Experimental validation of an adsorbent-agnostic artificial neural network (ANN) framework for the design and optimization of cyclic adsorption processes

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Abstract

The efficacy of an adsorbent agnostic machine-learning surrogate model for rapid design and optimization of a Skarstrom cycle vacuum swing adsorption (VSA) process is experimentally validated. The surrogate model is trained to predict the process performance using adsorbent features that include hypothetical Langmuir adsorption isotherm parameters, particle density, porosity and bed voidage, and process variables such as pressure, step duration and feed velocity. The training data was generated from a detailed process model for 20,000 unique combinations of the training variables. The model shows high accuracy of $R^2_{\text{adj}} > 0.99$ for predicting key performance parameters such as product purity, recovery and productivity. The ability of this surrogate to predict the experimental performance for the purification of O_2 from air on two adsorbents, namely 13X and LiX zeolites, was studied. Two separate multi-objective optimization studies, to maximize purity and recovery, and to maximize productivity and purity were performed. For these optimization studies, the volumetrically measured isotherms of N_2 and O_2 were used as inputs to the surrogate model. Note that these isotherms were not a part of the dataset used to train the model. Nine points were chosen from the Parteo curves and the corresponding decision variables were used as set-points in a two-column lab-scale rig. The average difference between the calculated and experimentally measured purity, recovery and productivity was 3%, 5% and 9%, respectively. This study provides the necessary confidence to use surrogate-based process models for adsorbent screening and adsorption process optimization.

Introduction

Gas adsorption is a mature separation process that is industrially deployed for a variety of applications, from small to large-scales¹⁻⁴. On the one hand, recent developments in the synthesis of novel adsorbents have reinvigorated the interest in adsorption processes, particularly in areas such as CO₂ capture^{5,6}. On the other hand, as seen from the COVID-19 pandemic, the need for the rapid development of oxygen concentrators has demonstrated the critical role that this technology can play. Fixed-bed adsorption processes are inherently cyclic, with a column switching periodically between adsorption and regeneration steps². Rigorous simulation of these processes requires modelling of the heat and mass transfer phenomena while accounting for pressure drop and non-linear adsorption isotherms. The model equations consist of partial differential and non-linear algebraic equations. The numerical simulation involves starting with an initial condition and sequentially solving each constituent step until a cyclic steady-state (CSS) condition is reached.^{2,7,8} It is also worth noting that the number of cycles required for reaching CSS depends on the process parameters and the adsorbate-adsorbent system. For instance, strongly adsorbing components, e.g., water on zeolites, could take thousands of cycles to reach CSS. The cyclic nature of the process requires the simulations to calculate the dynamics to estimate the CSS performance. Although there have been several attempts to accelerate these simulations⁹⁻¹¹, most simulation works still adopt the conventional technique described above. With advancements in computing technology, performing a single PSA simulation can be rather quick (e.g., a few minutes on desktop workstations). However, performing process optimization that could involve searching a multi-parametric decision variable space could be computationally challenging. Finally, the need to perform adsorbent screening from databases containing hundreds of thousands of materials by simultaneously optimizing the process conditions for each adsorbent can indeed be a daunting task^{6,12-14}.

Recent advances in surrogate machine-learning (ML) models have been effective in overcoming the bottlenecks of the huge computational burden described above^{6,15,16}. A variety

of surrogate models have been reported in the literature, Beck *et al.* showed that surrogate models could be used for effective multi-objective optimization of PSA processes^{17,18}. Khurana *et al.* used artificial neural networks (ANN) to predict the minimum energy of a CO₂ capture process using adsorption isotherm features as inputs¹⁹. Leperi *et al.*¹⁴ and Subraveti *et al.*²⁰ used ANN models to emulate adsorption processes. In these studies training data was obtained used detailed simulations. They further used these models for process optimization and demonstrated substantial reducing in computational times. Pai *et al.* developed an ANN-based surrogate model for a specific separation, namely CO₂/ N₂ on Zeolite 13X²¹. The surrogate model, trained using data from detailed models, was designed to predict various predicted performance indicators, such as purity, recovery, energy and productivity for an arbitrary set of operating conditions. The efficacy of the surrogate model was demonstrated by performing multi-objective process optimization. A set of operating conditions from the Pareto curve were then chosen as setpoints for PSA experiments, and it was shown that experimentally measured performance indicators showed excellent comparison with the surrogate model predictions. Pai *et al.*'s work demonstrated that ANN-based models could indeed be used for practical process design and optimization. It is worth noting that most of the above surrogate models were developed for a single adsorbent. While there are clear opportunities where these models can be deployed, e.g., process optimization, they are not generalized for any arbitrary adsorbent. In other words, these tools were not yet ready for large-scale adsorbent screening exercises.

Recent advances in adsorbent synthesis have created a plethora of adsorbents that an engineer can choose from to improve process performance. Databases that contain hundreds of thousands of adsorbents are now available and continue to grow^{22,23}. Recently studies have also shown that the use of metrics, e.g., selectivity, working capacity, etc., is unreliable and that any meaningful screening should include process simulations^{6,13,24,25}. This idea has been successfully explored in studies that have focused on integrated, in-silico process-optimization based screening of adsorbents^{6,12,13}. In such studies, atomistic simulations

predict adsorption isotherms of an adsorbate-adsorbent system. These adsorption isotherms then serve as an input for process simulations that evaluate the process performance, e.g., purity, recovery, energy consumption, productivity, cost, etc. This method allows the tuning of process variables to best suit the chosen adsorbent. For such problems, developing surrogate models for each adsorbent can indeed be time-consuming, and we may not be able to fully exploit the advantage of ML techniques. To overcome this, we recently reported a generalized data-driven surrogate model based on a deep neural network called machine-assisted adsorption process learning and emulation (MAPLE) framework²⁶. The training data for MAPLE included both material properties, e.g., Langmuir adsorption isotherm and process parameters, e.g., step times, pressure levels, velocities. A total of 20,000 unique combinations of adsorbent and process parameters were used to train the surrogate model. Once trained, MAPLE can predict the process performance indicators, such as purity, recovery, energy and productivity for a pressure-vacuum swing adsorption (PVSA) process for post-combustion CO₂ capture process for any adsorbent that followed a Langmuir adsorption isotherm at an arbitrary set of process operating conditions. Although the initial training efforts were large, it was shown that the investment in training could be recouped if more than five adsorbents needed to be screened. Further, for a database that contains 10,000 materials, while conventional process-based screening techniques can take up to five million core hours, MAPLE can complete the task in 4,000 core hours, a large part of which is the sample generation. This represents $\approx$ three orders of magnitude reduction in computational time for a database of 10,000 adsorbents. What is more, MAPLE also allows for the inverse design to investigate the properties of ideal adsorbents where both adsorbent properties and process conditions can be treated as decision variables (DVs)²⁷. This approach allows the prediction of performance limits, i.e., the best performance that can be achieved if the “ideal” adsorbent can be made and married to the operating conditions that maximize its performance. Such studies provide the tools for technology evaluation and understanding the innovation potential in developing new materials.

As described above, adsorbent-agnostic ML models have huge potential for adsorbent screening and process optimization. However, even though MAPLE can be validated using a detailed model, the importance of testing its reliability through experimental validation cannot be overstated. We observe that while several studies have demonstrated the advantages of ML-based techniques within the chemical engineering domain (beyond adsorption processes), very few have been experimentally validated. Further, when training the ML models, a very large range of operating conditions is used. However, actual materials and process conditions where the performance is maximized may fall within a smaller sub-space of the training space. Hence, the ability of the ML model to predict outcomes in this range needs to be verified. Finally, to promote the use of ML techniques, it is critical to evaluate its predictive capabilities through practical experimentation. This demonstration will create more confidence and perhaps the widespread use of such tools.

The main objective of the current study is to experimentally validate an adsorbent-agnostic ML-based surrogate model. We consider the classical problem of oxygen purification from the air to fulfill this objective. The MAPLE model is trained for a Skarstorm cycle suitable for raffinate purification in a VSA process. The training variables included Langmuir adsorption isotherm parameters for two gases and process operating conditions. The goal of the current work is *to verify if the MAPLE model that was trained to predict the process performance of any arbitrary hypothetical adsorbent for an arbitrary set of operating conditions could estimate the performance of two commercial adsorbents*. Two commercial adsorbents, LiX and 13X, were chosen for validation. A series of characterization experiments allowed the description of the isotherms of N₂, O₂ and Ar on these adsorbents. Their Langmuir isotherm parameters were taken as the input to the MAPLE model. Multi-objective optimizations to maximize purity, recovery, the productivity of the process for each of these adsorbents were performed by coupling MAPLE with an optimizer. Several points on the Pareto curves were chosen, and the corresponding operating parameters were translated into experiments on a two-column lab-scale PSA rig²⁸. The paper is organized as follows: the detailed model and

the training of the MAPLE model are illustrated. Following this, the experimental rig is described, along with the experimental determination of the adsorption isotherms. Finally, the multi-objective process optimization and the experimental validation are described.

Adsorbent Equilibria

Two commercial adsorbents, namely, a Lithium-exchanged zeolite (LiX) (Tradename: JLOX-103 from Jalon corporation, China) and Sodium-exchanged Zeolite (13X) (Tradename: UOP HP 13 X from Honeywell UOP, Italy), were used. As a first step, the adsorption equilibria of N₂, O₂, and Ar on the two adsorbents were measured using a volumetric system (Micrometrics ASAP 2020C, Norcross, USA). Before the experiments, the adsorbent was regenerated in-situ at a temperature of 350° C for a period of 8 hours. The experiments were run long enough until equilibrium was reached.

The measured adsorption isotherms at three different temperatures are shown in Fig. 1. As is well known in the literature, all gases have a higher capacity on LiX as compared to 13X²⁹. At around 1 bar pressure and 25° C, the N₂ loading on LiX was $\approx 1.2 \text{ mmol g}^{-1}$ compared to $\approx 0.4 \text{ mmol g}^{-1}$ on 13X. Within the range of pressures and temperatures investigated, Nitrogen exhibited noticeable non-linearity on LiX and a mild non-linearity on 13X. All other isotherms, namely of O₂ and Ar, were reasonably linear. A constant-selectivity single-site Langmuir (SSL) isotherm was used to describe the competitive adsorption equilibrium:

$$q_i^* = \frac{q_{\text{sat}} b_i C_i}{1 + \sum_i b_i C_i} = \frac{H_i C_i}{1 + \sum_i b_i C_i}, \quad i = \text{N}_2, \text{O}_2, \text{Ar} \quad (1)$$

Here, q_{sat} is the saturation capacity of the adsorbing gas, b_i is the equilibrium constant for component i , and q_i^* is the equilibrium solid phase loading. The product of q_{sat} and b_i is the Henry constant, H_i . The temperature dependence of the equilibrium constant is described by:

$$b_i = b_{0,i} e^{\frac{-\Delta U_i}{R_g T}} \quad (2)$$

Here, ΔU_i is the internal energy of adsorption for component i , R_g is the universal gas constant and, T is the temperature. For the three components, the SSL isotherm comprises of seven parameters, namely, q_{sat} , b_{0,O_2} , b_{0,N_2} , $b_{0,Ar}$, ΔU_{O_2} , ΔU_{N_2} , and ΔU_{Ar} . These parameters were fitted to the experimental measured data using non-linear regression. The q_{sat} value is fitted to the strongest of the three components, namely, N_2 , and was kept the same for O_2 , and Ar . This fitting procedure also yields a thermodynamically consistent formalism. The equilibrium data along with the fitted isotherms are shown in Fig. 1. The SSL isotherm provides a good description of experimental data. The fitted isotherm parameters are provided in Table 1, along with the 95% confidence intervals. The N_2/O_2 equilibrium selectivity, α , defined as:

$$\alpha_{N_2,O_2} = \frac{H_{N_2}}{H_{O_2}} \quad (3)$$

shows LiX to be a superior adsorbent compared to 13X; an observation that is well documented in the literature^{29,30}. For instance the α_{N_2,O_2} for LiX and 13X, were approximately 12 and 3, respectively.

Vacuum swing adsorption (VSA) experimental system

In this work, VSA experiments were carried out in a two-bed lab-scale system, the process schematic of which is shown in Fig. 2 a). It consists of two 300 cc Swagelok stainless steel columns (≈ 18 cm length and 2.52 cm diameter). Each column was packed with ≈ 200 g of adsorbent. Column and particle properties are provided in Table 2. A vacuum pump (Pfeiffer Vacuum MVP 040-2, Germany) was used to operate the unit at sub-ambient pressures. The vacuum pump operates at a constant volumetric flow rate of 30 SLPM. Appropriate mass

flow meters (MFM) and mass flow controllers (MFC) obtained from Alicat Scientific, Tucson, AZ, USA, were used to measure and control the gas flows. The MFCs have a maximum flow rate rating of 10 SLPM. A metering valve (MV-1) is placed in the light reflux line to maintain the pressure of the donor column in the coupled light-reflux step. The raffinate and extract products are collected in a tank before they are vented. The extract tank is connected to a vacuum pump with a check valve. An oxygen analyzer (Quantek Instruments, Model 906A, USA) was used to measure the raffinate O_2 composition downstream of the O_2 product tank. The composition of the extract product is measured using a mass spectrometer (MS, Pfeiffer Vacuum OmniStar GSD 320, Asslar, Germany). The VSA experiments were conducted using certified premixed cylinders from Linde, Canada containing dry air (20.5 mol% O_2 , 78.5 mol% N_2 , and 1 mol% Ar). Note that all MFCs and MFMs were calibrated before each experiment using an independent calibrator (DryCal, Mesa Labs). The oxygen sensor was calibrated using several known gas mixtures, i.e., pure O_2 , pure N_2 , dry air. The columns and the product tank were fully saturated with dry air prior to each experiment, i.e., the initial experimental conditions are equal to the feed conditions. The light product was collected in the first part of the adsorption step, while the second part was used to implement the reflux step for the other column. All experiments were run for 100 cycles, although the cyclic steady state was reached in ≈ 25 cycles.

In this study, three performance indicators namely, O_2 purity (Pu_{O_2}), O_2 recovery (Re_{O_2}), and process productivity Pr_{O_2} , are considered for evaluating performance. Lab-scale vacuum pumps are typically oversized and a reliable measurement of their energy consumption was not possible. Hence, the experimental O_2 purity is measured downstream of the product tank and is hence an average of the two columns. The experimental recovery is calculated as the ratio of the moles of O_2 leaving the product tank to that introduced in the feed into the bed in the pressurization, adsorption, and light reflux (donor) steps. The cycle-time used to calculate productivity is the sum of the duration of the four steps. The idle times in the experimental two-bed system are removed while calculating the productivity.

Process Modelling

Modelling an adsorption process requires a detailed description of mass and heat transfer and fluid dynamics inside the adsorption bed. Since these processes are inherently cyclic, the equations describing each step are iteratively solved until a cyclic steady state (CSS) is reached. In this study, we fix the column dimensions and the sizes of fluid movers to match the dimension/configuration of the lab-scale VSA testing rig described above, which is the same system that was described in an earlier work²⁸. The model has the following key assumptions: 1. The fluid is described by the ideal gas law; 2. An axially dispersed plug flow model describes the flow in the adsorption bed, meaning there are no radial effects; 3. The solid and fluid phases are in thermal equilibrium; 4. Mass transfer is described by a linear-driving force (LDF) model, assuming that the molecular diffusion in macropores controls the mass transfer³¹; 5. Darcy’s law is used to describe the pressure drop in the column. It has been shown that this assumption is sufficient for the testing rig used in this work and for the operating conditions studied²⁸. The isotherm parameters for Ar are assumed to be the same as that of O₂ in the detailed model. While we acknowledge that this can be a limitation, particularly for LiX that shows a slight difference in the affinities of O₂ and Ar, it simplifies the model without compromising much on its predictive capabilities. The column mass and energy balances result in a system of partial differential equations (PDEs). The PDEs are reduced to ordinary differential equations (ODEs) using a finite-volume scheme. They are solved using *ode23s*, an inbuilt solver in MATLAB. Boundary conditions for the different steps are applied as appropriate. Model equations and boundary conditions are provided in the supporting information. Properties associated with the column are provided in Table 2. The entire simulation strategy is detailed in a previous work³² and has been validated experimentally both at lab-scale²⁸ and pilot-scales³³.

Process cycle

The VSA process used in this study is a 4-step cycle with light product reflux (LR) and feed pressurization (FP), as shown in Fig. 2 b). This is popularly known as the Skarstrom cycle and consists of the following steps:

- An adsorption step, where the feed mixture consisting of synthetic dry air is introduced at the feed end ($z = 0$) of the column with an interstitial feed velocity v_F and pressure P_{ATM} , for a period of t_{ADS} . The raffinate product, which is predominantly O_2 , is collected at the outlet end ($z = L$).
- A light reflux step, where the outlet stream from the adsorption donor (D) step, is used to purge the column in the light reflux receiver (R) step.
- An evacuation step, where a vacuum pump reduces the pressure to a value, P_L through the feed end ($z = 0$) and column is regenerated.
- A light reflux step, where a portion of the product from the light reflux donor (D) step is directed to purge the column, which is maintained at P_L . This step helps to remove the adsorbed N_2 and keep the product end of the column filled with high purity O_2 .
- A pressurization step, where the pressure of the column is brought back from the P_L to P_{ATM} using the feed stream (FP) at the same flowrate as the adsorption step.

In this study, we considered only VSA operation. While it is well known that LiX works best under PVSA conditions and 13X is best operated at PSA conditions²⁹, the goal of the study was to validate the MAPLE model and not necessarily to optimize the entire process for each adsorbent. Hence, the study of the VSA process is considered sufficient.

MAPLE Sampling and Training

MAPLE is a data-driven surrogate model trained to emulate an adsorbent process using supervised machine learning²⁶. This model is trained for a generalized system with both

adsorbent and process-related inputs. The trained variables related to the adsorbent property are the five SSL parameters ($q_{\text{sat}}, b_{0,\text{N}_2}, b_{0,\text{O}_2}, \Delta U_{\text{N}_2}, \Delta U_{\text{O}_2}$), particle radii (R_{P}), particle voidage (ϵ_{P}), bed voidage (ϵ_{B}), and adsorbent particle density (ρ_{ADS}). The trained process variables include the low pressure (P_{L}), the durations of the adsorption step (t_{ADS}), and the light reflux step (t_{LR}), and inlet feed flowrate (v_{F}). Meaningful constraints were used for the training. For instance, N_2 is always the strongly adsorbed gas, i.e. $b_{\text{N}_2} \geq b_{\text{O}_2} + 0.5$ [m^3/mol] and, $|\Delta U_{\text{N}_2}| \geq |\Delta U_{\text{O}_2}| + 1$ [kJ/mol]. The duration of the adsorption step is longer than the light reflux duration, i.e., $t_{\text{ADS}} \geq t_{\text{LR}} + 1$ [s]. As mentioned earlier, for the sake of simplicity, the isotherm inputs for Ar are assumed to be the same as that of O_2 . Based on the parameters selected, the $\alpha_{\text{N}_2,\text{O}_2}$, is in the range of $2.5 \leq \alpha \leq 10^6$. Note that this range is substantially larger than the selectivities for LiX and 13X. Hence, the experimental testing is but a small sub-space of the range for which MAPLE is trained for. The inputs and their training ranges are shown in Fig: 2 b) and the ranges are provided in Table 2.

The dataset consisting of 20,000 samples was generated using Latin hypercube sampling (LHS). The dataset represents 20,000 unique hypothetical adsorbents paired with an equal number of random operating conditions. The various isotherms used for training are shown in Fig. S2. in the supporting information. The distribution of the variables in the training set is shown in Figs. S3-S5. The 20,000 points were run using a detailed process model until CSS was reached, and the outputs, namely, Pu_{O_2} , Re_{O_2} and Pr_{O_2} were saved. This data was then split randomly into a training and testing ratio of 90:10, and the model accuracy was evaluated using the R_{Adj}^2 of the test-set which is defined as :

$$R^2 = 1 - \frac{\sum_{j=1}^n (m_j - \hat{m}_i)^2}{\sum_{j=1}^n (m_j - \bar{m}_j)^2} \quad (4)$$

$$R^2_{\text{Adj}} = 1 - \frac{(1 - R^2)(n - 1)}{(n - k - 1)} \quad (5)$$

where n is the number of testing samples and k is the number of input descriptors, which in this work were 1000 and 13, respectively. m_j is the actual observed output, $\hat{m}_j$ is the

predicted output, and $\bar{m}_j$ is the mean of the set of actual outputs.

A network consisting of three hidden layers with 20 neurons each was chosen. The trade-off between layers/neurons and samples has been discussed in our previous work²¹. The network was trained using Bayesian regularization with backpropagation technique available in MATLAB. The training and validation mean squared errors (MSE) were evaluated for 200 epochs. Care was taken to avoid over-fitting the ANN. Achieving a test $R_{\text{Adj}}^2 \geq 0.99$ for each of the performance indicators was considered sufficient for the training exercise. To avoid the variation in model accuracy each time the model is trained and to get more robust predictions, an ensemble average of ten such trained neural networks was taken as the final model for each performance indicator. A parity analysis was also conducted using 1000 sampled data points. The testing results are shown as a parity plot for the various performance indicators in Fig. 3. The results from the MAPLE model show excellent prediction of the detailed model results. It is worth noting that the sampling for the training was completely randomized, and there was no bias in terms of data to be close to the experimental system. This is clearly illustrated in the supporting information where the distributions of the training variables are shown.

Process optimization and experimental validation

As described earlier, the goal of the study was to test whether the MAPLE model trained on a completely randomized set of adsorbent and process descriptors would predict the performance of actual adsorbents. We addressed this by considering two multi-objective optimization scenarios: the maximization of purity and recovery and the maximization of purity and productivity. In each of these optimization problems, the MAPLE model is coupled with a genetic algorithm optimization tool, namely the non-dominated sorting genetic algorithm (NSGA-2), available in MATLAB^{26,34}. Technically, the MAPLE model can accept any of the inputs for which it was trained as DVs. However, in our experimental campaign,

the adsorbents are fixed. Hence, in order to describe the performance of the selected adsorbents (LiX and 13X), the adsorbent-related parameters measured from the volumetric system were provided as inputs, and only the process-related parameters were considered as DVs.

An initial population consisting of 384 unique combinations of decision variables was chosen for each optimization. The optimization was run for 50 generations. The optimization was repeated multiple times by varying the initial populations to avoid local minima and stochastic variations in the final result. Multi-objective optimization results in Pareto curves representing the best trade-offs between two competing objective functions. All the points along the Pareto curve can be mapped to a specific set of DVs. The optimized DVs obtained were re-run in the detailed model. We emphasize that only the optimal points are run using the detailed model. Although not a requirement; running the optimal points using a detailed model ensures high accuracy avoiding spurious outliers.

The next step was the experimental validation. We selected a few points from the Pareto curves and identified the corresponding DVs. The selection included differing objectives, such as a high, medium and low purity. These DVs were used as setpoints for the experiments that were run until CSS. Both transient results and the performance indicators measured at CSS were recorded. The experimental observations were then compared to the values obtained from the MAPLE model. It is important to highlight that no parameter tuning is performed during the experiments. In other words, the model outputs are taken as-is for experimental implementation.

Purity-Recovery Optimization

One of the vital trade-off when designing an adsorption process are the countering objectives of process purity and recovery. In this case study, we perform an optimization to maximize these objectives. The optimization is run with fixed isotherm and particle parameters to the values of the two adsorbents shown in Table 2. The range of the operating parameters

that consist of step times, low pressure, and feed rate are also provided in Table 2. The resulting Pareto curves for the two materials are shown in Fig. 4 (a) as solid lines. This curve represents the best possible trade-off between purity and recovery obtained for the two adsorbents within the given range of operating conditions. The region to the top right of the curves is infeasible for each adsorbent, and the area below is sub-optimal. Note that the Pareto curve for 13X falls sharply at high purity values. This indicates that the use of 13X makes it difficult to simultaneously achieve high purity and recovery. The LiX sorbent outperforms 13X over the entire range by a substantial margin. For instance, for purity of $\approx 90\%$, 13X provides the best recovery of 35%, while LiX yields 75%. The dashed lines indicate the results obtained by running MAPLE with the DVs obtained from the optimization but using the 95% confidence interval values for the isotherm parameters.

Purity-Productivity Optimization

In a practical situation, it is highly desirable to maximize productivity while achieving high product purity. Hence, for the second case, we perform a multi-objective optimization to simultaneously maximize O_2 productivity and purity. Figure 4 (b) shows the Pareto curves for the performance indicators of purity and productivity for the two different adsorbents. The trend is very similar to the previous case, i.e., LiX outperforms 13X. In fact, in the high purity region, LiX has $\approx 2\times$ the productivity offered by 13X. This trend is again explained by the higher selectivity and working capacity offered by LiX compared to 13X. The maximum inlet flow rate was limited to 10 SLPM in the optimizations since this corresponds to the upper limit of flow delivered by the MFC. Hence, the performance shown in this work is not necessarily the best that the adsorbents can offer, but merely what can be achieved in the lab-scale rig. Similar to the previous case, the Pareto curves calculated by using the 95% confidence interval values from the isotherm are shown as dotted lines.

Experimental Validation

We choose operating conditions obtained for the different optimization case studies to validate the MAPLE predictions. Here, the outputs of the optimizer, namely, the DVs, i.e., the low-pressure values, duration of the adsorption step, feed flow rate, were programmed into the control system. The inlet flow rate controlled by MFC-2 was kept the same for the pressurization, adsorption and light reflux (D) steps. Before the experiment, the bed was saturated with the feed composition. The experiments were run for 100 cycles. The outlet flows and composition was recorded along with the dynamic bed pressure and temperature histories. The performance indicators, namely purity, recovery and productivity, are obtained by integrating the molar flows over one cycle.

The operating conditions and the performance of the various experimental runs are summarized in Table 3. Experiments 1 to 4 used LiX, while 5 to 9 used Zeolite 13X. Experiments 1-3 and 5-7 were chosen from the purity-recovery Pareto curve, while the others were from the purity-productivity Pareto curve. The points chosen for the experiments are shown in Figs. 4 along with the Pareto curves. The experimentally measured performance indicators and the ones predicted by MAPLE are provided in Table 3. In the figures, closed and open symbols correspond to the experimentally measured values and the corresponding MAPLE predictions. The average difference between the experimental values and the MAPLE predictions was 3% for purity, 5% for recovery and 9% for productivity. It is clear from both the figure and the table that the experimental values agree well with the MAPLE model. As a confirmation, the detailed model was used to predict the performance indicators for each of the nine experiments. These values are shown in Table 3. Once again, it is evident that these values are in very good agreement both with MAPLE predictions and experimental measurements.

It is important to note that MAPLE provides only performance indicators at CSS and is not trained to predict the transients. However, a wealth of dynamic information is collected from the experiments. The detailed model can be used to compare these transients. The

experimental conditions were simulated in the detailed model until CSS, and the obtained results are plotted alongside the experimentally obtained transients. Specifically, the transients of pressure and molar flow rates are shown in Figure 5 for all the nine experiments. In the figure symbols represent experiments, and the solid lines are obtained from the detailed dynamic model. Note that the idle steps needed to schedule the two-bed VSA process are included in Fig. 5. Since the simulations are performed using a uni-bed approach, idle steps are not explicitly included. However for the purpose of comparison, they are included in the plots. The pressure, and flow rate values at the end of the step preceding the idle steps are assumed to stay constant. The feed flowrate in the adsorption step, light reflux step, and pressurization step are kept the same as in the simulations. The pressure history for the evacuation step is predicted based on a constant volumetric boundary condition and has been shown in previous modelling works²⁷. The constant volumetric flow boundary condition captured the pressure histories for the evacuation step well. There is a pressure build-up in the adsorption steps in all the experiments due to undersized fittings downstream of the beds; this was not modelled in the simulation and showed up as discrepancies. Further, during the LR step, the column pressure increased slightly and remained flat over the duration of the idle step. In the experiment, during the LR step, the donor column is supplying the reflux to the receiver. This causes an increase in the pressure. Since the LR step is typically followed by an idle step wherein the solenoids at both ends are closed, the column pressure does not change. Although the discrepancy seems large, since the duration of the LR step itself is small, the difference does not have a major impact. The bottom two panels in each sub-figure show the raffinate and extract molar flow rates. There are sharp increases in simulated product flows that are not observed in the experiment. This observation is due to the fact that simulations do not consider the presence of tanks that are present in the experimental rig. Nevertheless, the area under the curve, i.e., the total number of moles collected in each step should be the same for both the simulation and the experiment. As shown in the legends of Figure 5, this is indeed the case.

Figure 6 shows the experimentally obtained purity, and recovery plotted as a function of the number of cycles along with the corresponding detailed model predictions. In all cases, the CSS purity and recovery values are in good agreement with the calculations. Experiments 5, 6, and 8 show a noticeable delay in the purity signal, which can be explained based on the product tank turnover delay owing to the relatively low product flow rate. Note that the tank turnover delay was not modelled, and it shows up as a discrepancy. For the other experiments, and the turnover rate is quick owing to high flows. This observation further validates the ability of the model to predict experimental trends.

Conclusions

This study trained an adsorbent-agnostic machine-assisted process learning and emulation (MAPLE) framework to learn the performance of a VSA process from sampled data obtained using a detailed process model. A Latin hypercube sampling strategy was used to sample input data that included both operating conditions and adsorbent features such as hypothetical Langmuir isotherm parameters for O_2 and N_2 , adsorbent density and bed voidage. The trained model is now adsorbent agnostic as it can predict the performance of any arbitrary adsorbent, real or hypothetical, at a given operating condition. Multi-objective optimization was performed for two commercially available adsorbents, namely LiX and 13X zeolites. The resulting optimized operating conditions for both adsorbents were used as set points on a lab-scale experimental rig to confirm the predictions. The experimentally measured performance indicators were in good agreement with the MAPLE predictions. Further, the simulations using a detailed model showed that the transients could also be well described.

The adsorption community is gradually moving towards process-based screening of adsorbents for a variety of applications. Owing to the computational challenges that exist in process simulation and optimization, ML-based techniques are gaining rapid attention. Since there are almost no experimental studies that exist, the practical relevance of such

screening approaches are still unknown. In fact there are substantial challenges in synthesizing new materials screened from large databases that contain hundreds of thousands of materials. Hence, one can use real materials as proxies to verify the efficacy of ML-based models, although they have not been specifically trained for these adsorbents. This goal is precisely what the current study has demonstrated. We believe that this opens up the opportunities for further work at the interface of adsorbent synthesis and process design that will accelerate the development of targeted solutions for a variety of gas separations.

Nomenclature

Roman Symbols

b, b_0	adsorption equilibrium constant [$\text{m}^3 \text{mol}^{-1}$]
C	fluid phase concentration [mol m^{-3}]
H	Henry constant [-]
i	component [-]
m	observed output [-]
$\hat{m}$	predicted output [-]
P	pressure [bar]
Pu_{O_2}	CO_2 product purity [%]
Pr_{O_2}	productivity [$\text{mol m}^{-3}\text{ads s}^{-1}$]
q^*	equilibrium solid phase loading [mol m^{-3}]
q_{sat}	solid phase saturation capacity [mol kg^{-1}]
R_g	universal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$]
Re_{O_2}	CO_2 recovery [%]
R^2	coefficient of determination [-]
t	time [s]
T	temperature [K]

ΔU	internal energy of adsorption [J mol ⁻¹]
v	interstitial velocity [m s ⁻¹]
y	composition in stream [-]

Greek Symbols

α	Selectivity [-]
ρ	density [-]
ϵ	voidage [-]
θ	reflux fraction [-]

Abbreviations, Subscripts and Superscripts

Adj	adjusted
ADS	adsorption
ANN	artificial neural network
CSS	cyclic steady state
D	donor
DV	decision variable
EVAC	evacuation
F	feed
FP	feed pressurization
H	high pressure
LDF	linear driving force
L	low pressure
LR	light reflux
MAPLE	machine-assisted adsorption process learning and emulation
MFC	mass flow controllers

MFM	mass flow meter
MV	metering valve
MS	mass spectrometer
NSGA	non-dominated sorting genetic algorithm
Opt.	optimization
PT	pressure transmitter
PSA	pressure swing adsorption
PVSA	pressure vacuum swing adsorption
R	receiver
SSL	single-site Langmuir
SV	solenoid valve
VP	vacuum pump
VSA	vacuum swing adsorption

Acknowledgements

Funding from Canada First Research Excellence (CFREF) through the University of Alberta’s Future Energy Systems is acknowledged. All computations were supported by Compute Canada’s resources for research groups grant. We thank Frank Tosto, Juan Segura, and Innotech Alberta for access to the VSA experimental rig. We thank UOP Honeywell, Italy for the contribution of the Zeolite 13X adsorbent.

Conflict of Interest

Authors have no conflicts of interest to declare.

Electronic Supplementary Information

Details of process models and boundary conditions; plots showing the distribution of training data, the binary isotherms are shown. An excel file with the data set containing 20000 samples that were used to train the ANN model and the mapping of the decision variables for the four optimization is provided.

Author credit statement

Kasturi Nagesh Pai: Conceptualization, Methodology, Software, Experimentation, Formal Analysis, Writing-Original Draft, Writing- Review and Editing; **Tai TT Nguyen:** Experimentation, Formal Analysis, Writing- Review and Editing; **Arvind Rajendran:** Conceptualization, Methodology, Writing- Review and Editing, Supervision, Funding acquisition; **Vinay Prasad:** Methodology, Writing- Review and Editing, Supervision.

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Table 1: Single site Langmuir isotherm parameters for three gases, namely, N₂, O₂, and Ar along with the 95% confidence intervals.

Zeolite Type	Gas	q_{sat} [mmol g ⁻¹]			b_0 [m ³ mol ⁻¹]			ΔU [kJ mol ⁻¹]		
		Value	95%-	95%+	Value	95%-	95%+	Value	95%-	95%+
LiX	N ₂	2.279	2.247	2.311	1.44×10^{-6}	1.60×10^{-6}	1.30×10^{-6}	-23.85	-24.13	-23.57
	O ₂	2.279	2.247	2.311	1.69×10^{-5}	1.77×10^{-5}	1.61×10^{-5}	-11.71	-11.84	-11.58
	Ar	2.279	2.247	2.311	6.38×10^{-5}	7.01×10^{-5}	5.79×10^{-5}	-7.801	-8.043	-7.56
13X	N ₂	2.471	2.051	2.871	9.35×10^{-6}	1.19×10^{-5}	7.38×10^{-6}	-14.96	-15.59	-14.34
	O ₂	2.471	2.051	2.871	2.02×10^{-5}	2.21×10^{-5}	1.84×10^{-5}	-9.92	-10.16	-9.675
	Ar	2.471	2.051	2.871	1.67×10^{-5}	1.78×10^{-5}	1.57×10^{-5}	-10.25	-10.41	-10.09

Table 2: Parameters used for detailed model simulations. Those indicated as “variable” are used for training the MAPLE framework and also used as decision variables.

Parameter	Type	Value
Column properties		
Bed length, L [m]	Measured	0.18
Column inner radius, r_{in} [m]	Measured	0.025
Column outer radius, r_{out} [m]	Measured	0.027
Density of the column wall, ρ_w [kg m ⁻³]	Fixed	7800
Tortuosity factor, τ [-]	Fixed	3.00 ⁸
Fluid properties		
Effective heat conduction coefficient, K_z [J m ⁻¹ s ⁻¹ K ⁻¹]	Fixed	9.03 × 10 ⁻²
Thermal conductivity of the wall, K_w [W m ⁻¹ K ⁻¹]	Fixed	16.00 ⁸
Inside heat transfer coefficient, h_{in} [W m ⁻² K ⁻¹]	Fitted	16.20
Outside heat transfer coefficient, h_{out} [W m ⁻² K ⁻¹]	Fitted	20.00
Gas specific heat capacity, $C_{p,g}$ [J kg ⁻¹ K ⁻¹]	Fixed	1010.60 ⁸
Adsorbed phase specific heat capacity, $C_{p,a}$ [J kg ⁻¹ K ⁻¹]	Fixed	1010.60 ⁸
Universal gas constant, R_g [m ³ Pa mol ⁻¹ K ⁻¹]	Fixed	8.314
Fluid viscosity, μ [kg m ⁻¹ s ⁻¹]	Fixed	1.72 × 10 ⁻⁵
Molecular diffusivity, D_M [m ² s ⁻¹]	Fixed	1.60 × 10 ⁻⁵
Adsorbent properties		
Adsorbent specific heat capacity, $C_{p,s}$ [J kg ⁻¹ K ⁻¹]	Fixed	1070.00 ⁸
Particle radius, r_p [m]	Variable	0.25 × 10 ⁻³ - 2.5 × 10 ⁻³
Bed voidage, ϵ [-]	Variable	0.35-0.45
Density of the solid particle, ρ_s [kg m ⁻³]	Variable	800.00-1200.00
Particle voidage, ϵ_p [-]	Variable	0.35-0.7
Adsorption saturation capacity, q_{sat} [mol kg ⁻¹]	Variable	0.50 to 10.00
Adsorption equilibrium constant of CO ₂ , b_{0,CO_2} [m ³ mol ⁻¹]	Variable	10 ⁻¹² to 10 ⁻¹
Adsorption equilibrium constant of O ₂ , b_{0,O_2} [m ³ mol ⁻¹]	Variable	10 ⁻¹¹ to 10 ⁻¹
Internal energy of adsorption of N ₂ , ΔU_{N_2} [kJ mol ⁻¹]	Variable	-7.00 to -30.00
Internal energy of adsorption of O ₂ , ΔU_{O_2} [kJ mol ⁻¹]	Variable	-3.00 to -25.00
Process properties		
Feed temperature, T_F [K]	Fixed	298.15
High pressure, P_H [bar]	Fixed	1.00
Evacuation step vacuum pump flow-rate, v_{EVAC} [SLPM]	Fixed	30
Adsorption step time, t_{ADS} [s]	Variable	10.00 to 110.00
Evacuation pressure, P_L [bar]	Variable	0.1 to 0.6
Feed flowrate, Q_F [SLPM]	Variable	1 to 10

Table 3: Optimal operating conditions and the measured performance of the VSA experiments, shown alongside the MAPLE model predictions for the same conditions. The units of productivity (prod) indicated as “*” are $\text{molO}_2 / \text{m}^3 \text{ ads} / \text{s}$. Experiments marked “PP”, and “PR” refer to those from the purity-productivity, and purity-recovery optimization Pareto curves.

Adsorbent	Experiment	Operating conditions					Experiment			MAPLE Model			Detailed model		
		t_{ads} [s]	t_{LR} [s]	P_L [bar]	Q_F [SLPM]	Purity [%]	Recovery [%]	Prod *	Prod *	Purity [%]	Recovery [%]	Prod *	Purity [%]	Recovery [%]	Prod *
LiX	1 ^{PP}	11.0	3.0	0.1	9.7	95.2	64.2	1.5	1.5	95.6	61.6	1.4	95.2	60.2	1.5
	2 ^{PP}	11.0	4.0	0.4	9.8	60.9	65.9	2.7	2.7	59.3	69.8	3.0	62.4	70.6	3.2
	3 ^{PP}	15.0	4.0	0.4	9.8	44.8	71.3	3.4	3.4	40.4	71.6	3.5	44.1	72.4	3.5
	4 ^{PR}	23.0	0.0	0.1	6.0	58.7	84.5	1.0	1.0	60.1	84.9	0.9	60.6	84.9	1.0
13X	5 ^{PP}	6.0	4.0	0.3	4.5	91.7	23.7	0.3	0.3	92.2	26.7	0.2	93.2	25.9	0.4
	6 ^{PP}	7.0	5.0	0.3	5.5	89.8	26.3	0.3	0.3	89.4	26.2	0.3	92.2	29.3	0.6
	7 ^{PP}	6.0	4.0	0.4	6.9	75.7	32.8	0.8	0.8	76.8	32.5	0.7	82.3	35.9	1.0
	8 ^{PR}	6.0	5.0	0.4	4.3	93.6	10.5	0.1	0.1	94.6	12.4	0.1	95.2	11.4	0.2
	9 ^{PR}	6.0	3.0	0.2	5.8	81.1	41.5	0.5	0.5	84.8	41.9	0.5	83.7	43.8	0.8

Figure 1: Measured adsorption equilibria of N_2 , O_2 , and Ar on LiX and 13X. The left and the right columns display the isotherms for LiX, and 13X, respectively. The symbols are experimentally measured values, and the lines are the SSL fit.

Figure 2: Experimental set-up and cycle studied (a) Schematic diagram of the bench-scale VSA test apparatus. (b) Illustration of the Skarstrom cycle along with the definition of the process variables. Note that the definition of reflux fraction is $\theta_{LR} = t_{LR}/t_{ads}$.

Figure 3: Parity plots of the prediction from MAPLE for different performance indicators against those obtained from the detailed model for a test-set of 1000 samples as inputs for the Skarstrom cycle. a) Purity, b) Recovery, c) Productivity. The shaded area indicates a 5% deviation from the diagonal.

Figure 4: Pareto curves for the multi-objective optimization of (a) simultaneously maximizing O_2 purity and recovery, and (b) simultaneously maximizing O_2 purity and productivity. The solid blue line corresponds to LiX, and the red line corresponds to 13X. The closed symbols represent the experimentally measured performance indicators, while the open symbols represent the same operating conditions in the MAPLE model. The dotted lines indicate the Pareto curves calculated based on 95% confidence interval for isotherm parameters.

Figure 5: Comparison of experimental and simulated transients for all the experimental runs. The pressure history for one cycle is shown along with the detailed model results for the same inputs. The middle row and bottom row in each subfigure show the outlet flow rate of the raffinate and extract product step, respectively. The symbols are from the experimental measurement, and the lines are obtained from the detailed simulations.

Figure 6: Comparison of experimental and simulated values of purity and recovery over 100 cycles for the Skarstrom cycle. Symbols represent the experimental purity and recovery averaged over each cycle, and solid lines are from the detailed model simulations.

Supplementary Information for Experimental validation of an adsorbent-agnostic artificial neural network (ANN) framework for the design and optimization of cyclic adsorption processes

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Process Modeling

Model Equations

Overall mass balance:

$$\frac{1}{P} \frac{\partial P}{\partial t} - \frac{1}{T} \frac{\partial T}{\partial t} = -\frac{T}{P} \frac{\partial}{\partial z} \left(\frac{P}{T} v \right) - \frac{1-\epsilon}{\epsilon} \frac{RT}{P} \sum_{i=1}^{n_{\text{comp}}} \frac{\partial q_i}{\partial t} \quad (\text{S1})$$

Component mass balance:

$$\frac{\partial y_i}{\partial t} + \frac{y_i}{P} \frac{\partial P}{\partial t} - \frac{y_i}{T} \frac{\partial T}{\partial t} = \frac{T}{P} D_L \frac{\partial}{\partial z} \left(\frac{P}{T} \frac{\partial y_i}{\partial z} \right) - \frac{T}{P} \frac{\partial}{\partial z} \left(\frac{y_i P}{T} v \right) - \frac{RT}{P} \frac{1-\epsilon}{\epsilon} \frac{\partial q_i}{\partial t} \quad (\text{S2})$$

Mass transfer rate:

$$\frac{\partial q_i}{\partial t} = k_i (q_i^* - q_i); k_i = \frac{C_i}{q_i^*} \frac{15\epsilon_P D_P}{r_P^2}; D_P = \frac{D_M}{\tau} \quad (\text{S3})$$

Pressure drop:

$$-\frac{\partial P}{\partial z} = \frac{150}{4} \frac{1}{r_P^2} \left(\frac{1-\epsilon}{\epsilon} \right)^2 \mu v \quad (\text{S4})$$

Column energy balance:

$$\left[\frac{1-\epsilon}{\epsilon} \left(\rho_s C_{p,s} + C_{p,a} \sum_{i=1}^{n_{\text{comp}}} q_i \right) \right] \frac{\partial T}{\partial t} = \frac{K_z}{\epsilon} \frac{\partial^2 T}{\partial z^2} - \frac{C_{p,g}}{R} \frac{\partial}{\partial z} (vP) - \frac{C_{p,g}}{R} \frac{\partial P}{\partial t} - \frac{1-\epsilon}{\epsilon} C_{p,a} T \sum_{i=1}^{n_{\text{comp}}} \frac{\partial q_i}{\partial t} + \frac{1-\epsilon}{\epsilon} \sum_{i=1}^{n_{\text{comp}}} ((-\Delta H_i) \frac{\partial q_i}{\partial t}) \quad (\text{S5})$$

Boundary Conditions

Figure S1: Typical operating configurations of the constituent steps in a P/VSA cycle

Table S1: Boundary conditions for the typical steps in a cyclic adsorption process.

Step	$z=0$	$z=L$
OPEN-CLOSED (FP)	$v _{z=L} = \frac{v_{\text{ADS}} P_{\text{ADS}} _{z=L}}{P _{z=L}}$	$\frac{\partial y_i}{\partial z} _{z=0} = 0$
	$D_L \frac{\partial y_i}{\partial z} _{z=L} = -v _{z=L} (y_{i,F} - y_i _{z=L})$	$\frac{\partial P}{\partial z} _{z=0} = 0$
	$\frac{\partial T}{\partial z} _{z=L} = -\epsilon v _{z=L} \rho_g C_{p,g} (T_F - T _{z=L})$	$\frac{\partial T}{\partial z} _{z=0} = 0$
OPEN-OPEN (ADS)	$v _{z=0} = v_F$	$P _{z=L} = P_H$
	$D_L \frac{\partial y_i}{\partial z} _{z=0} = -v _{z=0} (y_{i,F} - y_i _{z=0})$	$\frac{\partial y_i}{\partial z} _{z=L} = 0$
	$\frac{\partial T}{\partial z} _{z=0} = -\epsilon v _{z=0} \rho_g C_{p,g} (T_F - T _{z=0})$	$\frac{\partial T}{\partial z} _{z=L} = 0$
OPEN-OPEN (LR)	$P _{z=L} = P_L$	$v _{z=0} = v_{\text{ADS}}$
	$\frac{\partial y_i}{\partial z} _{z=L} = 0$	$D_L \frac{\partial y_i}{\partial z} _{z=0} = -v _{z=0} (y_{i,F} - y_i _{z=0})$
	$\frac{\partial T}{\partial z} _{z=L} = 0$	$\frac{\partial T}{\partial z} _{z=0} = -\epsilon v _{z=0} \rho_g C_{p,g} (T_F - T _{z=0})$
CLOSED-OPEN (EVAC)	$v _{z=0} = v_{\text{EVAC}}$	$v _{z=L} = 0$
	$\frac{\partial y_i}{\partial z} _{z=0} = 0$	$\frac{\partial y_i}{\partial z} _{z=L} = 0$
	$\frac{\partial T}{\partial z} _{z=0} = 0$	$\frac{\partial T}{\partial z} _{z=L} = 0$
		$\frac{\partial P}{\partial z} _{z=L} = 0$

Figure S2: Distribution of N_2 (top) and O_2 (bottom) isotherms used in the training set. JLOX LiX and UOP HP 13 X are shown as reference.

Figure S3: Training sample distributions of the SSL isotherm parameters. A total of 20000 samples are shown here.

Figure S4: Training sample distributions of the cycle specific operating parameters. A total of 20000 samples are shown here.

Figure S5: Training sample distributions of the adsorbent particle parameters. A total of 20000 samples are shown here.

Nomenclature

Roman Symbols

C	fluid phase concentration [mol m^{-3}]
C_p	specific heat [$\text{J kg}^{-1} \text{K}^{-1}$]
D_L	axial dispersion [$\text{m}^2 \text{s}^{-1}$]
D_M	molecular diffusion [$\text{m}^2 \text{s}^{-1}$]
D_P	particle diffusion [$\text{m}^2 \text{s}^{-1}$]
ΔH	heat of adsorption [J mol^{-1}]
i	component [-]
k	LDF coefficient [s^{-1}]
K_z	effective thermal conductivity [$\text{J m}^{-1} \text{s}^{-1} \text{K}^{-1}$]
P	pressure [bar]
q	solid phase loading [mol kg^{-1}]
r_P	particle radius [m^{-1}]
R_g	universal gas constant [$\text{J mol}^{-1} \text{K}^{-1}$]
t	time [s]
T	temperature [K]
ΔU	internal energy of adsorption [J mol^{-1}]
v	interstitial velocity [m s^{-1}]
y	composition in stream [-]
z	axial coordinate [-]

Greek Symbols

ϵ	voidage [-]
μ	viscosity [$\text{kg m}^{-1} \text{s}^{-1}$]

Abbreviations, Subscripts and Superscripts

Adj	adjusted
ADS	adsorption
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EVAC	evacuation
F	feed
FP	feed pressurization
H	high pressure
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L	low pressure
LR	light reflux
MAPLE	machine-assisted adsorption process learning and emulation
MFC	mass flow controllers
MFM	mass flow meter
MV	metering valve
MS	mass spectrometer
NSGA	non-dominated sorting genetic algorithm
Opt.	optimization
PT	pressure transmitter
PSA	pressure swing adsorption
PVSA	pressure vacuum swing adsorption
R	receiver
SSL	single-site Langmuir
SV	solenoid valve

VP	vacuum pump
VSA	vacuum swing adsorption