A MULTISCALE APPROACH FOR EVALUATING UTSA-16 ADSORBENT FOR POST COMBUSTION CARBON CAPTURE

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Abstract

UTSA-16 is considered as one of most promising Metal-Organic Frameworks (MOFs) for post combustion carbon capture in a vacuum swing adsorption (VSA) process. Current studies base their predictions on the equilibrium information for the crystalline material and assuming that the mass transfer is dominated by macropore diffusion. Performance of the real process depends not only on the equilibrium adsorption characteristics, but also on the morphology and mass transfer characteristics of the pellet. In this study, we use a series of complementary techniques to first characterize UTSA-16 pellets and develop a detailed understanding of the mass-transfer mechanisms in these pellets. Using the obtained data, we performed process simulations and optimization to explore performance of real UTSA-16 pellets in carbon capture VSA cycle. We have optimized a 4-step cycle with light product pressurization to identify operating conditions with minimum energy and maximum productivity subject to purity-recovery targets. Further, the performance of UTSA-16 was compared with that of the reference material Zeolite 13X.

Keywords: UTSA-16; vacuum swing adsorption (VSA), energy penalty, Zero length column (ZLC)

1. Introduction

Anthropogenic CO_2 emissions have been established as the major cause for global warming Therefore significant efforts are currently being pursued to limit the global temperature rise to below 2°C and carbon capture and storage (CCS) is being advocated as a possible solution to meet this challenge [1]. Adsorption processes using solid sorbents like Zeolites [2], Carbons [3] Metal organic frameworks (MOFs) [4], supported amine sorbents [5] and zeolitic imidazolate frameworks (ZIFs) [6] are currently being explored as potential candidates for carbon capture.

A typical post-combustion flue gas contains about 4-5% CO_2 for a natural gas combustion cycle and about 10-15% CO_2 in case of a pulverized coal combustion cycle along with a large amount of nitrogen. The adsorbent chosen must have a good CO_2 capacity and lower affinity to nitrogen to achieve high purity and recovery targets.

UTSA-16 is a metal organic framework that has been found promising for post-combustion carbon capture application by means of rigorous process optimization [7,8]. However, the process optimization was based only on the equilibrium information of a crystalline material and assuming that the mass transfer is dominated by macropore molecular diffusion. The morphology of the pellet and mass-transfer mechanisms also play an important role in the overall performance of the process.

An adsorbent pellet basically consists of microporous crystals bound together and intracrystalline macropores. Adsorption of a gas is governed either by the diffusion in the macropores, or micropores or both. In case of a macropore controlled diffusion process, the uptake is generally governed by the pellet size, i.e small pellets have a faster uptake than larger pellets. Moreover, smaller pellets also mean larger pressure drop and in case of a macropore diffusion-controlled process, the pellet size is a decision variable, which affects the performance of the adsorption process [9]. In case of a micropore controlled diffusion process, the uptake of CO_2 is not governed by the size of the adsorbent pellets. It is therefore important to establish the right mass transfer mechanism and the time constants to obtain the true performance of the adsorption process.

The aim of this work is to characterize UTSA-16 adsorbent (Figure 1) for obtaining information on adsorption equilibrium and kinetics and establish the mass transfer mechanism. Using this information detailed optimization of a 4-step vacuum swing adsorption (VSA) cycle was performed to identify operating conditions with minimum energy consumption and maximum productivity subject to 95% purity and 90% CO_2 recovery targets. The performance of UTSA-16 was compared with Zeolite 13X, the current benchmark sorbent for post-combustion carbon capture.

Figure 1: UTSA-16 extrudates used in this study.

2. Materials and methods

2.1. Volumetric apparatus

Single component CO_2 and N_2 adsorption isotherms were obtained using a commercial volumetric apparatus AUTOSORB IQ purchased from Quantachrome instruments. The volumetric apparatus was also used to study the diffusional time constant for pure CO_2 adsorption by recording the transient pressure response at different pressure steps. About 0.5 g of sample was used for the isotherm measurements and 11 mg of sample was used for the kinetic measurements

2.2. Zero length column (ZLC) apparatus

The zero-length column apparatus (ZLC) has been traditionally used for measuring diffusion in zeolites and other microporous sorbents [10,11] by providing a step input in concentration (CO_2+Carrier gas) and desorption is carried out by purging the column with the carrier gas. The advantage of this apparatus is that it uses relatively small amounts of sample thereby eliminating external mass and heat transfer resistances. Furthermore, it is possible to obtain both the equilibrium and kinetic parameters by simply varying the flowrate to carry out experiments in the equilibrium and kinetic regimes. For this work, a single UTSA-16 pellet weighing 11 mg was packed into a 1/8" Swagelok union. Experiments were done at different flowrates (7.5 cc/min to 30 cc/min) with a 10% CO_2-He mixture first to establish the kinetic regime. Once the kinetic regime was established, the carrier gas was switched to nitrogen. The volumetric experiments and the zero length column experiments were complemented with independent mercury intrusion experiments.

2.3. Process simulation

Next, a 4-step cycle with light product pressurization (LPP) [7,8] shown in Figure 2 was simulated using CySim software using the equilibrium and kinetic information obtained from the labscale experiments. The four steps are Adsorption with feed, co-current evacuation to an intermediate pressure, counter-current evacuation to low pressure and pressurization with light product. The cycle was optimized using NSGA-II to identify operating conditions with minimum specific energy consumption and maximum productivity subject to 95% CO_2 purity and 90% recovery.
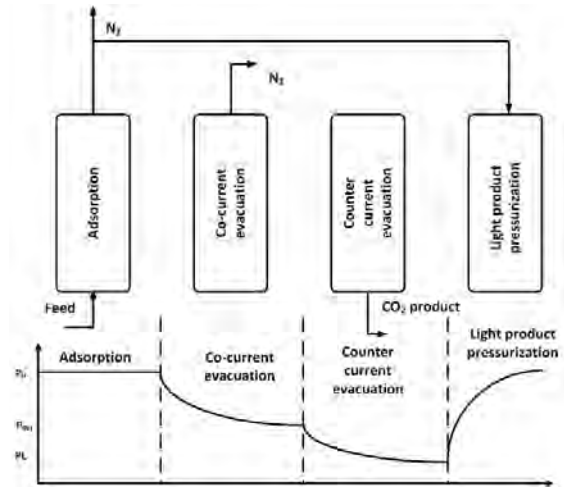

Figure 2: Schematic of the 4-step cycle with LPP

3. Results and discussion

3.1. Volumetric apparatus

The adsorption isotherms of CO_2 and N_2 are shown in Figure 3 and the experimental data was fitted to a Langmuir isotherm. It can be seen that the adsorption of CO_2 is stronger and the equilibrium loading corresponding to a pressure of 0.1 bar and 308 K is 1.2 mmol/g and these values are similar to the ones reported by Agueda et al., who observed 1.05 mmol/g at 313K [12].
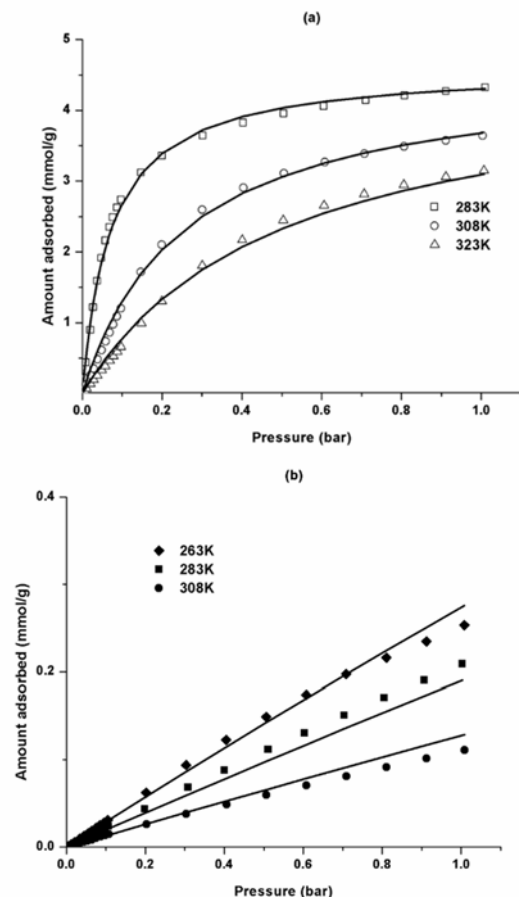

Figure 3: (a) CO_2 and N_2 adsorption isotherms in UTSA-16.

The transient pressure responses at 308 K for different pressure steps were analysed by a piezometric model developed by Brandani [13]. This involves analysing the normalized experimental curve with the piezometric model by fitting the valve co-efficient and the diffusional time constant for different pressure steps. More details about this method are given in earlier publications [14,15]. Figure 4a shows the comparison of the experimental pressure profile and the piezometric model. Figure 4b shows the diffusional time constant as a function of the pressure and one can see that the adsorption becomes faster

From the diffusional time constant, the effective diffusivity was calculated using the slope of the isotherm obtained from the initial and final pressure of the dosing and the particle porosity which was obtained from high pressure mercury intrusion experiments. Assuming macropore diffusion controlled

$$D_P^e = \frac{\varepsilon_p \dfrac{D_{macro}}{\tau}}{\varepsilon_p + (1 - \varepsilon_p)K}$$

(1)

The experiments correspond to a pure gas adsorption and therefore the macropore diffusion is governed by Knudsen, viscous and surface diffusion components. Neglecting surface diffusion, the macropore diffusivity is given by
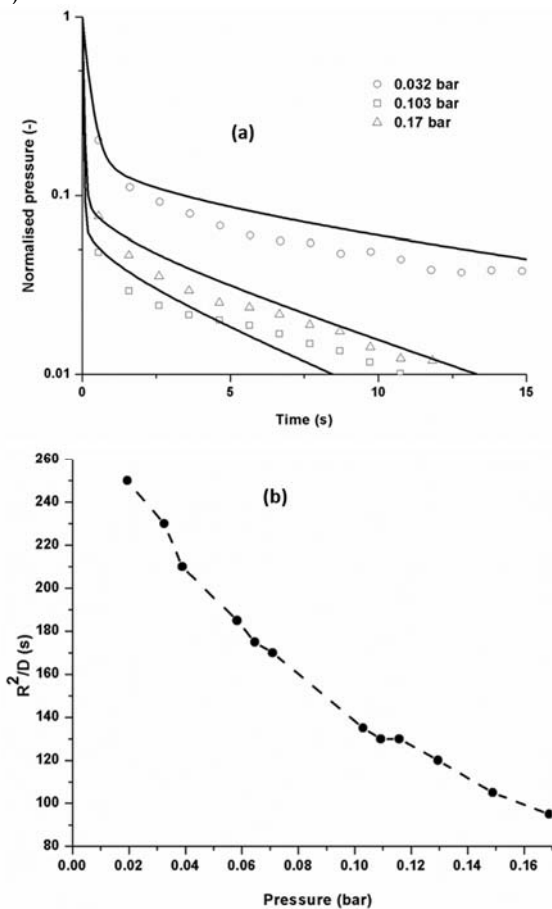
$$D_{macro} = D_{Viscous} + D_{Knudsen}$$

(2)

Using the effective diffusivity shown in Figure 4b and the macropore diffusivity calculated from the average pore size, which was obtained from the mercury intrusion, the average tortuosity was found to be 3.59 ± 0.1 and in Figure 5, the agreement between the measured and the predicted diffusivities are shown. From this analysis, it can be seen that there is a good agreement suggesting that the system is macropore diffusion controlled.
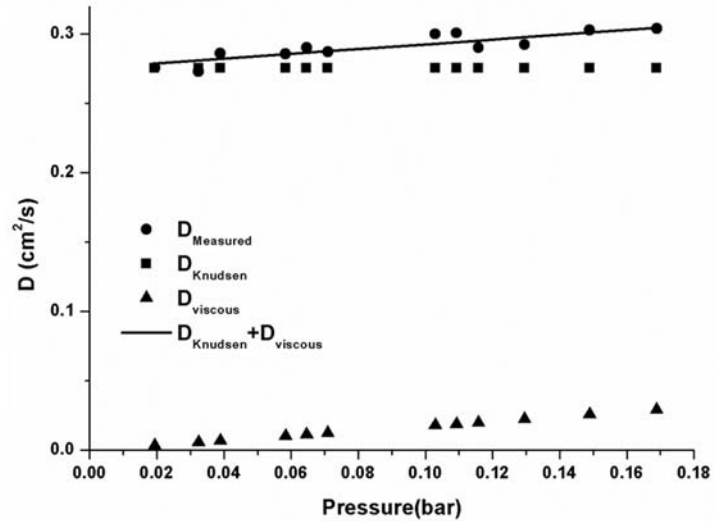

Figure 5: Summary of volumetric experiments for CO₂ adsorption at 308 K.

3.2. Zero length column (ZLC) apparatus

After the zero-length column experiments, the normalized concentration C/C_0 was plotted a function of flow rate x time. In Figure 6, the curves corresponding to two higher flowrates cross the lower flow rate curves indicating the kinetic regime. At this point, the carrier gas is switched to N_2 and experiments are repeated. One can see from Figure 7a that the slope of the long-time region (between 10^{-1} and 10^{-2}) is different for the two carrier gases. This clearly established the system was indeed governed by diffusion through macropores. If the adsorption was governed by micropore diffusion, then there would not have been any differences in the slope, i.e., the curves with two carrier gases would have overlapped one another. The curves were fitted using an automated ZLC tool (Figure 7b) to estimate the diffusional time constants and correspondingly the tortuosity [16]. The tortuosity values were estimated to be 3.57. This is in good agreement with the values obtained from the single component volumetric experiments.
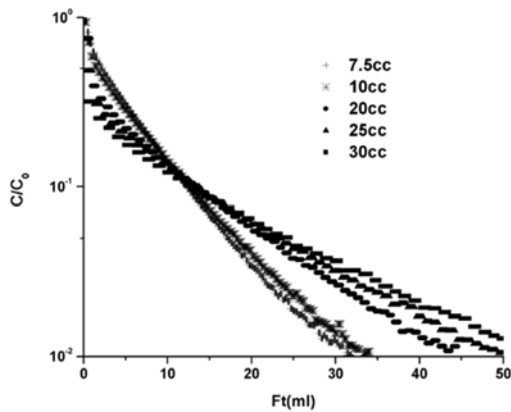
Figure 4: (a) Pressure response from experiments and (b) diffusional time constants with respect to pressure.

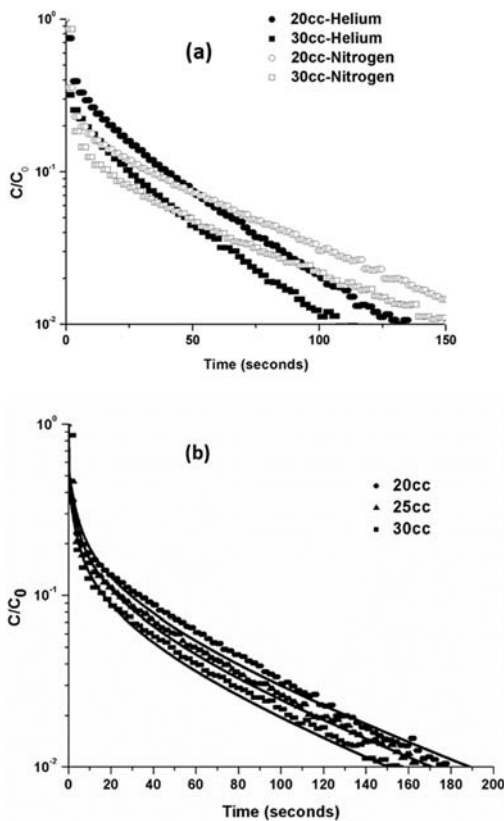Figure 6: ZLC curves for 10% CO2-He mixture

Figure 7: (a) ZLC curves with different carrier gases and (b) comparison of the experimental and simulated ZLC curves.

3.3. Process simulation

Figure 8 shows the pareto fronts for the UTSA-16 sorbent with the measured and assumed kinetic constants. The results are compared with that of Zeolite 13X. the current benchmark sorbent for CO_2 capture. UTSA-16 performed better than zeolite 13X both with respect to specific energy consumption and productivity. The minimum energy consumption and maximum productivity values for Zeolite 13X were 26.6 kJ/kg and 1.1 mol/m³ ads/s. In comparison, UTSA-16 had minimum specific energy value of 22.5 kJ/kg and a maximum productivity value of 1.25 mol/m³ ads/s,

respectively. The improvement in performance can be attributed to the fact that UTSA-16 had a lower affinity to nitrogen in comparison with Zeolite 13X. This meant that coarser vacuum was needed to remove the nitrogen in the co-current evacuation step for UTSA-16 than Zeolite 13X. The values of the co-current evacuation step pressure were 0.08-0.11 bar. In case of zeolite 13X, these values were 0.055-0.082 bar.

With a higher effective diffusivity (2.2 x 10 $^{-6}$ m²/s) a better performance in terms of productivity and specific energy. The minimum specific energy in two cases were 22.5 and 23.3 kJ/mol respectively. The maximum productivity values were 1.25 and 1.98 mol/m³ ads/s. The improvement in performance can be attributed to faster cycles (110 to 232 s vs. 180 to 280 s) and higher co-current evacuation pressure (0.1 to 0.15 bar vs 0.08 to 0.11 bar) chosen by the optimizer as seen from the figure 9.

Further, the energy penalty was calculated based on the maximum productivity values for 13X and UTSA-16 based on equations 3 and 4. We have considered a 600 MW power plant emitting 11690 kg-mole/hr CO_2 captured [17]. This translated into 95.5 MW power required to capture 90% of the CO_2 emitted by the power plant. Therefore, the energy penalty was 15.9%. For zeolite 13X, these values were 105.9 MW and 17.7% respectively. Therefore, a VSA process with UTSA-16 will be 10% more efficient than the one with Zeolite 13X adsorbent.

The power required for capture is calculated as

$$Power_{capture} =$$

$$CO_2 \text{ emission X Recovery X Specific energy consumption}$$

(3)

$$\text{Energy penalty} = \frac{Power_{capture}}{Power_{no\ capture}} \text{ X } 100$$
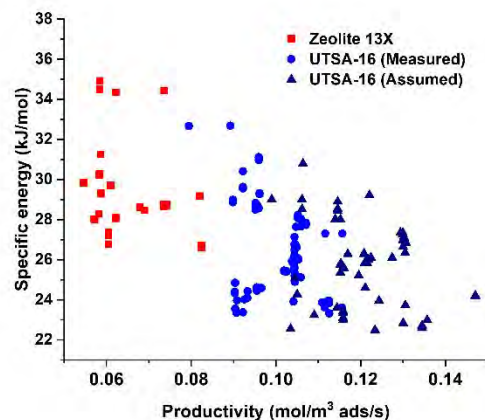
(4)

Figure 8: Specific Energy vs Productivity pareto fronts for Zeolite 13X and UTSA-16.
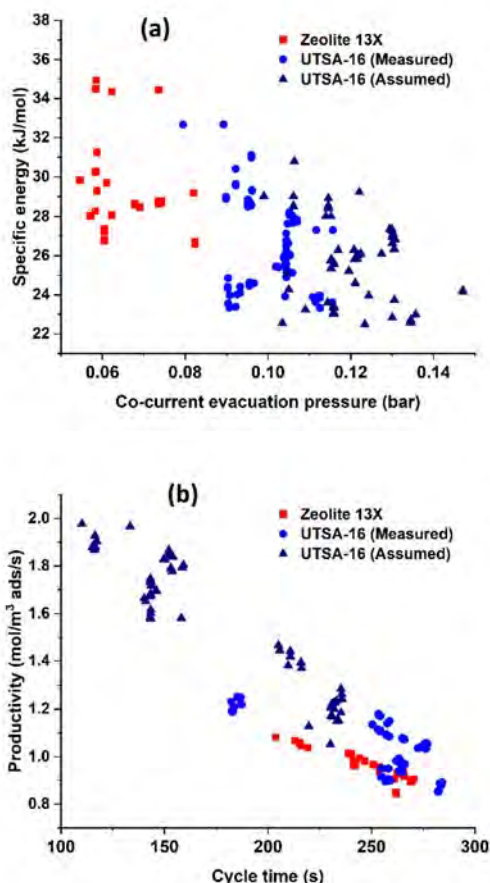
Figure 9: (a) Specific energy vs co-current evacuation pressure and (b) productivity vs cycle time.

Conclusions

UTSA-16 extrudates were synthesized by SINTEF up to 200g and these were characterized for adsorption equilibrium and kinetics at the University of Edinburgh. Using the information from the characterization, process optimization study was carried out and these results showed that UTSA-16 sorbent showed better performance than Zeolite 13X. This work also established the importance of establishing the mass transfer mechanism and the obtaining the right kinetic constants to obtain the true potential of an adsorbent.

Acknowledgements

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