

Highlights

Integrated Material and Process Evaluation of Metal-organic Frameworks Database for Energy-efficient SF₆/N₂ Separation

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- Multi-scale screening approach including the molecular-level and process-level simulations
- Screening of 2,890 MOFs for SF₆/N₂ separation GCMC simulations
- 87 and 74 top-performing MOFs from GCMC simulations
- Top 3 MOFs from VSA and PSA compared under different pump efficiency scenarios
- Experimental isotherms evaluation of the performance with PSA process

Integrated Material and Process Evaluation of Metal-organic Frameworks Database for Energy-efficient SF₆/N₂ Separation

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Abstract

In this work, we proposed multi-scale screening, which employs both molecular and process-level models, to identify high-performing MOFs for energy-efficient separation of SF₆ and N₂ mixture. Grand canonical Monte Carlo (GCMC) simulations were combined with ideal adsorption process simulation to computationally screen 14,000 metal-organic frameworks (MOFs) for adsorptive separation of SF₆ N₂. More than 150 high-performing MOFs were identified based on the GCMC simulations at the pressure and vacuum swing conditions, and subsequently evaluated using the ideal adsorption process simulation. High-performing MOFs selected for the VSA conditions are able to achieve the 90 % target purity level of SF₆, but none of the selected

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MOFs for PSA conditions could. Cascade PSA configuration was proposed and adopted to improve the purity level of the separated SF₆. Cascade PSA configuration was also adopted to improve the purity. In the pump efficiency scenarios of 80, 20, and 10 %, the VSA and cascade PSA cases were compared. Top-performing MOFs identified from the multi-scale computational approach were found to be able to produce 90% purity SF₆ with 0.10 - 0.4 and 0.5 - 1.4 MJ per kg of SF₆ for VSA and PSA, respectively. We used experimental isotherm data available in the literature to evaluate the process-level performance of top-performing materials (HKUST-1, UiO-67) along with other materials (MIL-100(Fe), UiO-66, and zeolite-13X) with experimental isotherm data. We found that there is a reasonable agreement between using simulated and experimental isotherm data.

Keywords: SF₆, High-throughput Screening, Adsorption process

1. Introduction

As we transition from centralized power systems (such as coal-fired power plants) to more decentralized ones (such as solar and wind) to power the planet, it becomes critical to reliably and securely distribute the electricity to where it demands. The central to the electricity supply chain is the switchgear, and a recent report indicates that the market for the high-performing switchgear is expected to reach 152 billion dollar by 2029 [1]. The most effective form of the switchgear is the gas-insulated switchgear (GIS), where the conductors and contacts are insulated by pressurized dielectric gas,

such as sulfur hexafluoride (SF_6). The high dielectric strength of SF_6 makes the gas useful in GIS, where SF_6 is typically mixed with relatively cheap N_2 . However, SF_6 has been identified as one of the main greenhouse gases in the Paris Agreement[2] due to its high global warming potential (GWP: 22,800 - 23,900). According to a report Simmonds et al. [3], the global SF_6 emission was increased by roughly 260 % from 1978 to 2018, which emphasizes the severity of the problem. Because of this, the development of advanced materials and separation processes that can selectively and efficiently capture the SF_6 from SF_6/N_2 mixtures is necessary to reduce the emission of SF_6 from the distributed electrical transmission systems. Because of this, the development of advanced materials and separation processes that can selectively and efficiently capture the SF_6 from SF_6/N_2 mixtures is necessary to reduce the emission of SF_6 from the distributed electrical transmission systems.

Moreover, SF_6 feed often becomes SF_6/N_2 mixture during the blowing process. Therefore, effective separation and recovery of SF_6 from the SF_6/N_2 mixture is important for recycling the expensive SF_6 and preventing the release of strong greenhouse gas into the atmosphere [4]. The small device of the pressure swing adsorption process is widely used for the separation, directly attached to the GIS is widely used to achieve the separation[5].

Recently, a number of advanced materials and separation processes, such as adsorption-based and membranes-based methods [6, 7, 8], have been proposed in the literature as a promising method to perform the SF_6/N_2 separation. For the adsorption-based separation process, there are two represen-

tative modes of operation: 1) vacuum swing adsorption (VSA), where the gas is adsorbed at the feed pressure and desorbed below the pressure, and 2) pressure swing adsorption (PSA), where the compressed gas is adsorbed and desorbed at the lower pressure. The key performance indicators (KPIs), such as product purity and recovery, for these two modes of operation heavily depend on the choice of the adsorbent material, which necessitates the development of high-performing adsorbent materials, such as metal-organic frameworks.

Metal-organic frameworks (MOFs) are a class of nanoporous materials that find their application in modern engineering applications, such as gas storage and separation, catalysis, and chemical sensing [9, 10, 11]. Several MOFs have been reported in the literature for SF₆/N₂ separation application [12, 4, 13]. For example, Senkovska and coworkers have reported HKUST-1 showed the best performance in SF₆ separation (SF₆ uptake 120 cm³/g at 18 bar), whereas MIL-101 (SF₆ uptake 276 cm³/g at 18 bar) and DUT-9 (SF₆ uptake 275 cm³/g at 18 bar) had the highest storage capacities. Another study by Chuah and coworkers have reported modified hierarchically structured HKUST-1 with both very high SF₆ uptake (4.98 mmol·g⁻¹ at 25 °C and 1 bar) and SF₆/N₂ selectivity (around 70 at 25 °C). Kim and coworkers have reported a zirconium-based MOF, UiO-67, with high SF₆/N₂ selectivity (30 – 37 at 10 bar). Nevertheless, the number of MOFs evaluated for this application is limited, and their full potential as part of the process modeling has not been evaluated in the literature.

Toward this end, computational high-throughput screening combined with multi-scale modeling, which involves both molecular and process-level simulations, could be used to quickly identify high-performing MOFs from large material databases [14, 15]. Computational screening has been applied to discover high-performing MOFs for energy storage applications, such as methane [16] and hydrogen storage [17, 18, 19], CO₂ capture [9], isomer separation [20], among others [21]. In this work, we carried out high-throughput, multi-scale computational screening of CoRE MOF 2019 database [22] to identify the high-performing MOFs for the SF₆/N₂ separation. The data obtained from the molecular-level simulations were directly used for the process-level simulation to evaluate the process-level performance indicators, such as the product purity, recovery, and the energy consumption of the process per mole of produced SF₆, of MOFs for VSA and PSA operations. Moreover, we explored ways to increase the product purity of PSA operation by introducing a cascade PSA configuration to achieve 90% purity level of produced SF₆. Our multi-scale screening study was able to identify top-performing MOFs for SF₆/N₂ separation for VSA and PSA conditions. We found the MOFs that are optimal for VSA and PSA operations have different physical and chemical properties. Energy consumption analyses show that the VSA operation was able to produce 90% pure SF₆ with 0.1 - 0.4 MJ per kg of SF₆ for 74 MOFs (out of 87 MOFs). None of the MOFs identified from high-throughput screening (using selectivity and working capacity metrics) for PSA operation were able to meet the 90% pure SF₆. Instead, we were able to meet the

90% SF₆ purity level using the cascade PSA configuration, which uses two PSA trains in series. Cascade PSA was able to produce 90% pure SF₆ with 0.5 - 1.4 MJ per kg of SF₆ for 36 MOFs (out of 74 MOFs). Further analyses showed that the cascade PSA operation could be more energy efficient mode of operation than VSA operation depending on the efficiency of vacuum pump used for the operation. While none of the MOFs that emerged as the top-performing MOFs for VSA process from this work were synthesized and tested to date, UiO-67, UiO-66 and HKUST-1, which have been previously tested for the SF₆/N₂ separation application for both VSA and PSA conditions, were identified as the top-performing MOFs to perform the separation using cascade PSA.

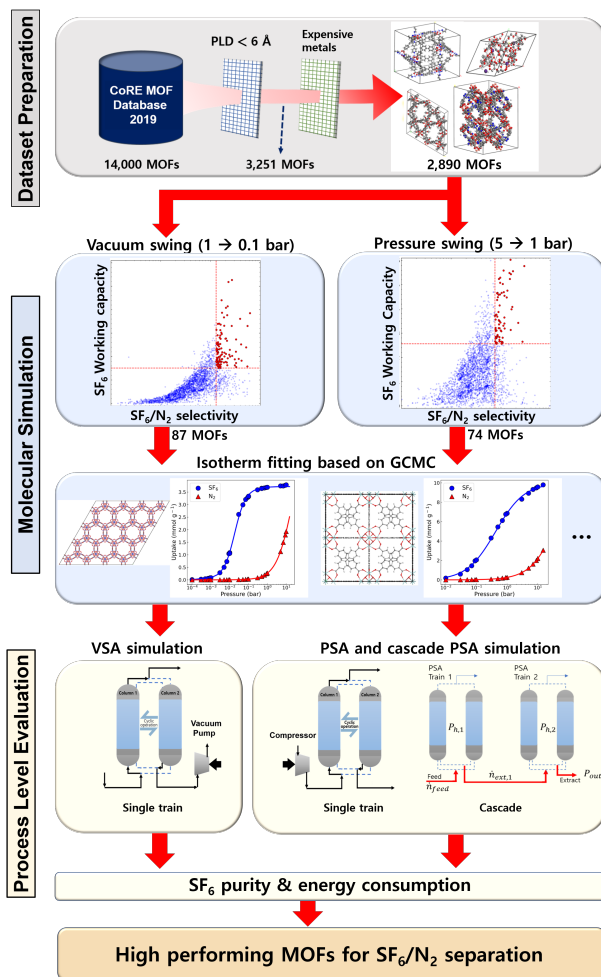


Figure 1: Computational workflow of high-throughput, multi-scale computational screening procedure employed in this work.

2. Computational Methods and Models

This section provides the procedure and methods of the adsorbent screening for MOFs. In Section 2.1, MOF CIF files were initially collected from the CoRE MOF 2019 database[22]. Two filtering criteria based on the pore limiting diameter (PLD) and the identity of metals were used to exclude the MOFs with pore limiting diameter (PLD) less than 6 angstrom and MOFs with expensive metals, which resulted in 2,890 MOFs. GCMC simulations were subsequently carried out on 2,890 MOFs to identify MOFs with high SF₆/N₂ selectivity and working capacity under VSA and PSA conditions. From the GCMC simulations, we identified 87 and 74 MOFs with high SF₆/N₂ selectivity and SF₆ working capacity under the VSA and PSA conditions. Single component GCMC simulations were additionally carried out for the 87 and 74 MOFs, and ideal VSA/PSA simulations were carried out on these materials to estimate the SF₆ purity and energy consumption under VSA/PSA conditions. e are selected by the in Section 2.5 to 2.9.

2.1. CoRE MOF database and Filtering Criteria

CIF files for MOFs and their physical properties were collected from CoRE MOF 2019 database[22]. To reduce the computational resources used for the screening, we first removed MOFs with the pore limiting diameter (PLD) smaller than 6 Å (which is slightly larger than the diameter of SF₆ model (5.6 Å) used in this work). We also removed MOFs with precious metals (see the Supplementary Information Table S1). Based on these two

filtering criteria, we arrived at 2,890 MOFs from 14,000 MOFs from the CoRE MOF 2019 database (Figure 1). We labeled each of 2,890 MOFs with a screening ID, and the screening ID is used throughout this work to identify a MOF. The high-throughput screening data and physical properties of all 2,890 MOFs are provided as a part of the Supplementary Information (HTS-result.csv).

2.2. Grand Canonical Monte Carlo (GCMC) Simulation

GCMC simulations were carried out to evaluate the SF₆ and N₂ adsorption properties of 2,890 MOFs using RASPA 2.0[23]. High-throughput GCMC simulations were carried out at fixed temperature 298 K with 1:9 SF₆ and N₂ mixture composition. For high-throughput screening, the SF₆ and N₂ mixture uptakes were calculated at three different pressure points – 0.1 bar, 1 bar and 5 bar. A GCMC simulation consists of 10,000 cycles for equilibration and 20,000 cycles for the ensemble averages, where a single cycle is equal to the number of adsorbate molecule in the system or 20 (whichever is greater). Translation, rotation, reinsertion and swap Monte Carlo moves were used with equal probabilities for sampling.

SF₆ (or N₂) working capacity and SF₆N₂ selectivity were calculated based on the GCMC simulation results. The working capacity, WC, was computed by taking the difference between the SF₆ or N₂ uptakes at the adsorption (1 bar for VSA and 5 bar for PSA) and desorption (0.1 bar for VSA and 1 bar for PSA) pressures (1):

$$WC = N_{ads} - N_{des} \quad (1)$$

Here, N_{ads} and N_{des} are the molecule loadings at the adsorption and desorption conditions. The selectivity between SF₆ and N₂, (α_{SF_6/N_2}) at the adsorption conditions (1 bar for VSA and 5 bar for PSA) was calculated using the following Eq. (2):

$$\alpha_{SF_6/N_2} = \frac{q_{SF_6}/q_{N_2}}{p_{SF_6}/p_{N_2}} \quad (2)$$

Here, q_{SF_6} and q_{N_2} are the uptake (mmol/g) of SF₆ and N₂, and p_{SF_6} and p_{N_2} are the partial pressure of SF₆ and N₂, respectively.

2.3. Force fields

The interaction between atoms in the systems were approximated with the van der Waals (vdW) interaction, which was modeled with the Lennard-Jones (LJ) 12-6 type Equation, Eq. (3). The interaction parameters between different atom types were approximated using the Lorentz-Berthelot mixing rules. A vdW cutoff distance of 12.8 Å was used to truncate the vdW interactions between atoms.

$$U_{ij} = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] \quad (3)$$

Here, U_{ij} is the interaction energy between atoms i and j , r_{ij} is the center-to-center distance between the two atoms. The LJ parameters for

all framework atoms were taken from the DREIDING force field[24]. If the atom types were not available in DREIDING force field, we have used the UFF force field [25]. The SF₆ molecule was modelled using a 7-site model from the work of J. Samios and coworkers[26]. The LJ parameter of N₂ was taken from the Transferable Potential for Phase Equilibria (TraPPE) force field[27]. All the LJ parameters are listed in the Table S2 and Table S3 of Supplementary Information.

2.4. Widom Particle Insertion

The heat of adsorption of SF₆ and N₂ for all MOFs were calculated using the Widom’s particle insertion method [28] as implemented in RASPA 2.0[23]. The affinity of a molecule with the framework can be expressed as the binding energy, or more generally, as the heat of adsorption at infinite dilution ΔH :

$$\Delta H = \Delta U - RT = U_{hg} - U_h - U_g - RT \quad (4)$$

where U is the internal energy, and U_{hg} , U_h , and U_g are the average internal energy of the guest molecule inside the host framework, the average internal energy of the host framework, and the average internal energy of the guest molecule, respectively. Since we used a rigid framework assumption, the average internal energy of the framework is zero. The internal energies of a molecule are also zero since the chemical bonds forming the adsorbates are fixed. The enthalpy of adsorption at infinite dilution is the difference

between the internal energy of a single molecule inside and outside the host framework.

2.5. Ideal Adsorption Process Simulation

In the studies focusing on optimizing or controlling a specific adsorption process with a single adsorbent, highly accurate model is important. However, because our study is about exploring hundreds or thousands of MOFs with limited information and limited computational resources, we focused more on how to screen out the MOFs based on the information we have and how to accelerate the computation for meaningful evaluation results.

We have resorted to using the simplified model that includes the most relevant information for the adsorption process modeling because of time and computational resource constraints to employ high-fidelity model for hundreds or thousands of MOFs. A high-fidelity model, which includes various parameters affecting the process performances, has been used in the literature [29][30]. However, only a small number of materials were evaluated so far and only for VSA operation. Besides the accuracy of those parameters used in the modeling, the high-fidelity model takes too much time to converge to obtain reasonable solutions. Because VSA and PSA processes typically operate in periodic cycles, the cyclic steady state (CSS) should be reached for a given operating condition by repeating the dynamic simulations. Moreover, optimizing the operating conditions for hundreds or thousands of MOFs requires significant computational resources. Depending on the process con-

figurations and adsorbents, severe numerical errors and convergence problems could occur, halting the whole evaluation procedure until these problems are addressed manually. In addition, even if we can consider more complicated aspects, some of those aspects cannot change the rankings of the MOFs.

Because of these reasons, we focused more on screening the MOFs based on the most critical information (e.g., adsorption isotherm data) to accelerate the computation that leads to a meaningful evaluation at the process level. A high-fidelity model may be employed for the top-performing materials identified from our screening to obtain a more accurate result in the future.

We adopted the ideal adsorption process concept, which has been recently proposed[31, 32], to quickly evaluate the upper limit performance of MOFs. The ideal adsorption process assumes optimal operation of the adsorption process so that the full potential of each MOF can be evaluated. Some key assumptions for the ideal adsorption process are:

- **Discrete pressure swing:** No loss in SF₆ purity and energy due to pressure gradient both across the cycle time and across the column, which leads to two operation steps (adsorption and desorption) for a single cycle.
- **Fast mass-transfer:** 100 % purity of raffinate (weakly adsorbing component stream) due to fast mass-transfer between bulk gas phase to adsorbed phase.
- **Isothermal operation:** Heat generated from adsorption is neglected.

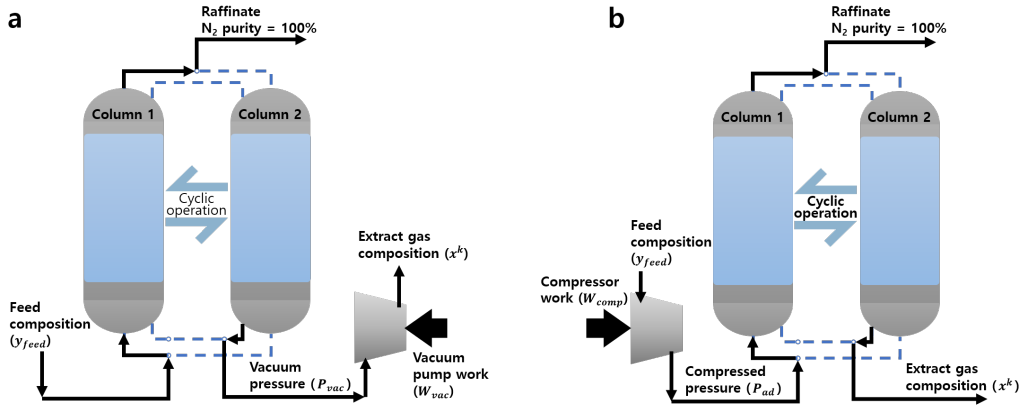


Figure 2: (a) Ideal VSA and (b) Ideal PSA progress diagram and key state variables

Figure 2 shows the cyclic operation of VSA and PSA process configurations that we considered in this work. For the VSA, a vacuum pump is located at the end of the process while for the PSA, a compressor is located at the beginning of the process configuration. Figure 2 (a) and (b) show the VSA and PSA operations where N_2 is produced as the raffinate stream, and the product SF_6 is produced as the extract stream. Note that N_2 component is also present in the extract stream as well since some N_2 molecules are adsorbed onto the MOFs along with SF_6 . In both VSA and PSA operations, two columns operate asynchronously in which the adsorption/desorption operations are occurring at the same time, and the cyclic steady-states (CSS) in both columns are assumed for both columns as part of the ideal adsorption process consideration. For both operations, two columns filled with the same MOFs are used for the simulation. During the adsorption period, all SF_6 and small amount of N_2 are trapped in the column while pure N_2 is

produced as the raffinate. This is because SF₆ is more strongly adsorbing component than N₂. During the desorption period, the trapped SF₆ and N₂ desorb from the MOFs and exit the column as the extract.

The mixture adsorption isotherm data at different bulk phase gas compositions are necessary to evaluate the performance of MOFs at the process-level. Single-component GCMC simulations were carried out for SF₆ and N₂ from 0.01 bar to 10 bar at 298 K. All the calculated GCMC isotherm data points were fitted using open-source python package, pyIAST[33] with following isotherm models expressed with Eq. (5) and Eq. (6):

$$\textit{Langmuir} : q = M \frac{Kp}{1 + Kp} \quad (5)$$

$$\textit{Quadratic} : q = M \frac{(K_a + 2K_b p)p}{(1 + K_a p + K_b p^2)} \quad (6)$$

Here, q is the uptake and p is the pressure of the system. (M, K) are the isotherm parameters for the Langmuir model and (M, K_a, K_b) are for the quadratic model.

We choose the Langmuir and/or Quadratic models because these two models provide robust convergence during the model fitting. In pyIAST, a limited number of isotherm models are available, and not all the models lead to convergent behavior during the fitting process. Since we cannot individually deal with the convergence issue due to the large amount of isotherm data, we tested different models to compute the errors. From our testing, we

found that the Langmuir and Quadratic models lead to good fitting results with an average root-mean square error (RMSE) value of 0.0417 and less than 0.3 RMSE for all data tested in this work.

The isotherm models and parameters of SF₆ and N₂ were combined with ideal adsorbed solution theory (IAST) to model the mixture adsorption uptake of a MOF at different bulk phase gas composition[34]. Between the two models, a model with the smaller RMSE was selected for the process-level simulation.

All the fitted parameters are provided as part of the the Supplementary Information.

2.6. Derivation of Product Purity and Sensitivity Analyses

To evaluate the process-level performance of a MOF, we used SF₆ purity and the energy consumption per unit SF₆ as the key performance indicators (KPIs). Using the ideal adsorption process formalism, we derive the composition of the extract to determine the SF₆ purity for a given MOF k (\mathbf{x} in Figure 2). For simplicity, we omitted the superscript k throughout the section for clarify.

In the bulk gas phase with n components, the mole fractions of each gas component i is represented by an element of \mathbf{x} vector:

$$\mathbf{x} \equiv (x_1, x_2, \dots, x_n) \tag{7}$$

For the binary component of SF₆ and N₂ mixture, we could further sim-

plify the above expression in terms of the mole fraction of SF₆ (x_1):

$$\mathbf{x} = (x_1, 1 - x_1) \quad (8)$$

where, x_1 is the bulk gas phase mole fraction of SF₆, which is equivalent to the SF₆ composition of the extract stream (i.e., SF₆ purity).

The bulk gas phase mole fractions of all components can be determined based on the feed and operating conditions. Feed conditions include feed composition and temperature (y_{feed}, T_{feed}), and the operating condition is the pressure the adsorption column undergoes.

In both ideal VSA and PSA operations, the system goes through the pressure swing between P_h and P_l while the other operating conditions, such as the feed velocity and step time, are assumed to be optimized at the fixed pressure swing range. In the VSA process, the vacuum pressure (P_{vac}) created by the vacuum pump is used for the low pressure (P_l) while 1 bar is used for the high pressure (P_h). For the PSA process, the adsorption pressure (P_{ads}) made by the compression of the feed flow is used for the high pressure (P_h) while the 1 bar is used for the low pressure (P_l).

The gas uptakes at adsorption/desorption conditions are based on the mixture isotherm function, $f_{iso,i}(\cdot)$.

$$q_{ads,i} = f_{iso,i}(y_{feed}, P_h, T_{feed}) \quad (9)$$

$$q_{des,i} = f_{iso,i}(\mathbf{x}, P_l, T_{feed}) \quad (10)$$

For the mixture isotherm, the IAST calculations of i component ($f_{iso,i}$) were carried out based on the following equations :

$$\pi_i(P_i^o) \equiv RT \int_P^{P_i^o} \frac{f_i^o(P, T)}{P} dP \quad (11)$$

$$x_i^{solid} \times P_i^o = P_i \quad (12)$$

$$\pi_1(P_1^o) = \pi_2(P_2^o) \quad (13)$$

$$\frac{1}{q_{tot}} = \sum_{i=1}^2 \frac{x_i^{solid}}{f_i^o(P_i^o, T)} \quad (14)$$

$$q_i = q_{tot} \times x_i^{solid} \quad (15)$$

Using the definition of *spreading pressure* (π_i^o) of Eq. (11), all the mole fractions of component i could be obtained via Eq. (12) and Eq. (13), and the obtained values lead to the uptake values with Eq. (14) and Eq. (15). These equations of IAST convert the pure isotherm models ($f_{iso,i}^o$) into the mixture isotherm model ($f_{iso,i}$), which indicates the procedure to find the uptake (q_i) satisfying the above equations. During the procedure, the recursive computations are required for solid phase mole fraction (x_i^{solid}) satisfying both Eq. (12) and Eq. (13). In the procedure, the hypothetical

pressure, partial pressure of each component, and total uptake are expressed with P_i^o , P_i and q_{tot} . In the above equations, R and T indicate gas constant and temperature. The thermal effect on the isotherm are generalized based on Clausius-Clapeyron equation [35]. More detailed expression is in Eq. (S1) and Eq. (S2) of Supplementary Information.

Note that during the adsorption period, the uptake in a MOF is defined as a function of feed flow mole fraction (y_{feed}) while the gas uptake at the desorption period is a function of bulk gas phase mole fraction (\boldsymbol{x}) to account for the equilibrium between the bulk gas phase and the residual gas remained in the adsorbed phase (i.e., inside the MOF). Since the feed and operating conditions are fixed during the CSS operation for ideal VSA and PSA simulations, we assume the following variables, y_{feed} , T_{feed} , P_{high} , P_{low} , are constant.

Based on the material balance, the uptake difference of component i in a MOF between the adsorption and desorption periods provides us with the information about amount of component i in the bulk gas phase during the desorption period. For component i , we could formally defined the uptake difference as:

$$\Delta q_i \equiv q_{ads,i} - q_{des,i} \quad (16)$$

Note that the uptake difference is not equivalent to the working capacity in that the uptake difference defined here accounts for different partial pres-

tures of SF₆ and N₂ at the desorption period. Here, $q_{ads,i}$ and $q_{des,i}$ are the adsorbed amount of component i in a MOF at adsorption and desorption conditions, respectively.

Next, we define the sum of the uptake difference between the two periods of all components, which is equivalent to the total amount of gas in the bulk gas phase during the desorption period, as following:

$$\Delta q_{tot} = \sum_{j=1}^2 \Delta q_j \quad (17)$$

From this expression, we can define the SF₆ purity (x_1) as the ratio of amount of SF₆ in the bulk gas phase (Δq_1) and the total amount of all components in the bulk gas phase during the desorption period as in Eq. (18):

$$x_1 = \frac{\Delta q_1}{\Delta q_{tot}} \quad (18)$$

To express a single cycle operation, a function for the extract composition of SF₆ (x_1) can be expressed as a function of the extract composition (\mathbf{x}) as follows:

$$h_1(\mathbf{x}) \equiv \frac{f_{iso,1,ads} - f_{iso,1,des}(\mathbf{x})}{f_{iso,1,ads} - f_{iso,1,des}(\mathbf{x}) + f_{iso,2,ads} - f_{iso,2,des}(\mathbf{x})} \quad (19)$$

Note that $f_{iso,1,ads}$ and $f_{iso,2,ads}$ are constants. To find the CSS condition (i.e., after repeated adsorption/desorption periods), we need to recursively call the function, $h(\mathbf{x})$ as in Eq. (20):

$$x_1 = h_1(h_1(\dots h_1(\mathbf{x}))) = h_1 \circ h_1 \circ \dots h_1(\mathbf{x}) \quad (20)$$

In the case for SF₆ and N₂, we need to consider two functions (h_1 and h_2) simultaneously. For the multi-component case (where $n > 2$), we should compute the mole fraction of all components using $n - 1$ number of Eq. (20), namely x_i for $i = 1, 2, \dots, n$, simultaneously.

For all gas components, we can write down H as follows:

$$\mathbf{x} = H \circ H \circ \dots H(\mathbf{x}) \quad (21)$$

To find the solution of Eq. (21), we employed the least-square optimization methods as implemented in the SciPy[36] with the formulation of Eq. (22):

$$\min_{\mathbf{x}} \|\mathbf{x} - H(\mathbf{x})\|_2^2 \quad (22)$$

$$\text{s.t. } \sum_{i=1}^n x_i = 100\% \quad (23)$$

Note that both VSA and PSA processes share the same equations for the composition of the extract stream produced during the desorption period.

Jupyter Notebook with analyses code and data are available as part of the Supplementary Information.

The above procedure discusses the numerical approach to locate the CSS for a given adsorbent and a given mode of operation (VSA or PSA). During the operation of VSA/PSA process, the previous cycle operation affects the next cycle operation as the initial condition. For example, higher solid phase concentration after the previous cycle hinders the next cycle adsorption whereas too low solid phase concentration encourages to capture more gas molecules. As the cycle continues, the state variables (e.g., solid/gas concentrations) converge to a certain point, and the system is deemed to have reached the CSS. Since cyclic swing adsorption processes normally operate under the CSS conditions, the performance of MOFs must be evaluated under the CSS condition. The Eq. (20) and (23) discuss the numerical approach to find each CSS for a given operating condition, and their results (e.g., desorption/adsorption pressures) are used to optimize the operating conditions of the VSA and PSA processes through Eq.(26) and (29).

2.7. Energy Consumption

The energy consumption to produce the desired product is directly related to the cost of the process operation. Energy consumption levels for the VSA and PSA were evaluated to compare the energy efficiency of these operations to produce 90 % purity SF₆. For the SF₆ separation case, several modifications to the original method from Ga and co-workers[31] were made

for both extract composition and energy consumption.

The key modification to the original method is the consideration of vacuum pump and compressor location (depending on the VSA and PSA). For example, different types of pressure driving equipment are required for VSA and PSA operations. Vacuum pump is required during the desorption period of the VSA operation while the compressor is required during the adsorption period of the PSA operation. Note that for the PSA operation, a compressor is located before the adsorption column so that the feed gas to the adsorption column is compressed, and then injected to the column. For the VSA operation, a vacuum pump is located after the column. The energy consumption required to produce a mole of SF₆ was calculated using the Eq. (24) and Eq. (25), for vacuum pump and compressor, respectively.

$$\begin{aligned} \frac{W_{vac}}{x_{SF_6} \dot{n}_{ext}} &= \frac{1}{x_{SF_6} \dot{n}_{ext}} \frac{\dot{n}_{ext} RT}{\eta_{isen}} \left(\left(\frac{P_h}{P_l} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \\ &= \frac{1}{x_{SF_6}} \frac{RT}{\eta_{isen}} \left(\left(\frac{P_h}{P_l} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \end{aligned} \quad (24)$$

where,

$$P_h = P_{feed},$$

$$P_l = P_{vac}$$

$$\begin{aligned}
\frac{W_{comp}}{x_{SF_6}\dot{n}_{ext}} &= \frac{1}{x_{SF_6}\dot{n}_{ext}} \frac{\dot{n}_{feed}RT}{\eta_{isen}} \left(\left(\frac{P_h}{P_l} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \\
&= \frac{1}{y_{feed}} \frac{RT}{\eta_{isen}} \left(\left(\frac{P_h}{P_l} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right)
\end{aligned} \tag{25}$$

where,

$$P_h = P_{ads},$$

$$P_l = P_{feed}$$

In Eq. (24) and Eq. (25), γ , η_{isen} , R and T are isentropic expansion factor (dimensionless), isentropic efficiency (dimensionless), gas constant (J/mol·K) and temperature (K), respectively. Using the ideal adsorption process formalism with 100 % purity of raffinate component and conservation of mass ($x_{SF_6}\dot{n}_{ext} = y_{feed}\dot{n}_{feed}$), the extract flowrate terms are cancelled out in Eq. (24) and Eq. (25). The energy per separated SF₆ defined here is independent of the process scale. Note that due to the compression (from compressor) and expansion (from vacuum pump) the column is operated at 313 K instead of 298 K for both PSA and VSA operations.

Decision variable	Symbol	Lower bound	Upper bound.
Vacuum pressure	P_{vac}	0.001	0.316

2.8. Optimization of VSA Operation

The required energy to separate SF₆ at the target purity (90%) was evaluated for the VSA process. The optimal desorption pressure was found for each MOF by minimizing the vacuum pump energy input with the purity constraint (i.e., 90 % SF₆ purity). Using the Eq. (7 - (23), the optimization problem can be expressed as Eq. (26) with decision variables and their upper/lower bounds listed in Table 1.

$$\begin{aligned}
 \min_{P_{vac}} \quad & \frac{W_{vac}}{x_{SF_6} \times \dot{n}_{ext}} \\
 \text{s.t.} \quad & \\
 & x_{SF_6} \geq 90\%
 \end{aligned} \tag{26}$$

2.9. Optimization of Cascade PSA Operation

For cascade PSA process, we defined $H_{css}(\cdot)$ as a solution of Eq. (22) and Eq. (23). Since the extract from the first train is used as an input to the compressor for the second train, and these two trains are in CSS, we need to solve for the extract compositions from two trains in series. From the feed composition, the extract composition of the first PSA train (x_{1st}) was obtained with Eq. (27), and the purity value was used in the second PSA process, calculating the second PSA purity (x_{2nd}) with Eq. (28).

Table 2: Decision variables and their bounds for the optimization of the cascade PSA operation.

Decision variable	Symbol	Lower bound	Upper bound
First PSA pressure	$P_{h,1}$	2.5	30
Second PSA pressure	$P_{h,2}$	2.5	30

$$x_{1st} = H_{css}(y_{feed}, T_{feed}, P_{h,1}, P_{low}) \quad (27)$$

$$x_{2nd} = H_{css}(x_{1st}, T_{feed}, P_{h,2}, P_{low}) \quad (28)$$

In these equations, the operating pressure employed for each PSA train is marked with $P_{h,1}$ and $P_{h,2}$ for the first and second train, respectively.

We compute the optimal combination of first and second train pressures that minimizes the energy consumption that satisfies the 90 % SF₆ purity constraint. This optimization problem could be expressed using Eq. (29) with the decision variables and their bounds listed in Table 2:

$$\begin{aligned} \min_{P_{h,1}, P_{h,2}} \quad & \frac{W_{comp,1} + W_{comp,2}}{x_{2nd} \times \dot{n}_{ext,2}} \\ \text{s.t.} \quad & \\ & x_{2nd} \geq 90\% \end{aligned} \quad (29)$$

Eq. (30) and Eq. (32) were used to calculate the energy consumption levels of the first and second PSA train ($W_{comp,1}$, $W_{comp,2}$).

The key parameters are used as displayed in Figure 6: SF₆ purity at the first and second PSA trains (x_{1st} , x_{2nd}), flowrates at feed and extract flows

in the first and second PSA trains (\dot{n}_{feed} , $\dot{n}_{ext,1}$, $\dot{n}_{ext,2}$). There are also SF₆ composition in the feed flow (y_{feed}), isentropic efficiency of the compressor (η_{isen}), isentropic expansion factor (γ), gas constant (R), and temperature (T).

$$\frac{W_{comp,1}}{x_{2nd}\dot{n}_{ext,2}} = \frac{1}{x_{2nd}\dot{n}_{ext,2}} \frac{\dot{n}_{feed} RT}{\eta_{isen}} \left(\frac{\gamma}{\gamma-1} \right) \left(\left(\frac{P_{h,1}}{P_{inlet}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (30)$$

$$= \frac{1}{y_{feed}} \frac{RT}{\eta_{isen}} \left(\frac{\gamma}{\gamma-1} \right) \left(\left(\frac{P_{h,1}}{P_{inlet}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (31)$$

$$\frac{W_{comp,2}}{x_{2nd}\dot{n}_{ext,2}} = \frac{1}{x_{2nd}\dot{n}_{ext,2}} \frac{\dot{n}_{ext,1} RT}{\eta_{isen}} \left(\frac{\gamma}{\gamma-1} \right) \left(\left(\frac{P_{h,2}}{P_{inlet}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (32)$$

$$= \frac{1}{x_{1st}} \frac{RT}{\eta_{isen}} \left(\frac{\gamma}{\gamma-1} \right) \left(\left(\frac{P_{h,2}}{P_{inlet}} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (33)$$

$$\begin{aligned} y_{feed,1st}\dot{n}_{feed} &= x_{1st}\dot{n}_{ext,1} \\ &= x_{2nd}\dot{n}_{ext,2} \end{aligned} \quad (34)$$

Using the ideal adsorption process assumptions and the mass conservation of SF₆ (34), the effect of flowrate could be removed from the equation, and the energy consumption could be expressed only as a function of each pressure ($P_{h,1}$ and $P_{h,2}$) as Eq. (31) and Eq. (33).

3. Results and Discussion

3.1. High-throughput Computational Screening

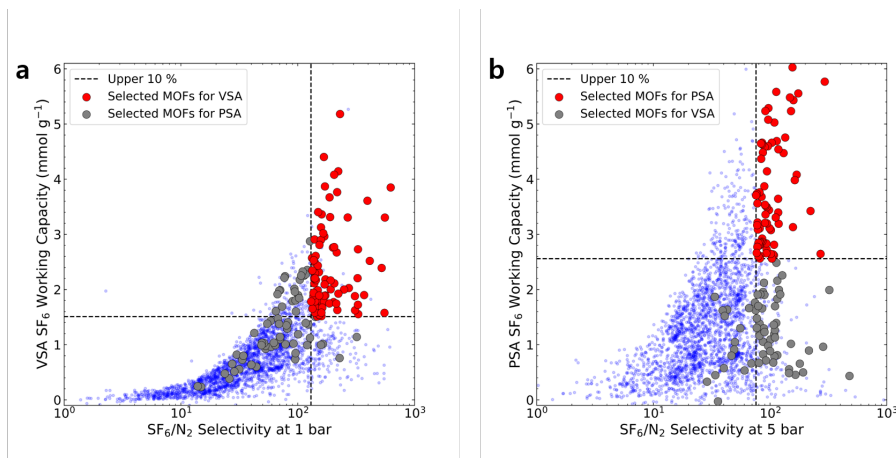


Figure 3: High-throughput computational screening (HTS) results for 2,890 MOFs. The potential targets for (a) VSA (1 bar \rightarrow 0.1 bar at 298 K for SF₆ working capacity) and (b) PSA (5 bar \rightarrow 1 bar at 298 K for SF₆ working capacity). The criteria were upper 10 % of both SF₆ working capacity and SF₆/N₂ selectivity.

In order to identify high-performing MOFs for the separation, we used the performance metrics, such as selectivity and working capacity, that are commonly used in the literature. Figure 3 shows the high-throughput GCMC simulation results for 2,890 MOFs. From these results, we selected the top 10 % MOFs based on the SF₆/N₂ selectivity and SF₆ working capacity at VSA and PSA conditions. The top-performing MOFs for VSA operation have high SF₆/N₂ selectivity in range of 130 - 624 (at 1 bar), and the working capacity in the range of 1.5 - 5.2 mmol/g. For PSA operation, the SF₆/N₂ selectivity is in the range of 76 - 293 (at 5 bar) while the SF₆ working capacity is in the range of 2.7 - 6.4 mmol/g. The number of top-performing MOFs for

VSA and PSA conditions are 87 and 74, respectively, and these MOFs were further evaluated using the process-level simulation. Note that none of the MOFs in top 10 % of VSA condition overlaps with the top 10 % materials from PSA condition.

3.2. Performance Evaluation based on Ideal PSA and VSA Simulations

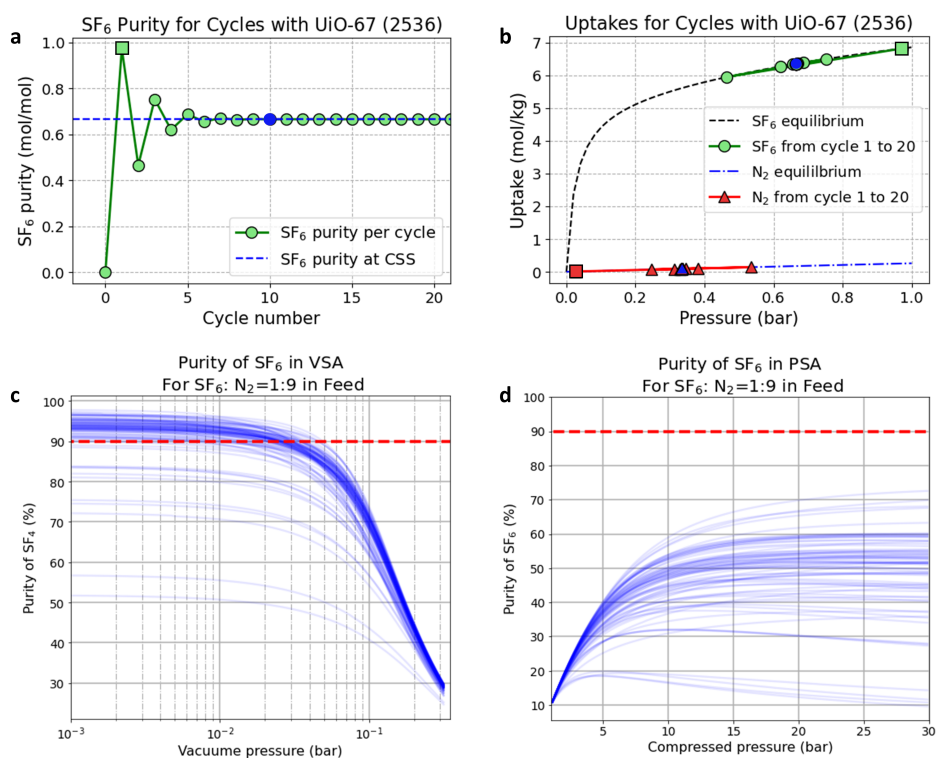


Figure 4: (a) SF₆ purity computed for each cycle of the ideal PSA process with UiO-67 (Screening ID: 2536) (b) SF₆ and N₂ uptake varying for cycles with UiO-67, whose first and 0.1 % CSS points are marked with square and blue markers, respectively (c) Ideal VSA and (d) Ideal PSA simulation results for the potential MOFs. SF₆ purity (%) at the raffinate.

For practical purposes, the performance evaluation metrics used for the screening should, in principle, correlate with the performance of MOFs in

the actual PSA and VSA processes. For binary gas separation cases, the selectivity and working capacity have been used frequently in the literature [37, 38, 39], but recent studies have shown that these commonly used metrics do not necessarily reflect the performance of MOFs at the process-level [40, 41, 42, 32]. We adopted an ideal VSA/PSA process simulation method to quickly evaluate the performance of MOFs at the process-level. The ideal VSA or PSA process simulation that we employed in this work provides what would be an upper bound performance that a MOF could physically achieve.

Figure 4 (a) and (b) show an example of the ideal adsorption process simulation for a given MOF. Here, the bulk gas phase concentration (Figure 4 (a)) and the adsorbed phase uptakes (Figure 4 (b)) after the first cycle are labeled with square markers, and the data points corresponding to the earliest cycle that satisfies 0.1 % CSS condition are colored in blue. At the first desorption step (i.e., end of the "first" cycle), the purity of SF₆ is close to 100 %. This is because there is not much N₂ adsorbed onto the MOF, and the extract initially contains highly concentrated SF₆. However, as the system reaches the CSS, the bulk phase SF₆ concentration (i.e., SF₆ purity) decreases from the initial concentration and reaches a steady-state value.

The calculations were repeated at different desorption pressure (up to 0.001 bar) and adsorption pressure (up to 30 bar) for all 87 MOFs and 74 MOFs for VSA and PSA, respectively. The results of the ideal VSA and PSA simulations for MOFs are shown in Figure 4 (c) and (d). For the VSA process, we find that the SF₆ purity increases as we apply more vacuum to the

system. Some MOFs show larger increase in SF₆ purity than the other MOFs as we pull more vacuum. Considering that a higher vacuum level requires more energy input to the VSA system, our results suggest that there could be a trade-off between the SF₆ purity and the energy consumption. The purity-energy diagram is in Figure S8 in Supplementary Information.

Figure 4 (d) shows the results of the PSA process. In this operation, the compressed pressure is the manipulating variable for the operation. Similar to the VSA operation, we find that the higher (instead of lower vacuum in the VSA) compressed pressure typically yields a higher SF₆ purity for the PSA process. However, we found the SF₆ purity of a few MOFs starts to decrease as we further increase the compression pressure. This is likely due to the rate of N₂ uptake swing increment is larger than that of SF₆, which originates from the fact that the SF₆ isotherms of these MOFs saturate early at relatively low pressure while the N₂ isotherms gradually increase.

From the simulation results shown in Figure 4 (c) and (d), we found 74 out of 87 MOFs could achieve the 90 % SF₆ purity for VSA. However, none of the MOFs was able to achieve the target purity with a single PSA train. This is striking because the selectivity and working capacity of the selected MOFs in each VSA and PSA have similar (Figure 3 and Supplementary Information Figure S1 to S3) values but some of the MOFs were able to meet the process target while the others were not able to do so.

We compared if the purity rankings of MOFs changes as we change the operating conditions for VSA and PSA. The Spearman's ranking correlation

coefficients (SRCCs) were calculated between 0.001 bar and 0.1 bar for VSA and between 5 bar and 30 bar for PSA. We found the SRCC for VSA and PSA are high (0.872 for VSA and 0.918 for PSA) suggesting that the purity rankings of these MOFs do not change as we change the operating conditions (Supplementary Information Figure S4).

3.3. Energy Consumption: Ideal VSA Process

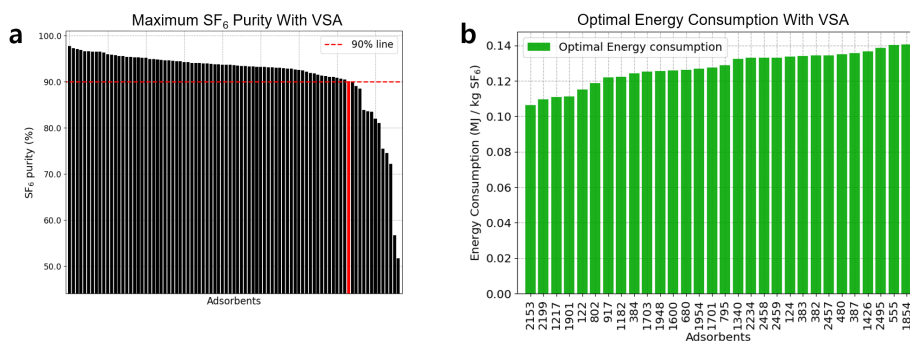


Figure 5: (a) Maximum SF₆ purity of each adsorbents in an ideal VSA process with desorption pressure ranging 1 mbar to 0.316 bar (b) Energy consumption with optimal operation of VSA for the selected adsorbents having over 90% maximum SF₆ purity

Figure 5 (a) shows the maximum SF₆ purity that can be reached under the ideal VSA process. Here we find 74 out of 87 MOFs could reach beyond the 90 % purity level. Since the SF₆ purity is a continuous function with respect to the vacuum pressure, we could instead change the operating pressure to produce the 90% target purity while reducing the energy consumption of the vacuum pump. Figure 5 (b) shows the optimal energy consumption required to produce 90% of target SF₆ purity under VSA condition. The energy consumption levels of different MOFs were computed and compared at

their optimal pressure swing ranges. For top-performing MOFs, the range of energy consumption required to produce 90 % purity level for the VSA is 0.10 - 0.14 MJ per kg of SF₆. The detailed information about the top-performing MOFs are provided in Table S4 in the Supplementary Information.

3.4. Cascade PSA Process

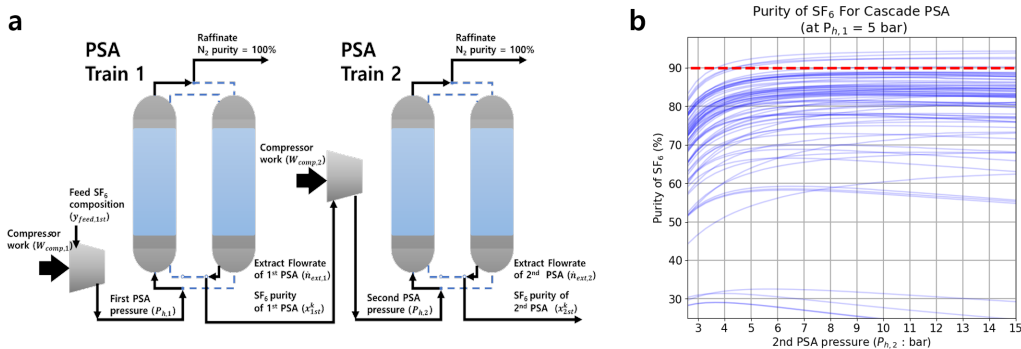


Figure 6: (a) Process flow diagram of the cascade PSA process and its key variables and (b) SF₆ purity from 74 MOFs in the extract flow of the second PSA train with different 2nd train pressure

We found that none of the high-performing MOFs identified from the high-throughput computational screening were able to separate SF₆ with 90% purity with a single train PSA process while many of the MOFs were able to meet the target with VSA process. In order to achieve the target SF₆ purity with PSA, we considered using two PSA trains in series (Figure 6 (a)) as an alternative strategy. The cascade configuration is advantageous because the configuration could be used achieve the target SF₆ product purity. In this configuration, the extract flow from the first train enters the second train with slightly increased SF₆ concentration, which allows the in-

creased purity of the extract flow in the second train. Another more subtle (but important) advantage is that the cascade configuration could reduce the energy consumption per kg of SF₆ by taking smaller pressure ratios of the two compressors. The optimal pressure combination that minimizes the energy consumption could be found using the equations (26) - (33).

We carried out the cascade PSA simulation on the 74 MOFs. We fixed the pressure of the first PSA train at 5 bar while varying the second PSA pressure ($P_{h,2}$) from 2.5 to 15 bar. The maximum SF₆ purity values of the 74 MOFs were found using the cascade PSA configuration with a 10:90 SF₆/N₂ mixture in the feed flow at 313 K immediately after the first compressor. The heat exchanger was used with 298 K cooling water and a 15 K minimum temperature difference approach was used to remove the heat of compression within the compression system. The same approach was used for the feed flow from the first train to the second train with different feed flow composition to the second train. We explored both pressure directions by setting the first and second PSA pressures between 2.5 and 20 bar.

Figure 6 (b) shows the results of the cascade PSA process. The SF₆ purity of the 74 MOFs are shown for a given range of the second PSA train pressure. Similar to the single train PSA, most of the curves exhibit the purity increase as the operating pressure increases. We also found few MOFs that show decrease in the SF₆ purity with increasing pressure after a certain pressure point, indicating that there is a purity maximum with the cascade PSA configuration for some MOFs. Using this configuration, 36 out of 74

MOFs were able to meet the target SF₆ purity level (90%).

3.5. Energy Consumption: Cascade PSA Process

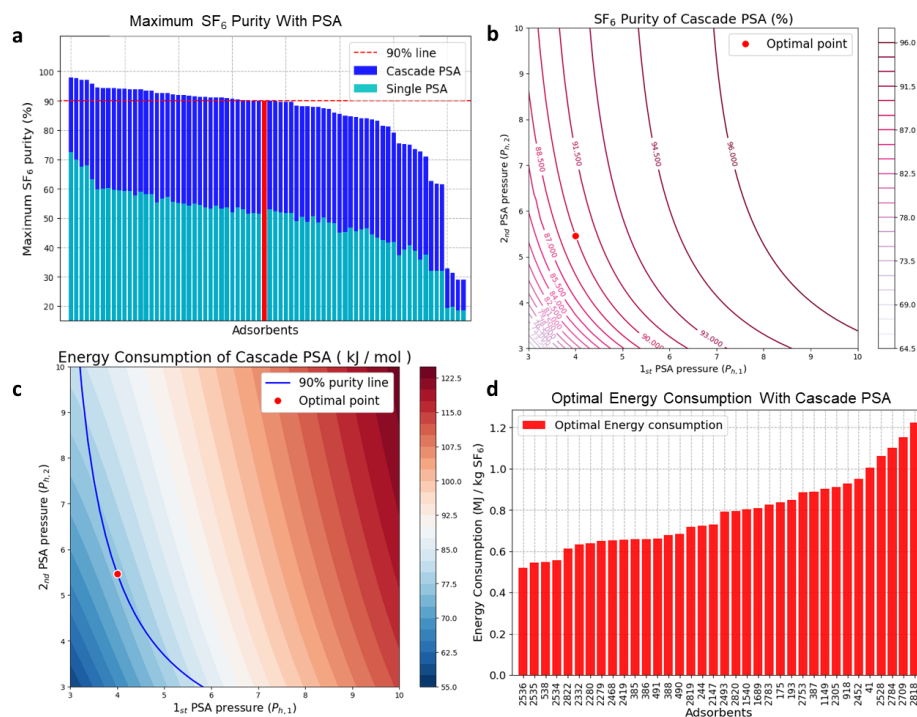


Figure 7: (a) Maximum SF₆ purity achievable with different MOFs in a cascade PSA process (blue) and in a single PSA process (cyan). 90% of target purity is shown in red dotted line; (b) an example contour plot for UiO-67 with different combinations of PSA pressures and corresponding SF₆ purity; (c) an energy consumption contour map of a cascade PSA for UiO-67 (screening ID: 2536) with varying pressure combinations with 90 % purity line (blue line) and the optimal operating condition (red dot); (d) Energy consumption of the cascade PSA process with each optimal operation for 36 MOFs.

Figure 7 (a) shows the results from both single PSA and cascade PSA operations where the maximum purity values between the two operations are compared. We found that the cascade PSA operation leads to improved purity values compared to the single PSA operation. The average purity of

the MOFs increased from 78.54% to 92.94%. For all the MOFs that were not able to reach the 90% target purity with a single train PSA, we discovered some MOFs have the maximum purity values exceeding the target with the cascade PSA operation. We calculated the energy consumption of the cascade PSA operation for 36 MOFs that were able to achieve the 90 % target purity level.

To illustrate how the optimization in the cascade PSA operates, the steps to find the optimal pressure combination that minimizes the energy consumption for UiO-67 (Screening ID: 2536) is shown in Figure 7 (b) and (c). Figure 7 (b) shows the SF₆ purity for varying pressure points. In the variable space, the feasible region is obtained based on the purity constraint in which the boundary is drawn with blue line as shown in Figure 7 (c). Among the feasible points in the region, the least energy consuming condition (i.e., pressure) is selected (red dot). The optimization results of all 36 MOFs are displayed in Figure 7 (d).

3.6. Comparison between VSA and PSA with Different Isentropic Efficiencies

We compared the results of VSA and cascade PSA processes. Because the VSA process has a pressure driving equipment at the extract gas, less amount of flowrate needs to be processed, which is advantageous when it comes to the energy consumption in the separation system. However, the use of strong vacuum is less preferable in the industrial application because

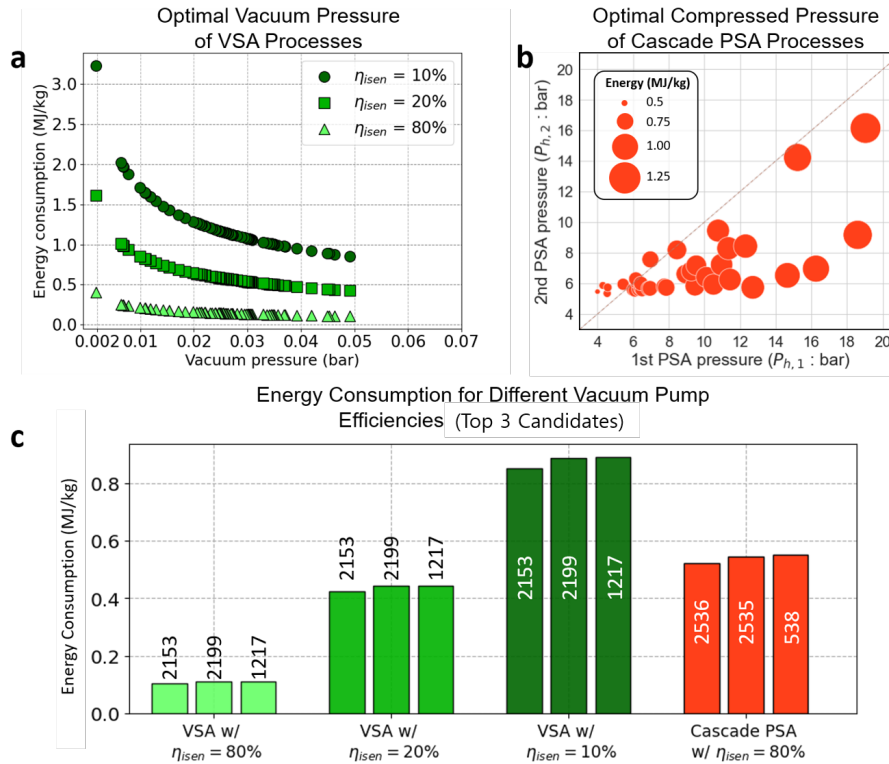


Figure 8: (a) Optimal vacuum pressure and energy consumption for 74 MOFs. 80, 20, 10 % isentropic efficiency results are marked with light green triangles, normal green squares, and dark green circles, respectively; (b) Optimal compressed pressures and energy consumption for the first and the second PSA trains for 36 MOFs; (c) Comparison of the energy consumption values for different vacuum pump efficiencies.

the strong vacuum is known for its low energy efficiency [43, 44, 45]. This can be worse when the pressure ratio becomes higher. On the the contrary, the PSA process uses a compressor with less pressure ratio, which contributes its favorable application to various areas. Still, the compressor should deal with a large flowrate because it is located before the PSA column. This means the PSA process spends more energy for compressing the N_2 than SF_6 .

Figure 8 (a) and (b) show the optimal operating pressures. As discussed

previously, each MOF has a pressure point that minimizes the energy consumption with respect to the 90% purity constraint. Figure 8 (a) shows the optimal pressure is distributed between 2 mbar to 0.05 bar for all MOFs that could achieve the 90% purity target with 0.1 - 0.4 MJ per kg of SF₆. The optimal pressure values of the cascade PSA process are shown in Figure 8 (b). The size of each point reflects the degree of energy consumption of a MOF for a given pressure combination. While the pressure ratio for the vacuum pump (VSA) is between 15 and 200, the pressure ratio for the compressor (cascade PSA) is between 4 and 20. We can see that the VSA process requires higher pressure ratio for the operation, which indicates that the system has less isentropic efficiency.

To consider the effect of isentropic efficiency for the VSA process, we computed the energy consumption of the VSA process with different isentropic efficiency scenarios, and the results were compared with the cascade PSA results. Figure 8 (a) shows the results with 80, 20, 10% isentropic efficiencies. Three top-ranked MOFs with 80, 20, 10% efficiency scenarios from the VSA process are displayed with the best performing MOFs from the cascade PSA process. In 80% and 20% scenarios, the energy required to separate SF₆ with a VSA process is lower than that of the cascade PSA case. However, when the isentropic efficiency is assumed 10%, the cascade PSA process outperforms the VSA process, showing lower required energy than that of the VSA process.

Table 3: Physical properties and their KPIs of Top 10 MOFs for optimized VSA condition.

Screening ID	LCD (Å)	PLD (Å)	SF ₆ Heat of Adsorption (kJ/mol)	Surface Area (m ² /g)	SF ₆ /N ₂ Selectivity (1 bar)	SF ₆ WC (1 - 0.1 bar) (mmol/g)	VSA Energy Consumption (MJ/kg)	References
2153	8.4	6.7	32.6	1313	325	2.2	0.1035	Ding et al. 2015[46]
2199	7.2	6.1	24	2121	413	2.5	0.1114	Hasegawa et al. 2007[47]
1217	10.5	9.4	26.7	2217	222	4.1	0.1233	Elsaidi et al. 2014[48]
1901	10.7	6.5	35.4	1124	309	1.6	0.1106	Brunet et al. 2017[49]
122	9.7	6.9	27.3	1387	327	2.7	0.1102	Zhang et al. 2011[50]
802	12.3	7.1	22.3	2363	394	3.6	0.1187	Zhang et al. 2015[51]
917	14.6	7.3	28.3	1829	551	1.6	0.1218	Vagin et al. 2008[52]
1182	14.8	8.2	16.8	3815	329	1.6	0.1223	Ramirez et al. 2016[53]
384	7.7	6.8	25	1996	273	2	0.1252	Hu et al. 2014[54]
1703	8.7	6.3	32.1	3687	521	2.4	0.1251	Duan et al. 2011[55]

Table 4: Physical properties and their KPIs of Top 10 MOFs for optimized cascade PSA condition.

Screening ID	LCD (Å)	PLD (Å)	SF ₆ Heat of Adsorption (kJ/mol)	Surface Area (m ² /g)	SF ₆ /N ₂ Selectivity (5 bar)	SF ₆ WC (5 - 1 bar) (mmol/g)	Cascade PSA Energy Consumption (MJ/kg)	References
2536	13	6.7	31.7	3062	90	3.2	0.5211	Hobday et al. 2016[56]
2535	13	6.7	25.3	3067	94	3.2	0.5452	Hobday et al. 2016[56]
538	13.3	6.7	18.6	2358	82	2.6	0.5498	Peterson et al. 2014[57]
2534	13	6.7	17	3058	98	3.4	0.5576	Hobday et al. 2016[56]
2822	13.2	6.6	43.6	2400	86	2.9	0.6125	Peterson et al. 2014[57]
2332	10.6	9.6	27.6	2341	81	3.8	0.6328	Park et al. 2011[58]
2280	11.7	6.1	20.5	5168	135	4.8	0.6381	Pang et al. 2016[59]
2279	12.5	6	33.1	5212	158	5.4	0.6512	Pang et al. 2016[59]
2468	9.2	6.5	21	3885	99	3.1	0.6544	Burtch et al. 2013[60]
2419	10.9	6.5	25.8	3276	77	3.2	0.6568	Wang et al. 2013[61]

3.7. High-Performing MOFs for SF₆/N₂ Separation

We identified top-performing MOFs with low-energy consumption from both VSA and cascade PSA processes Table 3 and Table 4, (full version in the Supplementary Information Table S4). Based on the data, we found that the physical properties of high-performing MOFs are different between VSA and PSA processes. For example, MOFs that optimizes the performance of the VSA process have the LCD average value of 10.5 Å while the MOFs that optimizes the cascade PSA cascade have the LCD average value of 12.0 Å. We also found that the process KPIs (SF₆ purity and energy consumption) do not show any correlation with selectivity, and working capacities (see Supplementary Information Figures S2 and S3). Figure S4 shows the molecular structure and the single component isotherms of the top 3 MOFs

for VSA and cascade PSA. Among the best performing MOFs of the PSA case, UiO-67 (screening ID: 2536, 2535) and HKUST-1 (screening ID: 538) are well-known MOFs in the literature that have been already validated for SF₆/N₂ separation[13, 4]. We found that top-performing MOFs from the cascade PSA process have different isotherm shapes than the VSA case. The best performing MOFs for VSA have the SF₆ adsorption isotherm that saturates quickly in the pressure range of 0.01 bar to 2 bar whereas the best performing MOFs for cascade PSA have SF₆ isotherms that gradually saturates near 10 bar. The maximum saturation loading is also different between the MOFs that are optimal for VSA and PSA. This is likely due to different structural properties of these MOFs and further research is required to draw the correlation between the structural properties of MOFs and their isotherm shape.

From the screening results, we found that the best performing MOFs are UiO-67 and HKUST-1 for a cascade PSA process and [H₂DABCO]·[Co(HPO₄)(bpdc)], [Cd(4-btapa)₂(NO₃)₂·6H₂O·2DMF]_n, and dia-7i-1-Co for a VSA process whereas top performing VSA MOFs have not been studied with SF₆ isotherm data, the top-ranked MOFs in the cascade PSA case have been reported as UiO-67 (screening ID: 2535, 2536) by Kim et al.[13] and HKUST-1 (screening ID: 538) by Chuah et al. [4]. Using the experimental isotherms obtained from the literature, we have carried out the process-level evaluation of these materials. For the comparative evaluation, the isotherm data of other well-known adsorbents tested for the application, including UiO-66, MIL-100(Fe),

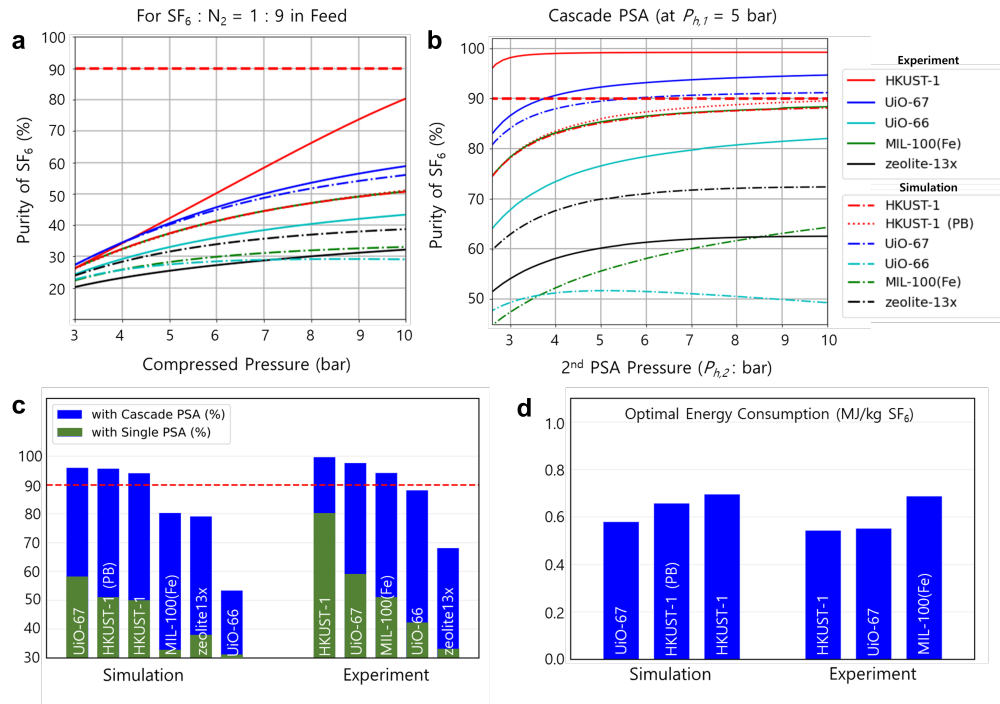


Figure 9: Comparison of the PSA process performance between the simulation and the experiment for porous material. (a) for PSA simulation, (b) for cascade PSA, (c) the SF_6 purity with cascade PSA, and (d) the energy consumption with optimal cascade PSA. MIL-100(Fe)[62], zeolite-13X[62], HKUST-1[4], UiO-66[13], and UiO-67[13] are included with their experimental data.

and zeolite 13X (the reference is listed in Table 5), were collected to evaluate their process-level performance. GCMC simulations were carried out on these materials to compare the simulated and experimental isotherms for these materials and the results are listed in Figures S6 and S7.

In Figure 9 (a), shows the process-level performance comparison based on experimental and simulated isotherm data for a single PSA train. Except HKUST-1, none of the materials reached 90 % SF₆ purity-level with a single PSA train based on either simulated or experimental isotherms. However, we should take the outcome with a grain of salt since the experimental isotherm data from HKUST-1 were only measured up to 1 bar. The isotherm data points beyond 1 bar were extrapolated. Nevertheless, the results are in line with the results from high-throughput screening work, where we found that none of the materials reached 90 % SF₆ purity-level with a single train PSA.

Figure 9 (b) shows the cascade PSA process results when the pressure of the first train is fixed at 5 bar, and the pressure in the second train is changing. We found that some of the materials reached 90 % SF₆ purity level. Notably, we found that UiO-67 and HKUST-1 reached above 90 % SF₆ purity level based on simulated and experimental isotherm data.

We need to see whether each adsorbent has any pressure condition achieving the 90 % purity target for all pressures. Therefore, by manipulating both the first and second PSA pressures, the maximum purity of each adsorbent was found, as shown in Figure 9 (c). The pressure domains of the first and second PSA pressures were between 3 bar to 10 bar, and the highest purity

was selected for each adsorbent. From the analysis, we found that UiO-67, HKUST-1 (PB), and HKUST-1 were able to reach 90 % purity based on the isotherms generated from simulations, and UiO-67, HKUST-1, and MIL-100(Fe) achieved 90 % purity based on the experimental isotherms.

With the adsorbents satisfying the 90 % target, the optimization of the operating pressures was carried out. We used the optimization problems formulated in Section 2.9, which minimizes the overall energy consumption with a 90 % SF₆ purity condition constraint. The optimized energy consumption values are sorted in Figure 9 (d). The UiO-67 and HKUST-1 are ranked at the top places based on both simulation and experimental isotherms.

Process-level performance between simulated and experimental results for MIL-100(Fe) is significant different. For example, Figure 10(b) shows that the process-level performance estimated with the experimental isotherms is higher than the performance estimated based on simulated isotherms. The result is, at first, counterintuitive since there is an excellent agreement between simulated and experimental isotherm data at 298 K (Figure S6) for MIL-100(Fe). MIL-100(Fe) reached 90 % SF₆ purity with experimental isotherm data as input but was not able to reach the level with simulated isotherm.

We further investigated the origin of the discrepancy in the process-level evaluation. We found the heat of adsorption value from the experiment and simulation differ significantly (57.54kJ/mol in the SF₆ simulation; 20.50kJ/mol in the SF₆ experiment), which is the main culprit of the mismatch in the process-level performance that we observed in Figure

10(b). During the process-level evaluation, the heat of adsorption value accounts for the increase in the temperature due to compression. Subsequently, the isotherm curve is updated to the new temperature based on the Eq. (S1) and (S2) as discussed in Supplementary Information. The magnitude of isotherm curve shifts is shown in Figure S9. Since we assumed a 15 K minimum temperature difference between the fluid of the heat exchanger located after the compressor and the SF₆/N₂ mixture gas, the new isotherm curve at 313 K is used in the process-level evaluation. Because of this, the different heat of adsorption values in the experiments and simulations significantly changed the isotherm curves, which considerably affected the process-level performances of MIL-100(Fe).

3.8. Limitation of Current Approach

Limitation of the molecular modeling

The present screening study relies on the accuracy of force field parameters that approximates the interaction between the adsorbate-framework and adsorbate-adsorbate interactions. Moreover, we assume the MOFs to be rigid during the simulation. We have compared the simulated and experimental adsorption isotherm data obtained from the literature to validate the force field used in this work (see Figure S6)[63].

Limitation of the screening strategy

As the second screening criterion, we adopted the working capacity and selectivity, which have been used in many previous studies. To find the most

critical factors directly influencing the capital expenditures (CAPEX) and operating expenses (OPEX) of a VSA or PSA process, the working capacity values should be found under the condition where the feed concentration is considered. At the same time, the optimal desorption (or adsorption for PSA) pressure satisfying the target SF₆ purity must be identified for the VSA process. However, calculating such working capacity values requires enormous computational expense. The mixture isotherm data is needed for a broad range of partial pressure (i.e., composition) of SF₆ and N₂ mixture to find the optimal pressures. Calculation of mixture isotherms for a broad range of partial pressure requires significantly high computational cost. To overcome this limitation, the Ideal Adsorbed Solution Theory (IAST) could effectively combine single isotherm data to generate mixture isotherms at different bulk phase partial pressure of SF₆. However, computationally generating the single isotherm data of the thousands of MOFs still requires significant computational resources.

We have used the working capacity and selectivity to remove the low to mid-performing MOFs from our dataset to reduce the computational effort in screening. Typically, MOFs with low working capacity and low selectivity exhibit low performance in the adsorption process. Note that the inverse is not necessarily true – i.e., MOFs with high working capacity and high selectivity never guarantee high process-level performance.

Limitation of Ideal V/PSA simulation model

In addition, as discussed in Section 2.5, the ideal VSA/PSA models that

we employed in this work do not consider the influence of adsorption kinetics. The process performances are affected by the kinetic parameters such as mass transfer coefficients; by broadening the concentration front during the adsorption operation. For instance, a low mass transfer coefficient can decrease the purity of the target component for a given operating condition. Incorporation of kinetics in the model requires the accurate estimation of inter- and intra-crystalline diffusion coefficients, which could, in theory, be obtained from Molecular Dynamics (MD) simulations or based on the transition-state theory (TST). However, it will take significant computational resources and time to estimate the diffusion coefficients using the methods. Moreover, even if we obtain diffusion coefficients related to the microscopic phenomena from the MD, overall mass transfer coefficients are also affected by other macroscopic factors, including the geometry of adsorbent beads, the velocity of gas flow.

4. Conclusion

In this work, more than 14,000 MOFs were computationally screened using a high-throughput, multi-scale evaluation method with two different process configurations (VSA and PSA), whose results were compared with the experimental data reported in the previous studies about porous adsorbents for the SF₆/N₂ separation[64]. Hierarchical filtering and screening methods were used to find 87 and 74 potential target MOFs for subsequent VSA and PSA process simulations, respectively. We found that the 74 MOFs (out of 87) were able to achieve a 90 % purity level but none of the MOFs selected for PSA were able to achieve the purity target. We explored the feasibility of achieving 90% SF₆ purity-level with a cascade PSA configuration, and found that 36 (out of the 74) MOFs were able to achieve 90% SF₆ purity-level with the cascade PSA configuration.

In terms of the energy consumption, we found top performing MOFs can produce 90% purity SF₆ with 0.10 - 0.4 and 0.5 - 1.4 MJ per kg of SF₆ for VSA and PSA, respectively. Furthermore, we revealed that the pressure ratio of VSA vacuum pump is higher than that of the PSA compressor (15 - 200 and 4 - 20 for VSA and PSA, respectively), which may impact the energy efficiency of the VSA process. We computed the energy consumption of MOFs with different isentropic efficiency values, and found that the cascade PSA process with 80% isentropic efficiency outperforms the VSA one with 10 % isentropic efficiency. The results suggest that the isentropic efficiency of the vacuum pump must be considered when choosing between the VSA

and PSA processes.

Finally, the structural properties of MOFs that optimizes the performance of the VSA process are different from the MOFs that optimizes the performance of the PSA process. $[\text{H}_2\text{DABCO}]\cdot[\text{Co}(\text{HPO}_4)(\text{bpdc})]$ (screening ID: 2153), $[\text{Cd}(4\text{-btapa})_2(\text{NO}_3)_2]$ (screening ID: 2199), and dia-7i-1-Co (screening ID: 1217) are the best performing MOFs for the VSA process, whereas UiO-67 (screening ID: 2535, 2536) and HKUST-1 (screening ID: 538) are the top-performing MOFs for the PSA process. None of the high-performing MOFs from the VSA process overlaps with the high-performing MOFs from the PSA process. The cascade PSA performance comparison with experiment data lends credence to this work. Notably, UiO-67 and HKUST-1 are ranked at the top places in both simulation and experiment structures. The most important factors responsible for the different results of the VSA and PSA processes are the isotherm shape and the pressure point at which the SF_6 uptake saturates. The saturation point of high pressure (over 1 bar) is favorable for the PSA process, and a relatively lower saturation point is required for the VSA process. The saturation point is likely determined by the structural properties of the MOFs. Top-performing MOFs for the PSA process have a larger LCD, PLD, pore volume, surface area, and void fraction than the top-performing VSA MOFs. Further research effort is necessary to draw the connection between the structural properties and the isotherm shape, and ultimately with the process KPIs.

Additionally, the heat of adsorption was found to be another key factor

since the heat of adsorption considerably affects the isotherm shape depending on the temperature change, which is caused by the heat generated by the feed gas compression. The example of MIL-100(Fe) exhibited how significantly the heat of adsorption affects the evaluation of adsorbents. Therefore, accurate measurement or estimation of the heat of adsorption is also a crucial point that we need to be conscious about during the evaluation of the MOFs.

5. Declaration of Competing Interest

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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