

MATHEMATICAL MODEL OF SOLVENT ELECTRODESORPTION FROM CAPILLARY-POROUS MATERIALS UNDER DECREASED PRESSURE OF THE MEDIUM

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A mathematical model of removal of adsorption-bound moisture from capillary-porous materials by decreasing the pressure in the presence of an internal heat source in the volume of the adsorbent is developed.

The usefulness of adsorption apparatuses in low-tonnage production depends on efficient methods of solvent desorption from porous sorbents [1]. The studies [2, 3] showed that one of the directions in this field is regeneration of the absorbing capacity of adsorbents by vacuum oscillation characterized by alternation of the processes of cooling of the material at a decreased pressure and convective heating of it at atmospheric pressure.

For current-conducting adsorbents such as activated carbon removal of the solvent can be accomplished by evacuation of the volume of the apparatus with simultaneous heating of the layer of disperse material by an electric current, upon passage of which through the conductor heat is released in accordance with Joule's law [4]. Development of a rational structure of an apparatus implementing the method of electrovacuum desorption from capillary-porous materials implies an analysis of the processes occurring in the vapor phase, the layer of disperse material, and a single particle.

The mathematical description of heat and mass transfer in the vapor phase is based on the assumption of ideal mixing of the components and absence of an inert gas (air). The latter circumstance is attributable to the fact that a voltage is applied to the electrodes at the moment of time $\tau = \tau_1$ of attaining the "threshold" residual pressure in the apparatus when formation of explosive vapor-air mixtures is ruled out.

The rates of change of the partial pressure of the i -th component of the mixture and its temperature have the form [2]

$$\frac{dp_i}{d\tau} = \frac{FR^*T}{V_{fr}\mu_i} j_i - p_i \left(\frac{V_{v,s}}{V_{fr}} - \frac{1}{T} \frac{dT}{d\tau} \right), \quad (1)$$

$$\frac{dT}{d\tau} = \left[\frac{FT_{m,s}R^* \left(\sum_{i=1}^n j_i \right)}{V_{fr} \sum_{i=1}^n \mu_i p_i} - \frac{V_{v,s}}{V_{fr}} \right] T, \quad (2)$$

and the residual pressure in the apparatus is calculated by Dalton's law [5]

$$P = \sum_{i=1}^n p_i. \quad (3)$$

All the particles of activated carbon are at the same conditions [2], the volume of micropores in them is 47%, of mesopores, 10%, and of macropores, 43% [1]. The share of adsorbent pores of a certain size and the differences in the mechanisms of their filling by the solvent in the saturation stage will determine the regularities of the desorption process. Since macropores are filled upon direct contact with the liquid, and mesopores, by prolonged capillary condensation, these pore varieties participate in desorption only as transport arteries. Owing to this we consider the liquid in the particles of activated carbon to be bound by adsorption forces, and the distribution of the moisture content and the temperature over the particle thickness bears a linear character [2]:

$$U_i = (U_{is} - U_{ic}) \frac{x - R}{R} + U_{is}, \quad (4)$$

$$T_m = (T_{m.s} - T_{m.c}) \frac{x - R}{R} + T_{m.s}. \quad (5)$$

The local moisture content in the region of absorption-bound moisture is determined by the Freundlich isotherm equation [6]

$$U_{ix} = a_i \left[\frac{p_{ix}}{p_{isat}(T_{mx})} \right]^{n_i^*} \quad 0 \leq x \leq R \quad (6)$$

The boundary conditions for the system of equations (4), (5) are written in the following form: the boundary conditions ($x = R$)

$$T_{m.s} = T, \quad (7)$$

$$-\lambda \frac{T_{m.s} - T_{m.c}}{R} - T_{m.s} \sum_{i=1}^n c_{iv} j_{is} + q_e = 0, \quad (8)$$

$$a_{mi} \rho_0 \left(\frac{U_{is} - U_{ic}}{R} + \delta_i \frac{T_{m.s} - T_{m.c}}{R} \right) + K_p \frac{p_{is} - p_{ic}}{R} - j_{is} = 0. \quad (9)$$

$$j_{is} = \frac{\beta_i \mu_i}{R^* T_{m.s}} (p_{is} - p_i); \quad (10)$$

the initial conditions

$$U_i(0, x) = U_i(\tau_1, x); \quad T_m(0, x) = T_m(\tau_1, x); \quad P(0) = P_{th}(\tau_1). \quad (11)$$

The last term in the left-hand side of Eq. (8) characterizes the volume heat source and is determined by the expression

$$q_e = \frac{U_e^2 R_v}{R_e V}. \quad (12)$$

The mathematical description of heat and mass transfer in the layer of disperse material with passage of electric current through the latter is based on the heat-balance equation

$$\left(m_m c_m + \sum_{i=1}^n m_{i\text{liq}} c_{i\text{liq}} \right) d\bar{T}_m + \sum_{i=1}^n r_i dm_{i\text{liq}} + F\bar{T}_m \sum_{i=1}^n c_{iv} j_i d\tau = IU_e d\tau. \quad (13)$$

The left-hand side of Eq. (13) characterizes the heat consumed for heating of the moist material and evaporation of the multicomponent liquid and the heat removed with its vapors, while the right-hand side describes the power of the electric source.

In accordance with Ohm's law the current strength in Eq. (13) can be expressed as

$$I = \frac{U_e}{R_e} = \frac{U_e S}{\rho_e H} = \frac{U_e V}{\rho_e H^2}. \quad (14)$$

Using relations characterizing the mass of the multicomponent liquid in the volume of the moist material

$$\sum_{i=1}^n m_{\text{liq}} = V \sum_{i=1}^n \rho_{\text{liq}} \bar{W}_i = m_m \bar{U}, \quad (15)$$

and the relationship between the humidity of the material and its moisture content

$$\bar{W}_i = \frac{\bar{U}_i}{1 + \bar{U}_i}, \quad (16)$$

we can express the volume of the moist material as

$$V = \frac{m_m \bar{U}}{\sum_{i=1}^n \rho_{\text{liq}} \frac{\bar{U}_i}{1 + \bar{U}_i}}. \quad (17)$$

Equation (13) with account for (14), (17) acquires the following form after transformations:

$$\frac{U_e^2 \bar{U}}{\rho_e H^2 \sum_{i=1}^n \rho_{\text{liq}} \frac{\bar{U}_i}{1 + \bar{U}_i}} = \left(c_m + \sum_{i=1}^n c_{\text{liq}} \bar{U}_i \right) \frac{d\bar{T}_m}{d\tau} + \sum_{i=1}^n r_i \frac{d\bar{U}_i}{d\tau} + \bar{T}_m \sum_{i=1}^n c_{iv} \frac{d\bar{U}_i}{d\tau}, \quad (18)$$

where the integral value and mean values of the process parameters \bar{U} , \bar{T}_m , \bar{U}_i determined by the relations

$$\bar{U} = \sum_{i=1}^n \bar{U}_i, \quad (19)$$

$$U_i = \frac{U_{is} - U_{ic}}{2} = a_i \left[\frac{p_{ix}}{p_{\text{isat}}(T_{mx})} \right]_{x=R/2}^{n_i^*}, \quad (20)$$

$$\bar{T}_m = \frac{T_{m.s} - T_{m.c}}{2}. \quad (21)$$

The change in the mean moisture content of the i -th component is determined from Eq. (6) provided that the coefficients a_i and n_i^* are constant quantities:

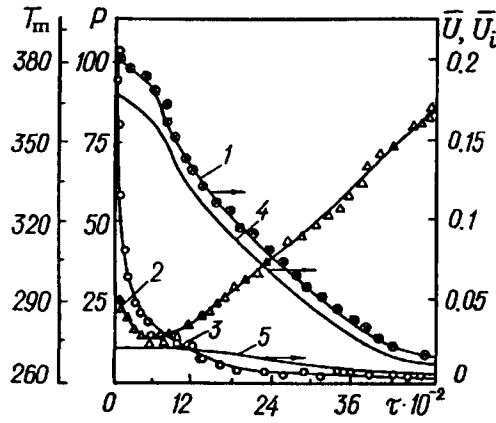


Fig. 1. Kinetic curves of electrovacuum desorption of a methylene chloride-water mixture from activated carbon, grade AR-V, at $U_e = 15-20$ V: 1) integral moisture content, 2) integral temperature, 3) pressure, 4) mean moisture content of methylene chloride, 5) mean moisture content of water.

$$\frac{d\bar{U}_i}{d\tau} = a_i n_i^* \frac{p_i^{n_i^*}}{p_{\text{isat}}(T_{\text{mx}})} \left[\frac{1}{p_i} \frac{dp_i}{d\tau} - \frac{1}{p_{\text{isat}}(T_{\text{mx}})} \frac{dp_{\text{isat}}(T_{\text{mx}})}{d\tau} \right]_{x=R/2}, \quad (22)$$

and the change in the saturation pressure of the i -th component of the mixture is determined from the Antoine equation [7]

$$\frac{dp_{\text{isat}}(T_{\text{m}})}{dT_{\text{m}}} = \exp \left(A_i - \frac{B_i}{T_{\text{m}}} \right) \frac{B_i}{T_{\text{m}}^2} \frac{dT_{\text{m}}}{d\tau}. \quad (23)$$

Let the moist material be represented in the form of two conductors connected in parallel, namely, the dry material and the liquid with the cross sections

$$S_{\text{m}} = S(1 - \epsilon); \quad S_{\text{liq}} = S\epsilon\bar{W} = S\epsilon \frac{\bar{U}}{1 + \bar{U}}. \quad (24)$$

Then the electrical resistance of the moist material is

$$\frac{1}{R_e} = \frac{1}{\rho_e \frac{H}{S(1 - \epsilon)}} + \frac{1}{\rho_{\text{liq.e}} \frac{H(1 + \bar{U})}{S\epsilon\bar{U}}}, \quad (25)$$

and the resistivity of the adsorbent is found from the relation

$$\rho_e = \frac{\rho_{\text{m.e}} \rho_{\text{liq.e}} (1 + \bar{U})}{\rho_{\text{liq.e}} (1 + \bar{U}) (1 - \epsilon) + \rho_{\text{m.e}} \bar{U}\epsilon}. \quad (26)$$

The electrical resistivity of the liquid mixture $\rho_{\text{liq.e}}$ entering the equation corresponds to the lowest value of the i -th parameter.

Equations (18), (26) and the transfer equations for the vapor phase (1)-(3) and a particle of the adsorbent (4)-(12) were solved by a numerical method [8].

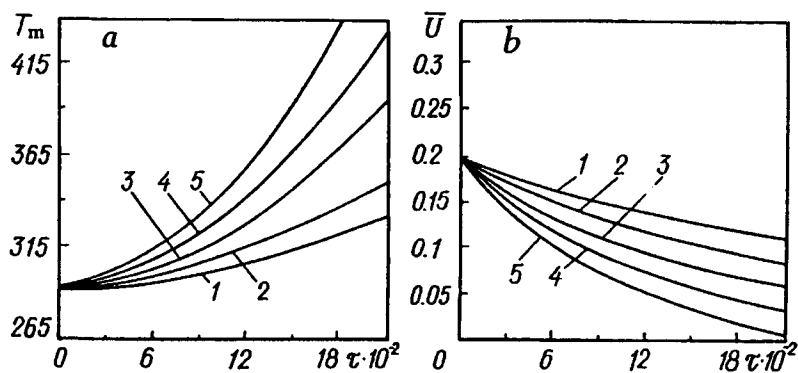


Fig. 2. Calculated kinetic curves of desorption of a mixture of isopropyl and ethyl alcohols from activated carbon, grade AR-V, at different electrode voltagea [1) $U_e = 10$ V, 2) 20, 3) 30, 4) 40, 5) 50]: a) integral temperature; b) integral moisture content.

The adequacy of the mathematical model was tested experimentally on a setup consisting of a chamber with electrodes, an autotransformer, an ammeter, and a voltmeter, a vacuum pump, a condenser, devices for recording the temperature of the material and the vapor phase and the absolute pressure. The composition of the condensate was determined on a chromatograph.

Figure 1 depicts calculated and experimental data on the kinetics of desorption of the two-component liquid methylene chloride–water from activated carbon, grade AR-V, by the electrovacuum method. An analysis of the curves reveals two stages of the process. In the initial stage, with a decrease in the pressure from atmospheric to "threshold" $P_{th} = 15-18$ kPa the solvent is removed. The integral moisture content decreases from 0.2 to 0.18 kg/kg, and the material temperature, from 293 to 275 K. To describe mathematically the process in this stage, use is made of system of equations (1)-(10) without the source term in Eq. (8) with the following initial conditions:

$$U_i(0, x) = U_{in}; \quad T_m(0, x) = T_{in}; \quad P_{in} = P_{at} + \sum_{i=1}^n p_i(T_{in}U_{in}); \quad j_i = 0.$$

In the second stage, a voltage $U_e = 15-20$ V was applied to the electrodes starting from the moment of time $\tau = \tau_1 = 600$ sec. As a result of the increase in the material temperature, the rate of liquid desorption from the adsorbent increased. After some time ($\tau = 4800$ sec) the magnitude of the moisture removal was $\Delta \bar{U} = \bar{U}_{in} - \bar{U}_f = 0.18-0.19$ kg/kg. In this case the material temperature increased to 360 K. For the mixture components, the mean moisture content changed from 0.18 to 0.01 for methylene chloride and from 0.02 to 0.003 for water.

A comparison of the results presented for electrovacuum desorption and data on moisture removal from capillary-porous materials under vacuum-oscillation conditions [3] revealed a more than threefold decrease in the duration of the process of adsorbent regeneration.

Figure 2 gives calculated kinetic curves for desorption of a mixture of isopropyl and ethyl alcohols for different voltages applied to the electrodes. An analysis of the curves shows that the intensity of moisture removal from the adsorbent increases proportionally to the voltage; however, here the material temperature increases considerably. To remove readily inflammable liquids, for safety purposes the voltage applied to the electrodes should be decreased in the course of the process so that the material temperature would be lower than the permissible value characteristic for the particular case.

NOTATION

P, p , total pressure of the mixture and partial pressure of the component, Pa; τ , time, sec; F , heat and mass transfer surface, m^2 ; R^* , universal gas constant, $J/(kmole \cdot K)$; T, T_m , temperature of the vapor mixture and the material, respectively, K; j , mass flow, $kg/(m^2 \cdot sec)$; $V_{v,s}$, volume capacity of the vapor removal system, m^3/sec ; V_{fr} , free volume of the apparatus, m^3 ; μ , molecular weight of the component, $kg/kmole$; R , particle thickness, m;

U , moisture content, kg/kg; x , current coordinate, m; a , n^* , coefficients in the Freundlich isotherm equation; λ , thermal conductivity, W/(m·K); c , heat capacity, J/(kg·K); q_e , density of the electric-power source, W/m²; R_V , reduced dimension, m; V , volume of the moist material, m³; a_m , mass conductivity, m²/sec; δ , relative coefficient of thermal diffusion, 1/K; K_p , molar-transfer coefficient, kg/(m·Pa·sec); β , mass-transfer coefficient, m/sec; m , mass, kg; r , latent heat of vaporization, J/kg; I , current strength, A; U_e , voltage, V; S , cross section of the layer, m²; H , height of the layer, m; ρ_e , electrical resistivity, $\Omega \cdot m$; W , humidity, kg/kg; ρ , density, kg/m³; R_e , electrical resistance, Ω ; ε , void content of the layer; n , number of mixture components. Subscripts: 0, dry material; m, material; liq, liquid; i , component of the vapor or the liquid; s, particle surface; c, particle center; fr, free; v.s, vapor system; sat, saturated; e, electrical; v, vapor; in, initial; f, final; at, atmospheric.

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