
THE EFFECT OF A SORBENT DILUTION WITH INERT MATERIAL ON ISOTHERMAL DYNAMIC ADSORPTION

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The derived expressions show the dependence of the efficiency of a sorption layer on dilution of this layer with inert material. The presence of the inert material in the space between granules has effect on the term of axial dispersion, while the same material inside the granules affects both the term of axial dispersion and the term of internal diffusion. The inert material presence can change in the isothermal sorption processes a relative importance of the individual rate steps. The derived expressions can be applied for testing the rate mechanisms and their dependence on the dilution extent.

In the preceding paper¹, we have used a separation of the overall kinetics from the effects of convection and axial dispersion, for evaluation of the effect of one type of dilution of a sorption layer with inert material.

Besides the earlier described insertion of inert particles between the adsorbent granules^{1,2}, we are considering in the present paper also the sorbent dilution inside the granules themselves. Such an analysis can be of importance if we are concerned with the zeolitic sorbents, since it illustrates, to certain extent, the influence of the presence of a binder which is used for holding the zeolite crystallites in the form of granules. In order to study the above effects, we shall not any more commence quite generally with differential equations describing the sorption dynamics in diluted columns but we shall use the results given in earlier papers^{1,3}. The corresponding conclusions can be found, on basis of these results, by simple considerations.

The Model of a Diluted Sorption Layer

We shall assume for simplicity that the sorbent filling consists of a mixture of spherical granules with identical radii R_b . In this case, we can write for a fraction φ_G of the sorption granules

$$\varphi_G = V_G / (V_G + V_i) = N_G / (N_G + N_i), \quad (1)$$

where V_G is the volume of the sorbent granules in a layer and V_i is the volume of inert particles.

Generally, it holds that $0 \leq \varphi_G \leq 1$. In the previous paper¹, we have formulated the conditions for φ and the volume distribution of a sorbent and the inert particles so that it was possible to regard this layer as a statistically homogeneous medium. For description of the mass balance, we have introduced two following distribution constants characterizing (for a linear adsorption isotherm), the distribution of molecules between the volume of column filling and the intergranular space:

$$K_L = \Delta \bar{a}_{L\infty} / \Delta c_\infty \quad (2)$$

In this expression, $\Delta \bar{a}_{L\infty}$ denotes the change of the amount of sorbate inside the particles of column filling per a unit volume of these particles; Δc_∞ is the change of the amount of sorbate in the intergranular volume per a unit volume of the intergranular space.

$$K_G = \Delta \bar{a}_{G\infty} / \Delta c_\infty \quad (3)$$

$\Delta \bar{a}_{G\infty}$ is the change of the amount of sorbate in the column filling per a unit volume of the sorbate particles. Simultaneously it holds that

$$K_L = K_G \varphi_G \quad (4)$$

In the next step, we shall discuss the internal structure of the sorbent granules, considering two basic forms of the presence of inert material in the granules,

Case (a) is shown schematically in Fig. 1a. We assume for simplicity that the sorbent granules have a form of spheres with identical radii r_A . From these, fraction φ_A represents the pure sorbent (*e.g.* zeolite crystallites) while fraction $1 - \varphi_A$ relates to inert material.

$$\varphi_A = V_A / (V_A + V_N) = N_A / (N_A + N_N) \quad (5)$$

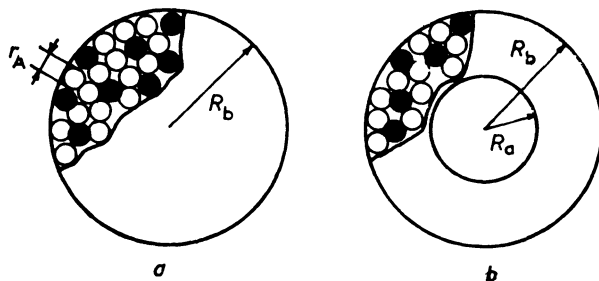


FIG. 1

Scheme of the section through a granule a) without inert core b) with inert core; full circles: the sorbent; open circles: inert material

V_A is the sorbent volume in a granule, N_A is the number of pure sorbent particles in a granule, V_N is the volume of inert in a granule and N_N is the number of inert particles in a granule.

A fraction of intercrystalline volume in zeolitic granules which represents the fraction of the transport pores is denoted as

$$\beta = V_b/V_G, \quad (6)$$

where V_b is the volume of the transport pores in the bed. Finally, we shall introduce the distribution constant K_A for the sorption in crystallites

$$K_A = \Delta \bar{a}_{A\infty} / \Delta c_\infty, \quad (7)$$

where $\Delta \bar{a}_{A\infty}$ is the change of the amount of sorbate in the crystallites per a unit volume of the crystallites.

Evidently:

$$K_G = \beta + (1 - \beta) \varphi_A K_A. \quad (8)$$

Case (b) is schematically shown in Fig. 1b. In this case, the diluted or undiluted layer is deposited on an inert core with the radius R_a :

$$K_G = \eta[\beta + (1 - \beta) \varphi_A K_A], \quad (9)$$

where

$$\eta = 1 - \xi^3, \quad (10)$$

η represents the volume fraction of the deposited sorption layer in the granules

$$\xi = R_a/R_b. \quad (11)$$

The Effect of Dilution on the Efficiency of a Sorption Bed

We shall take as a criterion of efficiency of a sorption bed, the number of theoretical plates of the column:

$$N = (\mu'_1)^2 / \mu_2, \quad (12)$$

where μ'_1 is the first normal moment and μ_2 the second central statistical moment of the outlet curve (for definition of the moments, see paper⁴). Let us assume that we have a bed with length L which is filled with the pure sorbent formed of granules with radii R_b . These are arranged in such a way that the intergranular volume α represents a fraction of the total volume of the bed. The granules consist of spheres

with radii r_A – with a volume fraction of the transport pores β . In the next step, we shall dilute the initial amount of the sorbent, with an inert, so that the parameters which characterize the above mentioned types of dilution will have values φ_A , φ_G and η . The internal geometry of the bed will remain unchanged. As a result of this operation, the length of the bed will extent to L' . Simultaneously, it is

$$L'/L = 1/\varphi, \quad (13)$$

where

$$\varphi = \varphi_A \varphi_G \eta. \quad (14)$$

The statistical moments of the outlet curves measured on the diluted beds can be written in a following way¹:

$$(\mu'_1)_\varphi = \frac{L'}{u} [1 + K_L(1 - \alpha)/\alpha]. \quad (15)$$

After substituting from the equations (4), (8), (13) and (14), we have

$$(\mu'_1)_\varphi = \frac{L}{u \varphi_G \varphi_A \eta} \{1 + \varphi_G \eta [\beta + (1 - \beta) \varphi_A K_A] (1 - \alpha)/\alpha\}, \quad (16)$$

where u denotes a linear velocity of the carrier gas along the column, related to cross section corresponding to the intergranular volume ($u = \dot{v}/\alpha S$, \dot{v} is the volume velocity of the carrier gas and S the cross section of a column).

For the second central moment $(\mu_2)_\varphi$ of the diluted bed, we can write¹:

$$(\mu_2)_\varphi = (\mu_1)_\varphi [(\tau_D)_\varphi + 2(\lambda)_\varphi (f_G)_\varphi], \quad (17)$$

where, $(\lambda)_\varphi$ is the mean penetration time of the sorbed molecules into particles of the diluted sorbent (the exact formula will be given below) and

$$\begin{aligned} (\tau_D)_\varphi &= 2(D_Z/u^2) \{1 + K_L(1 - \alpha)/\alpha\} = \\ &= 2(D_Z/u^2) \{1 + \varphi_G \eta [\beta + (1 - \beta) \varphi_A K_A] (1 - \alpha)/\alpha\} \end{aligned} \quad (18)$$

is the time constant describing axial dispersion in the column, which was introduced in paper¹.

$$(f_G)_\varphi = (\mu'_1)_\varphi^a / (\mu'_1)_\varphi \quad (19)$$

denotes a fraction of the total mean residence time of a molecule in the bed which the molecule spends inside the granules; D_Z is the coefficient of axial dispersion.

$$(f_G)_\varphi = \varphi_G \eta \frac{[\beta + (1 - \beta) \varphi_A K_A] (1 - \alpha) / \alpha}{1 + \varphi_G \eta [\beta + (1 - \beta) \varphi_A K_A] (1 - \alpha) / \alpha} \quad (20)$$

$(\mu'_1)_\varphi$ is the mean residence time which a molecule spends inside the sorbent particles on its way through the column. A general expression for the efficiency N_φ of a diluted layer can be obtained by substituting from Eqs (16–20), into (12). We shall, nevertheless, limit ourselves to the approximation (valid only for relatively small dilutions) which assumes that the accumulation of sorbate in the intergranular volume and in the transport pores is negligible against the accumulation in the granules and zeolite crystallites, respectively. Equations (16) and (20) must thus fulfil a condition

$$1 \ll \varphi_G \eta [\beta + (1 - \beta) \varphi_A K_A] (1 - \alpha) / \alpha \quad (21)$$

and in equations (16), (18) and (20)

$$\beta \ll (1 - \beta) \varphi_A K_A. \quad (22)$$

Applying the above expressions, we obtain for N_φ a relation which is analogous to Eq. (23) in the previous paper¹:

$$N_\varphi / N_1 \cong \frac{(\tau_D)_1 + 2(\lambda)_1}{(\tau_D)_1 \varphi + 2(\lambda)_\varphi}. \quad (23)$$

Indices “1” relate to the values λ corresponding to $\varphi = 1$ (i.e. to undiluted beds). The above equation differs from the equation (23) in the preceding paper¹ in that respect that instead of the original factor φ_G in the denominator, we get a factor $\varphi = \varphi_G \varphi_A \eta$. Also, the value of parameter $(\lambda)_\varphi$ depends in this case generally on the dilution. To get a complete picture of the influence of dilution on the bed efficiency, we must analyze the behaviour of parameter $(\lambda)_\varphi$.

The Effect of Dilution of Sorbent Particles on the Mean Time λ of Penetration of Molecules into the Granules

The dependence of $(\lambda)_\varphi$ on the degree of dilution can be evaluated only under the assumption that we know the concrete kinetic steps playing a role in the dynamics of the sorption process. It may be expected that the relative importance of the individual kinetic steps can be markedly affected by the extent of dilution. The described method could be then used for investigation of the individual kinetic steps in the dynamics of the sorption processes.

Granules without an inert core, $\eta = 1$. We shall postulate that the mass transport into granules consisting of a mixture of zeolitic crystallites and inert particles is described by the model applying two diffusion resistances^{5,6}.

We assume therefore that in zeolites proceed simultaneously both the intracrystalline and the intercrystalline diffusion, while external diffusion is negligible. It is further assumed that the factor of tortuosity τ_G , describing the diffusion in the granules is independent of the dilution degree. In addition to that, we take as a fact that the presence of inert material does not influence the access to the surface of the crystallites. Applying the well known solution of the problem of a diffusion into spherical particles with bimodal structure of the pores, we can write the following expressions:

$$(\lambda)_\phi = \frac{(R_b)^2 [1 + K_A \varphi_A (1 - \beta)/\beta]}{15(D_G/\tau_G)} + \frac{r_A^2}{15D_A} f_A = (\lambda_G)_\phi + \lambda_A f_A. \quad (24)$$

The first term on the right-hand side of Eq. (24) (*i.e.* $(\lambda_G)_\phi$) represents the contribution from intercrystalline diffusion (described by the diffusion coefficient D_G) to $(\lambda)_\phi$. This term depends on the factor of dilution φ_A of the granules. The second term depends primarily on the parameter λ_A , which represents the mean penetration time of molecules into the crystallites. λ_A is a function of the coefficient of intracrystalline diffusion D_A and within the framework of the bidisperse model it is independent of the dilution. Factor f_A shows a fraction of the sorption capacity of a granule which is represented by the sorption capacity of zeolitic crystals.

If we omit, as in the first case, the accumulation of a sorbate in the transport pores against the accumulation in the crystallites, we can write:

$$(\lambda)_\phi = (\lambda_G)_1 \varphi_A + \lambda_A \quad (25)$$

since also $f_A \rightarrow 1$. Then we get

$$(\lambda)_\phi / (\lambda)_1 \leq 1. \quad (26)$$

The mean penetration time of the sorbate molecules into the granules decreases with increasing dilution, or if the sorption kinetics is determined by the intracrystalline diffusion, it remains unchanged.

By substituting from Eq. (25) into (23), we obtain the final expression for the efficiency of the bed. As one can see, the bed efficiency can be further increased by a dilution of the granules

$$N_\phi / N_1 = \frac{(\tau_D)_1 + 2(\lambda_G)_1 + 2\lambda_A}{[(\tau_D)_1 \varphi_G + 2(\lambda_G)_1] \varphi_A + 2\lambda_A}. \quad (27)$$

Granules with an inert core, $\eta < 1$. Let us assume that we have a sorption layer which was diluted in a quite general way and then deposited on an inert core. We also assume that both diffusion mechanisms specified under (a) play a role in the above system.

The expression for $(\lambda)_\phi$ must have then the same form as Eq. (24), with only one difference concerning a factor adjoined to the first term of this equation. Instead of the original, generally valid value $1/15$, this factor appears now as a shape parameter, depending on the parameter $\xi = (1 - \eta)^{1/3}$.

In such a case, we obtain:

$$(\lambda)_\phi = f(\xi) \frac{(R_b)^2 [1 + K_A \varphi_A (1 - \beta)/\beta]}{D_G/\tau_G} + \frac{r_A^2}{15D_A}. \quad (28)$$

Kubín derived⁷ for $f(\xi)$ the expression

$$f(\xi) = \frac{1}{15} \left[1 - \xi^3 \frac{4 + 4\xi - 5\xi^2}{1 + \xi + \xi^2} \right]. \quad (29)$$

We can see that $f(\xi)$ varies within the range

$$\begin{aligned} f(\xi) &= 1/15 = 0.067 \quad \text{for } \xi = 0 \\ f(\xi) &= 0 \quad \text{for } \xi = 1. \end{aligned}$$

For the values ξ close to 1, we obtain after the expansion of Eq. (29) into the Taylor series, for the neighborhood of $\xi = 1$:

$$f(\xi) \cong (1/3)(1 - \xi)^2. \quad (30)$$

The course of the numerically evaluated dependence of factor f on ξ is evident from Fig. 2.

If we omit as before the terms corresponding to sorbate accumulation inside the pores, we obtain after substitution from Eq. (28) into (23), the expression for the efficiency of a bed

$$N_\phi/N_1 = \frac{(\tau_D)_1 + 2(\lambda_G) + 2\lambda_A}{[(\tau_D)_1 \varphi_G (1 - \xi^3) + 30(\lambda_G)_1 f(\xi)]_{\phi_A} + 2\lambda_A} \quad (31)$$

in which

$$\xi = \sqrt[3]{(1 - \eta)}.$$

We can see that the maximum effect is obtained for the case when intracrystalline diffusion is negligible, *i.e.* $\lambda_A \rightarrow 0$. Figs (3), (4) and (5) illustrate the effect of the parameters φ_G , η and φ_A , for the case $\lambda_A = 0$ and the typical values $(\tau_D)_1$ and $(\lambda_G)_1$.

It can be summarized that the derived expressions show in which way the efficiency of the sorption layer depends on dilution of this layer with inert material. A presence

of inert material in the volume between the granules affects the term of axial dispersion while the presence of inert material inside the granules has a positive effect both on the term of axial dispersion and on the term of internal diffusion.

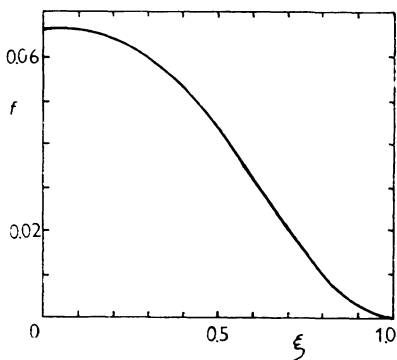


FIG. 2

The dependence of the factor f on ξ , for the particles with an inert core

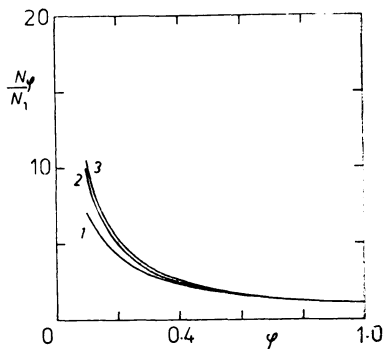


FIG. 3

The dependence of the efficiency of a diluted bed on the effects of parameters φ_G , η and φ_A , for $\lambda_A \rightarrow 0$, $(\lambda_G)_1 = 10$ s, $(\tau_D)_1 = 400$ s; 1: $\varphi_G < 1$, $\varphi_A = \eta = 1$; 2: $\varphi_A < 1$, $\varphi_G = \eta = 1$; 3: $\eta < 1$, $\varphi_A = \varphi_G = 1$

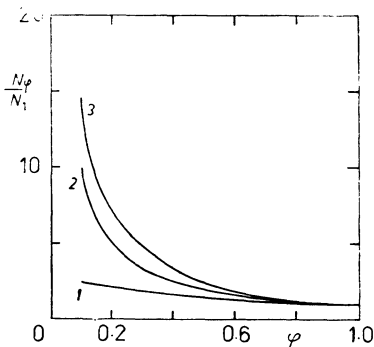


FIG. 4

The dependence of the efficiency of a diluted bed on the effects of parameters φ_G , η and φ_A , for $\lambda_A \rightarrow 0$, $(\lambda_G)_1 = 100$ s, $(\tau_D)_1 = 400$ s; 1: $\varphi_G < 1$, $\varphi_A = \eta = 1$; 2: $\varphi_A < 1$, $\varphi_G = \eta = 1$; 3: $\eta < 1$, $\varphi_A = \varphi_G = 1$

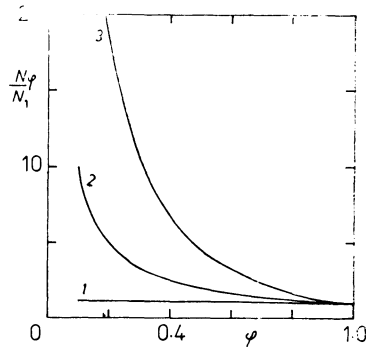


FIG. 5

The dependence of the efficiency of a diluted bed on the effects of parameters φ_G , η and φ_A , for $\lambda_A \rightarrow 0$, $(\lambda_G)_1 = 1000$ s, $(\tau_D)_1 = 400$ s; 1: $\varphi_G < 1$, $\varphi_A = \eta = 1$; 2: $\varphi_A < 1$, $\varphi_G = \eta = 1$; 3: $\eta < 1$, $\varphi_A = \varphi_G = 1$

It has been observed that in the case of isothermal sorption processes, the presence of inert material can change the relative significance of the individual rate steps.

The derived expressions can be used for testing the rate mechanisms and their dependence on the dilution degree.

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