Int. J. Heat Mass Transfer. Vol. 28, No. 4, pp. 859–866, 1985
Printed in Great Britain

0017–9310/85 \$3.00 + 0.00
Pergamon Press Ltd.

Mathematical modelling of countercurrent adsorption

J. NÉMETH, E. V. VASANITS and T. VIRÁG

Research Institute for Technical Chemistry, Hungarian Academy of Sciences, Veszprém Schönherz Z.u.2.
8200, Hungary

(*Received* 29 *August* 1984)

Abstract—The authors have studied mathematical models of countercurrent vapour adsorption and compared models obtained by various assumptions for the shape of the isotherm. A new iteration method is presented, which is capable of solving integral equations equivalent with differential equations describing the process. It is proved that the modelling of multiphase transport processes by integral equations makes it possible to take the partial backmixing of phases into consideration or to demonstrate the fact, that partial backmixing of adsorbent has much stronger effect on the concentration distribution along layer length, than partial backmixing of the gas.

1. INTRODUCTION

SEVERAL authors have investigated continuous countercurrent adsorbers [1–4]. However, the uniform mathematical description and calculation of the real adsorption process is still lacking. Methods hitherto used can be considered only as approximations mainly because of the simplifying assumptions concerning adsorption mechanisms and dynamics (linear and saturation isotherms, mixing free-flow of phases, perfect mixing of fluidized beds). In adsorption processes realized in practice (e.g. in case of solvent vapour/active carbon systems), however, equilibrium is nonlinear and phase currents are backmixed partially [5]. If calculations are performed on conditions not characteristic for the real process, deviations between calculated and measured data will be rather large and will reach in certain cases as much as ±63% [6].

Modelling of the adsorption process is not uniform *per se*. Residence time distribution of adsorbent in the fluidized bed is characterized by some authors by statistical methods [3], whereas others used for the same system the stagnating dead zone model of Cholette–Cloutier type [7].

Mathematical models of transport processes can be divided into two main groups, as far as solution methods concerned: linear models and nonlinear models. For the former group solution can be given in general in closed form (such as for the linear Miyauchi–Vermeulen model [11]), and the formula introduced can be evaluated rather simply. Nonlinear models however can be solved generally by numerical models only. We want to prove here, that in certain cases, due to complex formulae and difficulties in their numerical evaluation, it is more appropriate to use numerical methods or approximation models rather than substituting into the explicit solution even for linear models. As illustrations some different linear and nonlinear mathematical models of the adsorption process will be analysed, also providing their solution methods. Equilibrium state was characterized by three distinct isotherms. Both the gas phase and the aggregation of solid particles were considered as fluids. Flow and partial backmixing of the two phases were described by the axial dispersion model [11, 12].

2. THE MATHEMATICAL MODEL

The mathematical model of continuous countercurrent vapour adsorption must consider the partial backmixing of both phases. A similar system of conditions is incorporated in the Miyauchi–Vermeulen model [11] for gas–liquid systems in the linear equilibrium condition. Extension of this treatment to the two-phase gas–solid flow has determined the limitation of the proposed method as well. Thus we were forced to assume that the size of individual adsorbent particles is negligibly small compared to apparatus dimensions and length of the adsorption zone, and that concentration distribution within particles is uniform. This latter condition means that diffusion resistance within the particle was considered by the correction of the surface transfer factor. We think that this is not a coarser approximation than to consider the shape of commercially available adsorbent particles of variant forms and dimension distributions as spheres of equivalent diameter. The concept of corrected mass transfer factor is not new, it is used rather frequently in the literature [10], and the error of approximation thus obtained has been analysed already [13].

In other words, differential equations describing the phase current are actually Kolmogorov equations of a Markov process. The concentration distribution within particles is, if this is not uniform, as a matter of fact a memory mechanism, which contradicts the assumed post-effect-free nature of the Markov process.

The gas phase and the solid phase flowing with mean rates of v_g and v_a, have been considered in the

NOMENCLATURE

A, B	parameters in the equation of the Langmuir-type isotherm
c'_0	density of adsorbate in the gas phase fed into the adsorber [kg m^{-3}]
c'	density of adsorbate in the gas phase [kg m^{-3}]
c^*	equilibrium density of adsorbate in the gas phase [kg m^{-3}]
D_g	axial dispersion factor of the gas [m^2 s^{-1}]
D_a	mixing factor of adsorbent [m^2 s^{-1}]
H	apparatus length [m]
M	reciprocal of linear isotherm slope
M'	parameter in the equation of the broken-line isotherm
N_g	transfer unit number of gas phase
N_a	transfer unit of solid phase
Pe_g	Peclet number of gas phase
Pe_a	Peclet number of solid phase
q'	density of adsorbate in solid phase [kg kg^{-1}]
q'_0	saturation density of adsorbate in the solid phase [kg kg^{-1}]
v_g	linear gas velocity [m s^{-1}]
v_a	linear adsorbent velocity [m s^{-1}]
w	specific surface [m^{-1}]
x	length coordinate [m].

Greek symbols

β	transfer factor, corrected [m s^{-1}]
$\varepsilon_a, \varepsilon_g$	free volume fraction of gas and adsorbent
ρ	density of adsorbent [kg m^{-3}].

mathematical model as fluids. Phase flow has been described by the axial dispersion model.

Densities of adsorbates are denoted with c' in the gas phase and with q' in the solid phase. The local balance equation for these quantities will be for the steady, isotherm state, if volume changes are neglected:

$$-D_g\varepsilon_g\frac{\mathrm{d}^2c'}{\mathrm{d}x^2}+v_g\varepsilon_g\frac{\mathrm{d}c'}{\mathrm{d}x}+\beta w(c'-c^*)=0$$

$$-D_a\varepsilon_a\rho\frac{\mathrm{d}^2q'}{\mathrm{d}x^2}-v_a\varepsilon_a\rho\frac{\mathrm{d}q'}{\mathrm{d}x}-\beta w(c'-c^*)=0. \quad (1)$$

The first terms of equations describe conductive currents. Mixing occurs in the phases as an effect of these currents. The second term means the convective current, i.e. movement of media within the apparatus. Signs of these terms are different in above equations, since we deal here with countercurrents. The third term describes mass transfer, which is assumed to be proportional to the difference between equilibrium and actual concentrations. The gas-side transfer is the rate controlling process in our model.

Equations are solved according to the usual Danckwerts-type boundary conditions:

$$\left[\varepsilon_g v_g c'-\varepsilon_g D_g\frac{\mathrm{d}c'}{\mathrm{d}x}\right]\Bigg|_{x=0}=\varepsilon_g v_g c'_0$$

$$\left[-\varepsilon_a v_a \rho q'-\varepsilon_a D_a\rho\frac{\mathrm{d}q}{\mathrm{d}x}\right]\Bigg|_{x=H}=0 \quad (2a)$$

$$\left.\frac{\mathrm{d}c'}{\mathrm{d}x}\right|_{x=H}=0$$

$$\left.\frac{\mathrm{d}q'}{\mathrm{d}x}\right|_{x=0}=0. \quad (2b)$$

Let us introduce the following dimensionless variables:

$$c=\frac{c'}{c'_0};\quad z=\frac{x}{H};\quad Pe=\frac{vH}{D};$$

$$N=\frac{\beta wH}{v\varepsilon};\quad q=\frac{q'}{q'_0}. \quad (3)$$

With these, equations and boundary conditions can be described as follows:

$$\frac{\mathrm{d}^2c}{\mathrm{d}z^2}-Pe_g\frac{\mathrm{d}c}{\mathrm{d}z}-Pe_gN_g(c-c^*)=0$$

$$\frac{\mathrm{d}^2q}{\mathrm{d}z^2}+Pe_a\frac{\mathrm{d}q}{\mathrm{d}z}+Pe_aN_a(c-c^*)=0 \quad (4)$$

$$\left[\frac{\mathrm{d}c}{\mathrm{d}z}-Pe_gc\right]\Bigg|_{z=0}=-Pe_g;$$

$$\left[\frac{\mathrm{d}q}{\mathrm{d}z}+Pe_aq\right]\Bigg|_{z=1}=0 \quad (5a)$$

$$\left.\frac{\mathrm{d}c}{\mathrm{d}z}\right|_{z=1}=0;\quad \left.\frac{\mathrm{d}q}{\mathrm{d}z}\right|_{z=0}=0. \quad (5b)$$

We are concerned here with the discussion and solution of this equation system for various $c^*(q)$ isotherm relations (cf. Fig. 1.).

3. MODELLING WITH DIFFERENT ISOTHERM EQUATIONS

To determine the solution of equation system (4) with boundary conditions (5) we consider first various methods on the basis of isotherm linearization, then the solution considering a Langmuir-type isotherm.

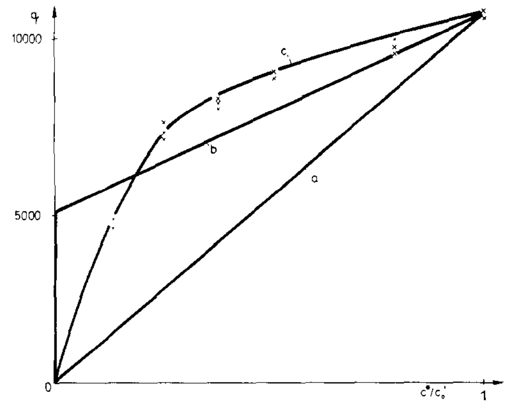

FIG. 1. Linear (a), broken-line (b) and Langmuir (c) isotherms according to equations (6), (12) and (13). The data are equilibrium data of benzene vapour measured at 20°C on active carbon Nuxit BO.

(A) Let us assume as a first approximation, that adsorbate concentration q and gas-side concentration c^* being in equilibrium with the former are in linear relationship (cf. Fig. 1a):

$$c^* = M \cdot q \tag{6}$$

In this case the solution of the boundary value problem (4), (5) can be given in a closed form [11] (it should be noted here, that the use of equations from [11] is rather difficult due to several printing errors). Solutions are looked for by this method as follows:

$$c = \sum_{i=1}^{4} A_i \, e^{\lambda_i z} \tag{7}$$

$$q = \sum_{i=1}^{4} B_i \, e^{\lambda_i z}. \tag{8}$$

Back-substituting into the equations and into the boundary conditions yields the following eigenvalue equation for λ_i [$i = 1, 2, 3, 4$]:

$$[\lambda^2 - Pe_g\lambda - Pe_gN_g][\lambda^2 + Pe_a\lambda - Pe_aN_aM] = Pe_gN_gPe_aN_aM \tag{9}$$

and yields moreover a linear equation system for A_i, B_i [$i = 1, 2, 3, 4$]. Eigenvalues were in the parameter range investigated and relevant to practical applications (cf. Table 1) in their order of magnitude as follows: -100, -1, 0, $+100$, respectively. The equation system for coefficient calculation seemed to be numerically correlated, thus there was no direct way to solve it. This is a considerable disadvantage for practical applications.

The numerical problems derived from the great deviation of eigenvalues can be eliminated rather easily on the basis of physical considerations. It can be seen from equations (7) and (8) that concentration distributions are influenced in the interior of the apparatus only by the two middle roots of the eigenvalue equation. The two extreme roots with highest absolute values influence the distribution functions only in the direct vicinity of starting and end points, there they break down at any rate. Thus exponential terms containing the largest and lowest roots of characteristic equation have been omitted from solution functions (7, 8) during approximative calculations. It is needless to say that this solution cannot satisfy all four boundary conditions, but only two of them. As a consequence we have omitted boundary conditions (5b) indicating zero character of conductive output flow, and retained boundary conditions (5a) having direct physical meaning and derived from the law of matter conservation. Fulfilment of these latter has been required also for the approximative solution, thus the following expressions have been obtained for concentration distributions:

$$\begin{aligned} c(z) &= \frac{(Pe_a+\lambda)(-\lambda^2+Pe_g\lambda+Pe_gN_g)\,e^{\lambda}-Pe_aPe_gN_g\,e^{\lambda z}}{(-\lambda^2+Pe_g\lambda+Pe_gN_g)(Pe_a+\lambda)\,e^{\lambda}-Pe_aN_g(Pe_g-\lambda)} \\ q(z) &= \frac{1}{M}\cdot\frac{(Pe_a+\lambda)(-\lambda^2+Pe_g\lambda+Pe_gN_g)\,e^{\lambda}-Pe_a(-\lambda^2+Pe_g\lambda+Pe_gN_g)(Pe_a+\lambda)\,e^{\lambda z}}{(-\lambda^2+Pe_g\lambda+Pe_gN_g)(Pe_a+\lambda)\,e^{\lambda}-Pe_aN_g(Pe_g-\lambda)}. \end{aligned} \tag{10}$$

Due to the character of the problem, zero always implies an eigenvalue. This has been substituted already into above formulae, whereas λ is the other eigenvalue nearest to zero. The relation is valid, if the two eigenvalues remaining are of absolute values larger by at least one order of magnitude.

No numerical problems were met during evaluation [9]. On the basis of result analysis we can say, however, that the model describes the process having nonlinear isotherm equations in reality only in its tendency. We have calculated for example with several parameters in

Table 1. Parameters and their values used during modelling

D_g	3.3×10^{-3}; 10^{-3}; 3.3×10^{-4}
D_a	4×10^{-6}; 1.2×10^{-7}; 4×10^{-8}
$\varepsilon_a, \varepsilon_g$	0.5
β	0.1
w	10^3
ρ	800
v_g	0.1
v_a	1.2×10^{-5}
H	0.1
M	10^{-4}
M'	2×10^{-4}
A, B	4×10^4; 3
Pe_g	3; 10; 30
Pe_a	3; 10; 30
N_g	200
N_a	1.67×10^6

experimentally well measurable ranges (cf. Table 1) solution curves and concluded, that their shapes were considerably distinct from those of experimentally measurable concentration distribution curves [5]. Consequently, it has been concluded that nonlinearity of adsorption isotherm must be considered at any rate.

(B) The next case investigated was where the adsorption isotherm was described in the saturation range by a general straight line (6b) approximating the former better than the straight line crossing the origin (cf. Fig. 1b):

$$c^* = M(q-q_0). \tag{11}$$

This case can also be discussed on the basis of [11], however, we do not want to go into details, as the model is according to our view physically erroneous. Although equation (11) approximates well the adsorption isotherm curve in the vicinity of the saturation range, in the continuously working adsorber we find always a section (namely in the neighbourhood of adsorbent feeding), where saturation is small, i.e. we are dealing with an isotherm section near the origon. Equation (11) yields here negative equilibrium concentrations, which is incorrect, and moreover has the consequence that the solution curve can take up negative values at certain sites, depending on parameter values. If such physically meaningless negative concentration values are replaced by zero, conservation laws postulated as the basis of the model would be violated.

(C) However, equation (11) can be made physically meaningful by a correction, which does not permit the value of c^* to turn negative:

$$c^* = \begin{cases} 0 & \text{if} \quad M(q-q_0) < 0 \\ M(q-q_0) & \text{if} \quad M(q-q_0) \geqslant 0. \end{cases} \tag{12}$$

This approximation, called a broken-shaped isotherm in the literature [10, 8], has been hitherto used (to our best knowledge) only for modelling discontinuous adsorption processes, where the adsorber has been considered infinite in both directions. We have therefore tried to solve the differential equation (4) according to boundary values (5) by the broken shaped isotherm (12). The solution can be given in principle in closed form, but for the determination of equation parameters a nonlinear equation system with nine unknowns must be solved. This is at least as difficult as to solve the nonlinear boundary value task describing the real equilibrium, especially if such numerical problems arise as outlined for the linear isotherm.

(D) The real equilibrium has been described by a Langmuir-type isotherm (cf. Fig. 1c):

$$c^* = \frac{q}{A-Bq}. \tag{13}$$

As can be seen from the figure, the curve calculated from (13) follows the measured values. Since the adsorption process could not be characterized by simple mathematical means and/or with necessary accuracy by the linear approximations as discussed for cases (A), (B) and (C), we want to describe here a method, by which the boundary value problem (4), (5) can be solved also for nonlinear source terms similar to (13).

4. TREATMENT BY INTEGRAL EQUATIONS

Solution of nonlinear boundary value problems is performed in the practice mostly by the so-called 'shooting' method [12]. As this method brings about several theoretical and practical problems, we have chosen another approach. The boundary value problem has been transformed into an integral equations system of Hammerstein type, followed by Newton iteration solution.

As a first step, differential equations (4) have been integrated for z:

$$\begin{aligned} &\frac{dc}{dz} - Pe_g c = Pe_g N_g \int_0^z (c-c^*)\,dz' - Pe_g \\ &\frac{dq}{dz} + Pe_a q = Pe_a N_a \int_z^1 (c-c^*)\,dz'. \end{aligned} \tag{14}$$

By selecting integration limits and constants as above, functions $c(z)$ and $q(z)$ satisfying equation (11) which also meet boundary conditions (5a) are found. Let us multiply the first equation of system (14) by $e^{-Pe_g z}$ the second by $e^{Pe_a z}$ and integrate:

$$\begin{aligned} e^{-Pe_g z} c &= Pe_g N_g \int_0^z e^{-Pe_g z''} \int_0^{z''} (c-c^*)\,dz'\,dz'' \\ &\quad + e^{-Pe_g z} + k_1 \\ e^{Pe_a z} q &= -Pe_a N_a \int_z^1 e^{Pe_a z''} \int_{z''}^1 (c-c^*)\,dz'\,dz'' + k_2. \end{aligned} \tag{15}$$

Double integrals on the RHS can be simplified by partial integration:

$$\begin{aligned} &Pe_g \int_0^z e^{-Pe_g z''} \int_0^{z''} (c-c^*)\,dz'\,dz'' \\ &\quad = -e^{-Pe_g z} \int_0^z (c-c^*)\,dz' + \int_0^z e^{-Pe_g z'} (c-c^*)\,dz' \\ &Pe_a \int_z^1 e^{Pe_a z''} \int_{z''}^1 (c-c^*)\,dz'\,dz'' \\ &\quad = -e^{Pe_a z} \int_z^1 (c-c^*)\,dz' + \int_z^1 e^{Pe_a z'} (c-c^*)\,dz'. \end{aligned} \tag{16}$$

Equations (16) are substituted back into equations (15).

We obtain by rearrangement:

$$\begin{aligned} c &= N_g\left[-\int_0^z (c-c^*)\,dz' + \int_0^z e^{Pe_g(z-z')}(c-c^*)\,dz'\right] + 1 + k_1 e^{Pe_g z} \\ q &= N_a\left[\int_z^1 (c-c^*)\,dz' - \int_z^1 e^{Pe_a(z'-z)}(c-c^*)\,dz'\right] + k_2 e^{-Pe_a z} \end{aligned} \tag{17}$$

Integration constants k_1 and k_2 can be determined from boundary conditions (5b):

$$\begin{aligned} c(1) = 0 &= N_g Pe_g \int_0^1 e^{Pe_g(1-z')}(c-c^*)\,dz' + k_1 Pe_g e^{Pe_g} \\ q(0) = 0 &= N_a Pe_a \int_0^1 e^{Pe_a z'}(c-c^*)\,dz' - k_2 Pe_a. \end{aligned} \tag{18}$$

If the relationships expressed for k_1 and k_2 are substituted back into equations (14), we obtain an integral equation system equivalent to the boundary value task (4), (5), which plays a central role at our further investigations:

$$\begin{aligned} c(z) &= 1 - N_g \int_0^1 K_g(z,z')\,[c(z') - c^*(z')]\,dz' \\ q(z) &= N_a \int_0^1 K_a(z,z')\,[c(z') - c^*(z')]\,dz'. \end{aligned} \tag{19}$$

Functions K_g and K_a appearing in the former equations are actually Green functions of the original boundary value problem. These are as follows:

$$\begin{aligned} K_g(z,z') &= \begin{cases} e^{Pe_g(z-z')} & \text{if } 0 \leqslant z < z' \leqslant 1 \\ 1 & \text{if } 0 \leqslant z' \leqslant z \leqslant 1 \end{cases} \\ K_a(z,z') &= \begin{cases} 1 & \text{if } 0 \leqslant z \leqslant z' \leqslant 1 \\ e^{Pe_a(z'-z)} & \text{if } 0 \leqslant z' < z \leqslant 1 \end{cases}. \end{aligned} \tag{20}$$

5. DISCUSSION OF RESULTS

The integral equation system of Hammerstein type (19) has been solved with the adsorption isotherms (6), (12), and (13) (cf. Fig. 1) and numerically by Newton's method (cf. Figs. 2 and 3).

Let us introduce some symbolism for better understanding of the solution method. The pair of functions $\{c(z), q(z)\}$ should be denoted with ¢, further $\mathbb{K}$ should be an operator, which computes for given ¢ or given $\{c(z), q(z)\}$ $c^*(z)$, which is substituted into the RHS of equation system (19), performs the necessary operations and calculates the LHS. Equation (19) can be written with above symbols as

$$¢ = \mathbb{K}¢. \tag{21}$$

It seems feasible to use the iteration method for the solution of the equation: if we start from an arbitrarily

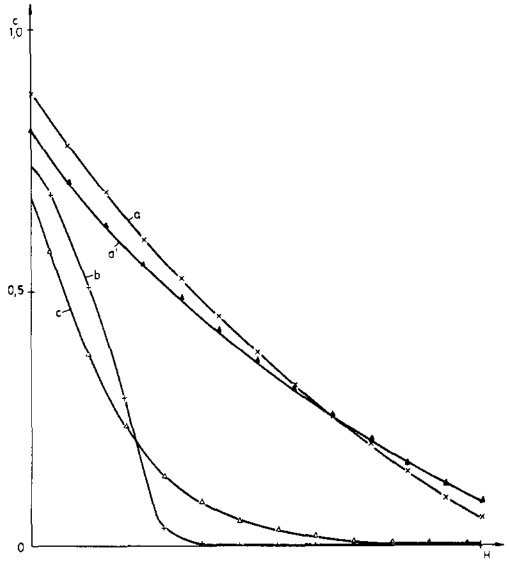

FIG. 2a. Concentration distribution of adsorbate in the gas phase of countercurrent adsorber calculated on the basis of identically marked isotherms with $Pe_a = Pe_g = 10$. (a) linear isotherm integral equation method and Miyauchi method; (a') linear isotherm, approximation (10); (b) broken-shaped isotherm, integral equation method; (c) Langmuir isotherm, integral equation method.

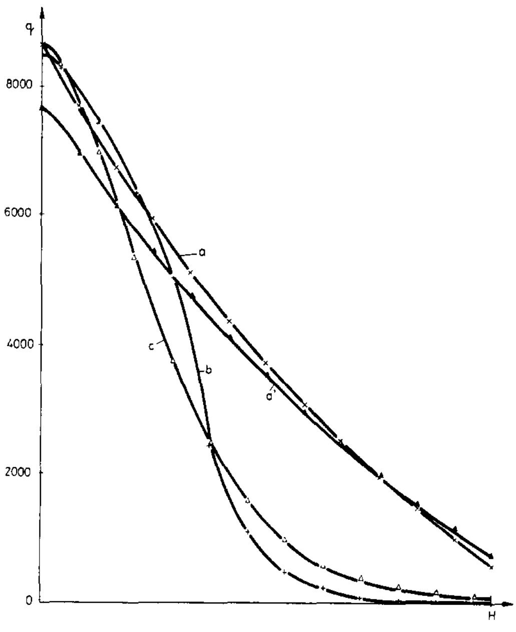

FIG. 2b. Concentration distribution of adsorbate in the solid phase of countercurrent adsorber according to isotherms marked identically with $Pe_a = Pe_g = 10$. (a) linear isotherm, integral equation method and Miyauchi method; (a') linear isotherm, approximation (10); (b) broken-shaped isotherm, integral equation method; (c) Langmuir isotherm, integral equation method.

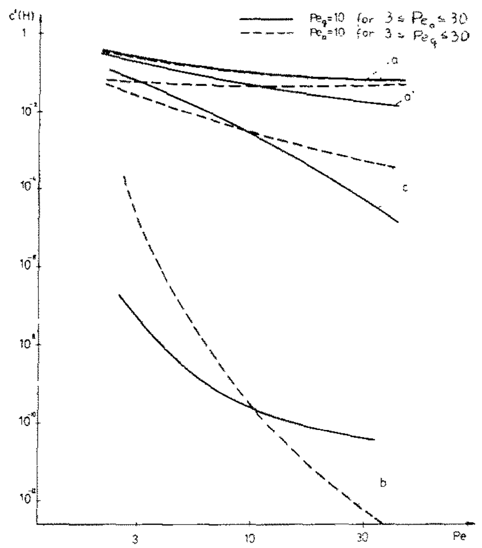

FIG. 3. Concentration of gas leaving the adsorber as function of gas phase and solid phase backmixing. (a) linear isotherm, integral equation method and Miyauchi method; (a') linear isotherm, approximation (10); (b) broken-shaped isotherm, integral equation method; (c) Langmuir isotherm, integral equation method.

chosen $\mathbb{c}_0$ we may expect that the series $\{\mathbb{c}_i\}_{i=0}^{\infty}$ created by the relation

$$\mathbb{c}_{i+1} = \mathbb{K}\mathbb{c}_i \tag{22}$$

converges to the solution of equation (21). If N_a and N_g are small, this is in fact the case, however, the series is divergent with parameter values as used by us.

It was possible to calculate solution functions by attenuated iteration [14], but convergence was very slow and required several hundred loops.

Thus we went over to Newton's method which possesses much better convergence characteristics. With Newton's method we can calculate from a given approximative solution $\mathbb{c}_i$ the error function $\mathbb{d}_i$:

$$\mathbb{d}_i = \mathbb{c}_i - \mathbb{K}\mathbb{c}_i \tag{23}$$

and from this we may calculate the improved value of the solution function by the formula

$$\mathbb{c}_{i+1} = \mathbb{c}_i + (\mathbb{K}' - \mathbb{I})^{-1}\mathbb{d}_i. \tag{24}$$

$\mathbb{I}$ in this formula denotes the Frechet derivative of operator $\mathbb{K}'$ whereas $\mathbb{K}$ is the identity operator. For a given $\mathbb{I}$ interval partition these operators are a matrix and a unit matrix, respectively, whereas inverting is matrix inverting. Such a serial improvement of solution functions is the local linearization of the isotherm around actual function values.

Integration was performed by partition of the interval [0, 1] into 12 parts according to the trapezoid rule. Although being relatively inaccurate, application of this method is advantageous for two reasons: this solution can be considered as an exact solution of a special cell model and possesses thus independent physical meaning, and on the other hand, the error derived from numerical integration can be assessed safely [12, 13].

Convergence was very fast in the vicinity of parameter values listed in Table 1: after starting from any feasible first approximation the solution was approached in the second or third step within 1%, and after 10 iteration loops were all the resulting digits accurate.

Calculations were performed on a personal computer (Sinclair ZX-81), where running for 10 iterations lasted for about 6 h. We estimated that approx. 5 h were needed for ten-fold matrix inverting.

6. CONCLUSIONS

A Hammerstein-type integral equation system (19) was solved for (a) linear, (b) broken and (c) Langmuir-type isotherms (cf. Fig. 1), and results were plotted for identical Peclet numbers ($Pe_a = Pe_g = 10$) in Fig. 2a for the gas phase, and in Fig. 2b for the solid phase. In Fig. 2 concentration changes as calculated from the axial dispersion model of Miyauchi and Vermeulen are also shown, where boundary conditions were similar. From Fig. 2 we may see that concentration values as calculated with Langmuir-type and broken isotherms (cf. curves (b) and (c) of Fig. 2) are similar to experimentally measured concentration distributions in continuous countercurrent adsorbers, whereas concentration distributions calculated from linear isotherms (cf. curve (a) of Fig. 2) and by the Miyauchi–Vermeulen model (cf. curve (a') of Fig. 2) are rather different.

On the basis of calculation results we may conclude that nonlinearity of the adsorption isotherm must be considered (modelling with broken isotherms or Langmuir-type isotherms seems to be feasible). The nonlinear boundary value problem thus obtained should be transformed into integral equations and solved in that form. Stability of integral equation handling is characterized by the fact, that equations could be solved even for nonlinear isotherms, where the numerical evaluation of the exact solution written for the linear isotherm was difficult.

For the engineering practice of adsorber construction and design the most important and characteristic value is the gas concentration leaving the adsorber, $c'(H)$. Figure 3 shows the concentration of the gas leaving the adsorber as a function of the Peclet number, where values calculated from appropriate isotherms can be compared on the basis of partial backmixing of gas and solid phases. It can be seen from the summarizing figure that there are minor deviations of output concentration values using linear and simplified linear isotherms (cf. curves (a) and (a')), whereas deviation is larger for the Langmuir-type isotherm and very large for the broken-line isotherm. When adsorbers are designed, the results of calculated curves as shown in Figs. 2 and 3 must be considered for the determination of concentration values jointly.

The present study considers partial backmixing of

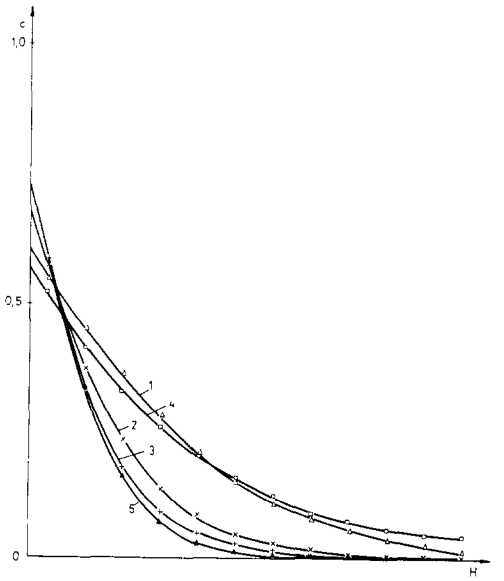

FIG. 4a. Concentration distribution of adsorbate in the gas phase as function of mixing (on the basis of a Langmuir-type isotherm).

both phases. Results are shown for the Langmuir-type isotherm on Fig. 4a for the gas phase and on Fig. 4b for the solid phase, respectively. We can conclude from the figures that modelling of solid phase mixing is not negligible for real countercurrent adsorption, since increased backmixing of the adsorbent deteriorates efficiency of the adsorber much more, than increasing gas flow mixing. Above results are similar to concentration changes of real adsorption processes, thus supporting the applicability of the axial dispersion model for the description of adsorption.

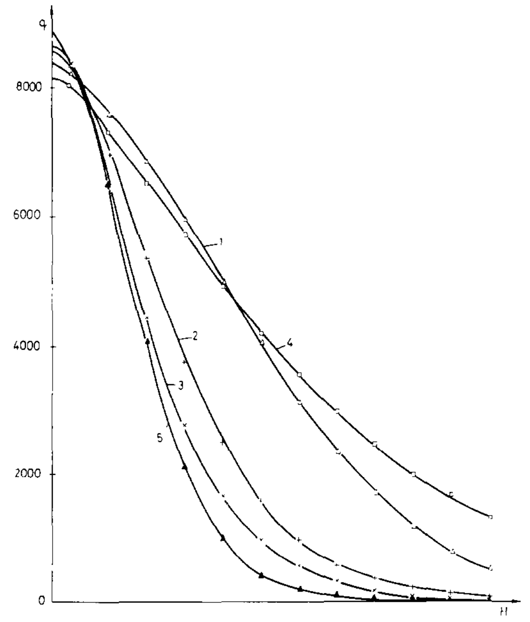

FIG. 4b. Concentration distribution of adsorbate in the solid phase as a function of mixing (on the basis of a Langmuir-type isotherm)

	Pe_g	Pe_a
1	3	10
2	10	10
3	30	10
4	10	3
5	10	30

Further it was possible to develop a computer program on the basis of the integral equation method described above, which is capable of modelling multiphase transport processes, where it is necessary (similar to the adsorption) to consider partial backmixing of phases [14].

Advantages of the treatment by integral equations can be summarized as follows:

(1) The method can be used independently of mixing character and shape of source functions.

(2) If Newton's method is used for equation solution, convergence is fast and reliable even at parameter values where numerical handling of explicitly given exact solution of the linear system is difficult.

(3) The method offers writing of compact and widely useful programs (the whole solution program consists of only 30 BASIC lines!). Disadvantages are the relatively large memory capacity needed and the slow program running.

REFERENCES

1. L. Szirmay, Process for gas separation on a moving adsorbent bed, *AIChE Symp. Series* **71,** 104–109 (1975).
2. J. Németh, Up-to-date methods of solvent recovery, *Magy. Kém. Lap.* **22,** 82–88 (1967).
3. P. G. Romankov, N. B. Rashkovskaya, V. F. Frolov, *Mass Transfer Process in Chemical Technology.* Chimiya, Leningrad (1978).
4. O. M. Todes, O. B. Zitovitsh, *Fluidized Bed Equipments.* Chimiya, Leningrad (1981).
5. J. Németh, Ph.D. thesis, Hungarian Academy of Sciences, Budapest (1978).
6. K. E. Goryuohov, A. I., Tamarin, Study of longitudinal mixing (effective diffusion) of a solid phase in a fluidized bed with mean-volume packing, *Inzh. fiz. Zh.* **40,** 271–277 (1981).
7. J. Vanderschuren, The plate efficiency of multistage fluidized bed adsorbers, *Chem. Engng J.* **21,** 1–9 (1981).
8. K. Ikeda, H. Ohya, O. Kanemitsu and K. Shimomura, Breakthrough curve of adsorption on a fixed bed for a favorable isotherm, *Chem. Engng Sci.* **28,** 227–239 (1973).
9. T. Blickle, J. Németh, T. Virág, A new approximation of continuous operation adsorption with backmixing of both phases, *Chem. Technik* **29,** 518 (1977).
10. J. W. Carter, H. Husain, The prediction of the performance of fixed-bed adsorptive gas purifiers, *Chemie- Ingr-Tech.* **49,** 517 (1977).
11. T. Miyauchi, Th. Vermeulen, Longitudinal dispersion in two-phase continuous-flow operations, *Ind. Eng. Chem. Fundamentals* **2,** 113–126 (1969).
12. T. Virág, Post graduate thesis, Hungarian Academy of Sciences, Bundapest (1979).
13. K. Polinsky, E. V. Vasanits, J. Fülöp, Approximate analytic determination of the average values of potential functions occurring in chemical transport phenomena. *Proc. Fifth International Heat Transfer Conference,* Tokyo (1974).
14. T. Blickle, J. Gyenis, G. Halász, Mathematical modelling of heat- and mass-transfer units in technical chemistry. II. *Magy. Kém. Lap.* **37,** 99–103 (1982).

MODELISATION MATHEMATIQUE DE L'ADSORPTION A CONTRE-COURANT

Résumé—Les auteurs étudient des modèles mathématiques d'adsorption de vapeur à contre-courant. Ils comparent les modèles obtenus par diverses hypothèses sur la forme de l'isotherme. Une nouvelle méthode d'itération est présentée qui est capable de résoudre des équations intégrales équivalentes aux équations différentielles qui décrivent le mécanisme. La modélisation des mécanismes de transport multiphasique par des équations intégrales peut prendre en considération le backmixing des phases et montrer que celui-ci pour l'adsorbant a un effet plus fort sur la distribution de concentration le long de la couche que celui pour le gaz.

MATHEMATISCHES MODELL FÜR DIE GEGENSTROMADSORPTION

Zusammenfassung—Die Verfasser untersuchten Modelle für die Gegenstromadsorption von Dampf. Sie verglichen Modelle, die sie durch unterschiedliche Annahmen über den Isothermenverlauf erhielten. Eine neue Näherungsmethode wurde vorgestellt, mit der Integralgleichungen ebenso wie Differentialgleichungen, die den Prozeß beschreiben, gelöst werden können. Die Autoren zeigten, daß die Beschreibung von Mehrphasen-transport-Prozessen durch Integralgleichungen es ermöglicht, die partielle Rückvermischung der Phasen zu betrachten. Ebenso kann dadurch bewiesen werden, daß die partielle Rückvermischung des Adsorbenten einen viel größeren Einfluß auf die Konzentrationsverteilung entlang der Grenzschicht hat als die partielle Rückvermischung des Gases.

МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ ПРОТИВОТОЧНОЙ АДСОРБЦИИ

Аннотация—Изучаются математические модели противоточной адсорбции пара. Сравниваются модели, полученные для различных форм изотерм. Представлен новый метод итераций, с помощью которого можно решать интегральные уравнения, эквивалентные дифференциальным уравнениям, описывающим процесс. Показано, что моделирование многофазных процессов переноса с использованием интегральных уравнений позволяет принять во внимание частичное обратное смешивание фаз и продемонстрировать тот факт, что частичное обратное смешивание адсорбента оказывает намного большее влияние на распределение концентрации вдоль длины слоя, чем частичное обратное смешивание газа.