DOI: 10.6060/ivkkt.20226508.6625

УДК: 661.935, 519.633.2

К ВОПРОСУ ИСПОЛЬЗОВАНИЯ УРАВНЕНИЯ ДУБИНИНА–РАДУШКЕВИЧА–АСТАХОВА В РАСЧЕТАХ ИЗОТЕРМ H_2, CO_2, CO ДЛЯ ПРОЦЕССА КОРОТКОЦИКЛОВОЙ БЕЗНАГРЕВНОЙ АДСОРБЦИИ ИЗВЛЕЧЕНИЯ ВОДОРОДА НА БЛОЧНЫХ ЦЕОЛИТАХ 13Х

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Расчет изотерм адсорбции компонентов синтез-газа в процессе короткоцикловой безнагревной адсорбции (КБА) для извлечения из него водорода на цеолитовых адсорбентах традиционно осуществляется с использованием уравнения Ленгмюра или производных от него уравнений. Недостатком его использования является необходимость получения экспериментальных изотерм адсорбции по каждому газу, входящему в газовую смесь на используемом адсорбенте. Такой подход является затратным, особенно в случае многокомпонентных смесей, таких, как синтез-газ. В статье продемонстрирован способ расчета изотерм адсорбции газов H_2, CO_2, CO в процессе КБА извлечения водорода из синтез-газа на перспективных блочных цеолитах 13Х с использованием уравнения Дубинина–Радушкевича–Астахова (ДРА). Получены экспериментальные изотермы адсорбции H_2, CO_2, CO при температурах 293 и 323 К, изотермы адсорбции N_2 при температуре его кипения 77,35 К на цеолитах 13Х трех образцов. С использованием экспериментальных изотерм решены задачи параметрической идентификации и определены параметры уравнения ДРА для газов H_2, CO_2, CO на блочных цеолитах 13Х. Установлено, что расчет изотерм адсорбции газов H_2, CO_2, CO на блочных цеолитах 13Х, характеристики которых попадают в интервалы предельного адсорбционного объема 0,258–0,296 см^3/г и характеристической энергии адсорбции 10279–13395 Дж/моль, можно корректно осуществлять с использованием уравнения ДРА в диапазоне температур 293–323 К и давлений 0–30 атм. При этом максимальная ошибка в рассогласовании между экспериментальными изотермами газов и рассчитанными по уравнению ДРА составила 14,69% по H_2; минимальная – 1,81% по CO_2. В отличие от традиционного способа, полученные коэффициенты аффинности позволяют осуществлять расчет изотерм адсорбции газов H_2, CO_2, CO в найденных интервалах предельного адсорбционного объема и характеристической энергии адсорбции всего лишь по одной изотерме стандартного газа (N_2) на используемом цеолите 13Х. Универсальность способа расчета по предложенной методике может быть использована для расчетов изотерм адсорбции различных газов, смесей и адсорбентов в циклических адсорбционных процессах.

Ключевые слова: короткоцикловая безнагревная адсорбция, цеолит 13Х, водород, синтез-газ, изотерма, уравнение Дубинина–Радушкевича–Астахова

ON THE ISSUE OF USING THE DUBININ–RADUSHKEVICH–ASTAKHOV EQUATION IN CALCULATING ISOTHERMS OF H2, CO2, CO IN THE PRESSURE SWING ADSORPTION PROCESS FOR HYDROGEN RECOVERY ON BLOCK ZEOLITES 13X

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The calculation of adsorption isotherms of synthesis gas components in the process of pressure swing adsorption (PSA) for hydrogen extraction on zeolite adsorbents is traditionally carried out using the Langmuir equation or equations derived from it. Its disadvantage consists in the necessity to obtain experimental adsorption isotherms for each gas in the gas mixture on the used adsorbent. This approach is expensive, especially in the case of multicomponent mixtures, such as synthesis gas. The paper demonstrates the prospects of an alternative method for calculating adsorption isotherms of H_2, CO_2, CO gases in the PSA process for hydrogen extracion from synthesis gas on block zeolites 13X using the Dubinin–Radushkevich–Astakhov (DRA) equation. Using zeolites 13X made by three samples, experimental adsorption isotherms of H_2, CO_2, CO at temperatures of 293 and 323 K, and adsorption isotherms of N_2 at a boiling point of 77.35 K were obtained. Using experimental isotherms, the problems of parametric identification were solved, and the parameters of the DRA equation for H_2, CO_2, CO gases on block zeolites 13X were determined. It has been found that the calculation of adsorption isotherms of H_2, CO_2, CO gases on zeolites 13X, the characteristics of which fall within the ranges of the limiting adsorption volume 0.258–0.296 cm^3/g and the characteristic adsorption energy 10279–13395 J/mol, respectively, can be correctly carried out using the DRA equation in the temperature range of 293–323 K and the pressure range of 0–30 atm. In this case, the maximum value of the mismatch between the experimental gas isotherms and those calculated by the DRA equation is 14.69% for H_2; the minimum value is 1.81% for CO_2. Certain affinity coefficients make it possible to calculate the adsorption isotherms of H_2, CO_2, CO gases in the obtained ranges of the limiting adsorption volume and characteristic adsorption energy using only one isotherm of the standard gas (N_2) on the zeolite 13X used. The versatility of the DRA equation can be used to calculate the adsorption isotherms of various gases, mixtures, and adsorbents in cyclic adsorption processes.

Key words: pressure swing adsorption, zeolite 13X, hydrogen, synthesis gas, isotherm, Dubinin-Astakhov equation

Для цитирования:

Голубятников О.О., Акулинин Е.И. К вопросу использования уравнения Дубинина–Радушкевича–Астахова в расчетах изотерм H_2, CO_2, CO для процесса короткоцикловой безнагревной адсорбции извлечения водорода на блочных цеолитах 13Х. *Изв. вузов. Химия и хим. технология*. 2022. Т. 65. Вып. 8. С. 39–47. DOI: 10.6060/ivkkt.20226508.6625.

For citation:

Golubyatnikov O.O., Akulinin E.I. On the issue of using the Dubinin–Radushkevich–Astakhov equation in calculating isotherms of H_2, CO_2, CO in the pressure swing adsorption process for hydrogen recovery on block zeolites 13X. *ChemChemTech* [*Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.*]. 2022. V. 65. N 8. P. 39–47. DOI: 10.6060/ivkkt.20226508.6625.

INTRODUCTION

Hydrogen is a promising source of energy, and its consumption in the world doubles every fifteen years. For 2020, more than 75 million tons of hydrogen are consumed in the world. More than 50% of hydrogen is consumed in the production of ammonia and more than 25% in the oil refining industry, and there is a constant increase in hydrogen consumption in the energy sector [1, 2].

Today, the main method of hydrogen production is the steam reforming of natural gas, which occupies 75% of the production volume and makes it possible to obtain production hydrogen at the lowest cost price of 2.5-5 $ per 1 kg [1, 2]. One of the key stages is the process of adsorption separation of steam reforming products in order to extract hydrogen of high purity (99.99% vol. and higher) from synthesis gas [3]. The main components accompanying hydrogen in synthesis gas are CO2, CO, CH4, and N2 [3]. The adsorption separation process is usually organized according to the principle of pressure swing adsorption (PSA) [4]. The PSA unit for hydrogen extraction is a complex technological object that includes four or more adsorbers, shut-off valves, receivers, and instrumentation. The principle of the unit operation consists in sequential alternation of adsorption and desorption processes in adsorbers filled with an adsorbent. This is achieved by providing different gas pressures at the adsorption and desorption stages (for implementing the PSA process, pressure at the adsorption stage must be higher than at the desorption stage). As a result, a continuous flow of product hydrogen with a purity of 99.99 vol.% and higher is formed at the unit outlet [3]. Both various brands of active carbons [5, 6] and industrial zeolites 13X [7, 8] and 5A [9, 10], which possess high selectivity for hydrogen-accompanying synthesis gas components CO_2, CO, CH_4, N_2, are most often used as microporous adsorbents for hydrogen extraction from synthesis gas. In addition, in recent years, new promising adsorbents for hydrogen extraction, such as metal-organic framework structures MOF, Cu-BTS, Cu-TDPAT, new block adsorbents and a number of others, have been developed [11-13].

The complexity and scale of the PSA unit and the processes occurring in it require high economic costs for their study by experimental methods. The computational capabilities of the modern computer technology allow for the study and optimal design of PSA units using mathematical modeling methods [3, 10, 14]. Mathematical models are systems of partial differential equations describing the fields of velocities, concentrations and temperatures [3, 15, 16]. Such systems are complex, since the variables of the model are in complex relationships with each other and with the transfer coefficients, and the solution of the systems is carried out before the onset of the cyclic steady state [17]. Currently, several approaches have been developed to solve the PSA models [14].

One of the main tasks in the construction of mathematical models is the correct calculation of adsorption – desorption isotherms. In the majority of works on modeling the PSA process for hydrogen extraction from multicomponent mixtures, the equations of Langmuir isotherms and derivative equations (extended Langmuir, dual-site Langmuir, Langmuir–Freundlich) are used [3, 7, 9, 10, 17-19]. The coefficient values of isotherm equations for specific gas mixtures are found by experimentally determining the isotherms of gases included in the mixture in the temperature range of 293-323 K (the range at which the PSA process for hydrogen extraction from synthesis gas is carried out) and then solving the problem of parametric identification of the coefficients. The analysis of the works shows that the values of the Langmuir isotherm coefficients for the same gases and zeolites can differ by whole orders of magnitude [3, 7, 9, 10, 17-19]. This discrepancy can be explained by the fact that the properties of industrial zeolites of the same type (for example, 13X or 5A) made by different manufacturers differ from each other due to the peculiarities of the production technology (the use of various binding components in different amounts, different production methods). Moreover, the properties of the zeolite adsorbent can also vary from the same manufacturer in different batches. Therefore, in order to achieve high accuracy of the PSA process model, it is necessary to experimentally determine the Langmuir isotherm coefficients for each gas included in the initial gas mixture, and not to use the literature data. This approach is expensive, especially in the case of multicomponent mixtures, such as synthesis gas (which can include up to 7 components).

An alternative method for calculating isotherms is the Dubinin–Radushkevich–Astakhov (DRA) equation based on the theory of volumetric filling of micropores (TVFM) [20]. According to TVFM, for any nature of adsorption interactions (i.e., under the action of dispersion, electrostatic, or other forces) that cause physical adsorption, an adsorption field created by a solid appears in the entire micropore space. Adsorption in micropores is characterized by volumetric filling of the adsorption space, while the molecules sequentially adsorbed in micropores do not form adsorption beds. Therefore, the main geometric parameter characterizing a microporous adsorbent is the volume of micropores, and not their surface. This theory gave birth to the Dubinin–Radushkevich–Astakhov (DRA) isotherm equation which was originally derived to describe adsorption isotherms at temperatures below critical for adsorptives using equilibrium standard states of components in equilibrium phases: limiting adsorption at the equilibrium saturated vapor pressure of the adsorptive [20]. The use of TVFM in the region of supercritical temperatures is usually limited to an interval extending to 100-150 K above the critical temperature [21].

However, a number of works [12, 21-32] shows that the DRA equation can be used to quantitatively describe experimental isotherms also at temperatures above critical by more than 100-150 K on active microporous carbons, zeolites, silica gels, and molecular sieves. In particular, the DRA equation can be used to describe the adsorption of CH_4, N_2, H_2 on Zeo-5A@MOF-74-1 zeolite at temperature $T = 298$ K and pressure $P = 0\text{-}22$ atm [12]; H_2 on active carbons [23, 24]; Ar on zeolite 13X [32]; CH_4 on zeolites 13X, CaLSX, KLSX, LiLSX at $T = 298\text{-}343$ K and $P = 0\text{-}1$ atm [31]; CH_4, N_2 on zeolites Cu-BTC and MaxSorb at $T = 298\text{-}303$ K and $P = 0\text{-}40$ atm [30]; CO on zeolite 13X at $T = 293\text{-}343$ K and $P = 0\text{-}1$ atm [27]. Works [22, 25] propose to replace the saturation pressure with standard pressures. With the help of molecular dynamics calculations, it is shown that this replacement leads to an increase in the accuracy of calculating isotherms using the DRA equation in subcritical temperature ranges for microporous carbons [22].

The application of the DRA equation for calculating adsorption isotherms is carried out according to the following procedure. First, it is necessary to experimentally determine the isotherm of the standard substance (for zeolites, the standard gas is usually N_2).

Then, with its help, the coefficient values of the limiting adsorption volume of the adsorbent W_0 and the characteristic energy of adsorption E are restored. To calculate the isotherms of other gases included in the gas mixture using the DRA equation, the affinity coefficients β (for a standard gas β = 1), which are determined experimentally or calculated using approximate equations, are used on this adsorbent. The most accurate method for determining the affinity coefficients β is experimental. The affinity coefficient β for the corresponding gas is thus determined from the ratio of the ordinates of the characteristic curves [20]. There are also several approximate equations for calculating the affinity coefficient, such as the parachor relation equation, molar heat capacity equation of the considered and standard substances; equations that take into account the polarity and non-polarity of adsorptive molecules, the multiplicity of bonds, the presence of quadrupole and dipole moments and a number of other effects [33]. However, in practice, all these equations are often inferior in accuracy to the experimental method, when commercial adsorbents are used as adsorbents suitable for the equation.

It should be noted that one experimental isotherm of the standard (model) gas, from which the coefficients W_0 and E are determined, is sufficient for using the DRA equation. The remaining isotherms of gases entering the gas mixture can be calculated using the found W_0 and E for the model gas and the affinity coefficient β for the gas under consideration.

The purpose of this work is to study the possibility of using the DRA equation for calculating the adsorption isotherms of synthesis gas components in the PSA process for hydrogen extraction (using perspective block zeolites 13X as adsorbents) and determining the ranges of coefficient values of the DRA equation for block zeolites 13X, which ensure the correct calculation of adsorption isotherms.

METHODS AND MATERIALS

To determine the equilibrium conditions in the gas mixture–adsorbent system, studies were carried out to obtain adsorption–desorption isotherms of H_2, CO_2, CO (which are the main components of synthesis gas – the initial gas mixture). Three samples of block zeolites 13X (Roskhimzashchita Corp.) made of zeolite powder from different manufacturers were selected as adsorbents. This is necessary for determining the ranges of coefficients W_0 and E of the DRA equation, where the correct calculation of adsorption isotherms is provided. The study used the following samples of zeolites: 13X-1 – block with equivalent diameter of pore channels d = 0.20 mm made from zeolite powder by Zeochem (Switzerland); 13X-2 – block with d = 0.26 mm made from zeolite powder by HKC Corp. (Hong-Kong, Chine); 13X-3 – block with d = 0.33 mm made from zeolite powder by KNT Group (Russia).

At the first stage, the process of obtaining adsorption–desorption isotherms for a model gas (N_2) was studied. Using an Autosorp IQ gas sorption meter (Quantachrome, USA), the complete N_2 isotherm was obtained at a boiling point of 77.35 K for each sample of zeolite 13X.

Further, according to M.M. Dubinin's methodology, the obtained isotherms were plotted in semi-logarithmic coordinates for the working pressure range of 0-30 atm, at which the PSA process for H_2 extraction from synthesis gas proceeds. For this purpose, the dependencies of the equilibrium concentration $a_{\mathrm{N2}}(P/P_{\mathrm{s}})$ are plotted in semi-logarithmic coordinates, where the values $\lg^2\left(\frac{P_{\mathrm{s,N2}}}{P_{\mathrm{N2}}}\right)$ are plotted along the x-axis, and the values $\lg(a_{\mathrm{N2}})$ are plotted along the y-axis. Next, according to the experimental points of the graph $\lg(a_{\mathrm{N2}})$ from $\lg^2\left(\frac{P_{\mathrm{s,N2}}}{P_{\mathrm{N2}}}\right)$, the regression equation $y = Dx + C$ is constructed, where the values of the regression coefficients D, C are determined.

The linearized isotherms for each zeolite sample are used to calculate the values of two coefficients of the DRA equation (1), i.e. the limiting adsorption volume W_0 (cm^3/g) and the characteristic adsorption energy E (J/mol):

$$a_k^* = \frac{W_0}{\upsilon_k^*}\exp\left[-\left(\frac{RT_{\mathrm{g}}\lg\left(\frac{P_{\mathrm{s},k}}{P_{\mathrm{p},k}}\right)}{\beta_k E}\right)^n\right], \qquad (1)$$

$$W_0 = \upsilon_{\mathrm{N_2}}^* 10^{\mathrm{C}}, B = \frac{D\beta_{\mathrm{N_2}}^2}{0.434T_{\mathrm{g}}^2}, E = 4.184 \times 4.574\sqrt{\frac{1}{B}},$$

$$\upsilon_k^* = \frac{10^{-3}\mathrm{M}_{\mathrm{g},k}}{\rho_k^*}, \rho_k^* = \rho_{\mathrm{b},k}10^{-0.434\alpha_k(T_{\mathrm{g}}-T_{\mathrm{b},k})},$$

$$\alpha_k = \frac{\lg\left(\frac{\rho_{\mathrm{b},k}}{\rho_{\mathrm{cr},k}^*}\right)}{0.434(T_{\mathrm{cr},k}-T_{\mathrm{b},k})}, \rho_{\mathrm{cr},k}^* = \frac{\mathrm{M}_{\mathrm{g},k}}{1000b_k}, b_k = \frac{R^*T_{\mathrm{cr},k}}{8P_{\mathrm{cr},k}},$$

$$P_{\mathrm{s},k} = \frac{\exp\left(\frac{A_k-F_k}{T_{\mathrm{g}}-C_k}\right)}{760}, P_{\mathrm{p},k} = P\frac{y_k}{100},$$

where k is the initial gas mixture component, $k = \mathrm{H_2, CO_2, CO}$; a_k^* is the equilibrium concentration in the adsorbent, mol/kg; υ_k^* is the molar volume of the adsorbate, cm^3/mmol; T_{g} is gas temperature; β_k is the affinity coefficient to standard gas (N_2); B is a parameter characterizing the predominant size of micropores, 1/K^2; R is a universal gas constant, J/(mol K), $R = 8.31$; $P_{\mathrm{s},k}$ is saturation pressure, atm; $P_{\mathrm{p},k}$ is partial pressure, atm; n is the exponent of the DRA equation; $M_{\mathrm{g},k}$ is the molar mass of the k-th component of the gas mixture, kg/kmol; ρ_k^* is the density of the adsorbate, g/cm^3; $\rho_{\mathrm{b},k}$ is the gas density at a boiling point, g/cm^3; $T_{\mathrm{b},k}$ is the boiling point of gas, K; α_k is the thermal coefficient of limiting adsorption; $T_{\mathrm{cr},k}$ is the critical temperature of the k-th component in the gas mixture; $\rho_{\mathrm{cr},k}^*$ is the density of the adsorbate at the critical temperature, g/cm^3; b_k is the molar volume constant, l/mol; R^* is the universal gas constant, l atm/(mol K), $R^* = 0.0821$; $P_{\mathrm{cr},k}$ is the critical pressure of gas, atm; A_k, F_k, C_k are Antoine equation constants; P is the current pressure of gas, atm; y_k is the volumetric gas concentration, vol.%. The initial data for calculating isotherms are taken from [34]. For $n = 2$, the DRA equation (1) is also known in the literature as Dubinin–Radushkevich (DR) equation, and for $n = 3$, it is called the Dubinin–Astakhov (DA) equation.

It should be noted that obtaining the complete isotherm of the model gas is an optional condition; a fragment of its isotherm is sufficient for the operating pressure range, at which the PSA process is carried out.

Since the PSA process for hydrogen extraction from synthesis gas proceeds in the temperature range of 293-323 K, then at the second stage, using an iSorb gas sorption analyzer (Quantachrome, USA), adsorption isotherms of H_2, CO_2, CO are obtained at gas temperatures of 293 and 323 K and pressures of 0-30 atm, which correspond to the operating range of temperatures and pressures of the PSA process under consideration.

Next, the affinity coefficients β_k of H_2, CO_2, CO gases included in the synthesis gas were determined. The β_k values for H_2, CO_2, CO gases were determined by solving parametric identification problems (2) – (4) presented below.

The problem was formulated as follows: for each k-th gas entering the synthesis gas ($k = \mathrm{H_2}, \mathrm{CO_2}, \mathrm{CO}$), it is necessary to find such values of the affinity coefficient β_k and the exponent n of the DRA equation, for which the mismatch RMS_k^* (root-mean-square error) between the adsorption value a_k determined experimentally and the equilibrium concentration a_k^* determined by the DRA equation will be the smallest.

case 1

$$\mathrm{RMS}_k^* = \min_n Q_n, \quad n = 1,2,3,4,5; \tag{2}$$

$$Q_n = \min_{0.01 \le \beta_k \le 10} \mathrm{RMS}_{k,n}; \tag{3}$$

$$\mathrm{RMS}_{k,n} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{a_{k,i}(P_i) - a_{k,i}^*(P_i, n)}{a_{k,i}(P_i)}\right)^2}\ 100\%; \tag{4}$$

case 2

$$\mathrm{RMS}_k^* = \min_{\substack{0.01 \le \beta_k \le 10 \\ 0.01 \le n \le 5}} \mathrm{RMS}_k; \tag{2′}$$

$$\mathrm{RMS}_k = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{a_{k,i}(P_i) - a_{k,i}^*(P_i)}{a_{k,i}(P_i)}\right)^2}\ 100\%; \tag{4′}$$

where RMS_k is the root mean square error; a_k is the adsorption value found experimentally, mol/kg; a_k^* is the equilibrium concentration found by the DRA equation (1), mol/kg; P is gas pressure, atm; i is a measurement number; N is the total number of measurements of the adsorption value for three samples of the same type of zeolite 13X.

In the optimization problem (3), case 1, the value of the affinity coefficient β_k for the k-th gas is determined, where the minimum value of the root-mean-square error $\mathrm{RMS}_{k,n}$ is achieved for a given integer value of the exponent n of the DRA equation (1). In the optimization problem (2), case 1, among the five values of $\mathrm{RMS}_{k,n}$ ($n = 1,2,3,4,5$) defined in problem (3), the smallest value $\mathrm{RMS}_{k,n}$ and the corresponding value of the exponent n of the DRA equation (1) is chosen for the k-th gas. If the final value of RMS_k^* is more than 15%, then another optimization problem is solved – (2′), where n is the optimized continuous variable $0.01 \le n \le 5$.

Problems (2)–(4) were solved in the MatLab software environment using the fmincon solver. The SQP sequential quadratic programming algorithm was chosen as the solution algorithm.

RESULT AND DISCUSSION

The complete isotherms of N_2 at a boiling point of 77.35 K on zeolites 13X are shown in Fig. 1. Table 1 shows W_0 and E coefficients determined by Dubinin's method for all samples of industrial zeolites 13X. Table 1 also shows the values of W_0 and E coefficients for zeolites 13X found in the works of other authors.

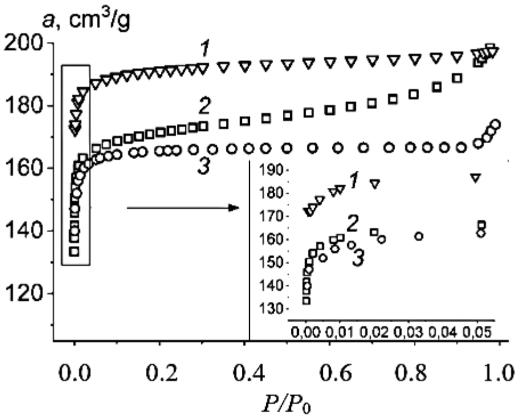

Fig. 1. Complete nitrogen isotherms at a nitrogen boiling point of 77.35 K on zeolites 13X: 1 – 13X-1; 2 – 13X-2; 3 – 13X-3
Рис. 1. Полные изотермы азота при температуре кипения азота 77,35 К на цеолитах 13X: 1 – 13X-1; 2 – 13X-2; 3 – 13X-3

Table 1

Coefficient values of the DRA equation for zeolites 13X (standard gas N_2)

***Таблица 1.* Коэффициенты уравнения ДРА для цеолита 13X (стандартный газ N_2)**

Source	W_0, cm^3/g	*E*, J/mol	*n*
[20]	0.235	7473	2
[13]	0.230	15750	4.52
[32]	0.269	13638	2
13X-1	0.296	13395	2
13X-2	0.262	12916	2
13X-3	0.258	10279	2

The results obtained in the course of experimental studies show that the values of the limiting adsorption volume and characteristic adsorption energy for block zeolite 13X are in the ranges of $W_0 = 0.258 - 0.296$ cm3/g and $E = 10279 - 13395$ J/mol. The spread of W_0 and E values is as follows: the spread of W_0 values is 14.73%, the spread of E values is 30.31%. This indicates that in order to calculate the PSA process for hydrogen extraction on zeolites 13X, it is recommended to clarify the values of these coefficients using experimental nitrogen isotherms (as a model gas) in the operating pressure range of the PSA process on the industrial zeolite 13X used (if the manufacturer differs from those presented in Table 1). If it is not possible to obtain an experimental isotherm on a specific zeolite 13X, it is necessary to take into account the obtained spread of W_0 and E coefficient values while calculating the isotherm using the DRA equation.

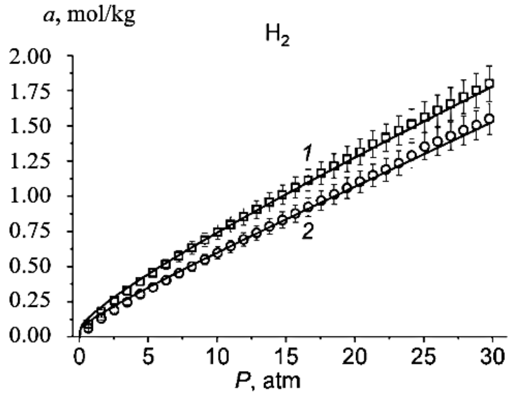

Fig. 2. Isotherms of H_2 on zeolites 13X at temperatures: 293 K (curve 1), 323 K (curve 2) and calculation using the DRA equation (solid line)

Рис. 2. Изотермы H_2 на цеолитах 13X при температурах 293 K (кривая 1), 323 K (кривая 2) и расчет по уравнению ДРА (сплошная линия)

Figs. 2-4 show the obtained isotherms of H_2, CO_2, CO at temperatures of 293, 323 K and pressures of 0-30 atm, as well as the calculation of the equilibrium gas concentration using the DRA equation, where the coefficients β_k and *n* were determined for H_2, CO_2, CO by solving parametric identification problems (2) – (4). The results of solving the problems are presented in Table 2 (the line "RMS*, %" contains the obtained minimum and maximum RMS).

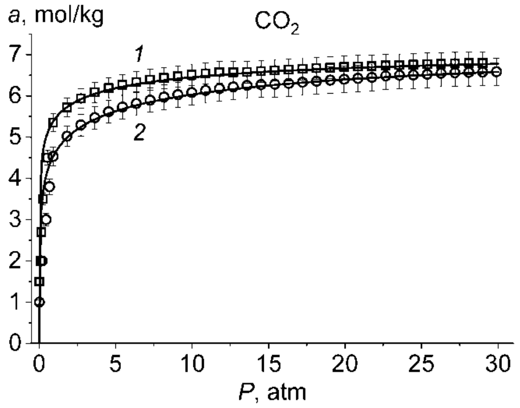

Fig. 3. Isotherms of CO_2 on zeolites 13X at temperatures: 293 K (curve 1), 323 K (curve 2) and calculation using the DRA equation (solid line)

Рис. 3. Изотермы CO_2 на цеолитах 13X при температурах 293 K (кривая 1), 323 K (кривая 2) и расчет по уравнению ДРА (сплошная линия)

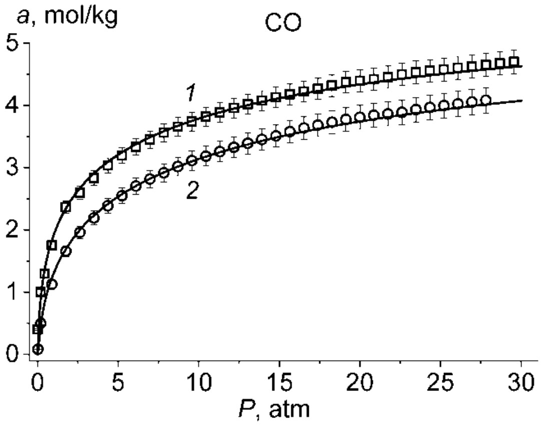

Fig. 4. Isotherms of CO on zeolites 13X at temperatures: 293 K (curve 1), 323 K (curve 2) and calculation using the DRA equation (solid line)

Рис. 4. Изотермы CO на цеолитах 13X при температурах 293 K (кривая 1), 323 K (кривая 2) и расчет по уравнению ДРА (сплошная линия)

Table 2

Results of solving the problem of identifying the affinity coefficients β and the exponent n of the DRA equation for zeolite 13X

***Таблица 2.* Результаты решения задачи идентификации коэффициентов аффинности β и экспоненты n уравнения ДРА для цеолита 13X**

Gas	β*	*n**	RMS*, %
H_2	0.13	0.81	6.74–14.69
CO_2	1.87	2	1.81–10.08
CO	1.06	2	7.95–10.59

As a result of solving the problem of identifying the affinity coefficients of the DRA equation, it can be concluded that the DRA equation allows to correctly describe the isotherms of H_2, CO_2, CO on block zeolite adsorbents 13X in the temperature range of 293-323 K and pressure range of 0-30 atm. The maximum mismatch does not exceed 14.69%, which is achieved when calculating the H_2 isotherm (Table 2). Thus, the calculation of adsorption isotherms of the PSA process for hydrogen extraction from synthesis gas (with the composition H_2, CO_2, CO) on block zeolites 13X can be carried out using the DRA equation.

It is important to illustrate the achieved advantage of calculating isotherms using the DRA equation. In the PSA process for H_2 extraction from synthesis gas with the composition H_2, CO_2, CO the number of isotherms that must be obtained experimentally will be:

using the Langmuir equation or its derivatives – six experiments (two adsorption isotherms for each H_2, CO_2, CO gas at two temperatures of 293 and 323 K);

using the DRA equation – one experiment for the operating pressure range of 0-30 atm (1 isotherm of N_2 obtained at room temperature or at a boiling point of N_2).

As it can be seen, the advantage is achieved by reducing the number of experimental isotherms that must be obtained for calculations.

It should be noted that for all gases, except H_2, the optimal exponent n of the equation was n = 2 (Table 2), which indicates the correctness of applying the particular case of the DRA equation for calculating adsorption isotherms, i.e. the Dubinin–Radushkevich equation. For hydrogen, the use of the Dubinin–Radushkevich equation for one of the samples gave the value of $\text{RMS} = 45.64\%$ for 13X-2, which is too large an error. The average RMS for all H_2 samples for the Dubinin–Radushkevich equation were $\text{RMS} = 35.15\%$ for 13X. The RMS values for integer values of the exponent $n > 2$ turned out to be even higher. The best result was obtained at $n = 1$. The average RMS for all samples at $n = 1$ were: $\text{RMS} = 24.68\%$ for 13X. Therefore, the identification problem for H_2 was also solved according to the second scenario, case 2, problem $(2'), (4')$, which made it possible to continuously vary the exponent of the DRA equation. This difference from other gases is explained by the fact that H_2 is rather poorly sorbed on zeolites 13X and 5A in contrast to other gases CO_2, CO, which is clearly seen from the isotherms shown in Fig. 2-4. Hydrogen is in the region of low fillings, and its isotherm in the pressure range of 0-30 atm and temperature range of 293-323 K is close to linear; therefore, it is difficult to use the Dubinin–Radushkevich equation $(n = 2)$. The DRA equation is a more general case and, using this equation, it is possible to find the values of the affinity coefficients β and the exponent n, at which acceptable RMS values are achieved (Table 2).

Table 3 shows the values of the adsorption heats ΔH for H_2, CO_2, CO gases on block zeolites 13X calculated on the basis of the obtained adsorption isotherms (Figs. 2-4), as well as the balance of the PSA process for hydrogen recovery using a mathematical model [3, 15, 16, 37].

Table 3

Values of adsorption heat ΔH (kJ/mol) for zeolite 13X

***Таблица 3.* Теплоты адсорбции ΔH (кДж/моль) для цеолита 13X**

Source	H_2	CO_2	CO
13X-1	7.28	31.56	22.95
13X-2	8.81	32.84	24.76
13X-3	10.17	43.22	19.53
[33]	–	46.0	23.6
[33]	11.2	43.3	26.1
[7]	9.5	31.6	23.3

As in the case with the coefficients W_0, E, the obtained values of the adsorption heat ΔH are also in the ranges of ΔH (kJ/mol): 7.28– 10.17 for H_2, 31.56– 43.22 for CO_2, 19.53– 24.76 for CO. The obtained intervals are valid for the temperature range $T = 293 - 323$ K and pressure range $P = 0 - 30$ atm. The spread in the adsorption heat ΔH values is: 39.70% for H_2, 36.95% for CO_2, 26.78% for CO. The resulting spread in the heat ΔH values is confirmed by a comparative analysis of the heat ΔH values presented in other works (Table 3). This spread must be taken into account when calculating the heat balance of the PSA process for hydrogen extraction from synthesis gas on industrial zeolites 13X.

Table 4 shows the values of the affinity coefficients β_k of the DRA equation for H_2, CO_2, CO gases using zeolites 13X presented in other works.

Table 4

Values of the affinity coefficients β of the DRA equation for zeolite 13X (nitrogen as a standard gas)

***Таблица 4.* Значения коэффициентов аффинности β уравнения ДРА для цеолита 13X стандартный газ N_2)**

Source	H_2	CO_2	CO
This work	0.13	1.87	1.06
[33]	–	1.89	1.38
[33]	–	1.86	1.37
[33]	–	2.31	1.30
[38]	–	2.43	1.39

In the comparative analysis of the affinity coefficients β of the DRA equation obtained in this work, some discrepancy with other works can be identified (Table 4). The discrepancy is explained as follows. Apparently, each of the works in Table 4 [33, 38] introduced the experimental studies carried out for zeolites 13X made only by one manufacturer. Their names are not given in the works presented in Table 4. In this study, the problem of identifying the affinity coefficients β and the exponent n (2)–(4) was solved using experimental data from several manufacturers. In fact, the found values of the affinity coefficients β and the exponent n cover the spread range of the coefficient values $W_0 = 0.258 - 0.296$ cm^3/g, $E = 10279 - 13395$ J/mol for zeolites 13X (Table 1). This range is the confidence interval for using the obtained affinity coefficients β and the exponent n (Table 2). Thus, in this work, the refined values of the affinity coefficients β and the exponent n of the DRA equation were obtained for calculating the adsorption isotherms of the PSA process for hydrogen extraction from synthesis gas on industrial zeolites 13X.

CONCLUSION

Using experimental methods for obtaining adsorption isotherms of gases and the theory of volumetric filling of micropores, the ranges of the coefficients of the DRA equation have been determined, where the correct calculation of sorption isotherms of H_2, CO_2, CO on block zeolites 13X is ensured (using three samples from different manufacturers): limiting adsorption volume $W_0 = 0.258 - 0.296$ cm^3/g and characteristic adsorption energy $E = 10279 - 13395$ J/mol. It has been established that the calculation of adsorption isotherms of H_2, CO_2, CO gases on industrial zeolites 13X, the characteristics of which fall within the obtained ranges for W_0 and E, can be correctly performed using the DRA equation in the temperature ranges of 293-323 K and pressure ranges of 0-30 atm, where the PSA process for H_2 extraction from synthesis gas with the composition H_2, CO_2, CO is carried out.

The use of the DRA equation for calculating the adsorption isotherms of H_2, CO_2, CO in the PSA process for hydrogen extraction from synthesis gas will eliminate costly experiments to determine the isotherms of H_2, CO_2, CO (included in the synthesis gas) in the temperature range of 293-323 K and pressure range of 0-30 atm. It is enough to be limited to only one experiment on the removal of the sorption isotherm of N_2 (as a model gas) on the selected zeolite 13X to refine the coefficients W_0 and E. If the obtained coefficients W_0 and E fall into the intervals for W_0 and E found in this work, then to calculate the isotherms of the remaining gases H_2, CO_2, CO it is necessary to use the obtained affinity coefficients and the exponent n of the DRA equation, which were determined as a result of solving parametric identification problems. The maximum value of the mismatch between the obtained experimental isotherms of H_2, CO_2, CO gases and the isotherms calculated using the DRA equation was 14.69% for H_2, and the minimum value was 1.81% for CO_2.

The approach proposed in the paper can be used to assess the applicability of the DRA equation for calculating adsorption isotherms of gases in various cyclic adsorption processes with various gas mixtures and adsorbents. The applicability of the DRA equation for calculating the adsorption isotherms of various gases in the PSA process on other zeolite adsorbents requires additional research.

The study was carried out at the expense of a grant from the Russian Science Foundation (Project No. 21-79-00092, https://rscf.ru/en/project/21-79-00092/).

The authors declare the absence a conflict of interest warranting disclosure in this article.

Исследование выполнено за счет гранита РНФ (проект № 21-79-00092, https:/rscf.ru/project/21-7900092/).

Авторы заявляют об отсутствии конфликта интересов, требующего раскрытия в данной статье.

REFERENCES
ЛИТЕРАТУРА

1. **Singla S., Shetti N., Basu S.** Hydrogen production technologies - Membrane based separation, storage and challenges. *J. Environ. Manag.* 2022. V. 302. P. 113963. DOI: 10.1016/j.jenvman.2021.113963.
2. **Dat V., Kang J., Oh M.** Dynamic model and performance of an integrated sorption-enhanced steam methane reforming process with separators for the simultaneous blue H_2 production and CO_2 capture. *Chem. Eng. J.* 2021. V. 423. P. 130044. DOI: 10.1016/j.cej.2021.130044.
3. **Li H., Liao Z., Sun J.** Modelling and simulation of two-bed PSA process for separating H_2 from methane steam reforming. *Chin. J. Chem. Eng.* 2019. V. 27. N 8. P. 1870–1878. DOI: 10.1016/ j.cjche.2018.11.022.
4. **Tavan Y., Hosseini S.H., Olazar M.** A note on an integrated process of methane steam reforming in junction with pressure-swing adsorption to produce pure hydrogen: Mathematical modeling. *Ind. Eng. Chem. Res.* 2015. V. 54. N 51. P. 12937-12947. DOI: 10.1021/acs.iecr.5b01477.
5. **Agarwal A., Biegler L., Zitney S.** Superstructure-based optimal synthesis of pressure swing adsorption cycles for precombustion CO_2 Capture. *Ind. Eng. Chem. Res.* 2010. V. 49. N 11. P. 5066–5079. DOI: 1021/ie900873j.
6. **Dowling A., Vetukuri S., Biegler L.** Large-scale optimization strategies for pressure swing adsorption cycle synthesis. *AIChE J.* 2012. V. 58. N 12. P. 3777–3791. DOI: 10.1002/aic.13928.
7. **Delgado J.A., Águeda V.I., Uguina M.A.** Adsorption and diffusion of H_2, CO, CH_4, and CO_2 in BPL activated carbon and 13X zeolite: Evaluation of performance in pressure swing adsorption hydrogen purification by simulation. *Ind. Eng. Chem. Res.* 2014. V. 53. N 40. P. 15414-15426. DOI: 10.1021/ie403744u.
8. **Abdeljaoued A., Relvas F., Mendes A.** Simulation and experimental results of a PSA process for production of hydrogen

used in fuel cells. *J. Environ. Chem. Eng.* 2018. V. 6. N 1. P. 338–355. DOI: 10.1016/j.jece.2017.12.010.

9. **Yavary M., Ebrahim H.A., Falamaki C.** The effect of number of pressure equalization steps on the performance of pressure swing adsorption process. *Chem. Eng. Process.* 2015. V. 87. P. 35-44. DOI: 10.1016/j.cep.2014.11.003.
10. **Xiao J., Li C., Fang L.** Machine learning–based optimization for hydrogen purification performance of layered bed pressure swing adsorption. *Int. J. Energy Res.* 2020. V. 44. N 6. P. 4475-4492. DOI: 10.1002/er.5225.
11. **Asgari M.** Synergistic material and process development: Application of a metal-organic framework, Cu-TDPAT, in single-cycle hydrogen purification and CO_2 capture from synthesis gas. *Chem. Eng. J.* 2021. V. 414. P. 128778. DOI: 10.1016/j.cej.2021.128778.
12. **Al-Naddaf Q., Rownaghi A., Rezaei F.** Multicomponent adsorptive separation of CO_2, CO, CH_4, N_2, and H_2 over core-shell zeolite-5A@MOF-74 composite adsorbents. *Chem. Eng. J.* 2020. V. 384. P. 123251. DOI: 10.1016/j.cej.2019.123251.
13. **Xiao Y., He G., Yuan M.** Adsorption equilibrium and kinetics of methanol vapor on zeolites NaX, KA, and CaA and activated alumina. *Ind. Eng. Chem. Res.* 2018. V. 57. N 42. P. 14254–14260. DOI: 10.1021/acs.iecr.8b04076.
14. **Akulinin E.I., Golubyatnikov O.O., Dvoretsky S.I.** Pressure swing adsorption for recovery hydrogen, oxygen and nitrogen from gas mixtures: mathematical modeling, optimization and units design. *ChemChemTech [Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol.].* 2021. V. 64. N 11. P. 8–29. DOI: 10.6060/ivkkt.20216411.6459.
    Акулинин Е.И., Голубятников О.О., Дворецкий С.И. Короткоцикловая безнагревная адсорбция для извлечения водорода, кислорода и азота из газовых смесей: математическое моделирование, оптимизация режимов функционирования и проектирование установок. *Изв. вузов. Химия и хим. технология.* 2021. Т. 64. Вып. 11. С. 8-29. DOI: 10.6060/ivkkt.20216411.6459.
15. **Ohs B., Lohaus J., Marten D.** Optimized hollow fiber sorbents and pressure swing adsorption process for H-2 recovery. *Ind. Eng. Chem. Res.* 2018. V. 57. N 14. P. 5093–5105. DOI: 10.1021/acs.iecr.7b05368.
16. **Moon D.-K., Lee D.-G., Lee C.-H.** H_2 pressure swing adsorption for high pressure syngas from an integrated gasification combined cycle with a carbon capture process. *Appl. Energy.* 2016. V. 183. P. 760-774. DOI: 10.1016/j.apenergy.2016.09.038.
17. **Shi W.-R., Tian C.-X., Ding Z.-Y.** Review on Simulation, Optimization and Control of Pressure Swing Adsorption. *Gaoxiao Huaxue Gongcheng Xuebao.* 2018. V. 32. N 1. P. 8–15. DOI: 10.3969/j.issn.1003-9015.2018.01.002.
18. **Liu B., Yu X., Shi W., Shen Y.** Two-stage VSA/PSA for capturing carbon dioxide (CO_2) and producing hydrogen (H_2) from steam-methane reforming gas. *Int. J. Hydrogen Energy.* 2020. V. 45. N 46. P. 24870-24882. DOI: 10.1016/j.ijhydene.2020.06.264.
19. **Ma S., Tong L., Ye F.** Hydrogen purification layered bed optimization based on artificial neural network prediction of breakthrough curves. *Int. J. Hydrogen Energy.* 2019. V. 44. N 11. P. 5324-5333. DOI: 10.1016/j.ijhydene.2018.12.142.
20. **Dubinin M.M.** Fundamentals of the theory of adsorption in micropores of carbon adsorbents: Characteristics of their adsorption properties and microporous structures. *Carbon*. 1989. V. 27. N 3. P. 457–467. DOI: 10.1016/0008-6223(89)90078-X.
21. **Tolmachev A.** Adsorption of gases, vapors, and solutions: II. Description and a priori calculations of adsorption equilibria. *Prot. Met. Phys. Chem. Surf.* 2010. V. 46. N 3. P. 291–308. DOI: 10.1134/S2070205110030020.
22. **Fomenkov P., Gumerov M., Tolmachev A.** On the possibility of application of the TVFM and lattice-model equations at temperatures above the critical values of an adsorptive. *Prot. Met. Phys. Chem. Surf.* 2018. V. 54. N 4. P. 565–568. DOI: 10.1134/S2070205118040044.
23. **Fomkin A., Pribylov A., Murdmaa K.** Adsorption of hydrogen in microporous carbon adsorbents of different origin. *Prot. Met. Phys. Chem. Surf.* 2019. V. 55. N 3. P. 413–419. DOI: 10.1134/S2070205119030134.
24. **Fomkin A., Pribylov A., Tkachev A.** The influence of the structural and energetic characteristics of the microporous structure of carbon adsorbents on hydrogen adsorption. *Colloid J.* 2019. V. 81. N 5. P. 607–612. DOI: 10.1134/S1061933X19050053.
25. **Kuznetsova T., Fomenkov P., Kryuchenkova N.** Thermodynamics of adsorption of light hydrocarbons on microporous active carbons at supercritical temperatures. *Prot. Met. Phys. Chem. Surf.* 2017. V. 53. N 3. P. 404–407. DOI: 10.1134/S2070205117030133.
26. **Fomkin A., Petukhova G.** Features of gas, vapor, and liquid adsorption by microporous adsorbents. *Russ. J. Phys. Chem. A.* 2020. V. 94. N 3. P. 516–525. DOI: 10.1134/S0036024420030097.
27. **Rege S., Yang R., Buzanowski M.** Sorbents for air prepurification in air separation. *Chem. Eng. Sci.* 2000. V. 55. N 21. P. 4827-4838. DOI: 10.1016/S0009-2509(00)00122-6.
28. **Erdem-Şenatalar A, Tatlier M.** The relationship of the geometric factor in the Dubinin-Astakhov isotherm equation with the fractal dimension. *Chaos, solitons and fractals.* 2000. V. 11. N 6. P. 953–960. DOI: 10.1016/S0960-0779(98)00321-X.
29. **Oh H., Lim S., Kim J.** Adsorption equilibria of water vapor on an alumina/zeolite 13X composite and silica gel. *J. Chem. Eng. Data.* 2017. V. 62. N 2. P. 804-811. DOI: 10.1021/acs.jced.6b00850.
30. **Gomez L., Zacharia R., Bénard P.** Multicomponent adsorption of biogas compositions containing CO_2, CH_4 and N_2 on Maxsorb and Cu-BTC using extended Langmuir and Doong–Yang models. *Adsorption*. 2015. V. 21. N 5. P. 433-443. DOI: 10.1007/s10450-015-9684-6.
31. **Epiepang F., Li J., Liu Y.** Low-pressure performance evaluation of CO_2, H_2O and CH_4 on Li-LSX as a superior adsorbent for air prepurification. *Chem. Eng. Sci.* 2016. V. 147. P. 100–108. DOI: 10.1016/j.ces.2016.03.022.
32. **Vyas R., Kumar S.** Determination of micropore volume and surface area of zeolite molecular sieves by D-R and D-A equations: a comparative study. *Indian J. Chem. Technol.* 2004. V. 11. N 5. P. 704–709.
33. **Kolganov V., Potolokov N., Fedorov V.** Calculating the similarity coefficients and adsorption energies for gases and vapors on zeolite NaX. *Russ. J. Phys. Chem. A.* 2005. V. 79. N 7. P. 1140–1144.
34. **Poling B., Prausnitz J., O'Connell J.** The properties of gases and liquids. McGraw-Hill. 2001. 803 p. DOI: 10.1036/0070116822.
35. **Behvandi A, Tourani S.** Equilibrium modeling of carbon dioxide adsorption on zeolites. World Academy of Science, Engineering and Technology. 2011. V. 52. P. 617–619.
36. **Alami A, Boucham B, Gouareh A.** Investigation on the energy efficiency of a geo-sol adsorption heat transformer in the algerian context. *Int. J. Heat Technol.* 2019. V. 37. N 3. P. 820-830. DOI: 10.18280/ijht.370319.
37. **Golubyatnikov O., Akulinin E., Dvoretsky S.** Numerical research to determine the dominant mechanism of mass and heat transfer in pressure swing adsorption processes. *Bull. of the South Ural State Univ., Ser.: Mathem. Model., Program. and Comp. Software.* 2021. V. 14. N 2. P. 39–51. DOI: 10.14529/mmp210204.
38. **Kolganov V.** Calculations of the similarity factor and initial adsorption heats of substances on LiX, NaX, and KX zeolites. *Prot. Met. Phys. Chem. Surf.* 2009. V. 45. N 2. P. 158-162. DOI: 10.1134/S2070205109020051.

Поступила в редакцию (Received) 30.03.2022
Принята к опубликованию (Accepted) 27.05.2022