CO_2 CAPTURE WITH STRUCTURED SORBENTS CONTAINING MULTIWALLED CARBON NANO TUBES AND POLYETHYLENEIMINE (PEI)

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Abstract

In this work monolithic adsorbents containing polyethyleneimine (PEI) and multiwalled carbon nanotubes obtained by 3D printing. CO_2 and N_2 isotherms were measured using a commercial volumetric apparatus. Breakthrough experiments were carried out with a synthetic flue gas containing 15% CO_2 and the rest N_2. The information was used to simulate and optimize a 6-step Vacuum swing Adsorption (VSA) cycle for post-combustion CO_2 capture from a flue gas stream containing 15% CO_2 and 85% N_2. Detailed process optimization revealed that it was indeed possible to achieve 95% CO_2 purity and 90% CO_2 recovery targets.

Keywords: *3D Printing, Vacuum swing adsorption, PEI*

1. Introduction

Processes that utilize solid adsorbents to capture CO_2 are promising alternatives to state-of-art technologies using water-based amine solutions as absorbents for capturing CO_2 from large point sources such as power plants. Although the energy needs of solid sorbent-based processes are low, the process footprint and consequently the capital cost connected to its implementation can be large due to the relatively long cycle times needed to get the required capture rate and purity of the CO_2 product. To overcome this challenge, processes having structured adsorbents like laminates, monoliths etc. are needed owing to their low pressure drop and better mass transfer characteristics [1, 2]. In recent times, 3D printing of structured adsorbents has been gaining significant attention due the versatility in shapes of the adsorbents and good control over the channel dimensions.

Even though there are several published studies in the context of structured adsorbents, they are mostly restricted to characterization of the adsorbents with respect to equilibrium and mass transfer[3-5]. Very few published studies exist on a process level demonstrating an improvement in the process performance in comparison with pellets[6, 7]. It has been shown that, the true potential of any adsorbent only be obtained through rigorous optimization of a cyclic adsorption process [8].

The aim of this work is to study a 3D printed sorbent for its suitability to post-combustion CO_2 capture. These adsorbents were then printed in the form of monoliths by the 3D printing technique called robocasting. First pure component CO_2 and N_2 isotherms were measured using a commercial volumetric apparatus. Breakthrough experiments were then carried out with a dry mixture of CO_2 and N_2. The information from the adsorbent characterization was then used to simulate and optimize a vacuum swing adsorption process in order to identify the operating conditions corresponding to 95% CO_2 purity and 90% CO_2 capture rate targets to capture CO_2 from a coal fired power plant containing 15% CO_2, 85% N_2.

2. Materials and Methods

2.1 3D Printing

CNT-PEI based pastes were prepared by AIMPLAS. These pastes were then printed by VITO using a technique called robocasting and the methodology is shown in Figure 1. The printing process is a computer-controlled extrusion of the paste. Once a structure with desired dimensions is printed, it is then dried in a furnace at 40°C overnight. Each structure was 2 cm in height and 2.1 cm in diameter. The average diameter of the channels in the middle of the monolith was 2 mm with a wall thickness of 0.7 mm.

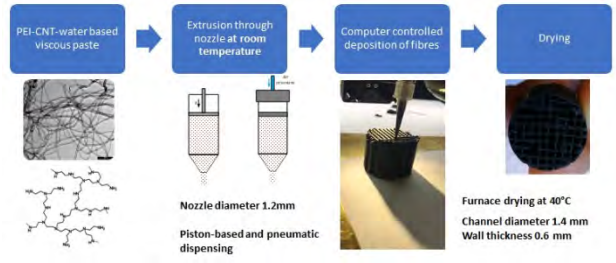

Figure 1: Schematic of the printing process

2.2 Adsorbent characterization

2.2.1. Volumetric apparatus

First, CO_2 and N_2 adsorption isotherms were obtained using a commercial volumetric apparatus. One of the printed structures was crushed and packed into the volumetric cell and regenerated overnight at 100°C. After regeneration, experiments were carried out with pure CO_2 and N_2 for pressures up to 1 bar. The CO_2 adsorption isotherms were measured for 4 different temperatures (70, 80, 90 and 100°C) and the nitrogen adsorption was carried out for 70 °C.

2.2.2. Breakthrough experiments

In the breakthrough apparatus, 2 structures weighing 4 g in total were packed in a column that was about 4 cm in length. Experiments were then carried out using a feed containing 15% CO_2 and 85% N_2 and this was followed by desorption using nitrogen purge. The adsorption part of the breakthrough experiment was analyzed using a 1D adsorption process model by fitting the adsorption rate equation co-efficient (Linear driving force co-efficient) and the heat transfer parameters. The analysis was done for multiple temperatures to obtain a meaningful set of parameters.

2.3. Process simulation and optimization

For the process simulations we chose a flue gas stream containing 15% CO_2 and 85% N_2 which is typical of a coal-fired power plant. In this work a 6-step vacuum swing adsorption cycle was simulated. The schematic of the 6-step cycle is shown in Figure 4 [9]. The steps in the cycle are as follows, adsorption with feed, rinse, co-current evacuation, counter-current evacuation, light reflux, and light product pressurization. A 1-D non-isothermal, non-isobaric model was used to simulate the 6-step VSA cycle. The model equations were discretized in the spatial domain by finite volume method and the resultant system of differential algebraic equations (DAEs) were solved in MATLAB. The simulations were performed up to cyclic steady state (CSS) and this was ensured the mass balance error was less than 0.5% for 5 consecutive cycles.

The next step was to optimize the cycle to identify operating conditions with minimum specific energy and maximum productivity for target CO_2 purity and recoveries of 95% and 90% respectively. The optimization was carried out using MATLAB's inbuilt multi objective genetic algorithm function gamultiobj. The use of genetic algorithm for optimization of VSA cycles is well-documented in literature [8, 10, 11] .

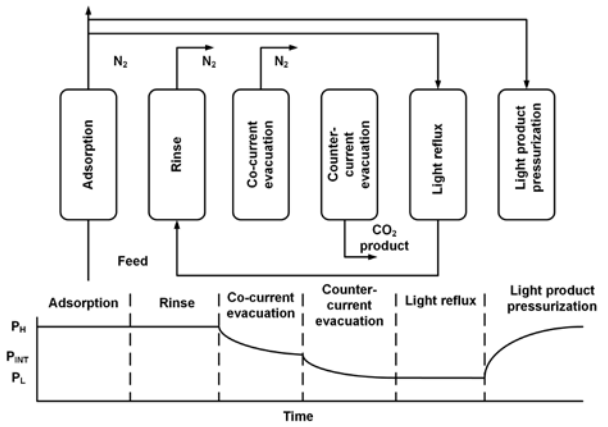

Figure 2: Schematic of the 6-step VSA cycle simulated in this study.

The performance indicators like CO_2 purity, recovery, specific energy consumption and productivity are defined in the following manner:

$$\text{Purity} = \frac{Moles_{CO_2,Cn-evac}}{Moles_{total,cn-evac}} \quad (1)$$

$$\text{Recovery} = \frac{Moles_{CO_2,Cn-evac}}{Moles_{CO_2,adsorption}} \quad (2)$$

$$\text{Productivity} = \frac{Moles_{CO_2,Cn-evac}}{V_{Adsorbent} t_{cycle}} \quad (3)$$

$$\text{Specific energy} = \frac{E_{compression} + E_{vacuum}}{Moles_{CO_2,Cn-evac}} \quad (4)$$

3. Results and Discussion

3.1 Adsorbent characterization

3.1.1. Volumetric apparatus

The adsorption isotherms of CO_2 and N_2 are shown in Figure 3. From Figure 3, one can see that the nitrogen adsorption is negligible, and the CO_2 is much more strongly adsorbed. The CO_2 data was fitted to a dual-site Langmuir model [12] and the heat of adsorption value obtained from the fitting was around 100 kJ/mol, typical of chemisorption mechanism. The adsorption isotherms of CO_2 on the structured sorbent and that of the pristine paste are shown in Figure 2b. The loss in capacity compared to the pristine paste could be due to the printing and drying processes. The adsorption isotherm parameters of CO_2 are shown in Table 1.

Table 1: Dual site Langmuir isotherm parameters

Parameter	Value
q_{s1}(mol/kg)	0.23
$b_{0,1}$(bar^{-1})	3.9 x 10^{-17}
ΔH_1 (kJ/mol)	–109.4
q_{s2}(mol/kg)	0.58
$b_{0,2}$(bar^{1})	7.4 x 10^{-11}
ΔH_2 (kJ/mol)	–58.7

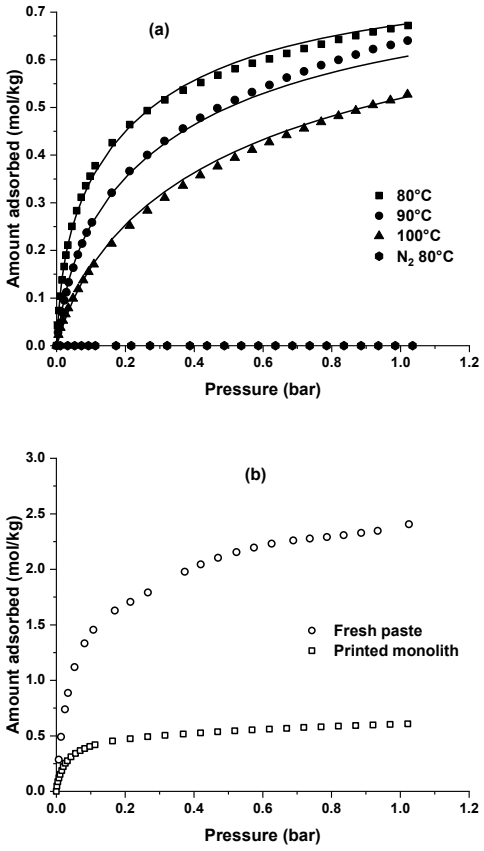

Figure 3: (a) CO_2 and N_2 adsorption isotherms in the 3D printed adsorbent and (b) comparison of capacities in the fresh paste and 3D printed monolith.

3.1.1. Breakthrough experiments

Breakthrough experiments were carried out at 4 different temperatures namely 70, 80, 90 and 100°C. As mentioned earlier, the residual between the experimental and simulated breakthrough curves by fitting the adsorption rate (LDF) coefficient and the heat transfer parameters

From the breakthrough curves shown in Figure 3, one can observe a good match between the simulated curves from the 1D model and experimental breakthrough curves. One can see a small kink in the CO_2 breakthrough curve and this kink could be due to the cracks present in the monolith which were formed during the drying. The other possibility could be due the differences in the channel sizes i.e., the channels in the corners are smaller than those in the middle of the monolith. Further studies either by experiments or by computational fluid dynamics modelling may help us to understand this phenomenon better.

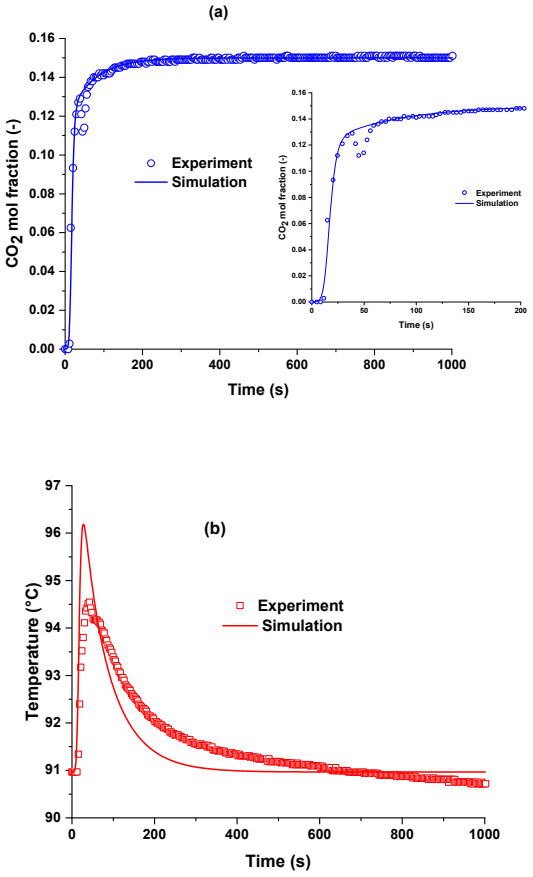

Figure 4: (a) concentration and (b) temperature breakthrough curves.

3.2. Process simulation and optimization

The 6-step VSA cycle was first validate using parameters and simulated profiles from literature [9]. Then detailed process optimization was carried out using MATLAB's in built non-dominated sorting genetic algorithm (NSGA-II) function for multi-objective optimization. In total 4200 simulations were performed.

Figure 5 shows the specific energy vs productivity pareto fronts and these points satisfy purity values of > 95% and recovery values are > 90%. The minimum specific energy was 0.67 MJ/kg, and the maximum productivity was 0.89 mol/m^3 ads/s. The average cycle time for points on the pareto front were approximately 2 minutes. The adsorption step time varied from 27 s to 49 s for the different conditions. It should be noted that the energy consumption reported is on an electricity basis.

Figure 6 shows the bed profiles at the end of the simulation and at cyclic steady state (CSS) conditions. Cyclic steady state means that the conditions in the column at a given cycle are the same as that of the previous cycle. Moreover, as mentioned earlier, the mass balance error is less than 0.5% for 5 consecutive cycles. Looking at the CO_2 concentration profile, one can understand what happens in very step. The inlet concentration at the adsorption step is the feed concentration. During the rinse step, the CO_2 concentration in the bed is enhanced by the stream coming from the light reflux step and nitrogen is

collected at the product. The co-current evacuation step removes the remaining nitrogen in the column so that high purity CO_2 product can be obtained from the counter-current evacuation step. The light product pressurization step uses nitrogen from the adsorption step and hence the concentration is lower.

As mentioned earlier, the adsorbent has a high heat of adsorption. This high heat of adsorption has high temperature swings inside the column. This also explains the spread in the CO_2 concentration profile i.e., the presence of considerable CO_2 close to the exit of the column.

In our simulations, we have not considered the presence of oxygen or water in the flue gas stream. The presence of oxygen is known to cause irreversible loss of capacity of these structured sorbents[13]. Secondly, the presence of moisture is known to enhance the CO_2 adsorption[14, 15]. Alternatively, it can also compete with the CO_2 adsorption which could further reduce the CO_2 capacity. Depending on the amine group used, it is also possible that these amines get leached with repeated use in a cyclic process. All these factors must be considered when we use these amine containing sorbents for cyclic adsorption processes.

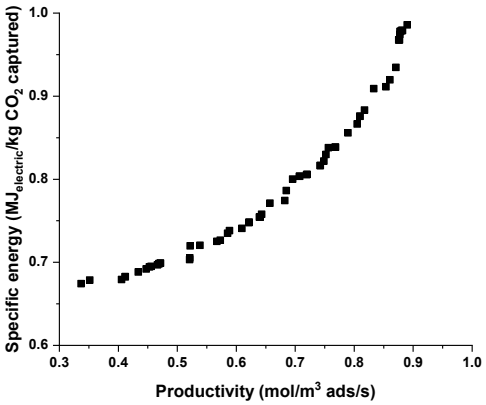

Figure 5: Specific energy vs productivity Pareto curve. All points on the Pareto curve satisfy >95% purity and >90% recovery.

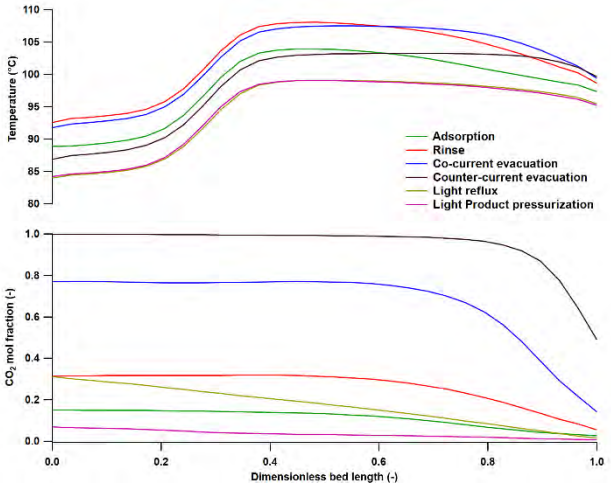

Figure 6: CO_2 concentration and temperature profiles in the column at CSS for maximum productivity.

4. Conclusions

In this work a structured sorbent made by 3D printing methods was characterized for adsorption equilibrium and kinetics. The information was fed to a process simulator and detailed process optimization of 6-step VSA cycle showed that it was indeed possible to achieve 95% purity and 90% recovery from a 15% CO_2 stream. While it is possible to produce structures with moderate CO_2 capacity values, still issues remain with respect to printing CNT-PEI pastes. First and foremost, the printing process was not stable, and this necessitated the use of additives. This affected the capacity of the structured sorbent. Secondly, the presence of water in the paste resulted in a large shrinkage of the final structure. While this is probably not a challenge in lab scale systems, it may pose a challenge when printing large structures on a pilot scale. Moreover, the printed structure also had cracks due to local gradients in drying rates and stress build up as well as the resistance to shrinkage due to the presence of a base plate. Therefore, further work is necessary for the optimization of pastes and the drying process to print structures with good capacity and mechanical stability.

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For more information on this project visit the project web page https://carmof.eu/

References

1. Ruthven, D.M. and C. Thaeron, *Performance of a parallel passage adsorbent contactor.* Separation and Purification Technology, 1997. **12**(1): p. 43-60.
2. Rezaei, F., et al., *Comparison of Traditional and Structured Adsorbents for CO_2 Separation by Vacuum-Swing Adsorption.* Industrial & Engineering Chemistry Research, 2010. **49**(10): p. 4832-4841.
3. Couck, S., et al., *3D-printed SAPO-34 monoliths for gas separation.* Microporous and Mesoporous Materials, 2018. **255**: p. 185-191.
4. Middelkoop, V., et al., *3D printed versus spherical adsorbents for gas sweetening.* Chemical Engineering Journal, 2019. **357**: p. 309-319.
5. Grande, C.A., et al., *Multiscale investigation of adsorption properties of novel 3D printed UTSA-16 structures.* Chemical Engineering Journal, 2020. **402**: p. 126166.
6. Mohammadi, N., *CO_2 Capture From Flue Gas By A PSA Process Using A Novel Structured Adsorbent*, in *College of Engineering and Computing*. 2017, University of South Carolina.
7. Sharma, I., et al., *Monolithic Adsorbent-Based Rapid-Cycle Vacuum Pressure Swing Adsorption Process for Carbon Capture from Small-Scale Steam Methane Reforming.* Industrial & Engineering Chemistry Research, 2020. **59**(15): p. 7109-7120.
8. Rajagopalan, A.K., A.M. Avila, and A. Rajendran, *Do adsorbent screening metrics predict process performance? A process optimisation based study for post-combustion capture of CO_2.* International Journal of Greenhouse Gas Control, 2016. **46**: p. 76-85.
9. Khurana, M. and S. Farooq, *Simulation and optimization of a 6-step dual-reflux VSA cycle for post-combustion CO_2 capture.* Chemical Engineering Science, 2016. **152**: p. 507-515.
10. Haghpanah, R., et al., *Cycle synthesis and optimization of a VSA process for postcombustion CO_2 capture.* AIChE Journal, 2013. **59**(12): p. 4735-4748.
11. Maruyama, R.T., et al., *Improving the performance of vacuum swing adsorption based CO_2 capture under reduced recovery requirements.* International Journal of Greenhouse Gas Control, 2020. **93**: p. 102902.
12. Krishnamurthy, S., et al., *Post combustion carbon capture with supported amine sorbents: From adsorbent characterization to process simulation and optimization.* Chemical Engineering Journal, 2021. **406**: p. 127121.
13. Sonnleitner, E., G. Schöny, and H. Hofbauer, *Assessment of zeolite 13X and Lewatit® VP OC 1065 for application in a continuous temperature swing adsorption process for biogas upgrading.* Biomass Conversion and Biorefinery, 2018. **8**(2): p. 379-395.
14. Sutanto, S., et al., *CO_2 removal from biogas with supported amine sorbents: First technical evaluation based on experimental data.* Separation and Purification Technology, 2017. **184**: p. 12-25.
15. Gelles, T., et al., *Recent advances in development of amine functionalized adsorbents for CO_2 capture.* Adsorption, 2020. **26**(1): p. 5-50.