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Робота присвячена теоретичному вивченню та моделюванню процесу адсорбції CO_2 на кліноптилоліті (Скоринське родовище, Закарпатська область, Україна) та процесу адсорбції SO_2, NO, і CO_2 на K_2CO_3-модифікованому – γ-оксид алюмінію. Математична модель динаміки сумісної газової адсорбції побудована на основі матеріального балансу в газовій та твердій фазі з урахуванням активність адсорбенту по відношенню до газу по змінними коефіцієнтами

Ключові слова: адсорбція, природний цеоліт, модифікований цеоліт, моделювання

Работа посвящена теоретическому изучению и моделированию процесса адсорбции CO_2 на клиноптилолите (Скоринское месторождение, Закарпатская область, Украина) и процесса адсорбции SO_2, NO, и CO_2 на K_2CO_3-модифицированном – γ-оксид алюминия. Математическая модель динамики совместной газовой адсорбции построена на основе материального баланса в газовой и твердой фазе с учетом активность адсорбента по отношению к газу по переменными коэффициентами

Ключевые слова: адсорбция, природный цеолит, модифицированный цеолит, моделирование

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SIMULATION THE GAS SIMULTANEOUS ADSORPTION OVER NATURAL AND MODIFIED ZEOLITE

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1. Introduction

Adsorption is of great importance. The unique advantage of adsorption over other separation methods is the higher selectivity that can be achieved by adsorbents. In addition, adsorption phenomena play a vital role in many solid state reactions and biological mechanisms. There are different adsorbents being used in industry such as Active Carbon,

silica gel, silicalites, activated clays, synthetic zeolites, natural zeolites (Clinoptilolite, Erionite, Mordenite), 4A, 5A, 13X molecular sieves, activated aluminas. For an adsorption process to be developed on a commercial scale requires the availability of a suitable adsorbent in tonnage quantities at economic cost. Actually Trans Carpathian region, Ukraine rich in natural zeolites such as Clinoptilolite [1]. The purpose of this work is theoretical study of the adsorption of harmful gases on different adsorbents and simulation these processes in order to conduct further experiments and to reach the industrial level.

2. Analysis of published data and problem statement

Recently, there has been intense interest in linking engineering models with rigorous simulation tools. Simulation approaches potentially provides an attractive alternative to costly and time-consuming experimentation. In order to know just how well the chosen adsorbent will perform, the adsorbent must be tested with the mix of pollutants that are to be adsorbed, and at the concentrations that are expected. Various multi-space adsorption models can predict how a combination of gas will adsorb, but these are all based on assumptions that fit the results to the individual experiment. In general, an adsorption isotherm is an invaluable curve describing the phenomenon governing the retention. Adsorption equilibrium (the ratio between the adsorbed amount with the remaining in the solution) is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time, with its adsorbate concentration in the bulk solution is in a dynamic balance with the interface concentration.

In article [2] the mathematical description of the dynamics behavior of the fixed-bed adsorption column was made using the integrated CFD model. The most significant disadvantage of the model is the definition of mass transfer coefficient only by macropore diffusion without taking into account the diffusion in micropores, which leads to considerable error in the calculation.

In work [3] for modeling the adsorption of pure components was used the double Langmuir (DL) model. The DL model was combined with the ideal adsorbed solution theory, provides an effective method to predict adsorption equilibrium of gas mixtures from the isotherms of the pure components. A major disadvantage of the DL model is that it assumes that there are only two different adsorbate locations in zeolites and all the components in the mixture conform to the rule analogous to Raoult's law. The chemical potential of the adsorbed solution is considered equal to that of the gas phase at equilibrium, these characteristics often do not meet the normal course of the process, is a significant limitation of the applicability of the model in practice.

The model developed here [4] is analogous to the bipore model developed in references [5] Authors assumed a cylindrical bed of microporous zeolite crystallites to be spherical, is exposed to a constant concentration of adsorbate in the gas phase. One face of this bed is permeable to the gas. In this case, one can consider that gas diffusion is linear in the macropores and radial in the micropores. There were done the following assumptions: *i*) during the evolution of the system towards equilibrium there has to be a concentration gradient in the macropores and/or in the micropores; *ii*) the effect of heat is negligible; *iii*) diffusion occurs in the Henry's law region of the adsorption isotherm. The analytical solutions of the proposed model can be obtained using the Laplace integral transformation and the Cauchy function methods. However, equations of the processes having feedback loops and processes partly or absolutely provided with means of automatic control, can be solved by this method with only a relatively low degree of complexity. When dealing with complex systems, Laplace transform method requires a huge number of algebraic operations and becomes almost unusable.

3. Purpose and objectives of the study

The purpose of this work is theoretical study of the adsorption of harmful gases on different adsorbents and simulation these processes in order to conduct further experiments and to reach the industrial level

In accordance with the set goal the following research objectives are identified:

1. Theoretical study of the adsorbents (natural and modified zeolite), the gas simultaneous adsorption processes over them.

2. Mathematical modelling of the dynamics simultaneous adsorption of gases over zeolites.

3. Checking the adequacy of the mathematical model to describe theoretical data.

4. Material for the adsorption. The adsorption process

Clinoptilolite is a member of the heulandite group of natural zeolites and it is the most abundant natural zeolite however remains largely uncommercialized for gas separation processes due to variation in the purity and composition of the various mineral deposits. Besides, low cost, ready availability, and versatility of synthetic zeolites has inhibited the commercialization of natural zeolites. Clinoptilolite is the most common natural zeolite found mainly in sedimentary rocks of volcanic origin. Such deposits aroused strong commercial interest because clinoptilolite tuffs are often rather pure and can be mined with simple techniques [6, 7]. γ-Alumina is one of the most frequently used versatile adsorbents because of its low cost, high mechanical strength, and good adsorption ability. Although γ-alumina is a kind of neutral adsorbent, there are both acidic and alkaline active sites on its surface. Furthermore, after specific modifications, the surface chemistry of γ-alumina can be manipulated and controlled; thus, it can be tailored for many special applications. γ-Alumina can be alkalized by impregnation with a K_2CO_3 solution. After alkalization, the amount of alkaline active sites increases a lot and c-alumina becomes alkalized alumina. As SO_2, NO_x, and CO_2 are all acidic gases, alkalized alumina may be used to adsorb them [8].

Adsorption of a gas on a solid is the enrichment of molecules in an interfacial layer adjacent to a solid wall. Here is two kind of adsorption: physical adsorption caused by van der Waals forces without a charge redistribution in the molecule and on the pore surface and chemical adsorption implies the creation of bonds and a change in the electron density between the adsorbent and the adsorbate. Furthermore, NO and O_2 interact with SO_2. Normally, chemical adsorption of SO_2 is an oxidation process in which the adsorbed SO_2 molecules are oxidized by O_2 to

SO_3, or react with active components to form sulfates and sulfites. On the surface of γ-alumina, NO and SO_2 can form unstable intermediates with the assistance of O_2 [9]. At low temperature, physical adsorption is predominant; the adsorption capacity first decreases as the temperature rises. At higher temperature, chemical adsorption is enhanced and becomes the main adsorption type, so that the adsorption capacity increases.

5. Simulation the dynamics adsorption of gases over zeolites

In isothermal adsorption systems, the equilibrium relationship between the adsorbent and adsorbate can be characterized by single curve or isotherm, where the solid phase solute concentration is a function of the gaseous phase solute concentration characterized by the mass balance in the gas and solid phase [10]. The fixed bed model is derived from the mass balance in gas and solid phase and from the experimental saturation capacities, with the following assumptions: no temperature gradients and no concentration gradients in a bed section perpendicular to gas flow direction, the regime is isothermal; the temperature gradients are absent; the diffusion of species is negligible, there is no deactivation of the adsorbent during the experiments [11] considering the activity of the adsorbent with respect to the gas by variable coefficients.

$$\frac{dy^{NO}_{out,i}}{dt}=\frac{2RT}{\varepsilon V_i P_t}\left[\frac{FP_t}{RT}(y^{NO}_{in,i}-y^{NO}_{out,i})-k^{NO}\cdot\overline{y_i}\cdot\theta_{V,i}\cdot q_{0\lambda}\cdot w_i\right],$$

$$\frac{dy^{SO_2}_{out,i}}{dt}=\frac{2RT}{\varepsilon V_i P_t}\left[\frac{FP_t}{RT}(y^{SO_2}_{in,i}-y^{SO_2}_{out,i})-k^{SO_2}\cdot\overline{y_i}\cdot\theta_{V,i}\cdot q_{0\gamma}\cdot w_i\right],$$

$$\frac{dy^{CO_2}_{out,i}}{dt}=\frac{2RT}{\varepsilon V_i P_t}\left[\frac{FP_t}{RT}(y^{CO_2}_{in,i}-y^{CO_2}_{out,i})-k^{CO_2}\cdot\overline{y_i}\cdot\theta_{V,i}\cdot q_{0\beta}\cdot w_i\right],$$

$$\theta_{V,i}=\frac{FP_t}{m_{ad}RT}(M^{NO}\cdot y^{NO}_{in,i}\cdot t_s+M^{SO_2}\cdot y^{SO_2}_{in,i}\cdot t_s+M^{CO_2}\times$$

$$\times y^{CO_2}_{in,i}\cdot t_s-M^{NO}\cdot\sum_0^{t_s}\frac{\overline{y_i}}{y^{NO}_{in,i}}dt-M^{SO_2}\cdot\sum_0^{t_s}\frac{\overline{y_i}}{y^{SO_2}_{in,i}}dt-$$

$$-M^{CO_2}\cdot\sum_0^{t_s}\frac{\overline{y_i}}{y^{CO_2}_{in,i}}dt),$$

$$i=\overline{1,k}.$$

Symbols:
F – gas flow rate, [l/h]
y_{in}, y_{out} – inlet and outlet mole fractions of adsorbate, [–]
$\overline{y_i}$ – the average gas mole fraction in the i layer, [–]
P_t – total pressure, [Pa]
R – ideal gas constant, [Pa*m^3/(kmol·K)]
T – temperature, [K]
V_i, w_i – volume and weight of the layer, [l, kg]
k – rate constant, [s^{-1}]
α, β, γ – species coefficients, [–]
q_0 – saturation amount of gas per kg. [kmol/kg]

Subscripts and superscripts:
i – property at *i* layer of an adsorbent bed in equation,
in – property at inlet of an adsorbent bed,
out – property at outlet of an adsorbent bed,
NO, SO_2, CO_2 – nitrogen monoxide, sulfur dioxide, carbon dioxide.

A normal linear system of differential equations with variable coefficients was solved by Taylor collocation method. Using the Taylor collocation points, this method transforms the ODE system and the given conditions to matrix equations with unknown Taylor coefficients. By means of the obtained matrix equation, a new system of equations corresponding to the system of linear algebraic equations is gained.

6. Verification of the adequacy of the mathematical model

In a result of the calculation of the model obtained concentrations of nitrogen monoxide, sulfur dioxide, carbon dioxide in the adsorbent in time for each new calculation, mass adsorbed oxides and the saturation capacity of the adsorbent. The calculation performed under the same conditions as in theoretical studies.

Table 1

The saturation time and the adsorption capacity of the clinoptilolite

		Gas flow rate, m/s		
		0,4	0,8	1,6
T=293 K	t_n, s	90	82	70
	m_{CO2}, g/100 g clinoptilolite	5,45	5,22	5,05
T=303 K	t_n, s	81	77	62
	m_{CO2}, g/100 g clinoptilolite	6,23	7,01	5,79
T=318 K	t_n, s	79	67	55
	m_{CO2}, g/100 g clinoptilolite	4,92	5,01	18,44

Table 2

The data of calculated points adsorption isotherm*

CO_2			NO			SO_2		
c, %	c/c_0	m, g	c, %	c/c_0	m, g	c, %	c/c_0	m, g
0,5	0,1	11,6	0,5	0,1	8,74	0,5	0,1	21,95
1,0	0,2	12,01	1,0	0,2	9,18	1,0	0,2	22,18
1,5	0,3	12,94	1,5	0,3	9,86	1,5	0,3	23,21
2,0	0,4	13,32	2,0	0,4	10,44	2,0	0,4	24,05
2,5	0,5	13,78	2,5	0,5	10,78	2,5	0,5	24,38
3,0	0,75	13,89	3,0	0,75	11,24	3,0	0,75	25,11
4,0	1	14,01	4,0	1	11,32	4,0	1	25,80

** Subject to: gas flow rate 0,5 l/min, SO_2 concentration at the inlet 2000 ppm, NO concentration at the inlet 1000 ppm, CO_2 concentration at the inlet 12 000 ppm, temperature 373 K.*

The experimental breakthrough curves of SO_2, NO, CO_2 adsorbed on alkalized alumina [8] and CO_2 on natural zeolite [12] were simulated Fig. 1, 2 respectively.

The adequacy of the data obtained as a result of the simulation is verified by the Fisher test. As a result, the model is adequate in 90 % of cases for the modified zeolite and in 75 % of cases for the natural zeolite. Since the natural zeolite has not ordered structures such as modified, the adsorption process more difficult to predict.

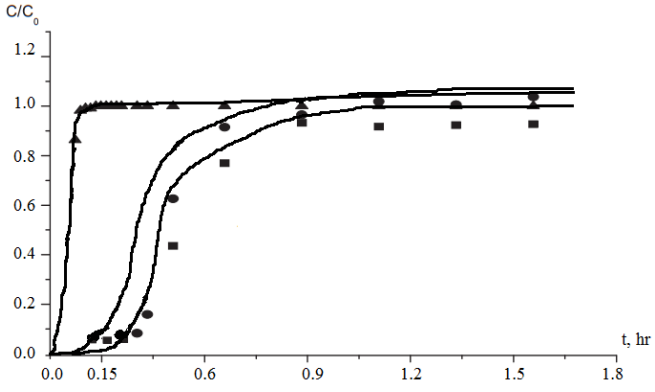

Fig. 1. Breakthrough curves of dynamics adsorption of SO_2, NO, and CO_2 over alkalized alumina (solid line — simulated data)

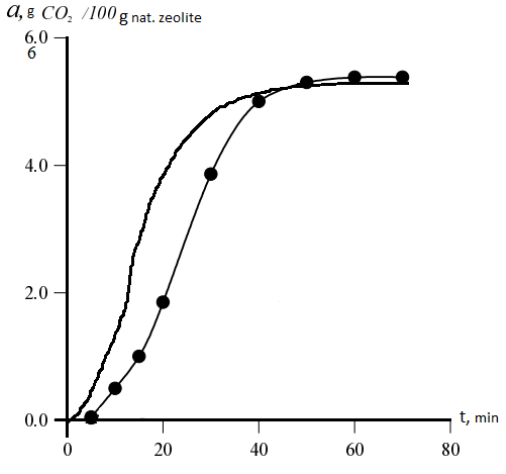

Fig. 2. Breakthrough curves of dynamics adsorption of CO_2 over natural zeolite (solid line — simulated data)

7. Conclusion

The adsorption process of CO_2 on the natural zeolite and SO_2, NO, and CO2 adsorption modified zeolite were theoretical studied and simulated by computer-mathematic methods. The developed mathematical model based on the mass balance in gas and solid phase, the experimental saturation capacities, considering the activity of the adsorbent with respect to the gas by variable coefficients. The model presented by a normal linear system of differential equations with variable coefficients, it was solved by Taylor collocation method. The breakthrough curves of SO_2, NO, CO_2 adsorbed on alkalized alumina and CO_2 on natural zeolite were reasonably well reproduced by the model (the adequacy of the model to the experiments result was carried out by Fisher Criterion, the expected value of which appeared far fewer theoretical). As a result, the model is adequate in 90 % of cases for the modified zeolite and in 75 % of cases for the natural zeolite. Thus, there is great sense to conduct further researches and simulations to reach the industrial level.

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