STOCHASTIC MODEL OF PERIODIC OPERATION
PERFORMANCE FOR THE CONTINUOUS COUNTER—CURRENT ADSORPTION PROCESS

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ABSTRACT

A stochastic model is developed to predict the periodic operation performance of the continuous counter—current adsorption process. The model takes into account the effects of random backmixing of particles, axial dispersion of liquid phase, liquid—film mass transfer, intraparticle diffusion and particle shape, and can reveal clearly the behavior of solid and liquid phase in adsorption process. The simulation results agree with the experimental data rather well.

Keywords: Periodic operation  Adsorption process  Stochastic model; Simulation.

INTRODUCTION

Adsorption has been widely employed in industry, specially in the removal and recovery of some metal or organic substances from solution. The continuous counter—current operation is favorable because of its high availability of adsorbent. The traditional simulation of fluidized bed adsorption process[1] involved some oversimplification, in which both the liquid and solid phases are supposed as plug flow. In fact, a certain backmixing is presented in both phases, a new model for fluidized bed adsorption[2] has described the backmixing by axial dispersion.

Because of the random backmixing, individual particle’s position is stochastic, and the stochastic process has an effect on the development of individual particle’s concentration profile and then on the mass transfer performance of adsorption process. But the effect of random backmixing on these hasn’t been considered yet in

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the models reported by previous authors.

In this paper, a stochastic model, which can reflect random backmixing of particles, is given for the counter—current adsorption process.

MODEL DEVELOPMENT

Assumptions

The governing equations of the model have been derived based on the following suppositions.

(1) In a multistage adsorption column, the hydrodynamic behavior of the fluidizing liquid can be described by the axial dispersion model\(^{[3]}\).

(2) The radial concentration gradients are negligible in the liquid phase of the column.

(3) The backmixing of adsorbent particles results from a great deal of random walk in the column\(^{[4]}\). Only the axial random walk of particles is taken into account. The random walk of individual particle can be described by Markov process.

(4) It is assumed that there isn’t backmixing of particles between any two stages of the column.

(5) The adsorbent particles are of uniform size.

(6) The shape of adsorbent particles is considered as sphere, cylinder or slice, depending on which the shape of particles is closest to.

(7) The adsorption process is sufficiently rapid so that a local equilibrium is established at the particle surface between concentrations in the solution and the adsorbed phase\(^{[5]}\).

(8) The rate of adsorption is limited by the intraparticle diffusional resistance and the mass transfer resistance in the laminar fluid boundary layer surrounding an individual adsorbent particle.

(9) The transfer of adsorbate into the particle can be described by the homogeneous solid diffusion model\(^{[6]}\).

(10) Thermal effects are negligible, i.e. the adsorber operates isothermally.

Derivation of the governing equations

(1) The transition probability matrix of individual particle in adsorber.

We discretize every stage of the column evenly as \((n_\Delta + 1)\) position points. So there are \(n(n_\Delta + 1)\) position points in \(n\) stages. We give serial numbers to these points as shown in Fig. 1.
In each operation period \((k-1)T < t < kT, k = 1,2,3,\ldots\), if a particle is in the inside of a stage, both of the probabilities of its walking to last position point and to next one in time \(\tau\) will be half, and if a particle is on the bound of a stage, both of the probabilities of its walking to inside adjacent point and keeping motionless will be half. Between two operation periods \((t = kT, k = 1,2,3,\ldots)\), the particles in each stage will transfer to last stage entirely. So we can get the transition probability matrix.

\[
P = \begin{bmatrix}
P_0 & P_0 & \cdots & P_0 \\
P_0 & \ddots & & \\
P_0 & & \ddots & \\
P_0 & & & \ddots \\
\end{bmatrix}
\]

\((when \ (k-1)T < t < kT, k = 1,2,3,\ldots)\) (1)
\[ P = \begin{bmatrix} O & E \\ O & E \\ & \ddots \\ & & O & E \\ & & & O \end{bmatrix} \quad \text{(1)} \]

\( (\text{when } t = kT, k = 1, 2, 3, \ldots) \)

and

\[ P_0 = \begin{bmatrix} 0.5 & 0.5 & 0 & 0 & \cdots & 0 & 0 & 0 \\ 0.5 & 0 & 0.5 & 0 & \cdots & 0 & 0 & 0 \\ 0 & 0.5 & 0 & 0.5 & \cdots & 0 & 0 & 0 \\ & & \ddots & & \ddots & \ddots & \ddots & \ddots \\ 0 & 0 & 0 & 0 & \cdots & 0.5 & 0 & 0.5 \\ 0 & 0 & 0 & 0 & \cdots & 0.5 & 0 & 0.5 \end{bmatrix} \quad \text{(1')} \]

Here, \( P \) is \( [n(n_A+1)] \times [n(n_A+1)] \) matrix, \( P_0 \) is \( (n_A+1) \times (n_A+1) \) matrix, \( O \) is \( (n_A+1) \times (n_A+1) \) zero matrix, \( E \) is \( (n_A+1) \times (n_A+1) \) unit matrix.

(2) The relation between walk pace \( \Delta \) and walk time \( \tau \)

According to the attribute of Markov process and the Kolmogorov's second equation, the connection between the walk pace \( \Delta \) and walk time \( \tau \) is obtained:

\[ \Delta^2 = \sigma^2 \tau \quad \text{(2)} \]

and \( \frac{1}{2} \sigma^2 \) is axial solid—phase dispersion coefficient.

(3) Particle's production and disappearance

According to the coming in and going out of adsorbent in periodic operation process, we have

\[ \begin{aligned} &\text{Particle's production,} M \text{ particles, whose beginning position points satisfy the} \\
&\text{even distribution of} \ (n-1)H \sim nH \ (\text{when } t = kT, k = 1, 2, 3, \ldots) \\
&\text{Particle's disappearance, all particles which is in } 0 \sim H \text{ at } t = kT^- \\
&\text{going out at } t = kT^+ \ (k = 1, 2, 3, \ldots) \end{aligned} \quad \text{(3)} \]

(4) Liquid—phase equation

From the \( \ldots \text{axial diffusion model} \), the liquid—phase equation is given by differ-
ential material balance for an infinitesimal layer:

\[
\epsilon \frac{\partial C}{\partial t} = E_\epsilon \epsilon \frac{\partial C}{\partial z} - \frac{\partial C}{\partial z} - \frac{\alpha k_f \epsilon C - \bar{q}_f / K}{x_0} \tag{4}
\]

\[
\begin{align*}
C(kT^+, z) &= C(kT^-, z) \\
C(t + kT, z) &= C(t, z) \\
B. C. & \quad z = 0: \quad C - \frac{E_\epsilon \epsilon}{u} \frac{\partial C}{\partial z} = C_f \\
& \quad z = H: \quad \frac{\partial C}{\partial z} = 0
\end{align*}
\]

(5) Adsorption kinetics equation

On applying the homogeneous solid diffusion model to the single particle which is traced, the generalized particle diffusion equation can be deduced from the differential material balance of sphere, cylinder and slice particle:

\[
\frac{\partial q}{\partial t} = \left( \frac{D_e}{x} \right) \frac{\partial^2 (x - 1) \frac{\partial q}{\partial x}}{\partial x} \tag{5}
\]

\[
\begin{align*}
I. C. & \quad t = 0: \quad q = 0 \\
B. C. & \quad x = 0: \quad \frac{\partial q}{\partial x} = 0 \\
& \quad x = x_0: \quad \frac{\partial q}{\partial x} = \frac{k_f}{\rho D_e} (C - q/K)
\end{align*}
\]

Here, \( \alpha \) is shape factor, which is 3, 2 and 1 to sphere, cylinder and slice respectively.

(6) The connection equation between phases.

The connector between both phases is average particle surface concentration:

\[
\bar{q}_a(t, z) = \frac{1}{m_z} \sum_{z \in (z - \frac{\bar{a}_z}{2}, z + \frac{\bar{a}_z}{2})} q(t, x) \bigg|_{x = x_s} \tag{6}
\]

From particle walk model equations (1)~(6) constitute a complete set of equations for simulating the periodic operation behavior of adsorption process in multistage fluidized bed. The model takes into account the effects of random backmix-
ing of particles, axial dispersion of liquid phase, mass transfer in liquid—film, intraparticle diffusion and particle shape. It reveals clearly the characteristics of solid and liquid phase in adsorption process.

SIMULATION ALGORITHM

The simulation of multistage fluidized bed adsorption process by particle walk model is described in the Fig. 2.

Fig. 2 Flow chart for simulation of adsorption process
EXPERIMENT FOR MODEL PARAMETERS AND THE MULTISTAGE FLUIDIZED BED ADSORPTION EXPERIMENT

By experiment with humic acid (the color) in monosodium glutamate solution as adsorbate and K15 GAC as adsorbent, all the model parameters were determined as shown in Table 1.

**TABLE 1** The model parameters determined by experiments

<table>
<thead>
<tr>
<th>parameters</th>
<th>results</th>
<th>experiment methods</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>418.4 ml/g</td>
<td>static method</td>
</tr>
<tr>
<td>D_e</td>
<td>8.169×10^{-11} m²/s</td>
<td>bottle-point method</td>
</tr>
<tr>
<td>K_i</td>
<td>8.13×10^{-7} m/s</td>
<td>single stage fluidized bed adsorption experiment</td>
</tr>
<tr>
<td>σ/2</td>
<td>6.60×10^{-4} m²/s</td>
<td>solid-phase backmixing experiment with resin as indicator</td>
</tr>
<tr>
<td>E_i</td>
<td>1.207×10^{-7} m³/s</td>
<td>RTD experiment</td>
</tr>
</tbody>
</table>

The experimental data for substantiating the simulation as shown in next section come from the multistage fluidized bed adsorption experiment with TPCIX column as adsorber and with the operation parameters shown in Table 2.

**TABLE 2** The operation parameters of the adsorption process in TPCIX column

<table>
<thead>
<tr>
<th>operation parameters</th>
<th>parameter value</th>
</tr>
</thead>
<tbody>
<tr>
<td>number of the stages in TPCIX column</td>
<td>5</td>
</tr>
<tr>
<td>adsorption period time</td>
<td>1 hour</td>
</tr>
<tr>
<td>stage height</td>
<td>0.30 m</td>
</tr>
<tr>
<td>average GAC particle radius</td>
<td>0.2368 mm</td>
</tr>
</tbody>
</table>

SIMULATION RESULTS AND DISCUSSION

With parameters shown in table 2, the simulation of adsorption process in TPCIX column was studied.

The relations between the concentration of liquid phase and time, position

We can get the concentration of liquid phase at a series of time points and position points by the simulation with Monte Carlo method. The result data can be plotted in graphs. But as the space in this paper is limited, we show only two of these graphs as an example.
Fig. 3 shows the relation between liquid—phase concentration and position at $t = 50 \text{min}$, from which we can find the concentration of liquid phase decreases as position $z$ increases, but the speed of decreasing slows down gradually.

Fig. 4 shows the relation between liquid—phase concentration at a stage exit ($z = 3H$) and time $t$, from which we can find the concentration of liquid phase decreases down to the lowest point quickly, then recovers slowly. And if we call the time at the lowest point as critical time, the critical time gets longer as column position $z$ increases.

From these graphs, we can find the simulation results agree with the experimental results rather well.

**Walk path of an individual particle in column**

In simulation, we trace a large number of particles and record the positions of every particle, which keeps walking up and down. So in the simulation, we can choose a particle in the sample and observe its behavior easily. As an example, Fig. 5 is the path of the particle, whose position is at $z = 4.4H$ ($H$ is stage height) when $t = 0$. From Fig. 5, it is easy to see that the particle came in the column when $t = 0$, walked randomly in fifth stage when $t = 0 - 1\text{hr}$, ..., the particle left the column when $t = 5\text{hrs}$. The figure shows that the frequency of the particle's walking is high, which indicates that the backmixing of solid phase in each stage is large.

**The development of individual particle concentration profile**
Fig. 6 shows the development of the concentration profile of the same particle as in Fig. 5. In this figure, the particle concentration profile is entirely zero when \( t = 0 \), as time increases, the profile curve becomes steeper. After \( t > 5 \text{hrs} \) (when the particle had left the column), the profile curve is very steep, which indicates that the intraparticle diffusion has great effect on adsorption process.

**Fig. 5** Walk path of an individual particle in column

**Fig. 6** The development of individual particle concentration profile

**Fig. 7** Effect of position on solid-phase section—average concentration

**Fig. 8** Effect of time on solid-phase stage—average concentration

The variation of solid—phase section—average concentration against time and position
With time as parameter, we can get curves of solid-phase section-average concentration against position. Fig. 7 is one graph as an example at \( t = 10\text{min} \). In this graph, the concentration decreases gradually from the first stage to the fifth stage and it changes only a little inside stage, which indicates the backmixing of solid phase in each stage is large.

**The relation between solid-phase stage-average concentration and time**

Fig. 8 shows the relation between solid-phase stage-average concentration and time, in which the concentration's variation against time is approximately linear and the slope decreases from the first stage to the fifth one.

**The distribution of particle-average concentrations in some certain time and position**

Fig. 9 shows the distribution of particle-average concentrations at \( t = 13.2\text{min} \) and \( z = 2.4H \). The figure was got by counting over 1000 particles which had occurred at the time and position point \((13.2\text{min}, 2.4H)\) in simulation. We can find from the figure that the distribution is not symmetrical. The characteristics of the distribution have never been got in the simulations reported by previous authors. Because it is not symmetrical, the simulation will have a certain deviation without taking account of the stochastic process.

**CONCLUSIONS**

(1) A stochastic model has been developed to predict the periodic operation performance of the continuous counter-current adsorption process. The model takes into account of random backmixing of particles, axial dispersion of liquid phase, liquid–film mass transfer, intraparticle diffusion and particle shape, and can reveal clearly the behavior of solid and liquid phase in adsorption process.

(2) The simulation of the stochastic model can furnish many important information of fluidized bed adsorption process such as concentration of liquid and solid
phase at any time and position, walk path of individual particle in bed and the development of its concentration profile, the distribution of particle—average concentration in some certain time and position.

'(3) It has been shown that the Monte Carlo method is useful to the simulation of continuous counter—current adsorption process successfully.

(4) The simulation results agree with the experimental data rather well.

**NOTATION**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>concentration of the adsorbate in the liquid phase</td>
<td>mol/m³</td>
</tr>
<tr>
<td>Dₐ</td>
<td>effective diffusivity of the adsorbate into the particle</td>
<td>m²/s</td>
</tr>
<tr>
<td>Eₐ</td>
<td>axial liquid—phase dispersion coefficient</td>
<td>m²/s</td>
</tr>
<tr>
<td>Eₚ</td>
<td>axial solid—phase dispersion coefficient</td>
<td>m³/s</td>
</tr>
<tr>
<td>H</td>
<td>height of a stage in adsorber</td>
<td>m</td>
</tr>
<tr>
<td>K</td>
<td>adsorption equilibrium constant</td>
<td>ml/g</td>
</tr>
<tr>
<td>kₐ</td>
<td>liquid—phase mass transfer coefficient</td>
<td>m/s</td>
</tr>
<tr>
<td>n</td>
<td>number of stages of adsorber</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>the transfer probability matrix</td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>adsorbate concentration in the particle</td>
<td>mol/kg</td>
</tr>
<tr>
<td>qₚ</td>
<td>average particle surface concentration</td>
<td>mol/kg</td>
</tr>
<tr>
<td>T</td>
<td>adsorption period time</td>
<td>s</td>
</tr>
<tr>
<td>t</td>
<td>time</td>
<td>s</td>
</tr>
<tr>
<td>u</td>
<td>superficial fluid velocity</td>
<td>m/s</td>
</tr>
<tr>
<td>x</td>
<td>position in the particle</td>
<td>m</td>
</tr>
<tr>
<td>xₑ</td>
<td>particle size</td>
<td>m</td>
</tr>
<tr>
<td>z</td>
<td>position in adsorber</td>
<td>m</td>
</tr>
</tbody>
</table>

**Greek letters**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>factor of particle form</td>
</tr>
<tr>
<td>Δ</td>
<td>walk pace of particle</td>
</tr>
<tr>
<td>εₐ</td>
<td>volume fraction of the liquid phase</td>
</tr>
<tr>
<td>εₛ</td>
<td>volume fraction of the solid phase</td>
</tr>
<tr>
<td>1/2 εₛ</td>
<td>axial solid—phase dispersion coefficient</td>
</tr>
<tr>
<td>τ</td>
<td>walk time each pace of particle</td>
</tr>
</tbody>
</table>

**Subscripts**
liquid phase

solid phase

REFERENCES