter of 1.3 mm. Figure 3a shows the zeolite particles in the CNT matrix. The particles are homogeneously distributed within the structure. Figure 3b shows the structure of SiC as a cluster of inorganic particles. The coating of SiC with PEI is thin and optically not distinguishable by microscopy.

Table 1: Properties of the SiC and CNT-zeolite fibers.

Parameter	SiC	CNT-zeolite
Pore diameter (nm)	500	1.6
Inner diameter (mm)	0.8	1.3
Outer diameter (mm)	1.8	1.5
Conductivity (kS m ⁻¹)	0.8	3.3

Two different impregnation methods were tested to immobilize PEI on the SiC fibers: a simple wet impregnation method and a combined impregnation and filtration method. The combined method leads to an increase in immobilized PEI of about 20% compared to the simple wet impregnation method (see Table 2).

An increased amount of immobilized PEI on the SiC support potentially leads to higher adsorption capacities while not only the amount of PEI but also a good distribution and the

Figure 3: Electron microscopy images of the surface topology and the cross section of CNT-zeolite (A and C) and SiC-PEI (B and D) fibers. Images have been adapted in brightness.

Table 2: PEI load on SiC fibers prepared by different impregnation methods (numbers in brackets represent the standard error of the mean).

Filtered PEI	Stirred PEI
$\text{mg}_{PEI}/\text{g}_{SiC}$	$\text{mg}_{PEI}/\text{g}_{SiC}$
97.6 (2.65)	81.3 (3.21)

available internal surface area are relevant for high adsorption capacities [36]. When testing the adsorption capacities of both impregnation methods with TGA in pure CO_2 , the filtration method yields 21.8 mg g^{-1} (2.3) at 30°C whereas the simple impregnation method only exhibits a CO_2 uptake of 8.2 mg g^{-1} (0.4). The corresponding working capacity ($30/80^\circ\text{C}$)

increased to 10.8 mg g^{-1} (0.3) from 4.2 mg g^{-1} (0.5) with the improved impregnation method (numbers in brackets represent the standard error of the mean). Detailed information on the CO_2 uptake at different temperatures is shown in Figure S2. For further testings, we used the filtration method to impregnate SiC fibers with PEI.

The specific CO_2 uptake of both fiber types at different temperatures and ambient pressure for pure CO_2 and a gas mixture of 15 vol % CO_2 and 85 vol % N_2 is shown in Figure 4. Both fibers exhibit a decrease in CO_2 uptake per gram fiber at increasing temperatures enabling desorption at elevated temperatures. The maximum CO_2 uptake for the SiC-PEI fibers is 19.2 mg g^{-1} under pure CO_2 and 8.3 mg g^{-1} under 15 vol % CO_2 at 30°C . The CNT-zeolite fibers attain a maximum of 209.6 mg g^{-1} under pure CO_2 and 102.2 mg g^{-1} under 15 vol % CO_2 at 30°C . The CNT-zeolite fiber thus shows nearly ten times higher values of adsorbed CO_2 per gram fiber than the SiC-PEI fiber. The differences are not only attributed to the different adsorbents zeolite and PEI but also to the different nature and density of the support materials CNT and SiC. When the CO_2 uptake is written in $\text{mg}_{\text{adsorbedCO}_2}$ per g_{PEI} , $21.8 \text{ mg/g}_{\text{SiC-PEI fiber}}$ correspond to $240 \text{ mg/g}_{\text{PEI}}$. The amine efficiency denotes the molar ratio of adsorbed CO_2 per amine group [26, 45] and is calculated to $0.23 \text{ mol}_{\text{CO}_2}/\text{mol}_{\text{amine}}$, which is comparable to data found in literature using low molecular branched PEI [26, 45]. The load of adsorbent material is significantly higher for the CNT-zeolite fiber with 80 wt % mass share of adsorbent, while the mass share of PEI on the SiC-PEI fiber comprises 9 wt %. However, altering the coating process, e.g. by using a higher PEI load in the impregnation solution may lead to higher mass shares and, consequently, higher CO_2 uptake per $\text{g}_{\text{SiC-PEI fiber}}$.

The difference in CO_2 uptake between 30°C and 80°C is used as an estimate for the expected CO_2 adsorption capacity measured with the module. The respective working ca-

Figure 4: CO₂ uptake per gram fiber at different temperatures measured by TGA under pure CO₂ or 15 vol. % CO₂ in N₂ (error bars represent standard error of the mean of three different fibers).

capacities between 30 °C and 80 °C based on Figure 4 amount to 10.8 mg/g_{Fiber} (0.3) and 86.3 mg/g_{Fiber} (1.0) for pure CO₂ on SiC-PEI and CNT-zeolite, respectively, and 3.9 mg/g_{Fiber} (0.1) and 49 mg/g_{Fiber} (1.7) for 15 vol % CO₂ for SiC-PEI and CNT-zeolite, respectively.

TGA measurements not only provide information about the working capacity but also about the kinetics of CO₂ adsorption on the fibers at different temperatures. A recent study on the CO₂ sorption kinetics on PEI-impregnated porous structures shows that changes in sorption mechanisms and heat of adsorption occur depending on the adsorption temperature [46]. Current research indicates that adsorption of CO₂ on PEI-impregnated adsorbents may be an intraparticle- or diffusion-controlled process and analyzing the relation between CO₂ pressure and temperature at a given CO₂ uptake is inaccurate [45, 47]. It is also assumed that the physisorbed CO₂ is not only in thermodynamic equilibrium with CO₂ in the gas phase but also participates directly in the reaction with the immobilized amine, resulting

in negative activation energies [48]. In this context, we do not want to presume to identify adsorption kinetics, since such complex behavior requires adequate, in-depth measuring methods exceeding the scope of this work.

The kinetics of the CNT-zeolite fibers for three different temperatures (30 °C, 50 °C, and 80 °C) were fitted by two models: The Avrami model was shown to accurately describe CO₂ adsorption on zeolites [49] and the recently proposed dual kinetic model (DKM) [50]. The Avrami model is a fractional kinetic model that describes the behavior of non-catalytic gas-solid reactions [51]. Detailed information and the model equations can be found in the Supporting Information. Experimental data and fits obtained with both models are shown in Figure S6. Both models are able to describe the kinetic behavior of the CNT-zeolite fibers precisely. Since time-dependent kinetics such as the Avrami model are difficult to implement and additionally, the DKM describes the kinetics more accurately (see Figure S6 and the coefficients of determination R^2 in Table S3 and S4) the DKM model was used in the simulation.

At higher temperatures (80 °C), the CO₂ uptake reaches a plateau-like region with very little increase after approximately 30 s while the kinetics slow down for decreased temperatures. At 50 °C, the CO₂ uptake plateaus at approximately 60 s while at 30 °C the uptake curve flattens out after 90 s. The working capacity between 30 °C and 80 °C after 90 s is 45.9 mg g⁻¹ (1.4) and thus, 93.5% of the working capacity after 45 min are obtained (see Figure 8). After 3 min, 98.7% of the working capacity after 45 min is reached (48.4 mg g⁻¹ (1.4)). This indicates the feasibility of short cycle times when using the CNT-zeolite fibers.

The adsorption isotherms measured by pycnometry from 0.004 bar to 1.1 bar are shown in Figure 5a for the SiC-PEI fibers and in Figure 5b for the CNT-zeolite fibers. The SiC-PEI

fibers exhibit a steep increase in adsorbed CO_2 up to approximately 0.05 bar to 5.3 mg g^{-1} followed by a slower increase to 14.6 mg g^{-1} at 1.1 bar. The Freundlich isothermal model has been used before to describe the behavior of amine-functionalized sorbents [52]. The Freundlich equation [53]

$$q_e = K_f \cdot p_{\text{CO}_2}^{1/n} \quad (5)$$

is an empirical model applicable to nonideal sorption on heterogeneous surfaces as well as multilayer sorption [54]. Here, q_e is the amount of CO_2 adsorbed at the partial pressure p_{CO_2} while K_f and n are constants of the model. It describes the behavior of the SiC-PEI fibers precisely as shown by the fit in Figure 5a. The model parameters are summarized in Table 3. Since no constant activation energy for a possible Arrhenius approach could be identified, the calculation of higher temperature isotherms requires additional experimental data. A drawback of the Freundlich isothermal model is that it allows indefinite increase in adsorption with pressure [55]. For further studies it could be beneficial to use the Langmuir-Freundlich isotherm instead. The steep increase in CO_2 uptake at very low partial pressures is in agreement with current literature on PEI adsorption of CO_2 [56] and could indicate good applicability of the SiC-PEI fibers for direct capture of CO_2 from air where it is currently present at around 400 ppm [57]. The discrepancy in CO_2 uptake measured by TGA and pycnometry (19.2 mg g^{-1} vs. 14.6 mg g^{-1}) are probably due to the isotherm being a single, representative measurement. Furthermore, the equilibrium time is different for each measurement method: TGA data points were calculated after 60 min adsorption time (cf. section 2.3) while the adsorption time for the last data point in the isotherm at 1.1 bar was

13 min (the total adsorption time for the entire isotherm was 11 h).

The adsorption isotherm of the zeolite-CNT fibers also shows different gradients but cannot be divided into two sections. No steep increase at very low partial pressures can be observed for the zeolite-CNT fibers. However, zeolites have previously been proposed as sorbents for direct air capture [58]. Isotherms of CO₂ adsorption on NaY zeolites have been found to be best described using the Langmuir isothermal model [59]. The Langmuir equation [60]

$$q_e = \frac{q_{sat} \cdot K_L \cdot P_{CO_2}}{1 + K_L \cdot P_{CO_2}} \quad (6)$$

assumes that adsorption takes place at specific homogeneous sites within the adsorbent and the adsorbent has a finite capacity for the adsorbate i.e., a saturation is reached [61]. Here, q_e is also the amount of CO₂ adsorbed at the partial pressure p_{CO_2} while q_{sat} is the amount of CO₂ adsorbed at saturation and K_L is a model constant. The fit obtained for the CNT-zeolite adsorption isotherm using the Langmuir equation describes the sorbent's behavior precisely as can be seen in Figure 5b. Thus, a temperature relation can be obtained when considering literature data for the activation energy [62, 63]. The Langmuir constants follow an Arrhenius type approach [64]. The model parameters are summarized in Table 3. A discrepancy between values obtained by TGA and pycnometry may possibly be attributed to different adsorption times to reach equilibrium (45 min for TGA and about 8 min for pycnometry).

Table 3: Constants for Freundlich and Langmuir isothermal models. K_f , K_L , and n are model constants, q_{sat} denotes the saturation of adsorbed CO_2 and R^2 is the coefficient of determination.

Para-	Unit	Freundlich	Langmuir
meter		SiC-PEI	CNT-zeolite
K_f	$\text{mmol g}^{-1} \text{Pa}^{-1}$	0.0104	
n	-	3.4208	
K_L	Pa^{-1}		$4.7 \cdot 10^{-5}$
q_{sat}	mmol g^{-1}		3.722
R^2	-	0.98	0.99

(a) SiC-PEI fibers. Data fitted with the Freundlich model.

(b) CNT-zeolite fibers. Data fitted with the Langmuir model.

Figure 5: Adsorption isotherm for both fiber types measured by pycnometry at ambient temperature and at higher temperatures for CNT-zeolite to be used in the simulation. Symbols represent experimental data while the lines represent a fit of that data.

3.2. Module design

We designed a gas-tight, electrically connectable lab scale module to test a bundle of 15 fibers in a proof-of-concept electric swing adsorption process. The module is made of aluminum and consists of two parts: the lower part contains a chamber for the fibers with electrical connections to a voltage source. The fiber chamber features a pressure and a temperature sensor and owns a gas inlet and outlet channel. A schematic drawing of the lower part can be found in the Supporting Information (Figure S4). The upper part serves as a lid to seal the fiber chamber squeezing a flat gasket between the upper and the lower part with twelve screws. To avoid a short-circuit between the fiber bundle and the module, two small pieces of rubber are placed under the wires. Temperature and pressure sensor are connected with push-in fittings with cylindrical threads to be gas-tight. To prove gas tightness of the module, the module was pressurized stepwise to 1, 2 and 3 bar with each step lasting at least 30 min. The pressure was monitored and the module was checked for gas bubbles under water. Figure 6 shows a fiber bundle of the SiC-PEI fibers in the fiber chamber of the module with attached electrical connections, a pressure sensor, and a temperature sensor.

3.3. ESA on fiber bundles

The module was used to test the electrical heatability of the fibers and to determine the working capacity of a fiber bundle between 30 °C and 80 °C using pure CO₂. When the fiber bundle was placed in the module, it was ensured that the temperature sensor touches the module. Under applied voltage both fiber types heat up and their temperature reaches a plateau at approximately 80 °C after 30 s, see Figure 7. The temperature remains stable for the course of the measurement (15 min).

Figure 6: Open fiber chamber of the aluminum module containing a bundle of SiC-PEI fibers with electrical connections as well as a pressure and a temperature sensor.

The working capacity of the two fiber types determined via different measurement methods can be seen in Figure 8. External heating means the "conventional" heating of the entire module in an oven while internal heating describes the direct heating of the fiber bundle using the Joule effect. Comparing both heating approaches enables testing the feasibility of Joule heating of the bundle. For both the SiC-PEI and the CNT-zeolite fibers, the working capacity measured with the module decreases slightly compared to the capacity measured with TGA, independent of the heating method within the module. The decrease can be attributed to the fact that no degas step was performed prior to the module experiments. Thus, both materials are expected to have residual water or gas adsorbed that might influence the results. Both fiber types yield similar adsorption capacities for external and internal heating, respectively. This emphasizes the feasibility of electrical heating for these fibers as a desorption strategy in a module configuration.

Figure 7: Temperature course of a SiC-PEI and a CNT-zeolite fiber bundle in the module recorded during an internal heating measurement.

3.4. Energy efficiency

To compare the two composite fibers with respect to their energy demand, Table 4 lists the energy requirement for heating the fibers from 30 °C to 80 °C. The energy demand comprises only the demand for heating calculated from the recorded voltage and current during the heat-up phase. The latent heat of adsorption was not considered since we aim at comparing the heating efficiency of the fibers independent of the two different latent heat demands. The energy demand is calculated with respect to the adsorbed amount of CO₂ measured with TGA according to the following equation

$$Q_{rel} = \frac{P_{\Delta 50^\circ C}}{m_{fibers} \cdot \Delta q_{\Delta 50^\circ C}} \text{ (MJ/kgCO}_2\text{)} \quad (7)$$

where P is the sum of the applied power measured in intervals of 0.4 s during the time of heating from 30 °C to 80 °C, m_{fibers} is the mass of the fiber bundle, and $\Delta q_{\Delta 50^\circ C}$ the working

Figure 8: Working capacity of the two different fiber types between 30 °C and 80 °C measured with TGA and with fiber bundles in the module using external and internal (electrical) heating. The y-axis is split. The error bars represent the standard error of the mean of three different fibers (TGA) or three different measurements with two different fiber bundles (module measurements).

capacity of CO₂ between 30 °C and 80 °C gained from TGA measurements in (mg/g_{fiber}).

While the two fiber types deviate in their mass related adsorption capacities nearly by a factor of 10 (10.8 mg/g_{SiC-PEI, fiber} vs. 86.3 mg/g_{CNT-zeolite, fiber}), the required energy demands per kg_{CO2} are in the same order of magnitude with CNT-zeolite being somewhat more effective. However, the mass share of PEI on SiC is still comparably low and may be improved with higher PEI contents in the coating solution. To conclude, with two different approaches of composite fibers for ESA application a comparable energy requirement is reached. The heating time required to reach 80 °C is approximately 25-30 s which is significantly faster than conventional heating [8]. Improved electrical connections could lead to an additional decrease in heating time and energy demand.

Table 4: Energy demand of the composite fibers measured at the fiber bundle. Time denotes the time required to reach 80 °C. Values in brackets represent the standard error of the mean.

Parameter	Unit	SiC-PEI	CNT-zeolite
Q_{rel}	J/(g _{Fiber} K)	3.1 (0.5)	15.8 (1.9)
Q_{rel}	MJ/kgCO ₂	14.5 (2.3)	9.2 (1.1)
Time	s	29.8 (3.9)	24.7 (0.8)

3.5. Mathematical modelling

To estimate the performance of our hybrid hollow fibers on a process level a mathematical model was established. The mathematical model is intended as a first indicator for the applicability of our fibers in a process. The model was thus implemented without optimization and only for CNT-zeolite fibers as they show a better performance compared with SiC-PEI. Since the equilibrium (Figure 5b) and kinetic (Figure S6) models of the CNT-zeolite fibers showed good accordance with experimental data, breakthrough, ad- and desorption cycles as well as general process behavior can be investigated.

Adsorption breakthrough curves were simulated for adsorption conditions of 25 °C and 1 bar. The molar CO₂ fraction in the gaseous phase at the column outlet is plotted over time in Figure 9. For the operating conditions of the reference case (cf. Table S2), CO₂ breakthrough occurs after 200 seconds when the fiber bundle was degassed completely prior to the adsorption step. For the steady-state process mode remaining gas with a CO₂ molar fraction of 11-15% from the preceding desorption and regeneration step exits the column outlet due to new feed flow. With desorption conditions of 140 °C and 0.5 bar a breakthrough

of the newly fed CO_2 occurs after 130 seconds. More complex modes of operation could lead to higher separation efficiency. For instance, Grande et al. [65, 66] presented a seven-step cycle and later a six-step cycle including internal rinsing and purging with recovered gas to improve the enrichment of CO_2 , doubling the enrichment factor compared to a four-step cycle.

Figure 9: Modelled adsorption breakthrough curve for CO_2 adsorption (gas composition: 15 vol % CO_2 in N_2) on a CNT-zeolite fiber bundle at 25°C and ambient pressure. The solid line represents the CO_2 molar fraction in the gaseous phase at the column outlet $L = 0.3\text{m}$ for a completely degassed column while the dashed line depicts the breakthrough behavior in steady-state.

Figure 10 shows three full cycles of electric swing adsorption on a CNT-zeolite fiber bundle according to the reference case conditions (cf. Table S2) and a desorption temperature and pressure of 140°C and 0.5 bar. The solid line represents the loading of the sorbent material at $1/3$ length of the fiber bundle while the dashed line depicts the loading at $2/3$ length. At $1/3$ length of the fiber module, the loading rises monotonically from about 20 mg g^{-1} to

its maximum of 65 mg g^{-1} in 350 s during the adsorption step. The loading at 2/3 length follows a similar course, resulting in a maximum of 55 mg g^{-1} . Subsequently, the desorption is initiated resulting in a sharp drop to a loading of 22 mg g^{-1} , which leads to a working capacity of more than 30 mg g^{-1} . The difference in working capacity calculated with the model and measured with the module (cf. Figure 8) results from the difference in CO_2 concentration during adsorption (15 vol % vs. 100%) and from the different desorption strategies. After the desorption step of 80 s, the column is cooled and pressurized to ambient conditions for 350 s. Here, an appreciable difference between the two locations of the bundle manifests, which can be explained by a heterogeneous temperature and concentration profile along the fiber length in the closed column. Lower temperatures and higher CO_2 partial pressure temporarily lead to a higher loading in the rear part of the column. The next adsorption step then starts with a slight decrease in loading due to the entering feed gas diluting the residual CO_2 -rich gas phase from the previous desorption step.

To examine the viability of CNT-zeolite fibers for the process described above, different operating points are simulated to calculate minimum energy requirements per kg CO_2 produced and the respective throughput as shown in Figure 11. The influence of different desorption temperatures and pressures on the process performance were simulated and analyzed. The best process performance was achieved when applying a low vacuum pressure of 0.2 bar, enhancing both CO_2 desorption with a throughput of $8.4 \times 10^{-3} \text{ kg h}^{-1}$ and its transport out of the column/bundle, resulting in an MER of $9 \text{ MJ/kg}_{\text{CO}_2}$ at 100°C . Due to fast pressure decrease and low pressure vacuum, the MER is almost constant over the presented temperature range, meaning that most of the product gas is recovered by pressure equilibrium. In contrast, when desorbing at ambient pressure a nearly linear temperature

Figure 10: Modelled ad- and desorption cycles for CO_2 adsorption (gas composition: 15 vol % CO_2 in N_2) on a CNT-zeolite fiber bundle. 1 denotes the adsorption step at ambient conditions, 2 the desorption step, which takes place at 140°C and a partial vacuum of 0.5 bar, and 3 the cooling and regeneration step to reach ambient conditions again. The solid line curve represents the adsorbent loading at $1/3$ length and the dashed line at $2/3$ length of the fiber bundle.

dependency is seen, decreasing from about $65 \text{ MJ/kg}_{\text{CO}_2}$ at 100°C to $35 \text{ MJ/kg}_{\text{CO}_2}$ at 140°C , showing a reduction in energy requirements of 50%. Here, the increment of the throughput of 40% between 100°C and 140°C shows a high potential for an application in TSA. For medium vacuum pressure operation at 0.5 bar and 0.7 bar, energy requirements are $22 \text{ MJ/kg}_{\text{CO}_2}$ and $29 \text{ MJ/kg}_{\text{CO}_2}$ at 100°C , respectively, and $18 \text{ MJ/kg}_{\text{CO}_2}$ and $19 \text{ MJ/kg}_{\text{CO}_2}$ at 140°C , respectively. When operating at vacuum pressures below 0.5 bar, high temperature operation becomes more energy intensive since the vacuum recovers most of the adsorbate.

Other simulation studies on ESA processes show lower energy requirements than the ones reported here. For instance, Lillia et al. [67] calculated an energy requirement of

2.86 MJ/kg_{CO₂} when capturing CO₂ from a stream containing 12 wt % CO₂ using a 13X zeolite / activated carbon hybrid material and an eight step cycle. Using a hypothetical adsorbent made from zeolites and graphite and adsorbing from a gas mixture with low CO₂ content (3.5%), representing flue gas from a natural gas power plant, Grande et al. [65] simulated a five step ESA cycle requiring 2.04 MJ/kg_{CO₂}. Obviously, the energy requirement calculated in our work exceeds these values. However, as stated before, our model is intended as a first indicator of the applicability of our fibers in a process and does not include any optimization. Different measures will lead to a decreased energy requirements. For instance, a more sophisticated process design should lead to a 50 to 60% reduction of the MER as reported by Grande et al. [66]. Additional optimization of the geometry and the fiber composition could lead to even lower energy demands. Additional approaches to improve the process model are discussed at the end of this section.

Figure 11: Minimal energy requirement per kg_{CO_2} for the ESA process at different operating points. The column was fully loaded every cycle and subsequently regenerated to its respective temperature and pressure equilibrium.

Low energy requirements are not the only advantage resulting from high temperature or low temperature plus low pressure operation. As presented in Figure 12, the product gas purity can be increased from 45% at 100 °C to 65% at 140 °C using the simple process configuration described above at ambient pressure. For medium vacuum pressures, the CO_2 purity improves from 63% to 75% in the same temperature range. Even higher purities can be achieved when applying a low pressure vacuum of 0.2 bar, resulting in a maximum purity of 81% at 140 °C and a promising enrichment factor of 5.4 for CO_2 . In order to reach such high purities in a three step TSA process, the column must be loaded to its maximum, since desorbed CO_2 will be mixed with remaining N_2 in the gaseous phase. This also means that the column must be fed even after CO_2 breakthrough at the outlet, resulting in lower recoveries (see Figure S5). For ambient pressure, CO_2 recovery is 21% at 100 °C increasing

to 32% at 140 °C and when applying low pressure vacuum up to 62% at 140 °C, for the fully loaded column.

Figure 12: CO₂ purity in product stream for different operating points. The column was fully loaded in every cycle and subsequently regenerated to its respective temperature and pressure equilibrium.

Overall, the results of the mathematical modelling prove the viability of our hollow fibers for ESA processes and indicate the optimization potential of the proposed model process conditions. Considering the results in terms of process development, future research should engage in more complex process design, optimization of fiber/bundle geometry and the identification of the capital cost trade-offs that relate to vacuum operation at high volume flows. Especially internal rinsing with recovered CO₂ and suitable purge steps are conceivable options to enhance energy demand, purity, and recovery.

4. Conclusion

Carbon capture remains one of the imperative measures to mitigate climate change and it necessitates research efforts. We presented two different hollow fiber types potentially suitable for CO₂ capture in an electrical swing adsorption process. Silicon carbide fibers were impregnated with PEI (SiC-PEI) while the other fiber type consisted of a carbon nanotube framework with embedded zeolite particles (CNT-zeolite). The adsorption capacity between 30 °C and 80 °C measured with TGA and a gas mixture with 15 vol % CO₂ in N₂ was 3.9 mg/g_{Fiber} (0.1) and 49 mg/g_{Fiber} (1.7) for SiC-PEI and CNT-zeolite, respectively. Higher capacities of the SiC-PEI fibers could be achieved by higher PEI loadings. Experiments with a bundle of 15 fibers in a module proved the electrical heatability of the fibers where 80 °C were reached within less than 30 s independent of the fiber type. The energy demand for heating was 14.5 MJ/kg_{CO₂} (2.3) and 9.2 MJ/kg_{CO₂} (1.1) for the SiC-PEI and the CNT-zeolite fibers, respectively. Better electrical connections could improve both the heating time and the energy demand. Adsorption experiments with the module yielded similar CO₂ adsorption capacities compared to the TGA measurements. The applicability of our hollow fibers for electrical swing adsorption was thus successfully demonstrated in a proof-of-concept module. Mathematical modelling of an ESA process with the CNT-zeolite fibers resulted in promising CO₂ purities of 81% when applying vacuum in the desorption step in addition to the temperature increase. Short cycle times of less than 500 s were needed to achieve working capacities of 40 mg/g_{Fiber}.

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