New hybrid membrane vacuum swing adsorption process for CO₂ removal from N₂/CO₂ mixture: modeling and optimization by genetic algorithm

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Abstract
In this study, a new innovative hybrid membrane/vacuum swing adsorption (VSA) process is developed, modeled, and optimized for removal of CO₂ from flue gases. The process benefits from the advantages of membrane simplicity and the high product quality of the adsorption system. The main advantage of this new process is the simultaneous increases of both CO₂ purity and its recovery. To achieve this objective, in the first step, a membrane system using PEBAX nano-composite membrane was modeled. In the second step, a VSA system using zeolite 13X was modeled. The adsorption equilibrium was predicted by the Toth isotherm. To increase the modeling accuracy, the mass transfer rate was calculated based on the quasi-second-order model. At the final step, the hybrid membrane/VSA process was modeled. Comparison of the new hybrid membrane/VSA with the stand-alone VSA process shows that the CO₂ product concentration was increased by 39% and the recovery was improved by 8%. To study the process limitations and increase the product quality, a sensitivity analysis was performed on vacuum pressure, membrane stage cut, and recycle ratio. Based on the results, decreasing the membrane stage cut to 15% and applying a recycle ratio equal to 2 will increase the product quality with the cost of increasing the equipment size. Finally, to achieve the required purity and recovery specification in industrial applications, the process was optimized using the genetic algorithm. Based on these results, it is possible to produce CO₂ with 94.7% purity and 99% recovery and N₂ with 99.9% purity and 97.3% recovery by regenerating the adsorbents at 0.01 bar, setting the membrane stage cut equal to 11%, keeping the recycle ratio at 1.89, and adjusting the purge-to-feed ratio to 2%.

Keywords CO₂ capture · Process combination · Membrane · Vacuum swing adsorption · Process modification

Introduction
The growth of the number of industrial plants has caused many environmental problems such as increasing anthropogenic greenhouse gas emissions and air pollution. Today, more than 85% of the required energy is provided by fossil fuels which have increased carbon dioxide concentration in the earth’s atmosphere by 40%, compelling the researching and industrial communities to devise CO₂ capture processes and methodologies to lower the greenhouse effects (Carapellucci and Milazzo 2003; Sabouni et al. 2014).

Various methods such as chemical and physical absorption, adsorption, membrane, chemical looping with metal oxides, cryogenic distillation, and microalgae bio-fixation have been adopted for CO₂ removal from flue gases. Unfortunately, none of these technologies satisfy the safety, efficiency, and economical requirements for CO₂ removal from large sources (Largitte and Pasquier 2016). The selection of each method depends on feed pressure, temperature, CO₂ concentration, impurities, and product quality. Researches show that the proposed processes have difficulties dealing with compression of flue gas and/or captured carbon dioxide, treatment of large gas volume with low CO₂ partial pressure, and large energy requirements for regeneration (Ben-Mansour et al. 2016). Amine absorption process is the most widely used in industries; even though applying this process...
is not recommended due to corrosion, presence of chemically unstable compounds, toxicity’s impacts on ecosystems, and oxidative/thermal degradation which necessitates fresh absorbent injection (Moioli et al. 2019). Recently, the application of ionic liquids (ILs) has been proposed as an alternative CO₂ absorption separation media (Liu et al. 2017). The comparison of amine properties with those of ILs shows that ILs have lower vapor pressure, wider liquid temperature range, higher thermal and chemical stability, and higher CO₂ solubility. However, there are limited industrial applications for ILs due to high manufacturing costs and high viscosity leading to lower diffusion rates (Shannon and Bara 2011). To extend IL applications, different combinations of membrane and ionic liquid processes have been introduced for CO₂ separation (Yan et al. 2019). Also, the separation of CO₂/N₂ mixture has been achieved by the application of a fabricated liquid membrane. The comparison of performances by NADES-SLMs and imidazolium-based SILM showed that the synthesized NADES provided performances comparable to its competition as well as its benefits of green environmental potential and low operating costs (Saeed et al. 2021).

Recently, CO₂ capture via the adsorption process has received attention in industrial applications. The process operates on the principle of different performances of the adsorbent in the adsorption/desorption processes. Adsorbent regeneration can be performed by heat in temperature swing adsorption (TSA) (Zhao et al. 2017), pressure in pressure swing adsorption (PSA) or vacuum swing adsorption (VSA) (Nikolaidis et al. 2018; Zarghampoor et al. 2017), and electricity in the electric swing adsorption (ESA) process. Due to the high polarizability and large quadrupole moment of CO₂, the traditional cycle design for recovering the less adsorbing component at high purity is not applicable (Joss et al. 2017). The important factors in the adsorption process include CO₂ selectivity of the adsorbent, adsorption capacity, ease of regeneration, adsorbent’s durability, and stability after several cycles. Physical adsorbents such as metal oxides, hydrotalcite-like compounds, activated carbons, and zeolites have been proposed for CO₂ capture (Ravanchi and Soleimani 2021). For example, CO₂ was adsorbed by piperazine-modified activated carbon adsorbents as well as activated carbon. As indicated by the results, CO₂ adsorption capacity decreases either by the application of more adsorbents or by increasing the particle sizes. Additionally, CO₂ adsorption will increase at higher pressures and will decrease at higher temperatures. Also, the performance will improve when the surface of activated carbon is modified (Ramezanipour Penchah et al. 2022). When selecting a suitable adsorbent, its selectivity, thermal stability, capacity, and flue gas impurities like NOₓ, SOₓ, carbon monoxide, and humidity which impact the adsorbent turnover are important (Ben-Mansour et al. 2016). Zeolites with a crystalline structure, high surface area, tunable pore size, and thermal and mechanical stability are common adsorbent choices for CO₂ removal. However, the CO₂ adsorption capacity by zeolite drops when moisture is present in the flue gas (Hefti et al. 2015). Due to the hydrophobicity of activated carbon, this physical adsorbent is used when the flue gas has moisture. Activated carbon has a high CO₂ adsorption capacity and low cost, and requires less regeneration energy compared to zeolites (Radosz et al. 2008). However, this adsorbent was also utilized for a high-pressure CO₂ capture application (Mazumder et al. 2006).

The membrane CO₂ separation system operates on the principle of solution-diffusion mechanism (Daramola et al. 2021). This technology is facing challenges to overcome plasticization and degradation caused by moisture, hydrocarbons, aromatic compounds, and high CO₂ concentration (Dodda et al. 2016). However, many modifications such as physical coating, chemical drafting, and polymer cross-linking have been applied to improve separation performance, membrane stability, and selectivity (Zhang et al. 2017; Zhang et al. 2018).

Recent studies have suggested that the application of a hybrid process for CO₂ removal will improve operational performance (Dong et al. 2021; Esteves and Mota 2002; Warmuzinski et al. 2013). Hybrid methods combine the advantages of each single-stage process to provide low-cost separation with higher efficiency, selectivity, and recovery (Hailong et al. 2018). The main disadvantages of hybrid methods are their capital cost and process complexity (Jaschik et al. 2020). Therefore, to have a truly integrated and stable hybrid process, it is imperative to study every single unit and then combine the processes (Akinlabi et al. 2007). Xiao et al. (2021) presented an integrating adsorption and solvent scrubbing system. The process combines a VSA and a MEA solvent scrubber. The results showed that the adsorption process enriched CO₂ to 50 mol% with a recovery of 90% and the CO₂ stream fed to the solvent scrubber had a significantly lower volumetric flow rate leading to a reduction of the diameter of the absorber column (Xiao et al. 2021). Lillia et al. (2018) reviewed a hybrid temperature electric swing adsorption (TESA) process for CO₂ capture. However, the analysis showed that TESA was uncompetitive as the required power was about 5 times higher than the one for the MEA absorption system (Lillia et al. 2018).

Esteves and Mota (2002) coupled PSA and membrane processes to develop two distinct schemes for the separation of different types of gas mixtures based on the permeability and selectivity of each component. The process takes advantage of high product purity, low regeneration cost, long-term stability, fast kinetics, and ease of handling the adsorption process (Eze and Agbo 2010). It then provides additional benefits via compactness, simplicity, modularity, ease of skid-mounting installation, low operating cost, and high efficient separation in membrane units (Khalilipour...
et al. 2015). The overall benefits will lead to high product purity and recovery and the least power consumption and space requirements. It is expected that an overall 10% purity and recovery enhancements are achieved with a PSA and membrane hybrid process (Asif et al. 2018). The pressure requirements for adsorption and permeation in Esteves and Mota’s (2002) coupled PSA and membrane process are provided by a compressor although it has been suggested to use a vacuum pump instead of a compressor to minimize the required operational energy (Zhang et al. 2008). Also, Ohs et al. (2019) concluded that a bulk membrane separation is an optimal design in a hybrid membrane pressure swing adsorption process. This conclusion leads to installing the membrane system at the first stage of a hybrid system.

In this research, the performance of a new hybrid membrane/VSA process for CO₂ removal from flue gas is studied by taking advantage of the low energy consumption in a vacuum swing adsorption process. For this purpose, a new high-performance and stable system for a hybrid membrane/VSA process is proposed and a corresponding mathematical model is developed as well. In this process, a stream with a flow rate of 3 L min⁻¹, containing 20% CO₂ and 80% N₂ at 50 °C is fed to the system. Polyether-block-amide membrane (PEBAX) was selected for the process as the nano-composite membrane due to its high permeability and selectivity. zeolite 13X was chosen as the adsorbent for its high capacity and selectivity. The reason for zeolite 13X higher CO₂ selectivity compared to N₂ is CO₂ polarizability and large quadrupole moment which enables CO₂ to be adsorbed significantly better than N₂ (Joss et al. 2017). To achieve mentioned goals, a membrane system and a single-stage VSA process were modeled in the first and second stages of the process development. Finally, the new hybrid system consisting of one membrane and two adsorption beds was modeled. To increase CO₂ product quality, sensitivity analyses on vacuum pressure, membrane stage cut, and product recycling were performed. Finally aiming to develop an industrially applicable process with CO₂ product purity of more than 95% and recovery of more than 80%, the tunable process parameters of the hybrid process were optimized via the genetic algorithm method.

**Hybrid system development**

**Process description**

The analyses of flue gases show that CO₂ concentration in flue gases is between 8 and 20 mole percent and the temperature is between 100 and 150 °C (Merkel et al. 2010; Olajire 2010; Songolzadeh et al. 2014). During the development of this new hybrid system and determining the equipment layout, it was decided to use a membrane in the first stage due to its high permeability and low CO₂ concentration. Figure 1 shows a schematic view of the recommended new hybrid membrane/VSA process. At first, the flue gas enters the membrane module and then the retentate stream is sent to the VSA cycle for further purification. Since the retentate contains a lesser portion of CO₂, the breakthrough time for the adsorption beds will increase dramatically. The required driving force for membrane permeation and adsorption bed regeneration is supplied by only one vacuum pump. If the membrane module were placed after the VSA cycle, then two vacuum pumps would be required to provide the necessary driving force, one to overcome membrane pressure drop at permeate side and another to provide the necessary adsorption/desorption pressure ratio in the VSA cycle. Another advantage of the proposed system is that the

![Figure 1: Schematic view of new recommended hybrid membrane/VSA process for CO₂ removal](image-url)
vacuum pump is not in the main feed stream, so it carries lesser loads than the compressor which would have been located in the mainstream in the PSA process. To increase CO\textsubscript{2} recovery and its purity in the proposed system, a portion of CO\textsubscript{2} product is recycled to the system and the rest is sent to the product storage tank.

The new proposed hybrid membrane/VSA process consists of six steps. Figure 2 shows the general trends in each step of this process. At first, the feed gas is sent to the membrane module. To increase CO\textsubscript{2} recovery and purity, a portion of CO\textsubscript{2} products is recycled and mixed with the feed stream. Since CO\textsubscript{2} is more permeable than N\textsubscript{2}, the retentate stream contains a lower CO\textsubscript{2} concentration. The retentate stream is sent to the adsorption column A for further purification. The reduction in CO\textsubscript{2} inlet concentration and flow rate will increase the adsorption column's breakthrough time. At the same time in the current step, the pressure in adsorption column B decreases and it becomes ready for purging. During the blowdown step, a portion of the adsorbent will be regenerated. To minimize adsorbent fluidization during the blowdown, a restriction orifice is installed at each bed’s outlet to control the flow rate. In the second step, a portion of the N\textsubscript{2} product is used as a purge gas to regenerate the adsorbent in column B while adsorption column A is purifying N\textsubscript{2}. Nitrogen purging will help to reduce CO\textsubscript{2} partial pressure and increase regeneration performance. In the third step, the regenerated bed is pressurized with some part of the retentate stream and column B becomes ready for adsorption. The adsorption column A is expected to be saturated at the end of step 3. In steps 4 to 6, the beds are interchanged. During these steps, adsorption column B purifies N\textsubscript{2} and column A is depressurized, purged, and pressurized in three steps.

Mathematical modeling of hybrid membrane/VSA process

The mathematical modeling of a hybrid membrane/VSA process requires the behavior prediction of each single stage. As all process parameters except initial conditions are the same for both the single-stage and hybrid methods, it is possible to use the single stage’s governing equations for the hybrid process as well.

Modeling of membrane process

The permeation in a nonporous membrane is modeled by the solution-diffusion method consisting of two steps. Originally, the gas is adsorbed on the surface and then permeates through the membrane (Drioli and Barbieri 2011; Freeman et al. 2006). To model the gas permeation, it is assumed that the gas and membrane surface are in equilibrium. This assumption implies that the chemical potential gradient through the membrane is continuous and the adsorption rate is much greater than the permeation rate. In the solution-diffusion model, the pressure across the membrane is assumed to be constant and the chemical potential gradient is only affected by concentration. The following assumptions are considered for the system:

1. Effects of impurities such as moisture, SO\textsubscript{x}, NO\textsubscript{x}, and solid particles are negligible.
2. Feed pressure, temperature, and composition are assumed constant.
3. Membrane selectivity remains constant during permeation and is equal to the ratio of CO\textsubscript{2} to N\textsubscript{2} permeability.
4. The flow pattern conforms to a perfect mixing plug flow model.
5. The formation of concentration polarization on the membrane surface is insignificant.

The model construction requires the selection of an element on the membrane. The mass balance equation for the membrane element is shown in Eq. 1:

\[ Q^* \frac{dx}{ds} = - \left( x - \psi y_p + x \frac{dQ^*}{ds} \right) \]  

(1)

where \( Q^* \) is the membrane stage cut, \( x \) is the upstream mole fraction, \( y \) is the downstream mole fraction, \( s \) is the dimensionless membrane area, and \( \psi \) is the pressure ratio across the membrane. The \( \text{CO}_2 \) and \( \text{N}_2 \) permeation rates are calculated based on the mass balance equation and expressed by Eqs. 2 and 3:

\[ -d(Qx) = \frac{P_{\text{CO}_2} P^*}{z} (x - y_p \psi) ds \]  

(2)

\[ -d[Q(1-x)] = \frac{P_{\text{N}_2} P^*}{z} [(1-x) - (1-y_p) \psi] ds \]  

(3)

where \( Q \) (m³/s) is the flow rate, \( P_{\text{CO}_2} \) (bar) and \( P_{\text{N}_2} \) (bar) are the partial pressures of \( \text{CO}_2 \) and \( \text{N}_2 \), respectively, \( P \) (bar) is the upstream pressure, and \( z \) (m) is the membrane thickness. The fraction of gas that permeates through the membrane is defined as stage cut which can be expressed by combining Eqs. 2 and 3 as shown in Eq. 4:

\[ \frac{dQ^*}{ds} = -\left( x - \psi y_p + \frac{1}{\alpha} (1-x - \psi (1-y_p)) \right) \]  

(4)

where \( \alpha \) is the membrane selectivity. To calculate the \( \text{CO}_2 \) removal performance of the membrane, it is necessary to calculate the permeate product’s concentration as defined by Eq. 5 and based on the overall mass balance and the combination of Eqs. 2 and 3.

\[ y_p = \frac{1}{1-y_p} \left( \frac{x - \psi y_p}{1-x - \psi (1-y_p)} \right) \]  

(5)

**Modeling of vacuum swing adsorption process**

The mathematical modeling of the adsorption process predicts the unsteady-state behavior of the adsorption bed. The model is constructed by simultaneous solution of a set of partial differential equations that represent mass, momentum, and energy balance, plus an ordinary differential equation that predicts the mass transfer rate (Hasan et al. 2012; Ruthven et al. 1994). The mathematical model will be constructed based on the following assumptions:

1. Adsorption beds operate at isothermal conditions.
2. Radial concentration gradients are negligible.
3. Bed pressure drop is calculated based on the Ergun equation.
4. Feed and purge gas conditions remain constant throughout the process.
5. Flow pattern behaves as an axially dispersed plug flow model.
6. Mass transfer rate is represented by a quasi-second order model.
7. Gas behavior is considered ideal.

The flow model for the adsorption process is based on packed beds (Ruthven et al. 1994). The mass balance equation includes axial dispersion, convection, gas phase accumulation, and adsorption rate as follows:

\[ -D_{ai} \frac{\partial^2 C_i}{\partial z^2} + \frac{\partial}{\partial z} (u_C i) + \frac{\partial C_i}{\partial t} + \left( \frac{1 - \epsilon_b}{\epsilon_b} \right) \rho_p \frac{\partial q_i}{\partial t} = 0 \]  

(6)

where \( C_i \) (mol. m⁻³) is the adsorbate concentration of component \( i \) in the fluid phase, \( u \) (m. s⁻¹) is the fluid velocity, \( z \) (m) represents the distance along the bed, \( t \) (s) is time, \( \epsilon_b \) is the bed void fraction, \( \rho_p \) (kg. m⁻³) is the particle density, \( q_i \) (mol. kg⁻¹) is the average concentration in adsorbent particle, and \( D_{ai} \) (m². s⁻¹) is the axial dispersion coefficient. The axial dispersion coefficient is defined by an empirical correlation as a function of Reynolds and Schmidt numbers as shown in Eq. 7 (Ruthven et al. 1994):

\[ \frac{\epsilon_b D_{ai}}{D_{mi}} = 20 + 0.5 \text{ScRe} \]  

(7)

where \( D_{mi} \) (m². s⁻¹) is molecular diffusivity of component \( i \), and Sc and Re are the Schmidt and Reynolds numbers, respectively. The mass transfer rate is defined based on different adsorption kinetics. It is recommended to use a quasi-second order model for a low concentration feed (Azizian 2004). Since \( \text{CO}_2 \) concentration in flue gas is between 8 and 15 mole percent, a quasi-second-order model is applied, and the general form of this model is defined in Eq. 8:

\[ \frac{\partial q_i}{\partial t} = K_{ai}(q'_i - q_i)^2 \]  

(8)

where \( K_{ai} \) (kg. mol⁻¹. s⁻¹) is the quasi-second-order mass transfer coefficient and \( q'_i \) (mol. kg⁻¹) is the adsorbed phase’s concentration at equilibrium with the fluid phase concentration. Due to monolayer adsorption of \( \text{CO}_2 \) and \( \text{N}_2 \) on zeolite 13X, the Toth isotherm is recommended for adsorption...
equilibrium prediction (Siriwardane et al. 2005). This relation is defined in Eq. 9 as follows:

\[ q_i^* = \frac{q_{i_{\text{max}}} K_{eq} P}{[1 + (K_{eq} P)^n]^{1/n}} \]  

(9)

where \( q_{i_{\text{max}}} (\text{mol.kg}^{-1}) \) is the maximum amount adsorbed at equilibrium, \( K_{eq} (\text{bar}^{-1}) \) is an equilibrium constant, \( P \) (bar) is the total pressure, and \( n \) is the Toth parameter. During the passing of the fluid through the empty spaces between adsorbent particles, the pressure may drop in the fluid. Equation 10 which is known as the Ergun equation is used to predict this pressure drop (Ruthven et al. 1994):

\[ \frac{\partial P}{\partial z} = -\frac{150\mu(1 - \varepsilon_b)^2}{\varepsilon_b^2 d^2_p} - u - \frac{1.75(1 - \varepsilon_b) \rho_g u^2}{\varepsilon_b d_p} \]  

(10)

where \( \mu \) (Pa. s) is the gas viscosity, \( d_p \) (m) is the particle diameter, and \( \rho_g \) (kg. m\(^{-3}\)) is the gas density. To evaluate the CO\(_2\) removal performance of the VSA cycle, it is necessary to calculate both its emission to the atmosphere and recovery. These parameters are calculated by Eqs. 11 and 12:

**CO\(_2\) Emmission** = \( \int_{t_0}^{t_{\text{adsorption}}} (1 - \text{purge/feed ratio}) \times \text{Flow}_{\text{CO}_2} \) dt  

(11)

**Recovery** = \( \frac{\text{CO}_2 \text{ obtained in adsorption} - \text{CO}_2 \text{ used for purging}}{\text{CO}_2 \text{ fed during pressurization & adsorption}} \)  

(12)

**Modeling of hybrid membrane/VSA process**

To predict the hybrid membrane/VSA process behavior, the above equations must be solved simultaneously. The set of partial differential equations describing VSA and membrane are discretized in the length direction and solved with MATLAB using the ODE15s method. Table 1 and Figure 3 provide the governing equations and flowchart of calculation steps.

**Table 1** Hybrid membrane/VSA process modeling equations

| VSA System | Adsorption Step | Blowdown Step | Purging Step |
|------------|-----------------|---------------|--------------|
| Presurization Step | Component i mass balance: | | Component i mass balance: |
| Total mass balance: | \( \frac{\partial \rho_{\text{eq}}}{\partial t} + \nabla \cdot (\rho_{\text{eq}} \nabla \psi) = 0 \) | | Total mass balance: |
| Continuity equation: | \( \nabla \cdot (\rho_{\text{eq}} \nabla \psi) = 0 \) | | Continuity equation: |
| Boundary conditions: | \( \rho_{\text{eq}_{\text{L}}} = \rho_{\text{eq}_{\text{initial}}} \) | | Boundary conditions: |
| | \( \rho_{\text{eq}_{\text{L}}} = \rho_{\text{eq}_{\text{initial}}} \) | | \( \rho_{\text{eq}_{\text{L}}} = \rho_{\text{eq}_{\text{initial}}} \) |
| | \( \rho_{\text{eq}_{\text{L}}} = \rho_{\text{eq}_{\text{initial}}} \) | | \( \rho_{\text{eq}_{\text{L}}} = \rho_{\text{eq}_{\text{initial}}} \) |
| Pressure drop & change: | \( \frac{\partial P}{\partial t} = -\frac{150\mu(1 - \varepsilon_b)^2}{\varepsilon_b^2 d^2_p} - u - \frac{1.75(1 - \varepsilon_b) \rho_g u^2}{\varepsilon_b d_p} \) | | Recovery of CO\(_2\): |
| Purity of component i: | \( \text{Purity} = \sum_{j=1}^{n_{\text{component}}} F_{dt} + \int_{t_0}^{t_{\text{purge}}} F_{\text{dt}} \) | | CO\(_2\) Emission to atmosphere: |
| Membrane System | Diffusion flux: | Fermentation rate: | Permeate product concentration: | Purity & Recovery: |
| | \( N_i = S_iD_i \left( P_{i_{\text{eq}}} - P_{i_{\text{eq}}} \right) \) | | Purity = \( \sum_{j=1}^{n_{\text{component}}} \) \text{Recovery} = \( \frac{\text{CO}_2_{\text{emission}}} {\text{Feed}_{\text{CO}_2}} \) |
| | Purity = \( \sum_{j=1}^{n_{\text{component}}} \) \text{Recovery} = \( \frac{\text{CO}_2_{\text{emission}}} {\text{Feed}_{\text{CO}_2}} \) |

where \( \gamma \) is the specific heat ratio, \( R \) (J. mol\(^{-1}\). K\(^{-1}\)) is the universal gas constant, and \( Q \) (m\(^3\). s\(^{-1}\)) is the volumetric flow rate of gas. As the required vacuum power varies during each step, the average power per unit mass of CO\(_2\) product is obtained.

\[ \text{Power}_{\text{avg}} = \frac{\sum_{j=0}^{6} \int_{0}^{t_{\text{step}}} \text{Power}_{\text{vacuum}} \, dt}{\int_{0}^{t_{\text{CO}_2}} \text{Flow}_{\text{CO}_2} \, dt} \]  

(14)
To evaluate the performance of the proposed hybrid membrane/VSA process, two case studies predicting CO$_2$ removal of a single-stage membrane and VSA are considered. The experimental data provided by Zhao et al. (2008) is used for the single-stage membrane process. Nano-composite PEBAX is used for this study due to its high permeability and selectivity. Next, the experimental data of equilibrium isotherms and adsorption bed parameters provided by Dantas et al. (2011) are used for the mathematical modeling of the VSA process. They used zeolite 13X as the adsorbent in the packed beds. Finally, a mixture of 20% CO$_2$ and 80% N$_2$ at 50 °C with a flow rate of 3 L·min$^{-1}$ at 1.3 bar is introduced to the membrane/VSA cycle. Membrane and adsorbent properties and process design parameters are reported in Table 2 and Table 3.

**Sensitivity analysis and process optimization**

The objective of process optimization is to produce the products with the highest possible purity and recovery that are acceptable in industrial applications. To determine the behavior and specify the lower and upper limits for independent operational process parameters, at first, a series of sensitivity analyses are performed. Then, the genetic algorithm model in MATLAB is applied as an optimization tool. In this tool, the response (purity and recovery) is considered to be a function of several independent process variables including pressure ratio, cycle time, purge-to-feed ratio, membrane stage cut, and recycle ratio.

Objective Function = $\max \{\text{purity}(CO_2, N_2) + \text{Recovery}(CO_2, N_2)\}$

(15)

**Results and discussion**

**Membrane process**

To evaluate the accuracy of the model in simulating the membrane separation process, the experimental data provided by Zhao et al. (2008) has been used in this study. A feed containing 14% CO$_2$ and 86% N$_2$ is introduced to the membrane system at 70 °C and 1 bar with a 100 m$^3$·h$^{-1}$ flow rate. A vacuum pump is used to provide permeate pressure of 0.03 bar. Figure 4 shows CO$_2$ and N$_2$ partial pressures on permeate and retentate sides of nano-composite PEBAX membrane during the separation process. As can be seen, the driving force for N$_2$ partial pressure is much higher than that for CO$_2$; and as the process continues, the CO$_2$ driving force decreases. This phenomenon makes the separation more difficult while the process continues.

To determine the CO$_2$ removal performance of the membrane, the recovery and product permeate concentration are calculated. However, simultaneous improvements of recovery and permeate concentration are mutually exclusive. Figure 5 shows the recovery versus product concentration for the PEBAX membrane. As the system recovery steps up to produce more permeates, the pressure driving force is also increased leading to higher N$_2$ partial pressure and more N$_2$ permeation through the membrane reducing the product concentration.
increase in recovery may increase the risk of membrane fouling by impurities like SOX, NOX, water vapor, and fine particles in the flue gas. Thus finding a balance between acceptable permeates product concentration and recovery is crucial.

### Table 3 Process design parameters (Dantas et al. 2011, Zhao et al. 2008)

| Process parameters | Membrane system | VSA stand alone | Hybrid membrane/VSA |
|--------------------|-----------------|-----------------|---------------------|
| Feed composition (mol%) | 86% N₂, 14% O₂ | 80% N₂, 20% O₂ | 80% N₂, 20% O₂ |
| Feed temperature (°C) | 70 | 50 | 50 |
| Feed pressure (bar) | 1.0 | 1.3 | 1.3 |
| Feed flow rate (LPM (STP)) | 1666 | 3 | 3 |
| Membrane | PEBAX | - | PEBAX |
| Stage cut | 1~20% | - | 20% |
| Membrane upstream side pressure (bar) | 1.0 | - | 1.3 |
| Membrane downstream side pressure (bar) | 0.03 | - | 0.1 |
| Adsorbent | - | Zeolite 13X | Zeolite 13X |
| Adsorption equilibrium model | - | Toth model | Toth model |
| Axial dispersion coefficient (m²/s⁻¹) | - | 7.81E⁻⁴ | 7.81E⁻⁴ |
| Global mass transfer coefficient (kg mol⁻¹s⁻¹) | - | CO₂: 0.106 , N₂: 5.014 | CO₂: 0.106 , N₂: 5.014 |
| Adsorption pressure (bar) | - | 1.3 | 1.3 |
| Desorption pressure (bar) | - | 0.1 | 0.1 |
| Adsorption bed length (m) | - | 0.8300 | 0.8300 |
| Adsorption bed diameter (m) | - | 0.0200 | 0.0200 |
| Adsorbent volume (L) | - | 0.26 | 0.26 |
| Adsorption bed void fraction | - | 0.6200 | 0.6200 |
| Pressurization time (min) | - | 22.4 (8% T_cycle) | 46 (8% T_cycle) |
| Adsorption time (min) | - | 112 (40% T_cycle) | 230 (40% T_cycle) |
| Blowdown time (min) | - | 84 (30% T_cycle) | 172.5 (30% T_cycle) |
| Purge time (min) | - | 61.6 (22% T_cycle) | 126.5 (22% T_cycle) |
| Cycle time (min) | - | 280 | 575 |
| Purge-to-feed ratio | - | 1/6 | 1/6 |
| Experimental data | Zhao et al. | - | Dantas et al. |

**Fig. 4** CO₂ and N₂ partial pressure on permeate and retentate sides of nano-composite PEBAX membrane during separation progress. Process parameters are provided in Table 3. The points show the results of Zhao et al.’s (2008) work.

**Fig. 5** Recovery vs. CO₂ permeate concentration for nano-composite PEBAX membrane. Process parameters are provided in Table 3. The points show the results of Zhao et al.’s work (2008) work.
Vacuum swing adsorption process

Evaluating the accuracy of the mathematical model for simulating the VSA system is provided via the experimental data provided by Dantas et al. (2011). Feed characteristics, bed properties, and equilibrium adsorption data are required to model a VSA system.

Choosing an appropriate adsorption isotherm ensures the accurate prediction of VSA cycle behavior. Based on the adsorption characteristic analyses for CO$_2$ and N$_2$ adsorption on zeolite 13X, the adsorption is monolayer and favorable (Siriwardane et al. 2005). This behavior can be predicted with most equilibrium isotherms with high accuracy. Figure 6 shows the results of CO$_2$ and N$_2$ equilibrium adsorption predictions by the Toth model at 50 °C. The results indicate that the maximum deviation error for equilibrium adsorption prediction is 2.5% for CO$_2$ and 2% for N$_2$.

To model the VSA process, a mixture of 20% CO$_2$ and 80% N$_2$ at 50 °C with a flow rate of 3 L min$^{-1}$ at 1.3 bar is introduced to the system. Process parameters including bed properties, bed pressure during adsorption and desorption, cycle time, and purge-to-feed ratio are listed in Table 3. Figure 7 demonstrates the modeling results of the VSA process in the zeolite 13X packed bed. Points show the experimental data provided by Dantas et al. (2011). As can be seen, N$_2$ is initially the one adsorbed in the bed, and it is then replaced by CO$_2$ molecules due to competitive adsorption. This phenomenon causes an oversooting peak on the N$_2$ breakthrough curve. The maximum cycle time is determined by CO$_2$ emission limitations. The energy consumption of the VSA unit depends on vacuum level and purge-to-feed ratio. The calculated energy consumption is equal to 4.2 MJ kg$^{-1}$ CO$_2$ in the VSA unit.

Hybrid membrane/VSA process

A comparison of the experimental data and modeling results by the membrane and VSA systems as explained in previous sections shows the accuracy of the model to predict the system’s behavior. Therefore, it is possible to trust the mathematical modeling results of the hybrid membrane/VSA process since the governing equations are the same as the single-stage systems, but with different boundary conditions. Figure 8 shows the performance results of CO$_2$ removal by the recommended new hybrid membrane/VSA process with process parameters reported in Table 3. In this system, the properties of the feed and adsorption beds are considered equal to those of the single-stage VSA system of Dantas et al. (2011), and membrane properties are incorporated from Zhao et al.’s (2008) work. Due to pressure variation in the system, flow rates are reported based on the standard condition. It should be noted that since the VSA cycle is an unsteady-state process, time-integrated flow rates and concentrations were used in the material balance calculations. As can be seen, the CO$_2$ concentration in the stream entering the membrane module is increased due to recycling a portion of the product, which increased the CO$_2$ product quality by 15%. The membrane’s retentate stream containing 14% CO$_2$ is sent to the adsorption system for further purification. The reductions of CO$_2$ inlet concentration and total flow rate fed to the adsorption section increased the breakthrough time by 31% which in turn can reduce the VSA bed size and its capital cost. The increased breakthrough time reduced the necessary times for bed regeneration and also improved its recovery. The pure N$_2$ will exit the VSA cycle with 99.9% purity.
When one bed is saturated, the bed pressure decreases via vacuum pump and then 15% of the N₂ product is used as a purge gas to regenerate the bed. During bed regeneration, the average CO₂ concentration exiting the bed is 31%. Finally, the membrane permeate stream and CO₂ product from the VSA cycle are mixed and sent to the storage tank.

One of the advantages of this process is using only one vacuum pump that lowers the capital cost. Also, installing the vacuum pump on CO₂ downstream reduces the energy consumption of the system. Imagine if a compressor is installed in the feed stream, the compressor would have to continuously increase the pressure of the feed with 3.25 standard liters per minute (SLPM) flow rate to create the required driving force for the membrane and adsorption beds, whereas the installed vacuum pump on the CO₂ stream needs to create a vacuum with a maximum of only 1.12 SLPM during steps 2 and 5, and about 0.75 SLPM during other steps. The energy consumption in the membrane-VSA hybrid process is 2.7 MJ.kg⁻¹ CO₂. The main reason for the reduction of energy consumption in the hybrid system is the increased CO₂ purity in the exiting product stream leading to less vacuum pump volumetric suction flow rate.

Figure 9 compares the behavior of similar zeolite 13X packed beds used in the hybrid membrane/VSA and VSA processes. As previously mentioned, in the single-stage VSA system, the feed containing 20% CO₂ enters the bed directly, while in the case of the membrane in the hybrid membrane/VSA processes, a portion of CO₂ in the feed is separated and the remaining retentate stream containing 14% CO₂ with a flow rate equal to 80% of the main feed goes to the VSA section. Reductions in CO₂ concentration and its flow rate in the stream fed to the VSA bed lead to an increase in the breakthrough time by 31%.

It should be noted that if the bed size for VSA and hybrid membrane/VSA is considered to be the same, then the VSA cycle time in the hybrid system can be increased to 575 min. Figure 10 shows the process performance comparison of single-stage VSA with hybrid membrane/VSA for CO₂ removal. As can be seen, the cycle time for the hybrid process is 105% longer than the one for the single-stage VSA process.

Figure 11 compares the recovery and CO₂ product concentration in the single-stage and hybrid membrane/VSA processes. As can be seen, the CO₂ product concentration is 30% with a 91% recovery for a single-stage VSA process with a 280-min cycle time, while the CO₂ product concentration will be 70% with a 99% recovery for a hybrid process with a 575 min cycle time. It should be noted that reducing the total cycle time to less than 280 min for the VSA process and less than 575 min for the hybrid system will reduce
product CO₂ concentration. The reason is that in a reduced total cycle time system, the packed bed is not saturated completely and excess N₂ gas is used during the purging step. Over-purging N₂ will dramatically decrease CO₂ product concentration. This means that during the design of the system, although oversizing the bed will guarantee N₂ product quality, CO₂ product concentration will be decreased.

**Sensitivity analysis for hybrid membrane/VSA separation system**

In industrial application, the required CO₂ purity is more than 95% for future transport and injection and also the attractive degree of CO₂ separation in the process is more than 80% (Mulgundmath and Tezel 2010). To identify the potential and limitation in the membrane/VSA system and to determine the impact of vacuum pressure, membrane stage cut, and product recycling on improving product quality in a hybrid membrane/VSA process, a sensitivity analysis is performed in this step.

**Effect of vacuum pressure** Previous studies have shown that it is beneficial to decrease vacuum pressure in the regeneration steps to improve bed regeneration (Zarghampoor et al. 2017). However, creating more vacuum will increase the operating cost. Figure 12 shows the vacuum pressure effect on improving CO₂ product quality. According to this figure, sensitivity analysis shows that a change of vacuum pressure in regeneration steps from 0.1 to 0.01bar results in improving product quality by 4%.

**Effect of membrane stage cut** One of the most important factors in modeling and optimization of the process is

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**Fig. 10** Comparison of the effect of cycle time on CO₂ emission in single-stage VSA and hybrid membrane/VSA processes. Process parameters are provided in Table 3

**Fig. 11** Comparison of the recovery and CO₂ product concentration in the (a) single-stage and (b) hybrid membrane/VSA process. Process parameters are provided in Table 3

**Fig. 12** Vacuum pressure effect on improving CO₂ product quality in hybrid membrane/VSA process. Feed properties are provided in Table 3
membrane stage cut. This parameter not only dramatically affects CO₂ product quality but also affects adsorption bed breakthrough behavior. Figure 13 shows the effect of membrane stage cut on CO₂ product quality and adsorption bed breakthrough time. As can be seen, decreasing the membrane stage cut from 20 to 15% will increase the product CO₂ quality by 10% while increasing the VSA side load which will decrease the adsorption bed’s break time by 25%. It should be noted that decreasing membrane stage cut from 15 to 10% has little impact on product quality while adsorption break time will decrease by 11.5%. So, it is recommended to keep the membrane stage cut to around 15%.

**Effect of recycle ratio** Recycle ratio is another design parameter that will affect product quality, process operating cost, and capital cost. The determination of the optimum recycle ratio in the hybrid process is one of the most important factors in the process design. An increase in recycle ratio increases the operating cost and packed bed volumes. Figure 14(a) shows the effect of recycle ratio on the required membrane surface area. It shows that increasing the recycle ratio from zero to two will decrease the required surface area by 35%. The reason is that with constant stage cut, increasing the recycle ratio increases CO₂ concentration in the membrane feed stream which increases the separation driving force.

Although increasing the recycle ratio will decrease membrane surface area, the breakthrough time in adsorption beds will decrease due to increased CO₂ concentration and its flow rate in the retentate stream. Figure 14(b) shows the recycle ratio’s effect on breakthrough time. Sensitivity analysis indicates that an increase in reflux ratio from zero to two will decrease the breakthrough time by 25% in adsorption beds.

Figure 14(c) shows the effect of recycle ratio on CO₂ product concentration. As can be seen, the product concentration would be 60% in the absence of product recycling and it will be improved by 12% during the recycling of a portion of products. It is not recommended to use any recycle ratio bigger than 2 since increasing the recycle ratio any more will have a very little incremental impact on CO₂ product quality while operating cost increases dramatically.

**Process optimization** The sensitivity analysis on the membrane separation process provided by Hosseini et al. (2016) shows that as membrane selectivity, feed/retentate pressure ratio, and CO₂ feed concentration increase, the CO₂ product quality will also increase. Additionally, the membrane with the highest permeability requires the minimum surface area which reduces its capital cost (Hosseini et al. 2016). So, it is recommended to choose the membrane with the highest selectivity and permeability, and provide the maximum
possible vacuum pressure on the permeate side of the membrane.

From sensitivity analysis of the VSA system in our previous work, it can be concluded that increasing the feed flow rate or its CO₂ content can reduce the breakthrough time which highly affects the VSA cycle time. Also, it is recommended to keep the vacuum pressure and purge-to-feed ratio at a minimum level as much as possible. Increasing the purge-to-feed ratio not only reduces CO₂ product quality and N₂ recovery but also has little impact on bed regeneration (Zarghampoor et al. 2017).

Sensitivity analysis on hybrid membrane/VSA system recommends setting the vacuum pressure at the most possible minimum level, keeping the membrane stage cut around 10 to 15%, and recycle ratio around 2.

In the optimization of the hybrid membrane/VSA system, five independent parameters are considered. A built-in genetic algorithm in MATLAB is used as the optimization tool. The upper and lower bounds of each parameter and the results are provided in Table 4. It should be noted that the population size is considered equal to 20 and the repetition equal to 30. Figure 15 shows the variation of the minimum value and the average objective function for each repetition. Best fitness refers to the fitness of the best individual in the current population and the mean fitness is the average of fitness values across the entire population. The behavior of average and best fitness implies that the final answers provided in Table 4 are global optimum and the answers are not trapped in a local optimum.

Modeling results based on reported optimized parameters demonstrate that CO₂ purity will be 94.7% in the CO₂-rich stream and its recovery is equal to 99%. Also, N₂ purity in the N₂-rich stream is 99.9% and its recovery is equal to 97.3%. It should be noted that reaching this high value of purity and recovery is not possible in the single-stage membrane or VSA processes. In the VSA system, it is possible to produce a pure N₂ product while having a CO₂ product with high purity requires an adsorbent with high selectivity which is not available in industries yet.

In the proposed hybrid membrane/VSA system, it is possible to reduce operating costs in the case of choosing membrane and adsorbent with higher selectivity which makes it possible to reach this high value of separation with lower reflux ratio and vacuum pressure.

### Conclusion

To evaluate the CO₂ removal performance of the new hybrid membrane/VSA process, at first, a membrane and a VSA system were modeled. The comparison of the results showed that the recovery and CO₂ concentration prediction accuracy in the membrane and VSA system was 1% and 2.5% respectively. Finally, based on the results for single-stage processes, the new hybrid system consisting of one membrane and two adsorption beds was modeled. The results showed that CO₂ product concentration in the single-stage VSA process was 31% with a 91% recovery, while the new recommended hybrid process operating under the same condition

### Table 4 Process parameters and optimum conditions for hybrid membrane/VSA system

| Parameters               | Lower bound | Upper bound | Optimum value |
|--------------------------|-------------|-------------|---------------|
| Vacuum pressure (bar)    | 0.005       | 0.1         | 0.01          |
| Membrane stage cut (%)   | 10          | 20          | 11            |
| Cycle time (min)         | 150         | 600         | 390           |
| Recycle ratio            | 0.5         | 2.5         | 1.89          |
| Purge-to-feed ratio      | 0.01        | 0.2         | 0.02          |

![Fig. 15](image-url)

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produced a CO₂ product concentration of 70% with a 99% recovery. The advantage of this process is using only one vacuum package for both the membrane and VSA systems leading to lower capital costs, and installing the package on the side stream leads to lower energy consumption. The energy consumption in the membrane-VSA hybrid process is reduced to 2.7 MJ.kg⁻¹ CO₂ compared to the energy consumption of 4.2 MJ.kg⁻¹ CO₂ in a stand-alone VSA unit. It should be noted that decreasing the purge-to-feed ratio to less than 5% will increase the product concentration to 87%. Also, the cycle time for the hybrid system was 105% longer than the time for a single stage. This means that it is possible to use a bed with 24% less adsorbent with equal cycle time in this hybrid system which will reduce bed size lowering capital costs.

To increase CO₂ product quality, sensitivity analyses on vacuum pressure, membrane stage cut, and product recycling were performed. Based on the results, it is recommended to reduce vacuum pressure as much as possible, setting the stage cut around 15% and recycling a portion of the product. In the absence of product recycling, the CO₂ concentration would be 60% whereas by recycling 50% of the product, the CO₂ concentration will reach up to 70%. It should be noted that increasing the recycle ratio will decrease the required membrane surface area at constant stage cut, but will increase packed bed loads which will decrease their breakthrough time. It is recommended not to use a recycle ratio bigger than 2 since it will have a very little incremental impact on the CO₂ product quality. Based on the results of process optimization, it is possible to reach a CO₂ product purity to 94.7% with 99% recovery and a nitrogen product purity of 99.9% with 97.3% recovery. In the optimized system, the required vacuum pressure is 0.01 bar, and the membrane stage cut is 11%. Only 2% of N₂ product is used to purge the VSA beds for adsorbent regeneration. The optimized system requires a portion of the product to be recycled with recycle ratio of 1.86. It should be noted that choosing membrane and adsorbent with higher selectivity makes it possible to reach this high level of separation with a lower reflux ratio and vacuum pressure to reduce the system operating cost in the future.

Nomenclature $C_i$(mol. m⁻³): molar concentration; $D_{ij}$(m².s⁻¹): molecular diffusivity; $D_{ij}$ (m². s⁻¹): axial dispersion coefficient; $d_i$(m): particle diameter; $i$: component $i$; $K_i$(bar⁻¹): equilibrium constant; $K_{eq}$(kg·mol⁻¹·s⁻¹): quasi-second order mass transfer coefficient; $n$: Toth parameter; $P$(bar): total pressure; $P_{CO_2}$(Barrier): CO₂ permeability; $P_{N_2}$(Barrier): N₂ permeability; $P$(bar): membrane upstream pressure; $Q$(m³. s⁻¹): gas flow rate; $Q^*$: membrane stage cut; $q^*$ (mol.kg⁻¹): maximum amount adsorbed at equilibrium; $q_{max}$(mol.kg⁻¹): adsorbed phase concentration in equilibrium with fluid phase; $q_i$(mol.kg⁻¹): average concentration in adsorbent particle; $Re$: Reynolds number; $Sc$: Schmidt number; $s$: dimensionless membrane area; $t(s)$: time; $u$(m. s⁻¹): fluid velocity; $x$: membrane upstream feed mole fraction; $y$: permeate mole fraction; $z$(m): distance along bed; $\alpha$: membrane selectivity; $v$: bed void fraction; $\mu$(Pa·s): gas viscosity; $\rho_s$(kg. m⁻³): gas density; $\rho_i$(kg. m⁻³): particle density; $\gamma$: pressure ratio in membrane; $\gamma$: specific heat ratio

Author contribution Mr. M. H. Zarghampoor carried out modeling for this paper and prepared figures and tables. Dr. M. Soleimani, Dr. M. Mozaffarian, and Dr. M. Takht Ravanchi wrote the main manuscript.

Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethical approval and consent to participate The research meets all applicable standards with regard to the ethics of experimentation and research integrity, and the following is being certified/declared true. As an expert scientist and along with co-authors of the concerned field, the paper has been submitted with full responsibility, following due ethical procedure, and there is no duplicate publication, fraud, plagiarism, or concerns about animal or human experimentation.

Consent for publication Not applicable.

Competing interests The authors declare no competing interests.

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