Lecture №10. Calculation of the adsorber batch and continuous action

Aim: Bring the equations of mono-, polymolecular adsorption and the Polani isotherm equation. Discuss the calculation of the adsorption process. Analyze the material balance equation of the countercurrent apparatus. Bring the equation of the average driving difference of the concentrations of the absorbed component.

Lecture summary: The adsorption equilibrium is characterized by dependencies of the amount of substance a^* absorbed by a unit mass or volume of a given adsorbent, on the concentration of the substance absorbed in the environment and temperature T. The equilibrium concentration of the adsorbent in the adsorbent can be represented as a function $a^* = f(c, T)$ or as a function of the partial pressure p and temperature in the case of gas adsorption $a^* = f'(p, T)$. The ratios between the values of the equilibrium concentrations a^* and c can be very diverse and depend on the ability of a particular substance to retain the target component by surface interaction forces. The dependence $a^* = \varphi(c)$ or $a^* = \varphi'(p)$ at a constant temperature is called absorption isotherm. Equilibrium dependencies are described by a number of empirical and theoretical equations. There are a number of theories of adsorption: monomolecular, polymolecular, bulk filling of pores, etc. In accordance with the proposed theories of adsorption, there are adsorption isotherm equations for adsorbents of various nature and structure used in the calculation of process characteristics. However, despite a significant amount of theoretical equilibrium studies, for practical calculations of adsorption processes, the most reliable equilibrium data are isotherms obtained on the basis of direct experimental measurements.

The monomolecular adsorption isotherm has the form of the Langmuir equation

$$\frac{a^*}{a_M^*} = \frac{bp}{1 + bp},$$

where the a_M^* maximum amount of adsorptive that can be absorbed by the adsorbent when filling all the adsorption centers on the surface of the pores of the adsorbent; b is the coefficient determining the dependence of the Langmuir isotherm type on temperature.

According to the theory of polymolecular adsorption of BET, the equilibrium state is described by the isotherm of the form

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$$\frac{a^*}{a^*_M} = \frac{C_1}{(1-p/p^*)\left[1-(C_1-1)p/p^*\right]}\frac{p}{p^*}$$

where p^* – adsorptive saturated vapor pressure at equilibrium process temperature; C_1 is a constant defined for each couple of adsorbent – adsorbate.

Theory of volumetric filling of micropores by an adsorbed component leads to the Polani isotherm equation

$$a^* = \frac{W_0}{v^*}\exp\left[-B\left(\frac{T}{\chi}\ln\frac{p}{p^*}\right)^2\right],$$

where W_0 is the total specific pore volume of the adsorbent, m^2/kg; v^* is the molar volume of the adsorptive in the state of the liquid phase, m^3/kmol; B is a constant characterizing the predominant influence of the micropores of the adsorbent, K^{-2}; χ is the affinity coefficient; T - temperature, K.

For the surface of mass transfer processes with a solid phase take the outer surface of the particles of the adsorbent. The specific surface of the contact phase is calculated by the equation $\sigma = 6(1 - \varepsilon)d$, where d is the diameter of the particles of the adsorbent.

The mass transfer rate to the porous material is determined by the mass transfer rate to the outer surface of the particles, characterized by the external mass transfer coefficient β_y, and the mass transfer rate to the inner surface of the adsorbent.

External mass transfer coefficients in the gas phase can be calculated by the equation

$$\beta_y = 0{,}355\frac{w}{\varepsilon}\left(\frac{w\rho_y d}{\mu_y}\right)^{-0,359}\left(\frac{\mu_y}{\rho_y D_y}\right)^{-0,667},$$

where ρ_y, μ_y, D_y – respectively, density, viscosity and diffusion coefficient for the environment.

To calculate the mass transfer coefficients β_y for adsorption on the active carbon ($d = 1.7–2.2$ mm, w of the flow $0.3–2$ m/s) use the equation (provided that the adsorption isotherm is described by Langmuir equation): $Nu' = 1{,}6\,Re^{0,54}$. The mass transfer coefficient β_y is calculated by the formula reduced to the calculated form:

$$\beta_y = 1{,}6\frac{Dw^{0,54}}{v^{0,54}\,d^{1,46}}.$$

Here $Nu' = \beta_y d^2/D$; $Re = wd/v$; D – adsorptive diffusion coefficient in gas at a process temperature, m^2/s; w – speed steam-gas mixture current, m/s; v — kinematic coefficient of viscosity, m^2/s.

The rate of internal mass transfer depends on the rates of diffusion in the pores of the adsorbent, on its inner surface and in the solid phase itself. Often, the rate of internal mass transfer is approximately characterized by mass transfer coefficients in pores β_p or in solid material β_{sol}.

Under the conditions of operation of the industrial adsorption apparatus, the external and internal diffusion resistances may be comparable in magnitude. To calculate the adsorption equipment, simplified expressions are used to describe the rate of adsorption:

$$\frac{da}{d\tau} = \beta_y(c - c_i) = \beta_\pi\left[(c_i - c^*(a)\right] = \beta_\tau\left[\frac{c_0}{a^*(c_0)}\right]\left[(a^*(c_i) - a\right],$$

where c_0 is the initial concentration of the adsorbed substance in the vapor-gas flow, kg/m^3; c_i is the concentration at the external surface of the adsorbent, kg/m^3; $a^*(c_0)$ - equilibrium adsorption capacity, kg/m^3.

The mass transfer coefficients in the pores and solid material are found from the corresponding diffusion coefficients by the following relations: $\beta_{por} = 10 D_{por}/d$:

$$\beta_\pi = 10\,D_\pi/d;$$

$$\beta_\tau = \frac{10 D_\tau}{d(1-\varepsilon)}\left[\frac{\rho_{\text{нас}}\,a^*(c_0)}{c_0}\right].$$

The total resistance to the process of mass transfer is represented as the sum of the outer (y) and inner (x) resistances:

$$K_y = 1 / (1/\beta_y + 1/\beta_x)$$

If the internal resistance to mass transfer is determined by diffusion in the pores, then the internal mass transfer coefficient $\beta_x = \beta_p + \beta_{sol}$. If the internal resistance depends on both the diffusion in the pores and the diffusion in the

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adsorbent or on its internal surface, then the internal mass transfer coefficient is $\beta_x = \beta_p + \beta_{sol}$.

The calculation of the adsorption process in the fixed bed of the adsorbent is reduced to determining the time during which the layer of a given thickness is able to remove the adsorbtive from the gas or liquid stream so that its content at the outlet does not exceed the predetermined value. This time interval τ_{pr} is called the time of the protective action of the layer and is determined by the Shilov empirical equation

$$\tau_{pr} = KH - \tau_0,$$

where K is the coefficient of the protective action of the layer, s/m; τ_0 - loss of time of the protective action of the layer, s; w - gas flow velocity, m/s; H - the height of the layer of adsorbent, m.

In the process of absorbing an adsorbtive, a concentration field of the absorbed substance is formed in the layer. The adsorption front moves over the layer. The adsorbent layer is characterized by the magnitude of the dynamic adsorption capacity (activity) a_d - the amount of absorbed substance by the layer of adsorbent until the moment when the adsorptive layer appears, $a_d = wc_0t_{pr}$.

The assumption that there are no resistances to the transfer of the adsorbent to the outer surface of the particles and inside their porous structure allows one to calculate the process of periodic adsorption in the fixed bed of the adsorbent on the basis of the material balance equation alone, according to which the amount of the component entering the layer with the flow gas in time τ, equal to the number of the target component, completely saturating part of the layer to a height h: $wc_0\tau = a*_0h$, where $a*_0$ is the equilibrium adsorption capacitance. The speed of the saturation front in this case is constant: $u = dh/d\tau = wc_0/a^*_0$. The time $\tau_{pr,M}$ of the complete filling of the entire layer H, which coincides with the time at which the initial concentration of the adsorptive c_0 immediately appears in the stream after the layer, is determined in this limiting case by the material balance equation, according to which it is proportional to the equilibrium adsorption capacity and inversely proportional to the amount of the adsorptive gas supplied with the carrier gas

$$\tau_{3,M} = \frac{a_0^* H}{wc_0}.$$

The coefficient of the protective action of the layer can be calculated by the formula $K = 1/u = a^*_0/(wc_0)$ where u is the rate of advance of the saturation front.

The real time τ_{pr} of the protective action of the layer due to the expansion of the adsorption front decreases in comparison with the maximum value of $\tau_{pr,M}$. In practical calculations, this circumstance is taken into account by introducing into the right-hand side of the Shilov equation the value of the loss of time of the protective action of the layer

$$\tau_3 = \frac{a^*_0 H}{wc_0} - \tau_0.$$

The loss of time of the protective action of the layer is mainly due to the fact that the formation of the adsorption front does not occur instantaneously. The numerical value τ_0 increases with an increase in the total diffusion resistance to the process of mass transfer, the degree of deviation of the adsorption isotherm from an extremely convex shape, and also with increasing intensity of longitudinal mixing in the flow of carrier gas passing through a fixed bed of adsorbent. The numerical values of the loss of protective action time τ_0 for the specific conditions of the periodic adsorption process by a non-moving layer are usually found experimentally.

The cross-section of the adsorber and, therefore, its diameter when designing a cylindrical apparatus is determined by the choice of the fictitious velocity of a gas or liquid. The cross-sectional area of the adsorber is determined from the flow equation

$$S = V / w,$$

where S – cross-sectional area of the apparatus, м^2; V – air-steam consumption, м^3/s; w – set or accepted linear velocity of flow through the apparatus, м/s.

The upper limit of the velocity is the rate of onset of the pseudo-liquefaction of the particles of the adsorbent. With an increase in speed, the mass transfer coefficient increases and the hydraulic resistance increases. The allowable fictitious speed can be calculated from the formula obtained on the basis of a feasibility study of the adsorbers:

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$$w = \sqrt{0{,}0167 \frac{\rho_{\text{нас}}\, d_{\text{э}}\, g}{\rho_{\text{г}}}}$$

where d_{eq} – the equivalent grain diameter of the adsorbent, м; ρ_{bulk} – the bulk density of the adsorbent, kg/m^3; ρ_g – gas density, kg/m^3.

The working flow rate in the adsorber is usually taken 25% less permissible.

The diameter of the apparatus is cylindrical $D = \sqrt{4S/\pi}$, and the height of his working area will be $H = V/S = w\tau$.

The adsorption process in the moving bed is organized in such a way that the dense layer of the adsorbent continuously moves towards the upward flow of the vapor-gas mixture. The advantage of carrying out the process of adsorption in apparatus with a moving layer of an absorber as compared with adsorption in a fixed bed is in the constant concentration of the adsorptive at the outlet of the apparatus. The purpose of the calculation process in a moving layer is to determine the required height of the layer, which would ensure the absorption of the target component in a given range of concentrations at the entrance and exit of the apparatus.

The material balance equation of such a counter-current process will be:

$$V(c_0 - c_c) = L\,(a_{ex} - a_{en}),$$

where V – carrier gas flow, м^3/c; L – adsorbent consumption м^3/c; c_0, c_c – the concentration of the absorbed component in the gas at the entrance to the adsorber and at the exit of it, кg/m^3; a_{en}, a_{ex} – adsorptive content in adsorbent at the entrance and exit of the adsorber, кg/m^3.

For given values of the content of the adsorptive at the beginning and end of the process, you can determine the minimum consumption of the adsorbent

$$L_{\text{мин}} = \frac{V(c_0 - c_{\text{к}})}{a^*(c_0) - a_{\text{н}}}.$$

The actual consumption of the adsorbent is taken with a margin $L = \varphi L_{min}$,

where φ – coefficient of excess adsorbent.

The joint balance equation of the component in the gas phase and the kinetics of mass transfer is written for the elementary height dh of the moving layer in the form

$$-Vdc = K_{Vc} S[c - c(a)]dh.$$

When integrating this equation over the entire desired height H of the moving layer, i.e. within the change in concentration in the flow from c_c at $h=H$ to c_0 at $h=0$ at a constant value of the mass transfer coefficient K_{Vc}, we obtain the equation for calculating the height of the adsorbent layer

$$H = \frac{V}{SK_{Vc}} \int_{c_\kappa}^{c_0} \frac{dc}{c - c^*(a)} = h_{\scriptscriptstyle9} n_{0c},$$

where n_{0c} – total number of transfer units; h – equivalent height of the transfer unit.

The calculation of fluidized bed adsorbers can be made using the general mass transfer equation, considered together with the material balance equations of the target component for the gas and solid phases:

$$K_{Vc}\Delta c_{cp}V_a = V(c_0 - c_\kappa) = L(a_{ex} - a_{en}),$$

where V and L – volumetric flow rates of carrier gas and disperse adsorbent, m³/s; V_a – luid bed adsorbent volume, m³; K_{Vc} – volumetric mass transfer coefficient, c⁻¹; c_0, c_c – the concentration of the absorbed component in the gas at the entrance to the adsorber and at the exit from it, kg/m³; Δc_{av} the average over the entire layer concentration difference absorbed component in the gas phase, kg/m³; a_{ex} – average concentration of the adsorptive at the exit of the apparatus, kg/m³; a_{en} is the content of the adsorptive in the adsorbent at the entrance to the adsorber, kg/m³.

The average driving difference in the concentrations of the absorbed component is calculated by the formula:

$$\Delta c_{cp} = \frac{\left[c_0 - c^*(\bar{a}_\kappa)\right] - \left[c_\kappa - c^*(\bar{a}_\kappa)\right]}{\ln \dfrac{c_0 - c^*(\bar{a}_\kappa)}{c_\kappa - c^*(\bar{a}_\kappa)}}$$

In multistage countercurrent adsorbers with a fluidized absorber layer, the volumetric mass transfer coefficient K_{Vc} varies from the plate, and the process rate can be limited by both external and intradiffusion kinetics. As the adsorbent flows onto the downstream plates, the proportion of intradiffusion resistance increases. It was experimentally shown that the value of β_0, which is called the average effective mass transfer coefficient, is close to the volume coefficient of the internal mass transfer, which is almost independent of the gas flow rate. On this basis, take $\beta_0 \approx K_{Vc}$.

The overall mass transfer coefficient is determined experimentally for each specific process condition. An example of the correlation ratio by which β_0 can be determined under fluidized bed conditions during the adsorption of benzene, methanol, and ethanol vapors from the air stream with granular activated carbons of grades AG-3, SKT-D, KAU, and AGK-1 is the equation

$$\frac{\beta_0 d^2}{D} = 1{,}55 \cdot 10^2 \chi \left(\frac{L_{уд} d}{D}\right)^{0{,}75} \left(\frac{c_S}{c_0}\right)^{0{,}35} \left(BT^2\right)^{-1{,}3} \left(\frac{d}{H}\right)^{1{,}25},$$

where d and H is the diameter of the particles of the adsorbent and the height of the fluidized bed, m; χ is the affinity coefficient; L_{sp} - specific consumption of adsorbent, m³/(m²·s); c_0 and c_S are the initial concentrations and the saturated vapor concentration of the adsorptive, kg/m³; B is the structural constant of the adsorbent, K^{-2}; D is the diffusion coefficient of the adsorptive, m²/s.

For systems of zeolite NaA - moisture vapor in the air, the value of the total mass transfer coefficient, referred to the unit volume of the fluidized bed, is calculated by the equation

$$\frac{\beta_0 d^2}{D} = 4.0\left(\frac{L_{уд}d}{D}\right)^{0,7}\left(\frac{c_S}{c_0}\right)^{0,35}\left(\frac{\chi^2}{BT^2}\right)^{1,1}.$$

The required volume of the adsorbent in the fluidized bed is determined by the equation

$$V_a = \frac{V(c_0 - c_к)}{\beta_0 \, \Delta c_{cp}}.$$

The volume of the fluidized bed is determined by the equation $V_{bed} = V_a/\varepsilon$, layer height is equal to $H = V/(0.785D^2)$.

Questions to control:

1. Bring the equations of mono-, polymolecular adsorption and the Polani isotherm equation.

2. Discuss the calculation of the adsorption process.

3. Analyze the material balance equation of the countercurrent apparatus.

4. Bring the equation of the average driving difference of the concentrations of the absorbed component.

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