# Modelling and optimization of vacuum pressure swing adsorption CO<sub>2</sub> capture pilot using MIL-160(Al)

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### **Abstract**

Global warming, driven by increasing CO<sub>2</sub> emissions from fossil fuel combustion, necessitates the development of effective carbon capture technologies. Among various approaches, Vacuum Pressure Swing Adsorption (VPSA) offers an energy-efficient solution for post-combustion CO<sub>2</sub> capture, especially in power plants and energy-intensive industries. This work focuses on validating a simulation model using a laboratory VPSA pilot with the Aluminum Metal-Organic Framework (Al-MOF) MIL-160(Al) and optimizing both lab-scale and industrial-scale VPSA pilots through simulation. Process modeling in Aspen Adsorption software simulated a 3-bed 6-step cycle using parameters from experimental adsorption isotherms and breakthrough curves. The simulation model was compared to previous lab-scale VPSA pilot experiments treating a synthetic 15/85 CO<sub>2</sub>/N<sub>2</sub> mixture at 1 Nm<sup>3</sup>/h, showing mean absolute errors of 1.47% for purity and 3.19% for recovery.

Surrogate models, including kriging and artificial neural networks (ANN), were used to optimize recovery and purity of the lab-scale pilot using a genetic algorithm (NSGA-II). The ANN model proved more accurate, especially in determining pareto fronts. The model was extended to an industrial VPSA pilot as part of the MOF4AIR project, designed to treat flue gas of 50 to 100 Nm<sup>3</sup>/h with three 41 L adsorption columns. Simulations showed that the pilot could achieve 95% purity and recovery for CO<sub>2</sub> concentrations ranging from 5 to 15%. The estimated energy consumption and productivity for 15% CO<sub>2</sub> gas were 413.19 kWh/tCO<sub>2</sub> and 3.03 tCO<sub>2</sub>/(m<sup>3</sup>ads.day) at a gas flow rate of 55.62 Nm<sup>3</sup>/h, demonstrating the technology's potential and competitiveness on a larger scale.

# <u>Keywords</u>

CO<sub>2</sub> capture; Vacuum pressure swing adsorption; Metal organic framework; Surrogate; Optimization

# <u>Highlights</u>

- Simulation model development for 3-bed 6-step VPSA cycle.
- Model validation at lab scale deviation: 1.47% for purity and 3.19% for recovery.
- Pareto front obtained with ANN model is equivalent to the one obtained with Aspen.
- Industrial VPSA pilot simulated can reach 95% purity and recovery.

# 1 Introduction

In 2024, the Earth's global surface temperature increased by  $\pm 1.55 \pm 0.13$ °C compared to the pre-industrial period (1850-1900) with more significant increases over land compared to the ocean. This warming trend has been accelerating since 1970 [1]. The consequences of climate change are diverse: rising sea levels, melting snowcaps, floods, drought, forest fires, heatwaves, and ocean acidification. One of the main contributors to global warming is the emission of greenhouse gases, especially CO<sub>2</sub> from fossil fuels combustion.

The 6<sup>th</sup> IPCC report (March 2023) emphasizes that to limit global warming to  $1.5^{\circ}$ C (as adopted in the Paris Agreement) or even 2°C, an immediate reduction in GHG emissions is required across all sectors in this decade [2]. Specifically, for CO<sub>2</sub> emissions, the reduction percentages from the 2019 level in the years 2030 is 48% and a global net zero emissions for 2050 to reach the objective of maximum +1.5°C. [2].

To reach these global targets, several measures must be implemented, including transitioning from fossil fuels without CCS (Carbon Capture and Storage) to very low or zero-carbon energy sources such as renewable or fossil fuels with carbon capture, improving energy efficiency, reducing energy consumption, and reducing non-CO<sub>2</sub> GHG emissions. In transition phase or for specific sectors CCS is highlighted as a crucial element of the solution, particularly in hard-to-abate sectors such as cement, lime and steel production or petroleum refining where a part of the CO<sub>2</sub> emission comes from chemical reactions [2,3]. CCU (Carbon Capture and utilization) is an alternative pathway to the storage of carbon dioxide in applications such as carbonatation, SNG (synthetic natural gas), methanol, and chemical products such as urea, enhanced oil recovery, or algae cultivation. According to the IEA [4–6], 8% of the CO<sub>2</sub> captured between 2020 and 2070 will be reused (CCU).

Post-combustion carbon capture involves separating the CO<sub>2</sub> from flue gas generated by fossil fuel combustion or chemical processes (*e.g.* boilers, industrial furnaces, cement kilns, blast furnaces). Different technologies exist for this purpose. Among them, chemical absorption with amines is the most mature technology (TRL9) but suffers from energy penalties due to high energetic consumption, solvent degradation, solvent loss, and high corrosiveness [7]. Alternatives to absorption techniques include membrane separation, cryogenic distillation, chemical looping, biological processes with microalgae, adsorption or a combination of these [8–11].

In adsorption processes, the separation is made by either changing the temperature (TSA: Temperature Swing Adsorption) or varying the pressure (PSA: Pressure Swing Adsorption). PSA processes are generally employed when the concentration of the compound to be retrieved is high while TSA processes are preferred for low concentrations [12][13]. Various types of adsorbents are used, including activated carbons, zeolites, silica membranes, or, more recently, metal organic frameworks [12]. Separation of gases by adsorption is already used in numerous fields such as air separation, H<sub>2</sub> purification, biogas upgrading, ... but need more development to be used for CO<sub>2</sub> capture [14–16]. VPSA processes are preferred to PSA for CO<sub>2</sub> capture as the use of vacuum is more economical since the flus gas to treat is already at atmospheric pressure, allowing to compress smaller gas flows (product stream) compared to PSA process (feed stream) [17].

The benchmark material for  $CO_2$  capture in flue gases through adsorption is zeolite 13X, a porous aluminosilicate material. At 25°C and a pressure of 1 bar, its reported  $CO_2$  adsorption capacity for a 15/85  $CO_2/N_2$  mixture is comprised between 2.5 and 3.8 mmol/g and a selectivity of  $CO_2$  over  $N_2$  between 100 and 700 [18,19]. However, zeolites are sensible to water which reduces drastically their  $CO_2$  adsorption capacity and active surface area, and to contaminants such as  $SO_x$  and  $NO_x$ . [20,21]. As an alternative, Metal Organic Frameworks (MOFs) have gained attention as a promising class of adsorbents for carbon capture over the past two decades. They exhibit microporous crystalline structures composed of central cation molecules (metal atoms or cluster) linked together by organic ligands (coordinate bonds) to form one, two or three-dimensional networks [13]. The large number of MOFs that can be synthesized results in materials exhibiting high adsorption capacity, high selectivity for  $CO_2$  versus  $N_2$ , finely tunable pore surface properties, and scalability for industrial applications [13].

Among these, Mg-MOF-74 has one of the highest CO<sub>2</sub> adsorption capacities, giving 5.9 mmol/g for a pressure of 1 bar, 15/85 CO<sub>2</sub>/N<sub>2</sub> mixture and 25°C, and a CO<sub>2</sub>/N<sub>2</sub> selectivity of 182 in the same conditions. Higher selectivity can be obtained with other MOFs such as the UTSA-16 (selectivity of 315) but with a lower adsorption capacity (2.06 mmol/g) for the same conditions as Mg-MOF-74 [22–24]. Mg-MOF-74 exhibits a high heat of adsorption (47 to 52 kJ/mol) while the UTSA-16 has a moderate heat of adsorption of 34.6 kJ/mol. Mg-MOF-74 has been reported to be sensitive to water decreasing the CO<sub>2</sub> capacity of the MOF in wet conditions, and also sensitive to SO<sub>2</sub> and NO<sub>2</sub> poisoning the adsorption sites due to high bounding energy [23,25,26]. UTSA-16 suffers from the same problem with a decrease of CO<sub>2</sub> adsorption capacity reported in the presence of water, SO<sub>2</sub> or NO<sub>2</sub> [27,28]. One of the most interesting MOFs for CO<sub>2</sub> capture is the Calgary Framework 20 (CALF-20), exhibiting high capacity (2.75 mmol/g for 0.15 bar of CO<sub>2</sub> at 20°C on the powder), high selectivity (230 for a 10/90 CO<sub>2</sub> /N<sub>2</sub> mixture) even in presence of water pressure vapor, moderate heat of adsorption (39 kJ/mol), stability over steam and acid gases. The raw materials needed for the production of this MOF are commercially available and the pathway of production can easily be applied in industry, showing a good scalability of this MOF for the industrial CO<sub>2</sub> capture [29].

The adsorbent scale properties (adsorption capacity, selectivity, heat of adsorption, ...) and metrics using its properties (Notaro, Ackley, Yang, Wiersum, ...) provide a way to screen the most promising adsorbents for CO<sub>2</sub> capture but are not sufficient to evaluate the performance of the adsorbent in adsorption cycle for CO<sub>2</sub> capture process [30,31]. These processes are usually evaluated by the recovery and purity of CO<sub>2</sub> which must be higher than 95% as recommended by the by the U.S. Department of Energy to be efficient [32]. Two additional metrics, energy consumption and productivity, are also evaluated in a process to compare economic competitiveness with other CO<sub>2</sub> capture technologies [17]. Process evaluation is made by either simulation or pilot experiments, this last option required enough adsorbent to be tested, in addition to high cost and time consumption. However, testing new material in realistic condition is important to validate the simulations made. Simulation of adsorption process allows to evaluate a material with parameters (adsorption isotherms, kinetic, geometry) which can be obtained from relatively small scale (a few dozen grams) and optimize the process to find the pareto front of energy/productivity for a recovery and purity higher than 95%. Nevertheless, simulations are relatively complex because of the need to simulate the dynamic behavior of the adsorption column for a sufficiently long time to reach steady state, resulting in runs that can last several hours [33,34].

Numerous adsorbents have been tested by simulations with different VPSA cycle configurations. Activated carbon, zeolite 13X, Mg-MOF-74, UTSA-16 and CALF-20 have been tested by simulations for a dry 15/85 CO<sub>2</sub>/N<sub>2</sub> flue gas with the 4-step cycle composed of adsorption, co-current evacuation, counter-current evacuation, and light product pressurization. The recovery-purity pareto obtained for the five materials shows better results for the UTSA-16 followed closely by CALF-20 and zeolite 13X. The three materials were able to reach 95% purity and 90% recovery but not 95% for both indicators simultaneously. Energy consumption and productivity obtained for UTSA-16 is equal to 116-120 kWh/t<sub>co2</sub> and 2.18-2.81 t<sub>co2</sub>/(m<sup>3</sup>.day). Nevertheless, these results were obtained with an evacuation pressure of 0.03 bar which is difficult to reach on an industrial scale. [30,35]. The 4-step cycle simulations were validated for zeolite 13X with a 2-bed pilot treating 56.9 Nm<sup>3</sup>/h of a 15/85 dry CO<sub>2</sub>/N<sub>2</sub> mixture, giving a mean error of 2.3% and 2.55% respectively for purity and recovery based on 8 experiments [36]. At smaller scale, a similar validation was performed with a pilot treating between 0.17 and 0.6 Nm<sup>3</sup>/h of a gas containing 15% CO<sub>2</sub> with four experiments showing a mean error for purity of 1.67% and 1.42% for recovery. It is interesting to note that for a same experiment repeated twice, the difference of purity and recovery was equal to 2.6% and 2.7% [37]. Another validation was

performed for the CALF-20 with a smaller 2-bed unit treating 0.05-0.11  $Nm^3/h$  of a 15/85 dry  $CO_2/N_2$  gas, giving 1.16% and 1.40% of mean error for purity and recovery based on 11 experiments [38].

Silica gel was tested experimentally on a PSA pilot using a dual-reflux cycle (composed of adsorption, equalization, evacuation, light and heavy reflux steps) with 2 beds containing 1.587 kg of adsorbent each. A  $15/85 \text{ CO}_2/\text{N}_2$  mixture with a flow rate of 0.16 Nm<sup>3</sup>/h was used and different parameters such as feed position, equalizing pressure method, light reflux flow rate were tested giving in the best conditions 99.18% purity and 99.62% recovery. This pilot was simulated to reproduce the different experimental results giving a maximum relative deviation of 1.38% between experimental and simulated results. By simulation the energy consumption was estimated to 538 kWh/t<sub>CO2</sub> for a productivity of 3.17 t<sub>CO2</sub>/(m<sup>3</sup>.day) [39].

A three beds cycle composed of seven steps (adsorption, co-current evacuation, heavy reflux, pressure equilibrium, co-current evacuation, light reflux, and second pressure equilibrium) containing zeolite 5A was tested with 32 to 46 Nm<sup>3</sup>/h of dry flue gas containing 15% of CO<sub>2</sub> giving a recovery of 79 to 91%, a purity of 71 to 85%, and experimental energy consumption of 658 to 867 kWh/t<sub>CO2</sub>. Simulation of this unit was performed showing good agreement in terms of recovery and purity, but also for the temperature and pressure profile. Nevertheless, no error or deviation values are given precisely [40]. Other cycle simulations have been validated with experimental data obtained on apparatus composed of a single column such as the Skarstrom cycle (adsorption, evacuation, light reflux, pressurization) with activated carbon and zeolite 13X. Simulation results are in good agreement with experiments but only a qualitative comparison was made [41,42].

Simulation of VPSA process can be also used as a screening tool to identify the best adsorbent for a given cycle or the best operating conditions for a given process. Optimization of the VPSA process is generally made by using a genetic algorithm such as the Non-Dominated Sorting Genetic Algorithm II (NSGA-II) [43] or NSGA-III [44] due to the ability of this method to find the global optimum between multiple objectives function by selecting and evolving solutions through a process of non-dominated sorting, crowding distance, and elitism to balance convergence and diversity in multi-objective optimization. This algorithm has been employed in numerous VPSA simulations to find the pareto between purity-recovery and/or energy consumption – productivity [34,37,38,45]. Since the utilization of an optimization algorithm required several hundreds to thousands of simulations to find the pareto front, surrogate models can be used to decrease the number of simulations required and thus increase the speed of optimization [46]. In surrogate modelling, a simpler mathematical model is constructed with a limited number of simulated data. In previous study, kriging model has been used for optimization of an extended Skarstrom cycle reducing the number of simulations by 2 to 5 with comparable results to the direct optimization of the VPSA process [47]. Hybrid algorithms using kriging have also been adapted to VPSA simulations using adaptative kriging where a global kriging is constructed with refinement of the model during the optimization by simulating additional points to increase the accuracy of the kriging [48].

Another popular surrogate model used in VPSA simulation is artificial neural network (ANN) which has been applied for pre-combustion  $CO_2$  capture but also post-combustion  $CO_2$  capture. Several works compare results obtained with process optimization using a full model compared to optimization with ANN. Subraveti et al. [49] have optimized an 8-step PSA cycle for  $H_2/CO_2$  separation, showing that only 1122 simulations were required to construct an ANN model with 8 decision variables able to predict the pareto front of this cycle. This optimization procedure can reduce the simulation time required by 10 compared to traditional optimization. Streb and Mazzotti [50] also investigate the use of ANN for the optimization of pre-combustion capture with a 12-step VPSA cycle with 9 parameters. The surrogate model constructed with 18 000 simulations is in very good agreement with the complete simulation model but shows its limitation when the model is used at the edge of the sampling domain or in areas where the sensitivity of the model to the parameters is high, requiring the estimation of the model error for its correct utilization. For post-combustion capture, Wang et al. [51] have optimized, with an ANN model, a 3-bed 7-step cycle using silica gel for a 15/85 CO<sub>2</sub>/N<sub>2</sub> dry flue gas. The model was constructed with 2000 simulations to optimize recovery, purity, energy consumption and productivity of the cycle with 6 decisions variables, showing R<sup>2</sup> higher than 99% between ANN and complete simulation model. Leperi et al. [52] used a different approach to model VPSA cycle with ANN. Instead of training the whole cycle with the surrogate model, they created different models for individual steps of a cycle, allowing to extend cycle with additional steps. This methodology was successfully applied to zeolite 13X and Ni-MOF-74 for the simulation of a 3-step cycle, Skarstrom cycle and 5-step cycle demonstrating the cycle synthesis using this method.

Artificial neural networks have been used more extensively by integrating adsorption isotherm parameters to the input of the surrogate model in order to simulate virtually any adsorbent for a given configuration and screen the best materials for  $CO_2$  capture. This methodology has been applied to the 5-step cycle (adsorption, co and counter-current evacuation, light reflux, light product pressurization) with a dual-site Langmuir isotherm, identifying materials such as h8155527 (hypothetic zeolitic structure), IISERP-MOF2 (hypothetical MOF) or UTSA-16 as the most promising to reduce the energy consumption and increase the productivity [31,53]. However, this method remains approximate because it uses only one type of isotherm, macropore diffusion as the single mass transfer resistance and constant adsorbent characteristics ( $c_p$ , density, size, etc.) without being based on actual measurements for the tested adsorbents.

In this work, the performance of the MIL-160(AI) in process conditions are studied by simulation. This MOF has been experimentally tested in our previous work with a laboratory scale pilot performing a 3-bed 6-step cycle (adsorption, heavy reflux, co and counter-current evacuation, light reflux, light product pressurization) giving a purity of 90% and recovery of 92.7% for the separation of a 15/85  $CO_2/N_2$  mixture with a moderate level of vacuum (0.1 bar) [54]. MIL-160(AI) exhibits numerous advantages such as high surface area and pore volume (1220 m<sup>2</sup>/g and 0.404 cm<sup>3</sup>/g respectively), a  $CO_2$  working capacity at 30°C of 0.85 mmol/g for partial pressures between 0.15 and 0.015 bar, a relatively low heat of adsorption (-33 kJ/mol for  $CO_2$ ), an IAST  $CO_2/N_2$  selectivity at 1 bar and 30°C of 34 for a 15/85 mixture and a resistance in presence of water, and a green path for the production of this MOF at kg scale, making it a promising candidate for post-combustion  $CO_2$  capture [55–58]. This MOF was studied experimentally and by simulation for biogas upgrading by Karimi et al. [59,60] showing interesting properties for the  $CO_2/N_2$  and  $CO_2/CH_4$  separation such as the fast kinetic of adsorption or the low heat of regeneration. Measurement on a laboratory scale PSA pilot for the  $CO_2/CH_4$  separation was performed with simulation of the results obtained showing a good agreement between the experiments and modelling.

A simulation model was developed in this work to simulate the 3-bed 6-step cycle with MIL-160(Al) and is compared to the experimental results obtained on the lab-scale pilot. The simulation model is then used to find the pareto fronts (recovery-purity and energy-productivity) of the VPSA pilot with a comparison between the direct optimization of the complete model and the use of surrogate models to reduce the computation time. Two models which have been used for approximating VPSA simulation were compared in this work: kriging and ANN. The accuracy and the number of simulations required were studied with the lab-scale VPSA simulation model to determine the best surrogate model. The validated model is finally used to determine operating conditions of the industrial pilot of the MOF4AIR project located at the Technology Centre Mongstad (TCM) test site with the data obtained at laboratory scale. This pilot is composed of three adsorption columns of 41 L to capture  $CO_2$ 

from 50 to 100 Nm<sup>3</sup>/h of flue gas coming from a residual fluid catalytic cracking unit (RFCC) containing around 14% of CO<sub>2</sub> or a process furnace containing 4 to 15% of CO<sub>2</sub> [61]. Optimization of energy consumption and productivity while reaching the target of CO<sub>2</sub> capture process (recovery and purity >95%) was performed for different flue gas composition.

# 2 Materials and methods

# 2.1 Experimental measurements

# 2.1.1 Materials

The MOF studied in this work is the MIL-160(Al) (Formula: Al(OH)( $O_2C-C_4H_2O-CO_2$ )) formed by aluminum chains linked via five-membered ring 2,5 furan di-carboxylate ligand, giving an helical shape with pore diameters ranging from 4 to 6 Å. This material exhibits interacting sites for CO<sub>2</sub> or H<sub>2</sub>O giving a good selectivity of CO<sub>2</sub> over N<sub>2</sub> [50,51]. This MOF has been reported to be resistant to water [57] and SO<sub>2</sub> with no structural degradation, although it shows a preferential adsorption of SO<sub>2</sub> compared to CO<sub>2</sub> [62]. However, molecular simulations have indicated that the material degrades upon exposure to H<sub>2</sub>S [63].

In this study, MIL-160(Al) was synthesized and shaped by MOFTECH using extrusion techniques, resulting in a cylindrical form. A total of 60 kg was produced for use in an industrial pilot in the demonstration site as part of the MOF4AIR project. An aliquot of this batch was sampled for testing at laboratory scale. The geometrical properties of the material were determined using a caliper (accuracy of 0.01 mm) and a scale (accuracy of  $10^{-4}$  g) on 20 pellets. The pellets have a cylindrical shape, with a mean diameter of 2.07 mm and a mean length of 4.20 mm. The measured pellet density is 554.65 kg/m<sup>3</sup>.

# 2.1.2 Adsorption isotherms

The  $CO_2$  adsorption isotherms were measured over a pressure range of 0.01 to 1 bar, while the  $N_2$  adsorption isotherms were measured from 0.1 to 50 bar using a gravimetric device [59]. This wide pressure range allows the application of the ideal adsorbed solution theory (IAST) under optimal conditions, where calculating the adsorbed amount requires extrapolating to lower pressures for the most adsorbed compound and to higher pressures for the less adsorbed one [64,65]. More information can be found in our previous paper [54].

# 2.1.3 Breakthrough curves

Breakthrough curves experiments were performed to determine adsorption kinetics and adjust the parameters of the heat transfer correlations used (see Section 2.2.2). Column of 30 cm height and 7.01 cm diameter was filled with the MIL-160(AI) and regenerated overnight at room temperature under vacuum (typical lowest pressure of the vacuum pump: 2 Pa). The column was then pressurized with pure nitrogen until temperatures inside the column were stabilized. The  $CO_2/N_2$  gas mixture used for breakthrough curve measurements was generated using two thermal mass flow controllers.

During a breakthrough curve, the gas was sent to the bottom of the column and the outlet composition was continuously monitored using a NDIR analyzer. The temperature profile during the experiment was recorded with two type K thermocouples placed inside an immersion sleeve at 5 cm and 25 cm from the bottom of the adsorption layer. Different flow rates (0.3 to  $1 \text{ Nm}^3/\text{h}$ ) and CO<sub>2</sub> concentrations (10 to 50%) were tested to separate kinetics from thermal effects. Breakthrough curve measurement lasted 30 minutes, followed by a 30 min desorption phase using pure nitrogen at the same flow rate.

# 2.1.4 Vacuum pressure swing adsorption cycles

The performance of MIL-160(AI) was evaluated using a home-made vacuum pressure swing adsorption pilot [54]. Three columns, identical to the column used for breakthrough curve measurements, were filled with MIL-160(AI). A set of valves allow to direct the gas flow into different sections of the pilot to perform the different steps of a VPSA cycle (adsorption, evacuation, reflux, ...) and therefore potentially all the cycles using two or three columns.

The cycle studied is the 6-step cycle described by Khurana and Farooq [45], which includes adsorption, heavy reflux, co-current evacuation, counter-current evacuation, light reflux, and light product pressurization. The cycle was adapted for a 3-column configuration and the different steps of the cycle are represented in Figure 1. This cycle is able to provide good separation performance with a moderate level of vacuum (0.1 bar) which is realistic for industrial applications. The performance of MIL-160(AI) had already been assessed in previous work [54], showing better results compared to the benchmark material, zeolite 13X.





Figure 1: Representation of the different steps of the 3-bed 6-step cycle with pressure level representation of bed 1 (HR: heavy reflux, co-evac: co-current evacuation, cn-evac: counter-current evacuation, LR: light reflux, LPP: light product pressurization).

The duration of each step can be defined by three variables when three adsorption beds are used. Adsorption time, light reflux time, and co-current evacuation time were chosen to define the cycle. The remaining step durations are determined using equations (1) to (3). The pressure levels of adsorption, co-current evacuation and counter-current evacuation and the flow rate of the flue gas, and the flow rate of light reflux are additional variables of the VPSA process.

$$t_{heavy\,reflux} = t_{light\,reflux} \,\#(1)$$

 $t_{counter-current\ evacuation} = t_{adsorption} - t_{light\ reflux} - t_{co-current\ evacuation} \#(2)$ 

 $t_{light \ product \ pressurization} = t_{adsorption} - t_{light \ reflux} #(3)$ 

The performance of the cycle is determined using four indicators: purity, recovery, productivity, and energy consumption [17]. Purity represents the  $CO_2$  concentration at the outlet of the VPSA process.

Since flow rate and concentration vary during one cycle, an average value is computed using equation (4). Recovery expresses the quantity of  $CO_2$  recovered at the VPSA outlet relative to the  $CO_2$  amount in the flue gas to be treated, as defined in equation (5).

Productivity is an image of the material's efficiency giving the amount of  $CO_2$  recovered per volume of adsorbent for a given time (typically one hour or one day). This indicator (equation (6)) gives an idea of the gas flow rate that can be treated per cubic meter of adsorbent or the VPSA unit size required for a given flow rate. Finally, energy consumption is the amount of energy required to obtain one ton of  $CO_2$  at the VPSA outlet, as defined in equation (7) where *E* is the energy consumption per cycle for the vacuum pump or compressor.

$$Purity [\%] = \frac{\sum_{cycle} Q_{product} Y_{CO_2 product}}{\sum_{cycle} Q_{product}} \#(4)$$

$$Recovery [\%] = \frac{\sum_{cycle} Q_{product} Y_{CO_2 product}}{\sum_{cycle} Q_{feed} Y_{CO_2 feed}} \#(5)$$

$$Productivity \left[ t_{CO_2} / (m^3.day) \right] = \frac{\sum_{cycle} Q_{product} Y_{CO_2 product}}{V_{ads}.t_{cycle}} \#(6)$$

$$Energy \ consumption \left[ kWh / t_{CO_2} \right] = \frac{\sum E}{\sum_{cycle} Q_{product} Y_{CO_2 product}} \#(7)$$

$$E \left[ kWh \right] = \sum_{cycle} \frac{Q.R.T}{\eta} \frac{\gamma}{\gamma - 1} \left( \left( \frac{p_2}{p_1} \right)^{\frac{\gamma - 1}{\gamma}} - 1 \right) \#(8)$$

With Q the molar flow rate, y the molar fraction,  $V_{ads}$  the volume of adsorbent used,  $t_{cycle}$  the time of one cycle, R the gas constant, T the temperature,  $\eta$  the isentropic efficiency,  $\gamma$  the heat capacity ratio,  $p_1$  the inlet pressure and  $p_2$  the outlet pressure.

#### 2.2 Modeling

## 2.2.1 Adsorption isotherms

The experimental adsorption isotherms obtained using the methodology described in Section 2.1.2 were modelled to predict the adsorbed amounts at different temperatures and partial pressures. A Langmuir model with temperature dependency (equation (9)) was used to fit the experimental data for pure CO<sub>2</sub> and pure nitrogen using the same saturation capacity  $(q_s)$  for both gases [14,66,67]. The nonlinear least-squares method using the trust region reflective algorithm was used within Matlab© software (Isqnonlin function) to determine the parameters of the model. The algorithm minimizes the cost function, defined as the sum of squared differences between the measured and modeled adsorbed amounts with the parameters to be identified. Moreover, a multistart procedure was applied to initialize the optimization procedure with various starting conditions to avoid convergence to local minimum. The 95% confidence intervals of the parameters were calculated using the Jacobian matrix provided by the solver [68]. The adsorbed amount for a CO<sub>2</sub>/N<sub>2</sub> mixture was computed using two methods which are compared: (i) The Ideal Adsorbed Solution Theory (IAST) using the Langmuir model (equation (9)) to represent pure component adsorption isotherms, as described in Section 1.1. of the Supporting Information [64,65], and (ii) the extended Langmuir model for mixture [14,67] defined by equation (10). The heat of adsorption ( $\Delta H$ ) was determined using the Clausius-Clapeyron method by fitting the experimental data with Langmuir model [67].

$$q = q_s \frac{b_0 \exp\left(-\frac{\Delta H}{RT}\right) p}{1 + b_0 \exp\left(-\frac{\Delta H}{RT}\right) p} \#(9)$$
$$q_i = q_s \frac{b_{0,i} \exp\left(-\frac{\Delta H_i}{RT}\right) p_i}{1 + \sum_j b_{0,j} \exp\left(-\frac{\Delta H_j}{RT}\right) p_j} \#(10)$$

 $R^2$  (coefficient of determination) and the normalized root mean squared deviation (NRMSD) (equations (11) and (12)) are used to assess the accuracy of the model in fitting the experimental data.  $R^2$  provides an overall score of the fitting expressed as a percentage while NRMSD quantifies the magnitude of error, also expressed as a percentage [68]. Therefore, a strong correlation between the model and experimental data is obtained when a high  $R^2$  value is combined with a low NRMSD.

$$R^{2} = \frac{\sum_{i}^{n} (q_{exp,i} - q_{model,i})^{2}}{\sum_{i}^{n} (q_{exp,i} - q_{mean})^{2}} \#(11)$$

$$NRMSD = \frac{\sqrt{\frac{\sum_{i}^{n} (q_{exp,i} - q_{model,i})^{2}}{n}}}{q_{exp,max} - q_{exp,min}} \#(12)$$

#### 2.2.2 Breakthrough curves

The adsorption bed was modeled using Aspen Adsorption © V14 software to determine the mass transfer coefficients of  $CO_2$  and  $N_2$  and to adjust the heat transfer coefficients. The gas phase properties (compressibility, enthalpy, ...) were calculated using the Peng-Robinson equation of state using Aspen Properties © V14 software embedded in Aspen Adsorption. The adsorption bed was divided into 30 axial nodes using the Van Leer scheme [69] to compute the mass, momentum, and thermal balance across the bed. The gas flow through the bed was represented by the axial dispersed plug flow model (equation (13)), assuming no radial effects. The dispersion coefficient was computed using equation (14) for  $CO_2$  and  $N_2$  applying the Chapman-Enskog equation to determine the molecular diffusion coefficient (full model in Section 1.2. of the Supporting Information) [14,70,71].

$$-D_{L,i}\frac{\partial^2 c_i}{\partial z^2} + \frac{\partial(vc_i)}{\partial z} + \frac{\partial c_i}{\partial t} + \left(\frac{1-\varepsilon_b}{\varepsilon_b}\right)\frac{\partial q_i}{\partial t} = 0\#(13)$$
$$D_{L,i} = \frac{D_m}{\tau_b} + \frac{v \, d_p}{Pe'_{\infty}\left(1 + \frac{13D_m}{\tau_b v d_p}\right)}\#(14)$$

With  $D_{L,I}$  the axial diffusion coefficient for compound i,  $c_i$  the gas phase concentration for compound i, z the axial distance, v the gas velocity, t the time,  $\varepsilon_b$  the bed porosity,  $q_i$  the adsorbed amount for compound i,  $D_m$  the molecular diffusivity,  $\tau_b$  the bed tortuosity,  $d_p$  the pellet diameter, and  $Pe'_{\infty}$  the limiting Peclet number.

The pressure drops across the bed was computed using the Ergun equation, which combines the Blake-Kozeny and Burke-Plummer equations, and is valid for a wide range of Reynolds numbers (from  $10^{-1}$  to  $10^{5}$ ). The equation is expressed in differential form by equation (15) [72,73].[69–71]

$$\frac{dp}{dz} = 150 \left(\frac{\mu v_0}{d_p^2}\right) \frac{(1-\varepsilon_b)^2}{\varepsilon_b^3} + \frac{7}{4} \left(\frac{\rho v_0^2}{d_p}\right) \frac{1-\varepsilon_b}{\varepsilon_b^3} \#(15)$$

With p the pressure,  $\mu$  the dynamic viscosity,  $v_0$  the superficial velocity, and p the density. Adsorbed amount in the bed was modelled using the Langmuir model (see Section 3.1 for multicomponent model selection). The mass transfer resistance between the adsorbed and gas phases was described using the linear driving force model (equation (16)).[71–73]

$$\frac{\partial q_i}{\partial t} = k_{LDF,i} (q_i^* - q_i) \# (16)$$

With  $k_{LDF}$  the linear driving force coefficient, and  $q_i^*$  the equilibrium adsorbed amount. Three energy balances were considered in the bed: energy balance of the adsorbent (i), gas (ii), and wall of the bed (iii). These lead to four heat transfer mechanisms in the adsorption bed: heat transfer between the gas and the adsorbent pellets (i), heat transfer between the gas and the column wall (ii), heat transfer across the column wall (iii), and heat transfer between the outer wall and ambient (iv). Equations (17) to (19) give the three energy balances in the bed [14,72,74]. Heat transfer coefficient between the solid and gas ( $h_s$ ) was obtained from [75] considering a bypass section of the gas due to the increase of void fraction near the column wall. This correlation is described in Section 1.3. of the Supporting Information, and is valid for low thermal Peclet numbers (<100) which can be encountered in gas adsorption processes such as the one studied here. The gas-wall heat transfer coefficient ( $h_w$ ) was estimated using the Yagi and Kunii model [76] (Section 1.4. in the Supporting Information). This correlation uses data from various packed bed with  $d_p/d_{bed}$  ratios between 0.02 and 0.17 and Reynolds numbers ranging from 20 to 2000 for different solid shapes. Finally, the heat transfer coefficient between the outer wall and ambient ( $h_{amb}$ ) was computed using classical heat transfer correlations [77,78] (see Section 1.5. in the Supporting Information.

$$\begin{split} \mathcal{C}_{v,s} \frac{\partial T_s}{\partial t} &= \frac{6h_s}{d_p} (T_g - T_s) + (-\Delta H) \frac{\partial \overline{q}}{\partial t} \# (17) \\ &- \frac{\lambda_g}{C_{v,g}} \frac{\partial^2 T_g}{\partial z^2} + v \frac{\partial T_g}{\partial z} + \frac{\partial T_g}{\partial t} + \left(\frac{1 - \varepsilon_b}{\varepsilon_b}\right) \left(\frac{C_{v,s}}{C_{v,g}}\right) \frac{\partial T_s}{\partial t} \\ &= \left(\frac{1 - \varepsilon_b}{\varepsilon_b}\right) \left(\frac{-\Delta H}{C_{v,g}}\right) \frac{\partial \overline{q}}{\partial t} - \frac{4h_w}{\varepsilon_b d_p C_{v,g}} (T_g - T_w) \# (18) \\ &- \lambda_w \frac{\partial^2 T_w}{\partial z^2} + \rho_w C_{p_w} \frac{\partial T_w}{\partial t} - h_w \frac{4 \ d_{b,in}}{d_{b,out}^2 - d_{b,in}^2} (T_g - T_w) + \\ \frac{2/d_{b,in}}{\lambda_w} + \frac{2}{h_{amb} d_{b,out}} \frac{4 \ d_{b,out}^2}{d_{b,out}^2 - d_{b,in}^2} (T_w - T_{amb}) = 0 \ \# (19) \end{split}$$

With  $C_{v,s}$  the volumetric heat capacity of the solid,  $T_s$  the temperature of the solid phase,  $T_g$  the temperature of the gas phase,  $\Delta H$  the heat of adsorption,  $\lambda_g$  the heat conductivity of the gas,  $C_{v,g}$  the volumetric heat capacity of the gas,  $T_w$  the temperature of the walls,  $\lambda_w$  the heat conductivity of the walls,  $\rho_w$  the density of the walls,  $C_{p,w}$  the isobaric heat capacity of the walls,  $d_{b,in}$  and  $d_{b,out}$  the inner and outer diameter of the column, and  $T_{amb}$  the ambient temperature outside the adsorption bed.

Parameters determination was made by linking Aspen Adsorption and Matlab to use the surrogateopt function. This optimization method builds an approximate model based on a limited number of simulations and optimizes this model instead of the full Aspen model [79]. The objective function minimized the squared difference between experimental and modelled breakthrough curves by adjusting the parameters to be determined. From this methodology, linear driving force coefficient for  $CO_2$  and  $N_2$ , gas-wall and outside heat transfer coefficients, bypass fraction (used in solid-gas heat

transfer coefficient calculation developed in Supporting Information), bed tortuosity (used in gas dispersion coefficient), and heat capacity of the adsorbent were estimated to fit the experimental data.

#### 2.2.3 Vacuum pressure swing adsorption cycles

The VPSA cycle described in Section 2.1.4 was implemented in Aspen Adsorption © V14 software using the same equations as in Section 2.2.2. The unibed approach was used for the interactions between the three adsorption beds, saving and replaying the flow rate, temperature, pressure, composition and enthalpy of the streams [80]. The cycles simulation was performed until the change in purity and recovery between two consecutive cycles was less than 0.1% (same stopping criteria as the experimental VPSA pilot [54]) assuming steady state is reached.

Two systems were investigated in this work. Firstly, the VPSA pilot was simulated under the same operating conditions as the experimental measurements to compare the results and validate the simulation for a  $15/85 \text{ CO}_2/\text{N}_2$  mixture with a flow rate of  $1 \text{ Nm}^3/\text{h}$ . The parameters for this simulation are given in Table S3 (Section 4 in the Supporting Information). The vacuum pump performance curve is used (Figure S2 in Supporting Information) and allows to compute the pumping speed based on the inlet pressure. The decrease of pressure in the adsorption column was computed using the mass balance (equation 15). The isentropic efficiency of the compressors was set to 85%, while the vacuum pump isentropic efficiency was estimated using equation 20, which is dependent on the vacuum level, giving a more realistic estimation of energy consumption [81].

$$\eta = 0.8 \frac{19.55p}{1+19.55p} \# (20)$$

The second system simulated is an industrial VPSA pilot located at Technology Center Mongstad (TCM), operating with the same adsorbent material as the laboratory pilot under the MOF4AIR project. Based on the laboratory-scale results, the pilot was simulated with a similar flue gas stream coming from a residue fluid catalytic cracking (RFCC) unit. Three CO<sub>2</sub> concentrations were considered: 15% of CO<sub>2</sub>, but also 10% and 5% CO<sub>2</sub> as these levels are representative of TCM's flue gas composition. The industrial pilot consists of three adsorption beds, each with a volume of 41 L, with a diameter of 0.3 m and a length of 0.58, operating the same VPSA cycle as the laboratory scale system. The vacuum pump performance curve of this pilot was also implemented in the simulation. However, unlike the lab-scale setup, this equipment does not have pressure regulation. As for the laboratory scale, the full list of parameters used for the industrial simulation is given in Table S4 in Supporting Information.

# 2.3 Surrogate and optimization

The study and optimization of the cycle at both laboratory and industrial scales were conducted using the surrogate model. Surrogate modelling allows to reproduce the behavior of a time-consuming model with a simplified model, built using a limited number of simulations. For the laboratory scale, two surrogate models were compared: kriging model which assumes a spatial correlation between the outputs and inputs of the model [46,79], and artificial neural network (ANN) which uses multiple layers of interconnected neurons using simple function between the inputs and the outputs [46,82]. The kriging model used in this work is composed of a constant term and a stochastic term using correlation functions (kernels). Four kernels were compared: Radial basis function (RBF), rational quadratic (RQ), Matern 3/2, and Matern 5/2 [46,83]. For each kernel, the constant term and the hyperparameters were fitted using training data. More details about the kriging model can be found in Section 5.1.1. of the Supporting Information. Feed forward network is used as ANN model to create a surrogate model since this network is able to represent numerous complex models, including VPSA [49–51,82]. Different network architectures were investigated to find the optimal number of layers and neurons. One- and two-layers networks with 10, 20, 30 or 40 neurons per layer were trained for this work. For

each architecture, the weights, biases, regularization terms, and activation functions were optimized using training data. More information on the ANN model can be found in Section 5.1.2 of the Supporting Information.

In practice, the surrogate models were implemented using the SciKit Learn library [84] in Python, employing the "GaussianProcessRegressor" model for Kriging and "MLPRegressor" for ANN. Latin hyper cube sampling, combined with the Enhanced Stochastic Evolutionary algorithm [85], was used to generate a set of parameters which will be simulated in Aspen Adsorption. The results obtained from VPSA simulations were then used to construct the surrogate models. The data obtained were randomly divided into a training set (70%) and a validation set (30%). Before training, input and output data were scaled to have a mean equals to zero and a unit variance to improve the fitting procedure [79,82,83]. Cross-validation with 10 folds is used during the training step to avoid overfitting and have a more robust model.

Surrogate models obtained can be used to study the effects of different variables on the VPSA unit or to find the optimal operating conditions with minimal computational resources. A multi-objective optimization was carried out using the Non-Dominated Sorting Genetic Algorithm II (NSGA-II) [43]. Genetic algorithms have previously been used for the optimization of VPSA unit [34,38,45,47,51] allowing to find the pareto between different variables (purity, recovery, productivity, and energy consumption). The Pymoo toolbox in Python [86] was used to implement NSGA-II by using the surrogate models built from Aspen Adsorption simulation results. NSGA-II was also directly applied with Aspen Adsorption to compare and validate the pareto obtained from the surrogate models.

For the lab-scale pilot, five variables were optimized for a unit treating a flow rate of 1 Nm<sup>3</sup>/h containing a 15/85 CO<sub>2</sub>/N<sub>2</sub> mixture: adsorption time [60-400 seconds], light reflux time [20-360 seconds], co-current evacuation time [20 – 40 seconds], co-current evacuation pressure [0.2 – 0.8 bar], light reflux flow rate [0.05 – 0.5 Nm<sup>3</sup>/h]. These parameter bounds were based on previous experimental studies [54]. These bounds have been expanded to explore a broader range of operating conditions while remaining consistent with the equipment used in the VPSA pilot. The adsorption pressure was set to 2 bar, and the counter-current evacuation pressure to 0.1 bar for all simulations.

Six variables were considered for the industrial case: the three times which defined the VPSA cycle as for the lab-scale unit (adsorption time [40 - 200 seconds], light reflux time [15 - 160 seconds] and co-current evacuation time [5 - 25 seconds]), the adsorption pressure [1.01 - 2 bar], the feed flow rate  $[30 - 100 \text{ Nm}^3/\text{h}]$ , the light reflux flow rate  $[0.1 - 20 \text{ Nm}^3/\text{h}]$ , and the CO<sub>2</sub> concentration in the feed gas [5 - 15%]. The lower and upper parameter bounds were derived from industrial pilot specifications and the flue gas available at the test site. The pressure levels during the two evacuation steps were not directly controlled and are related to the evacuation time and the vacuum pump performance curves.

# 3 Results and discussion

# 3.1 Adsorption isotherms

Experimental adsorption isotherms obtained for  $CO_2$  and  $N_2$  on MIL-160(AI), and the corresponding model fits, are presented on Figure 2. As observed, the Langmuir model is in good agreement with the experimental data, showing a R<sup>2</sup> of 99.07% for  $CO_2$ , and 99.89% for  $N_2$ . NRMSD values are also low, at 1.44% for  $CO_2$  and 0.59% for  $N_2$ , indicating a strong predictive capability of the model.



Figure 2: Experimental and simulated adsorption isotherms for  $CO_2$  and  $N_2$  on MIL-160(Al). Circle = 20°C experimental; square = 30°C experimental; triangle = 40°C experimental; dashed lines: Langmuir model.

The parameters obtained from the fitting of experimental data, along with their 95% confidence intervals, are given in Table 1 for both  $CO_2$  and  $N_2$ . The heat of adsorption, determined using the Clausius Clapeyron method at 0.1 mmol/g adsorbed, is 29.37 kJ/mol for  $CO_2$  and 16.16 kJ/mol for nitrogen. More details on working capacity and selectivity can be found in previous work [54].

	CO <sub>2</sub>	N <sub>2</sub>
q <sub>s</sub> [mmol/g]	5.14 ± 0.14	5.14 ± 0.14
b <sub>0</sub> [1/bar]	2.32x10 <sup>-6</sup> ± 1.80x10 <sup>-6</sup>	3.93x10 <sup>-5</sup> ± 2.37x10 <sup>-5</sup>
ΔH [kJ/mol]	34.01 ± 2.00	17.21 ± 1.56

Table 1: Langmuir model parameters obtained from experimental adsorption isotherms for CO<sub>2</sub> and N<sub>2</sub>.

The comparison between the extended Langmuir model, and IAST for co-adsorption prediction was made by generating 10 000 points for different temperatures (-10 to 50°C), pressures (0.001 to 2 bar), and CO<sub>2</sub> concentrations (0 to 100%) with a latin-hypercube design [87], and computing the adsorbed amounts obtained with the two models. Figure S1 in the Supporting Information shows the predicted adsorbed amounts for extended Langmuir versus the adsorbed amounts predicted by IAST. As represented by the straight lines, results obtained with IAST and extended Langmuir are similar, giving a R<sup>2</sup> of 1 for both CO<sub>2</sub> and N<sub>2</sub> adsorbed amount. The mean absolute error between both models is  $10^{-11}$  mmol/g, which is the numerical error made by the computer. Based on this, the extended Langmuir model will be used for simulating the VPSA process, as it significantly reduces computational expense while maintaining accuracy.

#### 3.2 Breakthrough curves

Elven breakthrough curve experiments have been carried out using the setup described in Section 2.1.3. Three different flow rates were tested: 0.3, 0.6 and 1 Nm<sup>3</sup>/h, in addition to different  $CO_2$  concentrations. For all flow rates 10%, 15% and 30% were tested, while for 0.6 Nm<sup>3</sup>/h, additional concentrations of 20% and 50% were also investigated. Results obtained are given in Figure 3. As observed, the breakthrough curves become sharper as the  $CO_2$  concentration increases for a given flow rate. For a given  $CO_2$  concentration, the curve profiles remain similar across different flow rates.

The simulated breakthrough curves are also represented on Figure 3 by the solid lines. R<sup>2</sup> and NRMSD were computed over the same time scale as in Figure 3. Results are also given in Table S1 in the Supporting Information. The simulation gives a good overall representation of the data, giving a mean R<sup>2</sup> of 97.91% and a mean NRMSD of 4.34%. The main difference between the experimental and simulated data occurs towards the end of the rise of the breakthrough curve, where simulations predict a sharper curve, especially at higher  $CO_2$  concentrations. This could be due to thermal effects which are not properly modelled, or gas channeling due to non-uniform adsorbent packing, leading to a lower packing density near the column walls which can occur even when the column to pellet diameter ratio is higher than 20 [88]. From the optimization procedure, the linear driving force coefficients for  $CO_2$  and  $N_2$  were estimated to 0.054 and 6.478 1/s respectively, the gas to wall heat transfer coefficient is 4.19 W/(m<sup>2</sup>.K), and wall to outside heat transfer coefficient is 4.29 W/(m<sup>2</sup>.K). The bypass fraction determined is 0.1040, the adsorption bed tortuosity is 1.8, and the heat capacity is 1326 J/(kg.K). The value of  $k_{LDF}$  found for CO<sub>2</sub> is close to the value of 0.052 1/s found by Karimi et al. [59] on the same material which seems to validate the results obtained. The gas to wall heat transfer coefficient is lower than the prediction of the Yagi and Kunii correlation [76] (20 W/(m<sup>2</sup>.K) for a flow rate of 1 Nm<sup>3</sup>/h), while the wall to outside heat transfer coefficient is close to the model with a wall emissivity of 0.4 – 0.5 (typical value for stainless steel [89]). The bypass fraction from the gas-solid heat transfer coefficient is close to the value of 2  $d_p/d_b$  (0.07) suggested by Martin [75], and the bed tortuosity close to the value of  $1/(0.45 + 0.55\varepsilon_b)$  (1.61) suggested by Ruthven [14]. Lastly, the heat capacity obtained is higher than the previously reported value for powder (1117 J/(kg.K)) [57].





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#### 3.3 Laboratory scale vacuum pressure swing adsorption pilot



#### 3.3.1 Simulation of experimental measurements

Figure 4: Purities and recoveries obtained by simulation versus experimental values. (a) Predicted vs actual value for purity, (b) predicted vs actual value for recovery, (c) error of the model compared to purity measured, and (d) error of the model compared to recovery measured.

The results of 42 experimental measurements and their corresponding simulations are represented in Figure 4 giving the simulated data versus the experimental data for purity (subplot(a)) and recovery (subplot (b)) and with the error (difference between simulation and experimental) for purity (subplot (c)) and recovery (subplot(d)). Numerical values are also available in Table S2 in Section 4 of the Supporting Information. As observed, most measurements are well represented by the simulation giving a mean error of 1.47% for purity and 3.19% for recovery. For comparison, the mean experimental uncertainty is 1.84% for purity and 2.36% for recovery. Some measurements are less well predicted, leading to larger errors and reducing the value of R<sup>2</sup> and increasing NRMSD (see Table 2). The maximum error obtained is  $\pm 4.57\%$  for purity and  $\pm 9.53\%$  for recovery. Most of the purity errors (35 points over 42) are located between -3% and +3%, and +5/-5% for recovery (32 points over 42). Numerous factors can explain the discrepancies between simulation and experiment. The plug flow model used to simulate the adsorption bed does not account for radial effects such as gas channeling or heat gradient in radial direction. Other elements of the VPSA pilot such as dead space, valve, vacuum pump, ... are probably not precisely modeled in the simulation model due to a lack of information from manufacturers.

Whatever, the mean error in recovery and purity is similar to values reported in other simulations works as discussed in the introduction : Krishnamurthy *et al.* [36] reported a mean normalized error

for purity and recovery of 2.3% and 2.55% respectively for the simulation of 8 experiments on a 2-bed 4-step pilot containing zeolite 13X. Estupinan Perez et al. [37] got a mean error of 1.67% and 1.42% for purity and recovery on four experiments performed on a lab-scale pilot with zeolite 13X. Nguyen et al. [38] achieved a mean error for purity and recovery of 1.16% and 1.40% respectively for the simulation of eleven measurements for 2-bed 4-step pilot with CALF-20. Nevertheless, the number of works comparing simulation and VPSA pilot are quite limited in the literature. Moreover, the number of experimental measurements performed on VPSA installation is lower than the number of experiments performed in this work.

	Purity [%]	Recovery [%]
Mean	1.47	3.19
Median	1.01	2.71
R <sup>2</sup> [%]	80.82	86.45
NRMSD [%]	7.97	9.69

Table 2: Value of different indicators obtained for the representation of purity and recovery by the simulation.

In extent comparison between experiment and simulation was performed for experiment 4 which achieved an optimal balance between purity (90.1%  $\pm$  1.9%) and recovery (92.8%  $\pm$  2.8%). As shown in Figure 5, the simulated pressure during the counter-current evacuation and purge steps closely matches experimental data. During co-current evacuation, the vacuum pressure sensor saturated at 1.1 bar explaining the constant value for 10 seconds. For the rest of this step, the simulated pressure profile is close to the experimental profile with small differences which are due to the pressure regulation in the VPSA pilot, which is difficult to reproduce by simulation. The same conclusion can be drawn for the flow rate profile. During counter-current evacuation and purge, the experimental and simulated profiles are close except during the transition between the two steps due to the opening and closing of the valves. For co-current evacuation, larger differences arise due to the pressure regulation. The CO<sub>2</sub> concentration profile predicted by the simulation matches experimental data, except after step transitions, which can be explained by pressure fluctuations in the gas analyzer due to valves operation, and the delay due to the distance between the vacuum pump outlet and the gas analyzer.



Figure 5: Comparison between pressure, flow rate and  $CO_2$  concentration profile between experiment (cross marker) and simulation (line) during evacuation and purge for the experiment n° 4. Red lines are the transition between two steps.

The same observations and conclusions can be drawn for other parts of the VPSA pilot or other experimental measurements. VPSA pilot dynamics seem to be well represented by the simulation even if disturbing elements such as valve opening and closing, or co-current evacuation regulations are hard to model and are not perfectly described by the simulation model.

Moreover, the simulation model can be used to study the column behavior via adsorbed amount profile in the column which are not directly measurable. Figure 6 presents the adsorbed amount profiles in the column for  $CO_2$  and  $N_2$  over one cycle in steady-state conditions for experiment 4. As observed, the adsorbed amount for  $CO_2$  and  $N_2$  are rapidly stable at the bottom of the adsorption bed during the adsorption step, meaning that the first layers of adsorbent are saturated (Figure 6b). From adsorption isotherm measurements, the adsorbed amount for a 15/85  $CO_2/N_2$  mixture at 2 bar and 20°C is equal to 2.29 mmol/g for  $CO_2$  and 0.37 mmol/g for  $N_2$  which are close to the values observed on Figure 6b. For middle (Figure 6c) and top (Figure 6d) of the column, the adsorbed amount of  $CO_2$  continuously increases while the  $N_2$  adsorbed amount decreases with the emergence of a saturation of adsorbed amount in the middle of the column. During heavy reflux step, the  $CO_2$  quickly propagates in the columns by the flow coming from the column in light reflux step (67%  $CO_2$ , 2 bar, 20°C) as represented by Figure 6a. The adsorbed  $CO_2$  amount has a sharp increase at the bottom of the column, and at the middle with a delay. This is due to the absence of plateau in the  $CO_2$  adsorption isotherm of MIL-160(Al) in the relevant range of  $CO_2$  partial pressures (Figure 2) that enables higher adsorbed quantities at higher partial pressures. The amount of adsorbed nitrogen decreases during this step. A

displacement of the CO<sub>2</sub> adsorbed amount occurred during the co-current evacuation step, with a decrease at the bottom, and an increase at the middle and top of the column. During this step, the N<sub>2</sub> adsorbed amount decreases sharply to reach almost 0 mmol/g at the bottom to the middle of the column. There is some nitrogen remaining at the top of the column. During counter-current evacuation and light reflux, the amount of CO<sub>2</sub> adsorbed in the column decreases with sharper variation at the middle and bottom. The effect of light reflux is more pronounced at the top of the column showing the importance of this step to reduce the adsorbed amount at this location. Finally, the adsorbed amount of N<sub>2</sub> increases as pressure rises during the light product pressurization step while the amount of adsorbed CO<sub>2</sub> remains constant. The 3D representation of adsorbed amount for CO<sub>2</sub> and N<sub>2</sub> are presented in Figure S3 in the Supporting Information.

On Figure 6a, we can observe that the top of the column keeps a low  $CO_2$  adsorbed amount during the whole cycle compared to the rest of the column despite the displacement of  $CO_2$  caused by heavy reflux and co-current evacuation, giving a good recovery. In addition, the adsorbed amount of nitrogen is very low at the start of the counter-current evacuation giving good purity. Optimization of the various cycle parameters is important in order to achieve an identical concentration profile for good  $CO_2$  recovery and purity.



Figure 6: Adsorbed amount in the adsorption column for experiment n°4 during one cycle in steady state. (a)  $CO_2$  adsorbed amount in the column in function of the time and distance in the column. (b) adsorbed amount at the bottom of the column (black =  $CO_2$ , blue =  $N_2$ ), (c) adsorbed amount in the middle of the column, (d) adsorbed amount at the top of the column. Red

lines are the transition between two steps. The steps are numbered in subfigure (a) : (1) Adsorption, (2) heavy reflux, (3) cocurrent evacuation, (4) counter-current evacuation, (5) light reflux, (6) light product pressurization.

# 3.3.2 Optimization

The optimization procedure described in section 2.3 was applied to the lab-scale VPSA pilot model in Aspen Adsorption to find the pareto plot of purity and recovery. A first optimization was performed using NSGA-II on the Aspen model to find the pareto between purity and recovery. A population size of 50 was chosen for the optimization, and 150 generations were performed giving a total of 7500 simulations to generate the pareto plot. On the other hand, 1400 simulations were performed to train the two surrogate models, and 600 additional simulations were used to validate the trained models. The same training and validation datasets were used for both models.

Four kernels were compared for the surrogate model, and 14 network topologies were investigated for the artificial neural network model. Figure S4 gives the MSE and R<sup>2</sup> values obtained for kriging, and the same results for the topologies of the ANN are given in Figure S6 in the Supporting Information. The best-performing kernel was the Matern 5/2 with a R<sup>2</sup> of 99.77% and 99.69% and NRMSD of 1.14  $10^{-2}$  and 9.2  $10^{-3}$  for recovery and purity respectively. RBF and Matern 3/2 kernels gave close results with R<sup>2</sup> higher than 99% and NRMSD lower than 0.02. The ANN topology is more impacting than the kernel choice as represented by Figure S6 in the Supporting Information. For a one-layer topology, increasing the number of neurons from 10 to 40 improved the accuracy of both recovery and purity. When adding a second layer, the best results were generally obtained when the size of the second layer is smaller than the first one. The (40,30) topology gave the best NRMSD value for recovery (8.1  $10^{-3}$ ), while the (40,20) topology was the best for purity (NRMSD equal to 6.2  $10^{-3}$  for purity but 9.2  $10^{-3}$  for recovery). ANN outperformed kriging in terms of R<sup>2</sup> and NRMSD for the validation set. Nevertheless, the R<sup>2</sup> is very high for both models (>99%) and NRMSD is relatively low (< 0.02).

The evolution of NRMSD and R<sup>2</sup> with the number of training points was studied for the Matern 5/2 kernel (Figure S5) and the (40,30) topology (Figure S7 in the Supporting Information). For the kriging model, NRMSD and R<sup>2</sup> trends suggest that additional simulations could improve accuracy, but the slope of the MSE curve seems to indicate that numerous simulations would be required to reach the same value of NRMSD as ANN model. For ANN, the slope of NRMSD seems stabilized at 1000 training points meaning that the model cannot be improved significantly by more simulations.

The surrogate models were then used to find the pareto front using NSGA-II. Figure 7 gives the graphical comparison between the purity-recovery pareto obtained with Aspen and with the kriging and ANN models. As observed, the ANN pareto front closely matches the one obtained from direct optimization of the Aspen model with small differences between the two curves. The optimization using the kriging model is less accurate with an overprediction of 4-5% of purity and recovery. Compared to the differences between simulation and the experimental results, the differences between the ANN model and the direct Aspen optimization are negligible. The pareto obtained shows that achieving both 95% of recovery and purity cannot be obtained under the investigated experimental conditions (1 Nm<sup>3</sup>/h feed gas with 15% CO<sub>2</sub>, adsorption pressure set to 2 bar, and an evacuation pressure of 0.1 bar). Nevertheless, for a recovery of 90%, the corresponding purity is 94% (with the ANN pareto). At a higher recovery of 95%, almost 90% of purity can be obtained. The performance of the pilot obtained by simulation is promising and close to the targets of a CO<sub>2</sub> capture process. Experimental results are also close to the pareto determined with experimental recovery/purity couple of (92.8%/90.1%) and (87.6%/96.0%) indicating that the experimental design carried out enabled us to find near-optimum conditions for the pilot.



Figure 7: Comparison of pareto obtained with direct optimization of the Aspen model, and optimization of the surrogate models. Experimental recovery/purity couples (92.8%/90.1%) and (87.6%/96.0%) are also represented.

The parameters giving the pareto plot obtained with Aspen are represented on Figure 8 with the red line representing the point with 95% purity, and the blue line the point with 95% recovery. Adsorption times are mainly comprised between 125 and 175 s, and light reflux times are in the range 60-120 s. Co-current evacuation times are in the narrow range of 20-26 s, except for some points with very high purity where this step lasts 40-45 s. It seems that minimizing this step duration enhances both recovery and purity. Co-current evacuation pressures range between 0.46 and 0.65 bar, except at very high recoveries, which require a pressure of 0.79 bar. Light reflux flow rates are comprised between 0.05 and 0.18 Nm<sup>3</sup>/h. From the Figure 8, the best purities are obtained with longer adsorption and light reflux times, lower co-current evacuation pressures, and lower light reflux flow rates. On the other hand, best recoveries are obtained with higher light reflux flow rates, lower light reflux times, and higher co-current evacuation pressures. The two highlighted points in Figure 8 correspond to different conditions, with adsorption time of 147 s, light reflux time of 79 s, co-current evacuation time of 23 s and pressure of 0.65 bar, and a light reflux flow rate of 0.17 Nm<sup>3</sup>/h for the recovery of 95% while the purity of 95% has an adsorption time of 175 s, light reflux time of 96 s, co-current evacuation time of 23 s and pressure of 0.52 bar, and light reflux flow rate of 0.12 Nm<sup>3</sup>/h.



Figure 8: Coordinate plot obtained for the pareto plot. Red line: best point for a purity of 95%, blue line: best point for a recovery of 95%.

#### 3.4 Industrial scale vacuum pressure swing adsorption pilot

The industrial pilot described in 2.2.3 was simulated using parameters obtained from the breakthrough curve simulation (Section 2.2.2), the size of the industrial columns, and the vacuum pump performance of the industrial pilot. Heat transfer coefficients between the gas and the inlet column wall are different from the lab-scale pilot ones and were computed using the equation described in Section 1.4 of the Supporting information. Coefficient between the outlet wall of the column and the ambient environment was calculated using the equations of Section 1.5. The complete list of simulation parameters is given in Table S4 of Section 4 in the Supporting Information. 3000 simulations were performed within the bounds specified in Section 2.3 to find the optimal operating conditions for the industrial pilot. An artificial neural network was used as a surrogate model since this model performed better in lab-scale simulations. The same strategy as the lab-scale pilot was used, 70% of the simulations were used to train the surrogate model for purity, recovery, and energy consumption, while the remaining 30% were used for validation. Different network topologies were studied to find the optimal configuration. Networks with one or two layers, containing 10, 20, 30, 40 or 50 neurons, were investigated. The accuracy of the surrogate model compared to validation points was evaluated using R<sup>2</sup> and NRMSD given in Figure S8 in the Supporting information. The best topology is not identical between purity, recovery and energy consumption: (50,40) network gives the lowest NRMSD for purity, the (50,30) network performed best for recovery, and the (40,40) network for energy consumption. The most suitable network for each indicator was used for the respective optimization of the industrial unit.

Four indicators are given in Table 3. The model obtained give a good representation of the validation points, with R<sup>2</sup> higher than 99%, and NRMSD lower than 1% for all three outputs. The mean absolute error (MAE) and median absolute error (MedAE) are both lower than 0.5% for purity and recovery which is well below the typical experimental error of a VPSA. The mean error in energy consumption is also low compared to the range of 250 to 2000 kWh/t<sub>CO2</sub> obtained in the 3000 simulations of the industrial VPSA pilot.

Table 3: Value of different indicators obtained for surrogate model of the industrial pilot against the validation points for recovery, purity and energy consumption.

Purity [%]		Recovery [%]	Energy [kWh/t <sub>co2</sub> ]	
R <sup>2</sup> [%]	99.79	99.92	99.93	

NRMSD [%]	0.48	0.60	0.38
MAE	0.10	0.34	5.26
MedAE	0.05	0.24	3.54

The effect of CO<sub>2</sub> inlet concentration, feed flow rate, and adsorption pressure on the purity/recovery pareto of the industrial pilot was studied using the surrogate model. Figure 9 gives the pareto front obtained with four feed flow rates: 40, 60, 80 and 100 Nm<sup>3</sup>/h. For each flow rate, three CO<sub>2</sub> inlet concentrations were investigated as represented by the light, normal and dark colors. Blue points were obtained for atmospheric pressure during the adsorption step, while red points indicate a pressure of 2 bar. As observed, the  $CO_2$  concentration in the feed has a low impact on the pareto front for a given flow rate and adsorption pressure. The 5% concentration can give slightly higher recovery compared to 10% and 15% at low feed flow rate, but the effect is negligible. As the feed flow rate increases, the pareto fronts shift to lower recovery, especially at atmospheric adsorption pressure. At this pressure, the VPSA pilot is able to reach 90% recovery for 95% purity with a feed flow rate of 40 Nm<sup>3</sup>/h. Compared to the lab-scale pilot, the industrial pilot's vacuum pump reaches a vacuum level lower than 0.1 bar during counter-current evacuation, which can explain the improved results. At 100 Nm<sup>3</sup>/h, the maximum recovery for 95% purity is only around 55% for the three inlet CO<sub>2</sub> concentrations. Increasing the adsorption pressure to 2 bar gives a beneficial effect on the pareto of the industrial pilot, shifting the curves toward higher recoveries (red dots). With this higher adsorption pressure, the target of 95% purity and recovery can be obtained for a feed flow rate slightly below 60  $Nm^3/h$  for the three  $CO_2$ concentrations.



Figure 9: Purity-recovery pareto for different feed flow rates, inlet  $CO_2$  concentrations and adsorption pressures on the industrial pilot. Light blue: 5%  $CO_2$  at atmospheric pressure, blue: 10%  $CO_2$  at atmospheric pressure, dark blue: 15%  $CO_2$  at atmospheric pressure, light red: 5%  $CO_2$  at 2 bar, red: 10%  $CO_2$  at 2 bar, dark red: 15%  $CO_2$  at 2 bar.

Since the targets of 95% purity and recovery can be obtained with the industrial pilot, the energy consumption and productivity of the VPSA unit were evaluated for the three  $CO_2$  concentrations. The same optimization procedure as for the recovery-purity pareto using NSGA-II was applied to find the pareto of productivity and energy consumption with a constraint of at least 95% purity and recovery. The optimization procedure was performed at adsorption pressures of 1.01 and 2 bar to study the impact of pressure on pilot performance. Results of the optimization are given in Table 4. For atmospheric pressure, the optimal adsorption time decreases with increasing  $CO_2$  concentration , ranging from 105 seconds for 5%  $CO_2$  to 73 seconds for 15%. Light reflux time and co-current evacuation times follow the same trend with light reflux time between 38 and 74 seconds, and co-current evacuation time between 7 and 11 seconds. Light reflux flow rate also decreases as the inlet  $CO_2$  concentration increases with a flow of 8.20 Nm<sup>3</sup>/h for 5%  $CO_2$  to 5.39 Nm<sup>3</sup>/h for 15%. The feed flow rate which can be treated to reach 95% purity and recovery with an atmospheric adsorption

pressure is quite low with only 30.92 to 37.06 Nm<sup>3</sup>/h. This leads to low productivity (0.67  $t_{CO2}/(m_{ads}^3.day)$  for 5% CO<sub>2</sub> to 1.69 for 15%). The low feed flow rate also impacts energy consumption leading to high values especially for 5% CO<sub>2</sub> in the inlet (up to 1432 kWh/t<sub>CO2</sub> at the lowest adsorption pressure).

Increasing the adsorption pressure up to 2 bar improves productivity by 70-80% but also surprisingly decreases energy consumption by 20%. This can be explained by the optimized feed flow rate, which is almost twice compared to the atmospheric pressure case, increasing the amount of CO<sub>2</sub> captured and thus increasing the denominator of the energy consumption, even if the numerator is larger due to the compression of the feed flue gas. Optimal operating conditions at 2 bar follow the same trends as at atmospheric pressure, where the adsorption and light reflux times are lower for higher  $CO_2$ concentrations. Co-current evacuation time and light reflux flow rate also follow the same trends as the atmospheric pressure case, with a slightly higher flow rate for the light reflux. Energy consumption obtained by simulation is close to values obtained with industrial adsorption pilot in literature: Krishnamurthy et al. [36] obtained a productivity comprised between 0.87 and 1.4  $t_{co2}/(m_{ads}^3.day)$  and an energy consumption comprised between 339 and 582 kWh/t<sub>co2</sub> with 2-bed 4-step pilot containing zeolite 13X and treating a flue gas of 56.9 Nm<sup>3</sup>/h with 15% CO<sub>2</sub>. It should be noted that this pilot operates with regeneration time higher than adsorption leading to non-continuous treatment of the gas. Wang et al. [40] studied a 3-bed 8-step pilot wit zeolite 13X and obtained 0.52-0.84  $t_{CO2}/(m_{ads}^3.day)$ as productivity and 497-867 kWh/ $t_{co2}$ . Compared with the simulation made by Khurana and Farooq [45] on the same cycle, the energy consumption obtained in this work is almost two times higher from the values obtained in their work with UTSA-16 (125 kWh/t<sub>CO2</sub> for minimum energy consumption and 289 kWh/ $t_{co2}$  for maximum productivity). They also obtained very high productivity (8-18 t<sub>co2</sub>/(m<sup>3</sup><sub>ads</sub>.day)) with UTSA-16 compared to the pilot in this work. This difference could be explained by the fact that the industrial pilot of this work is not able to regulate pressure, giving a lesser degree of freedom for optimization. Moreover, in the work of Khurana and Farooq [45], some evacuation steps are very short (15 seconds to reach 0.02 atm) which is not possible with the pilot of this work.

Case	5% CO <sub>2</sub>	10% CO <sub>2</sub>	15% CO <sub>2</sub>	5% CO <sub>2</sub>	10% CO <sub>2</sub>	15% CO <sub>2</sub>
	<b>p</b> <sub>atm</sub>	<b>p</b> <sub>atm</sub>	$p_{atm}$	2 bar	2 bar	2 bar
Adsorption time [s]	105	97	73	93	69	63
Light reflux time [s]	74	63	38	58	33	25
Co-current evacuation time [s]	11	8	7	11	9	8
Feed flow rate [Nm <sup>3</sup> /h]	37.06	33.30	30.92	68.87	59.03	55.62
Light reflux flow rate [Nm³/h]	8.20	6.19	5.39	10.30	7.73	6.26
Purity [%]	95.00	95.00	95.00	95.01	95.01	95.07
Recovery [%]	95.11	95.09	95.06	95.01	95.00	95.03
Productivity [t <sub>co2</sub> /(m <sup>3</sup> <sub>ads</sub> .day)]	0.67	1.21	1.69	1.25	2.15	3.04
Energy consumption [kWh/t <sub>co2</sub> ]	1432	784	531	1087	579	405

Table 4: Optimum found for a purity and recovery of at least 95% with different  $CO_2$  concentrations in the feed and different adsorption pressures.

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# 4 Conclusion

A unibed simulation model for the 3-bed 6-step cycle in Aspen Adsorption software was developed in this work, including interactions between process steps and the actual behavior of the vacuum pump for enhanced accuracy. The pure adsorption isotherms on MIL-160(AI) were measured and adsorption parameters were determined by fitting the Langmuir model. The column model including mass, momentum, and energy balances, was then used to fit breakthrough curve experiments performed on a lab-scale VPSA pilot. Kinetic parameters, heat capacity, and heat transfer parameters were obtained from this procedure, giving an overall good fitting with a mean R<sup>2</sup> of 97.91% between experimental data and breakthrough curve simulations. All the parameters obtained were used to simulate a laboratory VPSA pilot performing the 3-bed 6-step cycle with a feed flow rate of 1 Nm<sup>3</sup>/h containing a 15/85 CO<sub>2</sub>/N<sub>2</sub> mixture. 42 experimental measurements were compared with the simulation model, giving a mean absolute error on purity and recovery of 1.47% and 3.19% respectively. The comparison was further extended by analyzing pressure, flow, and composition profiles, showing a good agreement between model prediction and experimental measurements.

Optimization of the VPSA model for laboratory scale was performed using the NSGA-II both directly within Aspen Adsorption and via a surrogate model. A comparison between direct optimization, kriging, and artificial neural networks revealed that ANN performs better for the representation of the complete simulation model, especially when computing the pareto front. The study of different topologies was important in minimizing differences between ANN and the complete simulation model.

Finally, the validated model was used to simulate an industrial VPSA pilot to be operated within the MOF4AIR project. A surrogate model using ANN was used to compute the pareto front for different feed flow rates,  $CO_2$  concentrations, and adsorption pressures. Feed flow rate and adsorption pressure play an important role in the pareto front. Optimization of energy consumption and productivity for purity and recovery higher than 95% resulted in an energy consumption of 413.19 kWh/t<sub>CO2</sub> and a productivity of 3.03 t<sub>CO2</sub>/(m<sup>3</sup><sub>ads</sub>.day) for a flue gas composition of 15% CO<sub>2</sub>.

#### **Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### **CRediT** authorship contribution statement

**A. Henrotin:** Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **N. Heymans:** Writing – review & editing, Writing – original draft, Validation, Supervision, Methodology, Investigation, Data curation, Conceptualization. **M.-E. Duprez:** Writing – review & editing, Project administration. **G. De Weireld:** Writing – review & editing, Validation, Supervision, Project administration, Funding acquisition, Conceptualization.

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