

Theoretical Description and Simulation of the Hydrodynamics and Porous Layer Structure during Mass Transfer in an Adsorption Apparatus with Ion-exchange Resins

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This work is a part of the project for investigations of hydrodynamics and mass transfer in an adsorption apparatus with ion-exchange resins during the extraction of stevioside from stevia extract. Nowadays the issues of improving the structural-sorption characteristics while increasing selectivity to certain substances, expanding the range, simplifying the manufacturing technology and reducing the cost of production of industrial adsorbents are extremely relevant. The submitted work is devoted to mathematical modeling and a theoretical description of adsorption in the layer of expanded ion-exchange resins. By this, the main aspects of adsorption in a layer of porous material have been considered, and a model of the geometric structure of the adsorption layer has been developed. The original contribution of the work and its scientific novelty lie in the fact that a mathematical model of the evolution of a two-component dispersed phase has been developed and qualitatively analyzed taking into account competitive adsorption and the non-equilibrium nature of mass transfer between the adsorption surface of the porous material and the dispersed phase. The results and conclusions of the work are recommended to be used in planning and conducting research work in the field of intensification of heat and mass transfer processes and engineering design of adsorption chemical apparatuses and adsorption columns.

1. Introduction

Adsorption apparatuses based on layers of ion-exchange resins (Dong Wang et al., 2019) have been widely used in recent years (Alexandratos, 2021) both to purify multicomponent mixtures from impurities (Silva and Rodrigues, 2006) and as an intermediate adsorption step for extracting useful components (Huang et al., 2021). In the production of porous adsorbents (Lee and Chang, 2020), one of the main tasks is to create high porosity (Hainan Zhang et al, 2020), which should be also characterized by a uniform distribution of pores throughout the volume of the layer (He Xu et al., 2021). These requirements determine the method and parameters of the molding process (Kabtamua et al., 2020), as well as the type of porous structure and properties of the products (Tian Li et al., 2022). The rheological characteristics of the binder in the production of porous materials with a cellular structure from viscous-flowing compositions by swelling depend on the consumption of the binder and the duration of the mixing and molding cycles (Kaldybekova et al., 2023). Ensuring optimal modes of swelling process (Raelison et al., 2021) that is accompanied by the creation of a developed porous internal structure of the layer, and achieving the necessary geometric characteristics of the adsorption layer (Yiran Man et al., 2021) requires both an understanding of the features of the formation of the layer structure and a theoretical description of this complex process (Satayev et al., 2024). The rheological properties when producing highly porous adsorbents can be controlled by using a set of various techniques (Dullien, 2012): external influences on structured mixtures, in particular vibrations that cause a thixotropic effect, or the introduction of surfactants, temperature changes, etc (Kun-Yu Wang et al., 2023). The need for such a combination of different techniques is due to the fact that none of the known techniques is without drawbacks (Wang et al., 2023).

Water, highly volatile liquids, and burnable solid additives are used as blow-forming agents. When using burnable additives, as a rule, a cellular porous structure is formed; when using evaporating liquids, a porous-

capillary structure is formed (Xiaodu Liang et al., 2021). If the mass concentration of the pore-forming agent in the material and the mass concentration of the structure-forming material are known, then the porosity of the resulting material can be calculated in advance.

One of the most widely used methods is swelling (Kaldybekova et al., 2023). This method is based on the release or introduction of a gas phase into a plastic-viscous mass in the form of hydrogen, oxygen, carbon dioxide, water vapor, air, isopentyl, Freon, or other substances.

As a result of saturation of the mass with the gas phase, its volume increases - swelling occurs (foaming). During swelling, a cellular porous structure is formed, the total volume of porosity of which depends on the amount of the gaseous component introduced and retained by the mass. Common to all types of swelling is the plastic-viscous state of the porous masses during the period of their porosity, i.e., the porous masses must have the ability to irreversibly deform (flow) without breaking the continuity. However, the process of swelling of the ion-exchanged resins has some peculiarities (Huang et al., 2021). Namely, in this system, the so-called lamellar porosity is observed due to the sliding apart of the grains of the dispersed system by interpacket water, which turns into a vapor state when the grains are heated. In the case of using a porous binder in the form of a foam mass, the material is obtained with cellular porosity, consisting of the porosity of the grains and the porosity of the binder (indices m and s respectively) (Satayev et al., 2024):

$$\varepsilon = \varepsilon_m + \varepsilon_s \quad (1)$$

The results of studies of the internal structure of adsorption layers using adsorption isotherm methods leads to the conclusion that the internal surface of the porous layer is characterized by an extremely complex developed shape (Dullien, 2012). This problem can be solved by using fractal geometry methods (Satayev et al., 2024). In this case, the inner surface of the layer is characterized by a fractal dimension higher than the "usual" geometric dimension of the surface (Satayev et al., 2024):

$$2 \leq D \leq 3 \quad (2)$$

The specific value of porosity and internal surface depends on the initial geometric characteristics of the layer, i.e. the size of the granules and the method of their laying.

This paper is devoted both to mathematical modeling of the geometric structure of porous adsorbents with account of the peculiarities of substances exposed to swelling and to building a govern model for describing mass transfer of two-phase liquids flowing through the adsorbent porous layer.

2. Theoretical details

2.1 Modeling the geometric structure of high porosity adsorbents

The specific value of porosity and internal surface depends on the initial geometric characteristics of the layer, i.e. the size of the granules and the method of their laying.

The characteristic size during swelling is of the order of the average grain size δ . With a length scale determined by the smallest adsorption area

$$\sigma_{\min} \approx \delta^2. \quad (3)$$

the amount n of substance adsorbed on a layer with a fractal surface will change according to the law:

$$n \sim \delta^{-D} \approx \sigma_{\min}^{-D/2}. \quad (4)$$

The main question, therefore, comes down to determining two characteristics of the layer: the minimum adsorption surface, which is related to the porosity of the layer, and the fractal dimension, which depends on the size and method of laying the granules.

Thus, the following estimates can be made.

Let R - be some characteristic radius, which is taken equal to the radius of the sphere circumscribed around the grain. This size is determined so as to take into account the size of the grain, the layer of the substance adsorbed on it and the neighboring adsorbent grains in contact with this grain. Then the characteristic volume is determined as usual:

$$V \sim R^3 \quad (5)$$

And to estimate the characteristic free surface around the grain in the fractal layer of the adsorbent, the appropriate relation reads:

$$s \sim V^{D/3} \quad (6)$$

It is necessary to take into account the correction for the volume of the adsorbed monomolecular layer of molecules:

$$\Delta V = l_1 \Phi V^{2/3} \quad (7)$$

Where Φ is the grain shape factor (Kaldybekova et al., 2023). This factor is introduced to describe the influence of the deviation of the grain surface from a spherical shape on the intensity of adsorption.

Then, from the above relations it follows

$$R \approx \sqrt[3]{V + \Delta V} \quad (8)$$

An assessment of the porosity (1) of a layer of a plate-like adsorbent, in particular, vermiculite, taking into account two characteristic scales, can be made based on the following relationship (Raelison et al., 2021):

$$\varepsilon \approx (l_1/l_2)^{3-D} \quad (9)$$

From here an estimation for the fractal dimension of the swollen adsorbent layer can be obtained as follows

$$D \approx 3 - \left[\ln \left(\frac{\varepsilon_1}{1.4} + \varepsilon_0 \right) / \ln(l_1/l_2) \right] \quad (10)$$

Here the indices 1 and 0 for porosity ε refer to the final and initial states of the layer, respectively. The derivation of Eqs (9) and (10) is based on the ideas proposed in the work (Kaldybekova et al., 2023)

2.2 Simulation of two-component fluid flow in a layer of porous adsorbent

Typically, the main source of data on disperse systems is the results of rheological experiments. At the same time, it is known that during the flow of multicomponent multiphase liquids in porous structures, nonlinear effects are observed, which manifest themselves both in the form of adsorption effects, which affects the dynamics of adsorption efficiency indicators, and at the level of specific rheological effects, for example, in the form of a blocking effect flow ((Shukre et al., 2023). Therefore, the dynamic properties of complex disperse systems are not determined only by rheological characteristics.

Unusual flow regimes of complex multicomponent liquids in porous media are manifested in the nonuniform distribution of the adsorbed substance in the adsorption layer. This is explained by the interaction of the components with each other and their competition when filling free adsorption centers on a solid surface, since many multicomponent mixtures are colloidal systems in which surfactant components form a dispersed phase. This paper presents a mathematical model of the movement of a two-component dispersed phase, taking into account competitive adsorption and the non-equilibrium nature of mass transfer between the adsorption surface of the porous layer and the dispersed phase.

The basic system of model equations for a flow one-dimensional layer scheme is as follows:

$$\varepsilon \frac{\partial c_i}{\partial t} + \frac{\partial a_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2} - u \frac{\partial c_i}{\partial x}, \quad (11)$$

$$\frac{\partial a_i}{\partial t} = \beta_i \left(c_i - b_i a_i^2 \left(1 - \sum_k \lambda_k a_k \right)^{-2} + \sum_{j \neq i} k_{ij} a_i a_j \right), \quad (12)$$

The mathematical model (11), (12) is not closed and must be supplemented with a relation for the connection between equilibrium and non-equilibrium concentrations of components in the adsorbed state. In the work by A. Brener (Brener, 2006) it was proposed to use the simplest form of such a connection:

$$\tau \frac{\partial a_i}{\partial t} + a_i = \tilde{a}_i \quad (13)$$

Here \tilde{a}_i is some pseudo-equilibrium value, and τ is the characteristic relaxation time.

System of equations (11), (12) is solved under the following initial and boundary conditions:

$$c_i(0, t) = c_i^0, \quad \left. \frac{\partial c_i}{\partial x} \right|_{x=L} = 0, \quad t \geq 0 \quad (14)$$

$$a_i(x, 0) = 0, \quad c_i(x, 0) = 0, \quad 0 < x < L \quad (15)$$

However, taking into account the relaxation time requires modification of the basic transport equation (1). Therefore, in this paper it is proposed to use the methodology of, based on the concept of relaxation transfer kernels (Brener, 2006). In addition, this approach makes it possible to study the effect of non-isothermal process on the intensity of adsorption.

This paper presents for the first time a system of equations, which is a development and adaptation of equations, which were derived in work (Brener, 2006). The methodology proposed in the mentioned Brener's work is based on the representation of transport equations in the form of integro-differential equations, which make it possible to take into account the phenomena of nonlocality and delay using a special form of kernels of integral operators in the equations. By implementing this approach for a two-component system, the following govern system of equations for mass and heat transfer has been derived, which differs from the system of equations (11, 12)

$$\begin{aligned} & \frac{\partial^3 (\varepsilon c_i + a_i)}{\partial \hat{t}^3} - \left(\frac{1}{\tau_m} + \frac{1}{\tau_h} \right) \frac{\partial^2 (\varepsilon c_i + a_i)}{\partial \hat{t}^2} + \left(\frac{1}{\tau_m \tau_h} - \frac{1}{\tau_x^2} \right) \frac{\partial (\varepsilon c_i + a_i)}{\partial \hat{t}} + \\ & + \frac{\eta_{m_i}}{\tau_h} \nabla (\nabla v_i / T) + \frac{\eta_x}{\tau_x} \Delta (1/T) + \eta_m \frac{\partial}{\partial \hat{t}} \nabla (\nabla v_i / T) = 0 \end{aligned} \quad (16)$$

$$\begin{aligned} & \frac{\partial^3 E}{\partial \hat{t}^3} - \left(\frac{1}{\tau_m} + \frac{1}{\tau_h} \right) \frac{\partial^2 E}{\partial \hat{t}^2} + \left(\frac{1}{\tau_m \tau_h} - \frac{1}{\tau_x^2} \right) \frac{\partial E}{\partial \hat{t}} + \\ & + \frac{\eta_x}{\tau_x} \nabla (\nabla v / T) + \frac{\eta_h}{\tau_m} \Delta (1/T) + \eta_h \frac{\partial}{\partial \hat{t}} (\Delta (1/T)) = 0 \end{aligned} \quad (17)$$

The more detail analysis of the derived equations of adsorption kinetics showed the possibility of the existence of two types of solutions to the model, namely: solutions of the traveling concentration wave type for the case when the speed of adsorption or the degree of adsorption activity on the surface of a porous medium for one of the components clearly exceeds the others, as well as specific solutions describing oscillatory concentration processes of more complex dynamics (Yegenova et al., 2022). At the same time, the detail analysis of the stability of the solutions obtained yet should be completed. Note that the resulting system of equations contains the entire variety of discovered solutions, and it describes the corresponding modes of adsorption processes. This gives grounds to propose the model outlined in the submitted paper for a detailed description of the flow of a two-phase liquid in a layer of a porous adsorbent of complex structure.

3. Typical results of preliminary analysis of the model

For a more detailed study of the system, a bifurcation diagram was constructed for a "nested" dynamic system of equations (16, 17) at a fixed point in space ($x=0$). As a result, it was revealed that in the various range of

control parameters values the phase portrait can consist of unstable nodes, stable nodes and saddles. These states correspond to damped or unfading oscillations in the concentrations of adsorbed components. In all cases when the system exhibits oscillations in a nested “dynamic” system, a response to them appears in the form of a nonmonotonic distribution of concentrations of substances in the flow over space. The case of fading (A) and unfading oscillations (B) is presented in Figure 1.

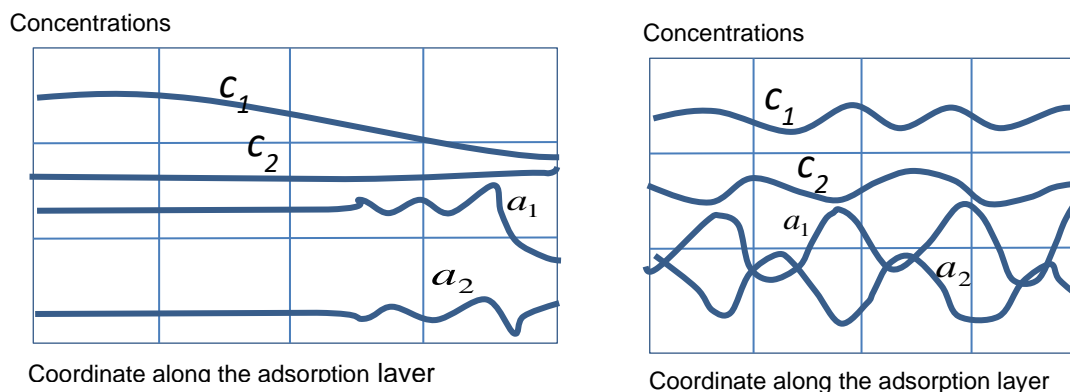


Figure 1: Distribution of concentrations of substances in the flow (c_1, c_2) and in the adsorbed state (a_1, a_2) in space (A- fading oscillations at $b_1 = -0.005, b_2 = 0.5$; B- unfading oscillations at $b_1 = -0.005, b_2 = 0.1$).

A larger volume of computer research remains to be carried out, as well as a comparison of the results obtained with known experimental data. Such work will require separate specialized training to clearly define the verification concept.

4. Conclusions

The work develops the proposed in the previous works of A. Brener an approach for describing heat and mass transfer processes in non-equilibrium systems based on the methodology of relaxation transfer kernels as applied to describing the dynamics of the adsorption process of a two-component liquid in a layer of swollen ion-exchange resin. A novel model for describing the dynamics of heat and mass transfer in such a system has been constructed. The numerical experiment carried out is preliminary in nature. At the same time, the main result of the investigation can be considered both in confirming the possibility for various alternative situations for the development of the studied complex system and identification of the main its behaviour types explicitly. The fractal structure of the swollen layer is also considered and corresponding estimates of the geometric parameters of the layer are given. Further efforts will be aimed at identifying areas of different dynamics in the space of control parameters of the proposed new model.

Nomenclature

a_i – concentrations of the components	in the adsorbed state, mol/m ³
b_i – adsorption coefficient	u – flow velocity, m/s
c_i – concentrations of the components	V – characteristic volume of granules, m ³
in the flow, mol/m ³	x – longitudinal coordinate, m
D_i – diffusion coefficient for component i , m ² /s	\mathcal{E} – porosity
D – fractal dimension	β_i – effective mass transfer coefficient, mol/m ³ s
E – internal energy, J	τ_m – relaxation time for mass transfer, s
k_{ij} – coefficient of intermolecular interaction of	τ_h – relaxation time for heat transfer, s
adsorbed components	τ_m – relaxation time for mass transfer, s
l_1, l_2 – characteristic semi-axis of adsorbent	τ_x – relaxation time for cross transfer, s
R – characteristic radius of granules, m	λ_k – filling coefficient of the monomolecular layer
s – characteristic surface of granules, m ²	ν_i – chemical potentials, J/mol
T – temperature, K	η – specific coefficients in relations (16,17)

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