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Optimizing Pressure-Swing Adsorption Processes and Installations for Gas Mixture Purification and Separation

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The paper formulates and provides a solution of the problem of determining the design parameters (the inner diameter of the adsorber, the length of the adsorbent layer, the diameter of the adsorbent granule, the capacity of the inlet and exhaust valves) and the regime (control) variables (pressure at the compressor outlet, the adsorption–desorption cycle time, the backflow coefficient regularities, changes in the degree of opening of the inlet and exhaust valves over time), under which the maximum degree of oxygen recovery is achieved in a two-adsorber installation pressure swing adsorption (PSA) with zeolite adsorbent 13X. The solution takes into account fulfillment of the constraints for oxygen purity, unit capacity and resource-saving of granular adsorbent. The computational experiment was used to study the effect of optimal regime (control) variables on the degree of recovery and purity of product oxygen, gas flow rate in the front layer of the adsorbent, and the capacity of the PSA unit. It is established that the complete abrupt opening of the inlet and exhaust valves does not provide for the fulfillment of constraints on the air flow rate in the front layer of the adsorbent (≤0.2 m / s), which leads to abrasion, dusting and shortening the life of the granular adsorbent in cyclic adsorption-desorption processes and requires defining the regularities of changes in the degree of valve opening in terms of time, the implementation of which eliminates hydraulic shock and destruction of the adsorbent.

1. Introduction

In recent decades, cyclic adsorption processes and, in particular, pressure swing adsorption (PSA) have become the most common way of separating gas mixtures and concentrating the target products in them. PSA processes are widely used in industry for the non-heating separation of hydrocarbons, extraction of methane, carbon dioxide, hydrogen from hydrogen-containing process flows, and oxygen and nitrogen from atmospheric air (Khajuria, 2011). The advantages of PSA units are their autonomy, mobility, reliability, and quick process stabilization (Ruthven et.al., 1993). The number of consumers of air separation products is increasing annually, and the annual growth in oxygen demand is on average ~ 4–5% due to increased demand in the steel industry, chemical industry, aluminium production and other industries. At the same time, a significant proportion of consumers utilise not pure oxygen as such, but air enriched with oxygen from 40 % vol. up to 90% vol. The use of PSA units with a capacity of up to 4 L / min for air separation is most profitable for consumers who need oxygen not constantly, but periodically (Xu et al., 2018, Kim et al., 2015, Rao et al., 2010, Santos et al., 2006).

One of the urgent tasks is designing medical oxygen concentrators which ensure the purity of oxygen from 40 % vol. up to 90% vol. and capacity from 1 L / min to 4 L / min (Moran et al., 2018, Rao et al., 2010, Santos et al., 2006, Cruz et al., 2005). The specified values of oxygen concentration and productivity (depending on the purpose of the concentrator) are ensured by fulfilling the technological limitations used in solving the problem of optimizing the operating modes of the medical oxygen concentrator.

The problems of optimizing PSA systems for extracting oxygen from atmospheric air were considered Santos et al. (2006), Rao et al. (2010), Beeyani et al. (2010), and others. In particular, Santos et al. (2006) shows the results of the PSA and VPSA optimization (vacuum PSA) optimization problem solution for medical oxygen concentrators models Oxysiv 5, Oxysiv 7 and MS S 624. It is shown that it is reasonable to use the oxygen

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extraction rate as optimization criterion, as it has the highest sensitivity to changes in design and regime parameters of the unit. In the work of Rao et al. (2010) the problem of optimizing PSA units for concentrating oxygen on zeolite adsorbents 5A and Ag-Li-X was formulated and investigated.
Analysis of numerous works of international and Russian researchers in the field of adsorption separation of multicomponent gas mixtures and optimization of operating regimes of PSA installations made it possible to establish the degree of relevance and promise of the current study.
The goal of this work is to formulate and study the optimization problem for the design and regime parameters of the PSA two-adsorber unit for air oxygenation, ensuring the maximum degree of oxygen extraction when the process regulations requirements on product purity (from 40% vol. to 90% vol.), unit capacity (from 1 L / min up to 4 L / min) and resource saving of granular adsorbent are met.

2. Stating the problem of optimization of design and regime parameters of air oxygenation PSA unit

We will analyze the technological process of air separation and oxygen concentration in two-adsorber PSA unit with a zeolite adsorbent 13X and a capacity of up to 4 L / min, designed to concentrate oxygen with a purity of 40 vol. % up to 90% vol. (Keltsev et al., 1984). During adsorption of N_2, O_2, Ar and adsorbent 13X, the following mass and heat exchange processes take place in the adsorbers of the PSA unit: 1) diffusion of N_2, O_2, Ar in the gas-air mixture flow; 2) mass transfer of N_2, O_2, Ar and heat exchange between the gas phase and the adsorbent; 3) the adsorption of predominantly N_2 and in significantly smaller amount of O_2 and Ar on the surface and in the micropores of zeolite adsorbent granules with the release of heat and the desorption of these components from micropores and from the surface of the granules with the absorption of heat.
The mathematical model of the PSA separation process of a three-component gas-air mixture includes the following equations (Akulinin et al., 2018): 1) component-wise material balance in air flow, taking into account the longitudinal mixing in the adsorbent layer; 2) Linear Driving Force (LDF) adsorption–desorption kinetics model; 3) heat propagation in the gas and solid phases, taking into account the convective component and thermal conductivity; 4) changes in the flow rate of the gas mixture and the pressure of the gas mixture along the height of the adsorbent layer; 5) pressure changes in the receiver; 6) air flow through the installation valves. The adsorption equilibrium on the microporous adsorbent 13X was described by the Dubinin-Radushkevich equation (Dubinin, 1972). As a result of the experimental studies, the following values for Dubinin equation coefficients were determined: limiting adsorption volume W_0 = 0.17 cm^3/g , parameter B = 6.55×10^{-6} $1/K^2$. The affinity coefficient for oxygen and argon is 0.68. Weight and heat transfer coefficients were determined by the formulas given in Akulinin et al. (2017).
To solve the resulting system of partial differential equations with the corresponding initial and boundary conditions (Akulinin et al., 2017), the method of lines (Rice et al., 2012) was used in the Matlab software environment. The equations of the model (Akulinin et al., 2018) were solved before the onset of the stationary periodic operation mode of the PSA unit, i.e. after ~ 20-30 adsorption–desorption cycles.
The analysis of the accuracy of the mathematical model was performed using the relative error of the mismatch calculated by the model and experimental values of the product oxygen concentration; the maximum value of the error did not exceed 11.5% (Akulinin et al., 2017).
In the course of the research, it was established that with an abrupt opening of the inlet and exhaust valves at a gas flow rate in the front layer above 0.15-0.25 m / s, hydraulic shocks may occur in the adsorbent layer, which leads to mechanical abrasion and dusting of the granular adsorbent (Skvortsov et al., 2018; Kheifets et al., 2004; Akulov, 1996). This scientifically established fact must be taken into account when solving problems of optimization and design of PSA units for separating gas mixtures. The rate limit in the front layer of the adsorbent can be achieved by controlling the degree of opening of the inlet and exhaust valves of the PSA unit according to a certain regularity, which is found as a result of solving the optimization problem.
Studies conducted in by Moran et al. (2018), Xu et al. (2018), Kim et al. (2015), Rao et al. (2010), Beeyani et al. (2010), Santos et al. (2006), Akulinin et al. (2017), and Skvortsov et al. (2018) allowed to determine the most effective controls u: pressure at the outlet of the compressor P^{in}, half-cycle duration $t_{ads} = t_c / 2$, backflow coefficient θ and the regularities of opening the inlet and exhaust valves $\Psi_i^{j*}, \Psi_{i+2}^{j*},\ i = 1, 2,\ j = \overline{1,m}$; the most dangerous perturbations z: temperature T_{env}, pressure P_{env} and composition of atmospheric air y_{env}; design parameters d of the PSA unit: internal diameter of the adsorber D_A, height of the adsorbent layer L, diameter of the adsorbent granule d_{gr}, throughput capacity of inlet and exhaust valves K_v; output

variables y of the PSA unit: concentrations y^{out} of oxygen, nitrogen, and argon in the product flow, unit capacity G^{out}, and oxygen recovery rate η.

The problem of optimization of the design and regime parameters of the PSA two-adsorber unit for air oxygenation is formulated as follows: for fixed values of disturbing influences z, which also include the worst case for operating the PSA unit, it is necessary to determine such design parameters $d^* = \{D_{\text{A}}^*, L^*, d_{\text{gr}}, K_{\text{v}}^*\}$ and control variables $u^* = \{P^{\text{in}}, t_{\text{ads}}^*, \theta^*, \psi_i^{j*}, \psi_{i+2}^{j*},\ i = 1, 2,\ j = \overline{1,m}\}$ so that the average oxygen recovery rate $\eta(u)$ in the time interval $[0, t_{\text{st}}]$ reaches a maximum η^*, i.e.

$$I(d^*, u^*, z) = \max_{d,u} \frac{1}{t_{\text{st}}(d,u)} \int_0^{t_{\text{st}}(d,u)} \eta\,(d, u, y^{\text{out}}(t), z)dt \tag{1}$$

with links in the form of mathematical model equations (Akulinin et al., 2018) and constraints:

on product oxygen concentration $y_{1,\text{def}}^{\text{out}} - y_{1,\text{st}}^{\text{out}}(d, u, z) \le 0$; (2)

on unit capacity $G_{\text{def}}^{\text{out}} - G^{\text{out}}(d, u, y_{1,\text{st}}^{\text{out}}, z) \le 0$ (3)

on gas mixture flow rate in the adsorbent layer $\max\limits_{t \in t_{\text{c}}} \left|v_{\text{g}}(t, d, u, z)\right| - v_{\text{g}}^{+} \le 0$ (4)

on pressure changes in the adsorbent layer
$$\max_{t \in [0, t_{\text{c}}/2]} \left[P_{\text{ads}}^{\text{in}}(t, d, u, z) - P_{\text{ads}}^{\text{out}}(t, d, u, z)\right] \le \Delta P_{\text{ads}}^{+}$$
$$\max_{t \in [t_{\text{c}}/2,\, t_{\text{c}}]} \left[P_{\text{des}}^{\text{in}}(t, d, u, z) - P_{\text{des}}^{\text{out}}(t, d, u, z)\right] \le \Delta P_{\text{des}}^{+} \tag{5}$$

on controls $\underline{t_{\text{ads}}} \le t_{\text{ads}} \le \overline{t_{\text{ads}}}$, $\underline{P^{\text{in}}} \le P^{\text{in}} \le \overline{P^{\text{in}}}$, $\underline{\theta} \le \theta \le \overline{\theta}$, $0 \le \Psi_i^j \le 1,\ i = \overline{1,4},\ j = \overline{1,m}$ (6)

on design parameters $\underline{D}_{\text{A}} \le D_{\text{A}} \le \overline{D}_{\text{A}}$, $\underline{L} \le L \le \overline{L}$, $\underline{d}_{\text{gr}} \le d_{\text{gr}} \le \overline{d}_{\text{gr}}$, $\underline{K}_{\text{v}} \le K_{\text{v}} \le \overline{K}_{\text{v}}$ (7)

where: v_{g}^{+} – the maximum permissible (critical in terms of adsorbent destruction) air flow rate in the front layer of the adsorbent; , and $t_{\text{c}}, t_{\text{st}}$ are the duration of the “adsorption–desorption” cycle and the time needed for the installation to reach a stationary periodic mode, respectively.

The formulated argument optimization problem Eq(1)-(7) with the assumption of the approximation of continuous control functions Ψ_i^{j*} and Ψ_{i+2}^{j*}, i=1.2 over a time interval $[0, t_{\text{c}}]$ by piecewise constant functions, belongs to the class of nonlinear programming problems. To solve it, the method of sequential quadratic programming (Rice et al., 2012) was used in the Matlab software environment. The initial data, the variation ranges of the design and regime parameters of the PSA two-adsorber unit are given in the table below.

Table 1: Initial data for solving the problem of optimization

Initial data and parameter variation ranges	
Controls u:	Design parameters d:
$2 \le P^{\text{in}} \le 6$ 10^5 Pa, $1 \le t_{\text{ads}} \le 40$ s	$0.0212 \le D_{\text{A}} \le 0.0732$ м, $6D_{\text{A}} \le L \le 14D_{\text{A}}$ m
$0 \le \theta \le 5$, $0 \le \Psi_i^j \le 1$ relative units	$0.5 \le d_{\text{gr}} \le 2$ mm, $5 \le K_{\text{v}} \le 20$ L / min
Disturbances z:	Maximum permissible values of:
$y_{\text{env}} = \{20.3, 78.2, 1.5\}$ % vol.	product purity $y_{1,\text{def}}^{\text{out}}$ = {40, 60, 90} % vol.
$T_{\text{env}} = 303$ K	unit capacity $G_{\text{def}}^{\text{out}}$ = {1, 2, 4} L / min
$P_{\text{env}} = 1 \cdot 10^5$ Pa	gas flow rate v_{g}^{+} = 0.2 m / s

3. Results and discussion

Analysis of the graphs presented in Figure 1 shows that an increase in the oxygen concentration at the PSA unit outlet from 40 % vol. to 90 % vol. is achieved with a respective change in the main structural dimensions of the PSA unit by two or more times, and throughput of valves – by three times (Figure 2b). In this case, the optimal values of the regime (control) variables change as follows: the pressure at the compressor outlet P^{in} almost doubles (from 2.25 · 105 Pa to 4.0 · 105 Pa), the backflow rate θ increases 3.34 times (from 0.6 to 2), and half cycle duration $t_{ads} = t_c / 2$ grows by1.4 times (from 10 s to 14 s).

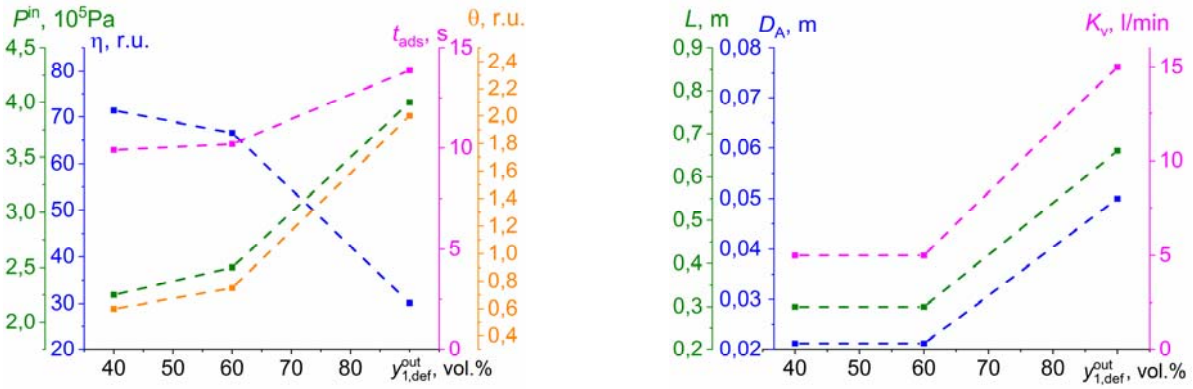

Figure 1: Optimal values of the control (a) and design parameters (b) at the required concentration of product oxygen 40, 60, 90 and the unit capacity of 1 L / min.

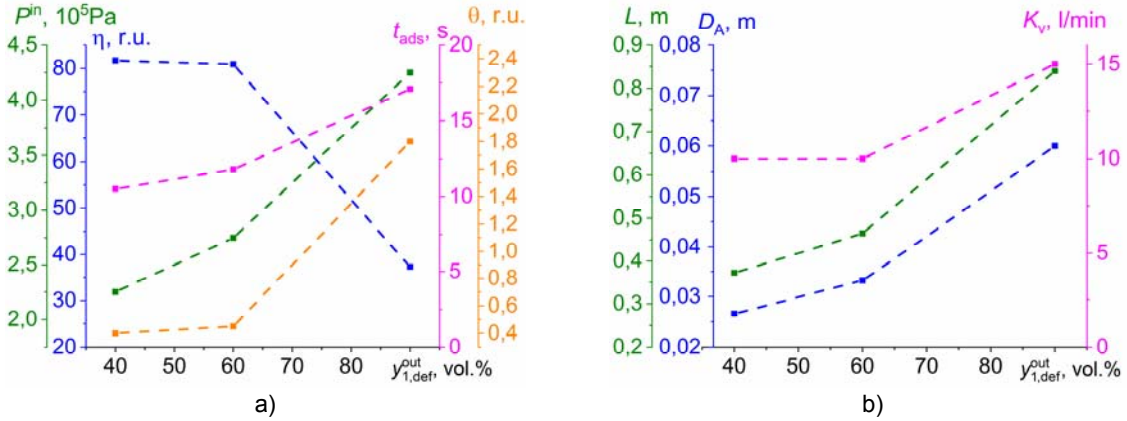

Figure 2: Optimal values of the control (a) and design parameters (b) at the required concentration of product oxygen 40, 60, 90 and the unit capacity of 2 L / min.

With an increase in the time of adsorption pressure set-up and, accordingly, the duration of the adsorption stage t_{ads}, the equilibrium nitrogen concentration in the adsorbent also increases (Ruthven et al., 1993; Dubinin, 1972), which leads to an increase in the purity of the product from 40% vol. % up to 90 % vol. Thus, an increase in the θ value is associated with the need for a deeper regeneration of the adsorbent at the desorption stage with an increase in the purity of the product $y^{out}_{1,def}$. And, finally, to increase the flow of atmospheric air in the PSA unit feed, a corresponding increase in K_v valve capacity is required.

An increase in the PSA unit's performance capacity from 1 L / min to 4 L / min is achieved with a corresponding change in the main structural dimensions of the unit (Figure 1b, 2b, 3b): the internal diameter of the adsorber D_A and the length L of the adsorbent layer increase by 1.5 times on average and the throughput of valves K_v practically does not change when the purity of the product $y^{out}_{1,def}$ = 90 % vol. In this case, the optimal values of the regime (control) variables are changed as follows: the pressure at the compressor outlet

P^{in} increases by more than 1.2 times (from 2.25 10^5 Pa to 2.75 10^5 Pa) with product purity $y^{out}_{1,def}$ = 40 % vol. and by 1.4 times (from 0 · Pa to 5.5 10^5 Pa) with product purity $y^{out}_{1,def}$ = 90 % vol. Backflow rate θ will decrease by 1.5 times (from 0.6 to 0.4) with product purity $y^{out}_{1,def}$ = 40 % vol. and by 1.25 times (from 2 to 1.65) with product purity $y^{out}_{1,def}$ = 90 % vol., respectively. The duration of a half-cycle $t_{ads} = t_c / 2$ increases 1.2 times (from 10 s to 12 s) with product purity $y^{out}_{1,def}$ = 40 % vol. and 1.55 times (from 14 s to 22 s) with product purity $y^{out}_{1,def}$ = 90 % vol. There is a slight decrease in the value of coefficient θ, which is due to the fact that a smaller amount of the product flow is used for the regeneration of the adsorbent with increasing pressure P^{in} and, accordingly, pressure P^{in}_{ads} in the adsorber (Akulinin et al., 2017).

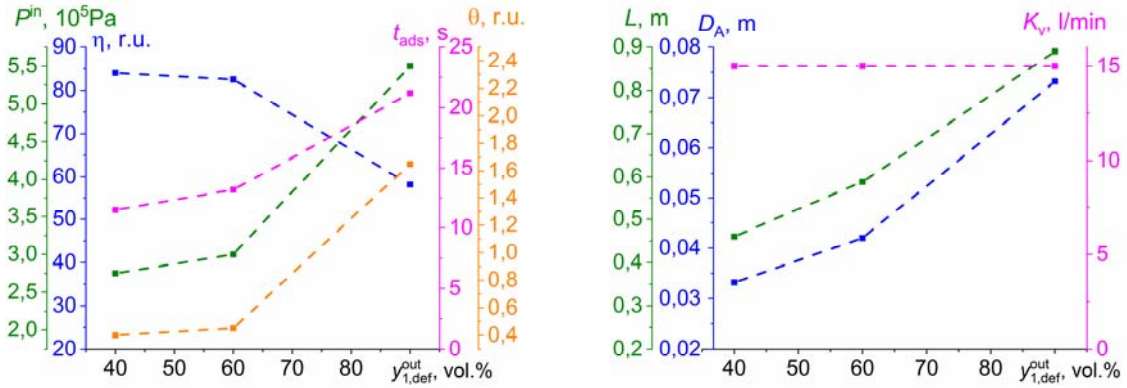

Figure 3: Optimal values of the control (a) and design parameters (b) at the required concentration of product oxygen 40, 60, 90 and the unit capacity of 4 L / min.

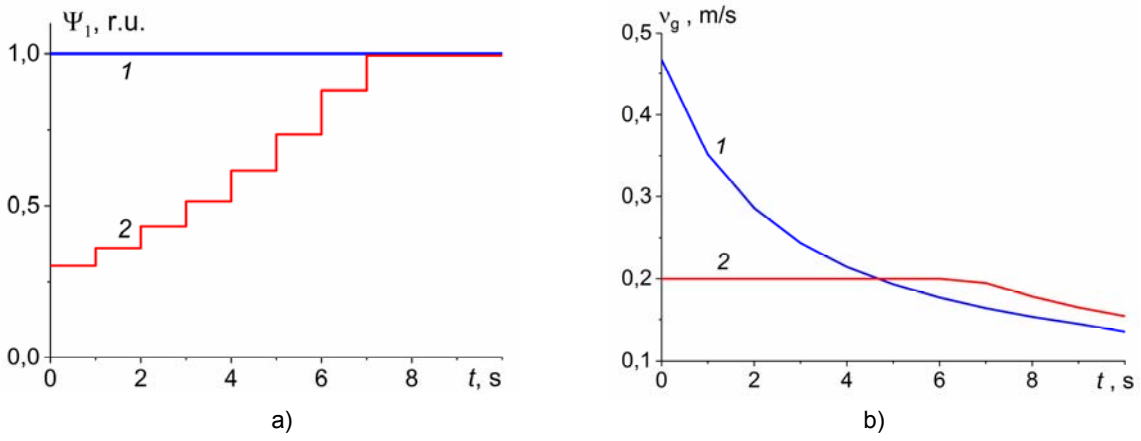

Figure 4: Dynamics of the degree of opening of the unit's inlet valves (a) and the flow rate in the front layer of the adsorbent (b) at the optimal values of design and regime (control) parameters: 1– with abrupt opening of the inlet valve; 2– with stepped opening of the inlet valve.

Figure 4a presents the regularities of the variation in time of the degree of opening the PSA unit's inlet valve, and Figure 4b – the corresponding gas flow rates in the front layer of the adsorbent when fulfilling constraints on the specified values of purity $y^{out}_{1,def}$ = 90 % vol. of production oxygen and productivity G^{out}_{def} = 1 L / min. From the analysis of the graphs, it follows that with an abrupt opening of the inlet valve (curve 1 in Figure 4a), the gas flow rate in the front adsorbent layer reaches 0.47 m / s (curve 1 in Figure 4b), which leads to the destruction of the zeolite adsorbent and contamination of the product flow. With a stepped (smooth) opening of the inlet valve (curve 2 in Figure 4a), the flow rate in the front layer of the adsorbent does not exceed a critical value of 0.2 m / s (curve 2 in Figure 4b).

4. Conclusions

With the use of modern methods of system analysis, mathematical modelling and optimization, new results were obtained for the design of medical concentrators with a capacity of 1 to 4 L / min and a product purity of 40 % vol. up to 90% vol.: 1) with increasing purity of the product, the degree of oxygen recovery decreases accordingly; so, for a PSA unit with a capacity of 1 L / min, an increase in the concentration of oxygen from 40 % vol. up to 90 % vol. leads to a decrease in the degree of recovery by 2.4 times; 2) with increasing unit capacity, the degree of oxygen recovery (especially at high concentrations) increases, which is explained by an increase in pressure at the outlet of the compressor (and, accordingly, at the stage of adsorption), as well as a decrease in the backflow coefficient; so, with a product purity of 90 % vol. increase in unit capacity from 1 to 4 L / min allows to increase the degree of recovery twice (from 30% to 58%), and a similar increase in unit capacity with a product purity of 40% vol. – 1.16 times (from 72% to 84%).
The problem formulation and optimization of the operation regimes of the two-adsorber PSA unit for air oxygenation can be used in the design of new resource-saving processes and PSA units for the separation and purification of multicomponent gas mixtures under uncertainty of the initial design data.

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