

# Mathematical model of a semi-flow stirred adsorber

A. BRUNOVSKÁ and J. ILAVSKÝ

Department of Chemical Engineering, Slovak Technical University,  
880 37 Bratislava

Received 11 July 1973

Accepted for publication 13 March 1974

A mathematical model of a semi-flow adsorber in which the solid phase (spherical particles) and gaseous phase are ideally stirred is described. By using the relationships derived from this model it is possible to determine the time dependence of the composition of the gaseous phase provided the diffusion coefficients measured in a nonflow adsorption device are known.

The sorption processes proceeding according to certain physical or physicochemical laws are very difficult to express mathematically by a system of equations respecting all the given conditions and valid relations. Even if we succeed in establishing these equations, the system of equations is usually complicated and contains a great number of parameters so that the solution is very difficult to handle. Therefore the formulation of this problem requires such a model to be constructed in which only the relationships essential for a correct description of the process are involved. A review of the papers of various authors who in their calculations of adsorption devices started from the analysis of certain physical models is presented in [1]. The analysis of the models according to *Timofeev* [2, 3] and *Kel'tsev* [4] is given in [5]. These models describe the adsorption of individual substances in a flow of an indifferent gas in a static layer.

The aim of this study is to design a mathematical model of an adsorber satisfying the following requirements:

1. The device works under isothermal conditions.
2. The spherical particles of adsorbent are ideally stirred [6] in the adsorption device (concentration of the adsorbate on individual particles of the adsorbent is the same at

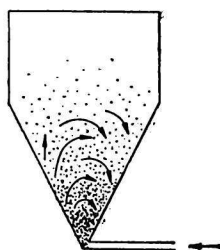


Fig. 1. Adsorber with a spouted bed.

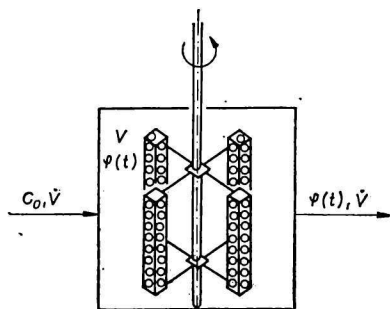


Fig. 2. Adsorber with adsorbent in the blades of the stirrer.

a certain time). This condition may be fulfilled by fluidization of the particles in the spouted bed (Fig. 1) or by placing the adsorbent in the blades of the stirrer (Fig. 2).

3. The gaseous phase flowing through the adsorber is ideally stirred [7]. Its composition is equal in the whole volume of adsorber and is identical with the composition of the outlet stream.

4. For  $t \leq 0$ , the device contains only pure adsorbent.

5. At  $t = 0$  the adsorbate of concentration  $C_0$  carried by the flow of inert gas starts to enter into the adsorber.

On these assumptions the material balance may be written as follows:

$$\begin{aligned} & \{\text{change in the concentration at the outlet stream}\} = \\ & = \frac{1}{V} [\{\text{entering amount of adsorbate}\} - \{\text{adsorbed amount}\} - \\ & \quad - \{\text{amount of leaving adsorbate}\}]. \end{aligned} \quad (1)$$

The mathematical formulation of this balance may be written in the following way

$$d\varphi(t) = 1/V [C_0 \dot{V} dt - N M'(t) dt - \varphi(t) \dot{V} dt], \quad (2)$$

where  $\varphi(t)$  is the concentration of the gaseous phase at time  $t$ ,  $M(t)$  is the adsorbed amount on one particle of the adsorbent at time  $t$ ,  $V$  is the volume of the gaseous phase in the adsorber,  $\dot{V}$  is the volumetric flow rate of gas, and  $N$  is the number of particles of the adsorbent in the adsorber.

In order to determine the quantity  $M(t)$ , we start from the physico-mathematical interpretation of diffusion formulated in the II Fick's law

$$\frac{\partial C}{\partial t} = \text{div } D \text{ grad } C, \quad (3)$$

where  $D$  is the diffusion coefficient. By transforming eqn (3) into spherical coordinates and assuming that the concentration field inside a particle is spherically symmetric and the coefficient of diffusion is constant, we obtain [7]

$$\frac{\partial C}{\partial t} = D_e \left( \frac{\partial^2 C}{\partial r^2} + \frac{2}{r} \cdot \frac{\partial C}{\partial r} \right). \quad (4)$$

Provided the initial concentration in a spherical particle of radius  $a$  is zero and is on the surface there is a variable concentration  $\varphi^*(t)$ , i.e.

$$\begin{aligned} C &= 0 & 0 < r < a & \quad t = 0 \\ C &= \varphi^*(t) & r = a & \quad t > 0 \end{aligned} \quad (5)$$

we can use the Laplace transform to obtain the solution of eqn (4) in the form of infinite series

$$C(t, r) = -\frac{2D_e}{r a} \sum_{n=1}^{\infty} (-1)^n e^{-D_e n^2 \pi^2 t / a^2} n \pi \sin \frac{n \pi r}{a} \int_0^t e^{D_e n^2 \pi^2 \lambda / a^2} \varphi^*(\lambda) d\lambda, \quad (6)$$

where  $C(t, r)$  gives the concentration of the adsorbed component as a function of time and position in a spherical particle.

The total amount adsorbed on a particle is given by

$$M(t) = 4\pi \int_0^a C(t, r) r^2 dr. \quad (7)$$

By substituting eqn (6) into eqn (7) and rearranging we obtain

$$M(t) = \int_0^t \Psi(t - \lambda) \varphi^*(\lambda) d\lambda, \quad (8)$$

where

$$\Psi(t) = 8\pi a D_e \sum_{n=1}^{\infty} e^{-D_e n^2 \pi^2 t / a^2}. \quad (9)$$

This relationship gives the amount of adsorbed substance  $M(t)$  in a spherical particle of radius  $a$  at time  $t$  and variable surface concentration  $\varphi(t)$ .

The substitution of eqn (8) into eqn (2) gives the resulting relationship for determining the composition of the gaseous phase at the outlet from the adsorption device

$$\frac{d\varphi(t)}{dt} = \frac{1}{V} \left[ C_0 \dot{V} - N \frac{d}{dt} \int_0^t \Psi(t - \lambda) \varphi^*(\lambda) d\lambda - \dot{V} \varphi(t) \right]. \quad (10)$$

By integrating, eqn (10) assumes the following form

$$\varphi(t) = 1/V [C_0 \dot{V} t - N \int_0^t \{\Psi(t - \lambda) + \dot{V}\} \varphi(\lambda) d\lambda]. \quad (11)$$

The function  $\Psi(t)$  necessary for solving eqn (11) can be calculated from eqn (9) on the basis of the coefficients measured in a nonflow device.

Eqn (11) is a special type of linear integral equation of the Volterra type, the so-called renewal equation with kernel  $K(t) = \{\Psi(t - \lambda) + \dot{V}\}$ . This equation has been intensively studied recently mainly owing to its frequent occurrence in operations analysis.

Though the kernel  $K(t)$  is not bounded ( $\lim_{t \rightarrow 0^+} \Psi(t) = \infty$ ), it is nevertheless integrable which can be established by termwise integration and subsequent passing to the limit for  $t \rightarrow 0$ . For such kernels the mathematical theory of equations of the Volterra type has been thoroughly elaborated.

Since the solution of eqn (11) cannot be found in a closed form, neither the use of the Laplace transform seems to be practicable, it is necessary to use some approximation method, e.g. infinite series or approximation by a difference equation.

We intend to generalize the method for the case of the diffusion coefficient depending on concentration. Since the introduction of the concentration dependent diffusion coefficient provides a nonlinear partial differential equation, it will be necessary to solve the numerically simultaneous system of eqns (2), (3), and (7) in this case.

In further investigations we shall verify the above model by means of the experimental results obtained on a semi-flow stirred adsorber with an adsorbent placed in the blades of the stirrer.

### Symbols

$a$	radius of the spherical particle of adsorbent
$C$	concentration
$C_0$	concentration of the adsorbate in inlet flow

$D$	diffusion coefficient
$D_e$	effective diffusion coefficient
$M(t)$	adsorbed amount of substance
$N$	number of the particles of adsorbent in adsorber
$r$	radial coordinate
$t$	time
$V$	volume of the gaseous phase in adsorber
$\dot{V}$	volumetric flow rate of gas
$\varphi(t)$	concentration of the gaseous phase in adsorber and outlet flow
$\varphi^*(t)$	concentration on the surface of particle in equilibrium with $\varphi(t)$

### References

1. Kossaczký, E., Bobok, D., Sitnai, O., and Ilavský, J., *Ropa a Uhlíe* **11**, 11 (1969).
2. Timofeev, D. P., *Zh. Fiz. Khim.* **23**, 11 (1958).
3. Timofeev, D. P., *Kinetika adsorptsii*. (Adsorption Kinetics.) Izd. Akad. Nauk SSSR, Moscow, 1962.
4. Kel'tsev, N. V., Toposhchenko, N. S., and Shumyatskii, Y. I., *Izotermicheskaya desorptsiya etilena iz sloya tseolita*. Materialy X. Vses. soveshchaniya po tseolitam. Izd. Nauka, Moscow, 1965.
5. Ilavský, J., *Habilitation Thesis*. Slovak Technical University, Bratislava, 1970.
6. Danckwerts, P. V., *Chem. Eng. Sci.* **2**, 1 (1953).
7. Crank, J., *The Mathematics of Diffusion*. Oxford University Press, London, 1964.

Translated by R. Domanský