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APPLICATION OF THE THEORY OF MARKOV CHAINS TO MODEL THE PROCESS OF ION EXCHANGE

ZASTOSOWANIE TEORII ŁAŃCUCHÓW MARKOWA DO MODELOWANIA PROCESÓW WYMIANY JONOWEJ

Abstract

The paper suggests a simple but informative approach to model the process of ion exchange at different levels of the process decomposition by means of the theory of Markov chains. Two aspects of the process are modeled on the basis of the same algorithm: diffusion of impurity into a bead of ionite with ion exchange reaction inside it, and the ion exchange in an apparatus with immovable layer of ionite. Some results of modeling are presented and discussed.

Keywords: ion exchange, diffusion, mass transfer, Markov chain, state vector, matrix of transition probabilities, impurity concentration

Streszczenie

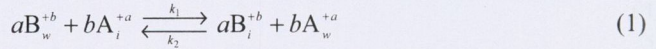
W pracy przedstawiono proste ale pouczające podejście do modelowania procesu wymiany jonowej na różnych poziomach dekompozycji procesu za pomocą teorii łańcuchów Markowa. Dwa aspekty procesu modelowane są na podstawie tego samego algorytmu: dyfuzja zanieczyszczeń w złożu jonitu z reakcją wymiany jonowej oraz wymiana jonowa w aparacie z nieruchomym złożem. Wybrane wyniki modelowania zostały przedstawione i omówione.

Słowa kluczowe: wymiana jonowa, dyfuzja, wymiana masy, łańcuch Markowa, wektor stanu, macierz prawdopodobieństw przejścia, stężenie zanieczyszczeń

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1. Introduction

The objective of the study is to propose a simple but informative model of the process of ion exchange both in a single ionite bead and in an ion exchange reactor. It is supposed that an appropriate mathematical tool for this purpose is the theory of Markov chains that was successfully used to model similar processes in chemical and related technologies [1÷3]. It is known [4] that the ion exchange is a chemical reaction in which mobile hydrated ions of a solid are exchanged, equivalent for equivalent, of ions of like charge in solution. For cation exchange this reaction can be written as follows:



where A and B are exchanging ionic species, a and b represent their charges, w and i designate solution and resin (exchanger) phases, k_1 and k_2 are the constant of direct and inverse reaction.

The kinetic equation of the reaction can be written as:

$$\frac{dC_B}{dt} = -k_1 \cdot C_B^a \cdot C_A^b + k_2 \cdot C_B^a \cdot C_A^b \quad (2)$$

where C is the concentration of a species, B is related to ions of impurity, and A is related to ions of ionite.

The reaction (1) occurs when the both species of ions are in contact. In order it to happen the ions of impurity must travel from a solution to the surface of ionite bead and then inside it though interconnecting pores. Thus, finally the total process of ion exchange can be interpreted as a diffusion process with the concurrent chemical reaction (1). When building a model it is not very important what exactly kind of reaction occurs. Therefore, in order to make the description not too cumbersome, we suppose that $k_1 \gg k_2$, and $a = b = 1$.

2. Modeling the ion exchange in a single ionite bead in immovable solution

The beads of ionite are placed in a reactor in the state of random packing. Nevertheless, the volume of solution per one bead can be found. Let us present this volume as a spherical layer pleased around the bead of ionite as it is shown in Fig. 1. It allows reducing the problem to a spherically symmetrical one that strongly simplifies its description.

Then let us separate the total spherical volume into m spherical layers of the identical small width Δr with mean radiuses r_j , $j = 1, \dots, m$ where the indices $1:m_j$ are related to the ionite bead, and the indices $m_1+1:m$ are related to surrounding the bead solution. The state of the process at a moment of time can be presented as the column vectors: $\mathbf{M}_B = [M_{B1} \dots M_{Bm}]^T$ for the impurity mass in solution, $\mathbf{C}_B = [C_{im1} \dots C_{imm}]^T$ for the impurity concentration in solution, $\mathbf{M}_A = [M_{A1} \dots M_{Am}]^T$ for the ions mass in ionite, $\mathbf{C}_A = [C_{im1} \dots C_{imm}]^T$ for the ions concentration in ionite. The vectors of mass and concentration are connected according to the relationship $\mathbf{C} = \mathbf{M} / (4 \cdot \pi \cdot \Delta r \cdot \mathbf{r})$ where the operator $/$ means element by element division of vectors. In vector/matrix notation evolution of the system can be described by the following set of recurrent matrix relationships:

$$\mathbf{M}_B^{k+1} = \mathbf{P} \cdot \mathbf{M}_B^k \quad (3)$$

$$\mathbf{C}_B^{k+1} = \mathbf{C}_B^k - k_1 \cdot \mathbf{C}_B^k \cdot \mathbf{C}_A^k \cdot \Delta t \quad (4)$$

$$\mathbf{C}_A^{k+1} = \mathbf{C}_A^k - k_1 \cdot \mathbf{C}_B^k \cdot \mathbf{C}_A^k \cdot \Delta t \quad (5)$$

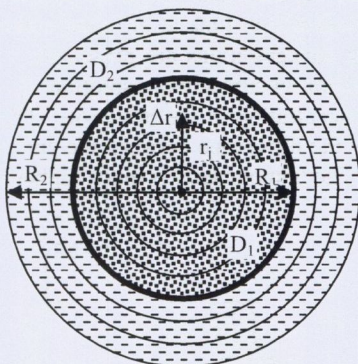


Fig. 1. Computational scheme of the cell model for a single ionite bead

Rys. 1. Schemat modelu obliczeniowego komórki pojedynczego ziarna jonitu

Equation (3) describes diffusion of impurity within the complex domain shown in Fig. 1, equation (4) describes impurity absorption by ionite, and equation (5) – ions of ionite consumption. The process of diffusion is controlled by the transition matrix \mathbf{P} . The general rules of its constructing are described in details in [1, 2]. The fragment of it, which is related to the border of inner and outer substance (see Fig. 1) is shown below:

$$\mathbf{P} = \begin{bmatrix} \dots & \dots & \dots & \dots \\ \dots & d_1 \cdot \left(1 - \frac{2 \cdot \Delta r}{r_{m1}}\right)^2 & \dots & \dots \\ \dots & p_{m1,m1} & d_1 \cdot \left(1 - \frac{2 \cdot \Delta r}{r_{m1+1}}\right)^2 & \dots \\ \dots & d_1 \cdot \left(1 + \frac{2 \cdot \Delta r}{r_{m1}}\right)^2 & p_{m1+1,m1+1} & \dots \\ \dots & \dots & d_2 \cdot \left(1 + \frac{2 \cdot \Delta r}{r_{m1+1}}\right)^2 & \dots \\ \dots & \dots & \dots & \dots \end{bmatrix} \quad (6)$$

where $d = D \cdot \Delta t / \Delta r^2$.

Some examples of modeling are shown in Fig. 2 and Fig. 3. Fig. 2 shows evolution of concentration distribution of impurity in solution and ions in ionite at identical value of d ($d_1 = d_2 = 0.3$). The initial state of the system corresponds to the homogeneous distribution of impurity in the outer solution and its absence inside the bead. The impurity distribution over the bead radius is more or less homogeneous except the initial time interval. On the opposite, the ions of ionite consumption is non-homogeneous. Its concentration near the bead core decreases much slower than near the bead periphery. Fig. 3 shows variation of impurity concentration in solution with time at different combinations of d inside and outside the bead. The following concentrations are presented: 1 – mean concentration inside the bead; 2 – mean concentration in surrounding solution; 3 – local concentration near the bead periphery; 4 – local concentration in the bead core. The process homogeneity inside the bead can be estimated by the difference between the curves 3 and 4 and their closeness to the mean concentration 4. The homogeneity is much higher at the bottom graph.

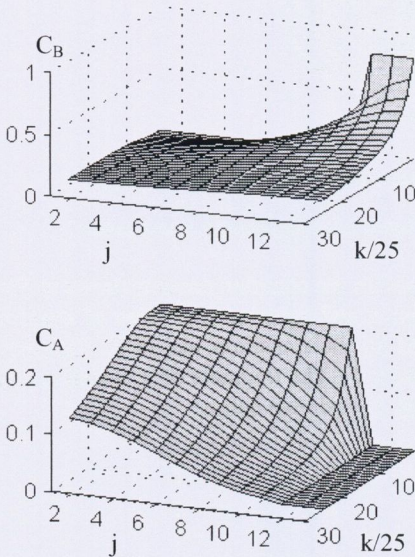


Fig. 2. Evolution of concentration distribution of impurity in solution and ions in ionite at $d_1 = 0.3; d_2 = 0.3$

Rys. 2. Ewolucja rozkładu stężeń zanieczyszczeń w roztworze i jonów w jonicie dla $d_1 = 0,3; d_2 = 0,3$

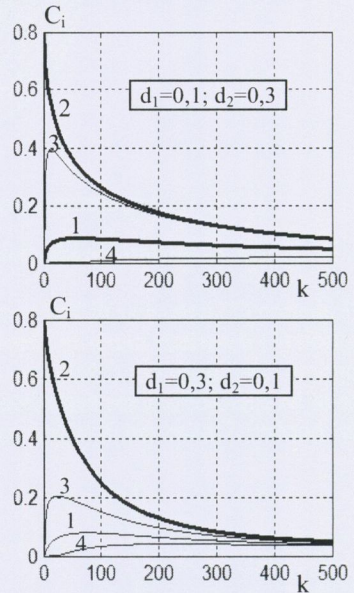


Fig. 3. Variation of impurity concentration in solution: 1 – mean concentration inside the bead; 2 – mean concentration in surrounding solution; 3 – local concentration near the bead periphery; 4 – local concentration in the bead core

Rys. 3. Zmienność stężenia zanieczyszczeń w roztworze: 1 – średnie stężenie w złożu; 2 – średnie stężenie w roztworze otaczającym; 3 – lokalne stężenie na peryferiach złoża; 4 – lokalne stężenie w rdzeniu złoża

3. Modeling the ion exchange in an apparatus with immovable ionite and moving solution

A real apparatus for ion exchange contains a big amount of ionite beads, a solution moves through which. Application of the model describes above to each bead is too cumbersome and computational time consuming. The model can be simplified by using the surface mass exchange relationships that presupposes that the limiting stage of the process is namely impurity mass transfer through the bead surface, and diffusion to the surface and inside ionite goes much faster. The schematic presentation of the process is shown in Fig. 4. Solution (water plus impurity) moves through the beads of ionite that are packed regularly or randomly. The impurity in solution due to mass transfer through the bead surface penetrates inside the bead and is absorbed by ionite. Thus, the solution moves to the apparatus outlet losing the impurity and leaves it with smaller impurity concentration. The theory of Markov chain appears to be a convenient tool to describe the process too.

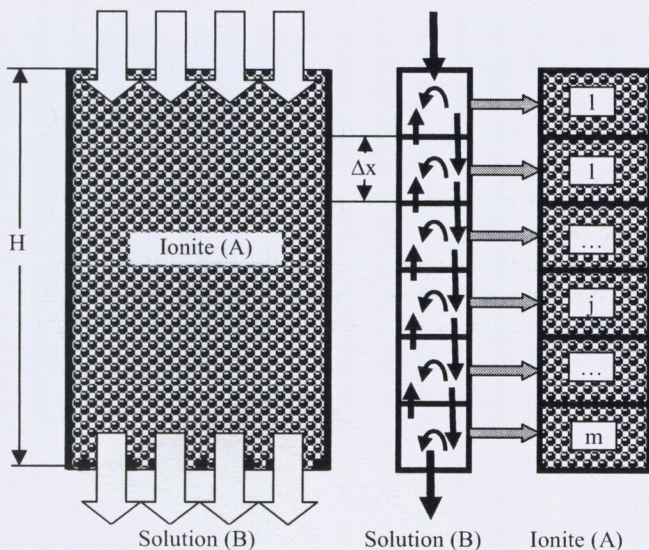


Fig. 4. Computational scheme of the process and its cell model

Rys. 4. Schemat modelu obliczeniowego procesu

Let us separate the operating volume into two parallel zones (one for moving solution, and one for immovable packed beads), and then separate each zone into a chain of perfectly mixed cells. The process kinetics can be described by the following set of recurrent matrix relationships:

$$M_{Bw}^{k+1} = \mathbf{P}(M_{Bw}^k - \Delta M_{Br}^k + \Delta M_{Bf}^k) \quad (7)$$

$$M_{Br}^{k+1} = \mathbf{P}(M_{Br}^k - \Delta M_{Bi}^k + \Delta M_{Br}^k) \quad (8)$$

$$M_{Ai}^{k+1} = M_{Ai}^k - \Delta M_{Br}^k \quad (9)$$

where \mathbf{M}_{Bw} is the vector of impurity mass in solution (water), \mathbf{M}_{Bi} is the same for ionite, $\Delta\mathbf{M}_{Br}$ is the impurity mass that penetrates into the beads due to mass transfer during one time transition, $\Delta\mathbf{M}_{B_r}$ is the impurity mass that disappears inside the beads due to the ion exchange reaction, \mathbf{M}_{B_f} is the impurity source vector – the mass of impurity that comes with water into the first cell during one time transition, \mathbf{M}_{Ai} is ions mass capable for exchange in the beads. Thus, the neighboring cells of the chains exchange mass of impurity, and the impurity travels over the water chains with water. This travel is controlled by the transition matrix \mathbf{P} [1, 2], which elements can be calculated with the following formulae: $P_{j,j+1} = d$; $P_{j+1,j} = d + v$; $P_{j,j} = 1 - \sum_{i=1}^m P_{ij}$; $d = D \cdot \Delta t / \Delta x^2$; $v = V \cdot \Delta t / \Delta x$ where D is the longwise dispersion coefficient of the water flow, V is the water flow speed.

The elements of transfer vectors $\Delta\mathbf{M}_{Br}$ and $\Delta\mathbf{M}_{B_r}$ can be calculated as follows (index of the cell number is omitted):

$$\Delta M_{Br}^k = \beta \cdot F \cdot (C_{Bw}^k - C_{Bi}^k) \cdot \Delta t = \beta \cdot F \cdot \left(\frac{M_{Bw}^k}{V_c \cdot \varepsilon} - \frac{M_{Bi}^k}{V_c \cdot (1 - \varepsilon)} \right) \cdot \Delta t \quad (10)$$

$$\Delta M_{B_r}^k = [k_1 \cdot C_{Bi}^k \cdot C_{Ai}^k \cdot \Delta t] \cdot V_c \cdot (1 - \varepsilon) = k_1 \cdot \frac{(M_{Bi}^k + \Delta M_{Bi}^k) \cdot M_{Ai}^k}{V_c \cdot (1 - \varepsilon)} \cdot \Delta t \quad (11)$$

where β is the mass transfer coefficient, V_c is the volume of the cell, F is the total surface of mass transfer in the cell.

Thus, the model gives the complete process description if the transfer coefficients and parameters of reaction are known. An example of modeling is presented in Fig. 5 where the evolution of impurity concentration distribution over the apparatus length is shown.

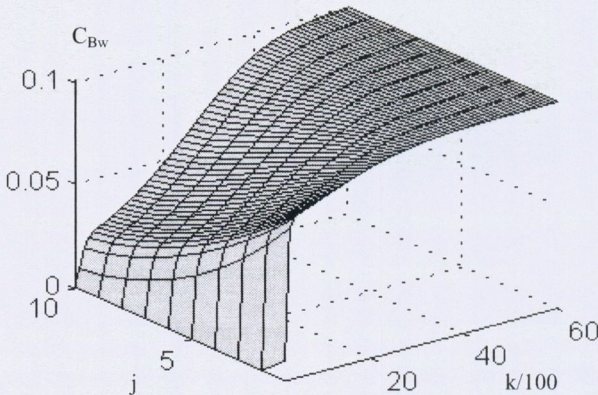


Fig. 5. Evolution of impurity concentration distribution over the apparatus length

Rys. 5. Ewolucja rozkładu stężeń zanieczyszczeń wzdłuż aparatu

At the initial stage of the process the intense absorption of impurity can be seen. Its concentration at the outlet is much less than at the inlet. However, the fixed volume of ionite little by little loses the ability for ion exchange, and the impurity concentration at the outlet is growing with time. After about 6000 time transitions it becomes practically equal to the inlet concentration, i.e., purification stops. The right moment of time for transition to ionite recovery can be chosen with such diagram.

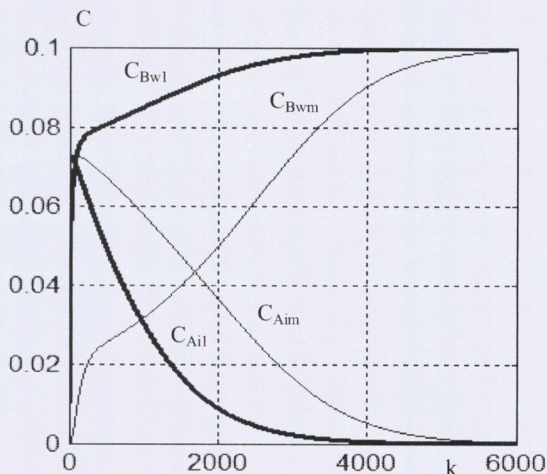


Fig. 6. Variation with time of components concentration at apparatus inlet and outlet

Rys. 6. Zmienność w czasie koncentracji składników na wlocie i wylocie z aparatu

Fig. 6 shows two cuts of the previous graph as variation with time of components concentration in the first and the last cells, i.e., at apparatus inlet and outlet. The difference in the impurity concentration in water between inlet and outlet is high at the beginning of the process. As ionite is used up the difference decreases, i.e., the impurity concentration at outlet grows.

It is not difficult to transit to modeling the process with movable ionite. It is enough to allow the ionite travelling through its chain (see Fig. 1), i.e., to draw the arrows similar to ones for the solution chain and to introduce the matrix of transition probabilities for ionite beads. However, describing the model is beyond the objectives of the present paper.

4. Conclusions

One of the main results of the investigation is demonstration of the fact that the theory of Markov chains is very convenient mathematical tool to model ion exchange at different level of the process decomposition. It allows describing the process at the level of single bead of ionite as a diffusion process with jump variation of diffusion coefficient at the bead

surface as well as the process in an ion exchanger. The main feature of the models structure is that they describe the process for local difference of transfer potentials, not for their average values over an apparatus. Depending on objective of model constructing the proposed approach allows the complete description of the process on required level of decomposition if the transfer parameters are known quantitatively that obviously needs experimental investigation of the process local details.

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