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MODELING METHODOLOGY OF EXCHANGING DIFFERENTLY CHARGED IONS IN WATER TREATMENT МЕТОДОЛОГИЯ МОДЕЛИРОВАНИЯ ОБМЕНА ИОНОВ РАЗНОГО ЗАРЯДА В ВОДОПОДГОТОВКЕ

Summary. The features of complex calculations, which are revealed, will help teachers and students implement the proposed methodology in the educational process. The mathematical models of statics and dynamics for exchanging ions from bi-charged to singly-charged and methods for their solution in MathCAD are proposed. Equation of the initial distribution of concentration along the filter is reasoned. The method of characteristics is adapted for analysis of the distribution of bi-charged ions in a filter. The model, which is proposed, provides varying technological and design parameters as input data in order to estimate their effect on the exchange process quality.

Key words: ion exchange, exchange isotherm, bi-charged ion, mathematical model, dynamics of the equilibrium exchange.

Аннотация. Раскрыты особенности сложных расчетов, которые помогут преподавателям и студентам реализовать предложенную методологию в учебном процессе. Разработаны математические модели обмена ионов разного заряда в статических и динамических условиях и предложены методы их решения в пакете MathCAD. Обосновано уравнение начального распределения концентрации в фильтре. Метод характеристик адаптирован для анализа распределения двухзарядных ионов в фильтре. Предложенная модель варьирует различными технологическими и конструктивными параметрами в качестве исходных данных для оценки их влияния на качество процесса обмена.

Ключевые слова: ионный обмен, изотерма обмена, двухзарядные ионы, математическая модель, динамика равновесного обмена.

Introduction. The scientific and technological progress of the last decades is based on the widespread use of computer technologies in any processing of experimental data, designing of modern productions, creation of automated control systems. The technical high school has an important task - to educate and train specialists in chemical technology and engineering, who can to actively use modern software packages and shells. The article is an example of mastering complex ion-exchange calculations in MathCAD. This article is a logical continuation of our article [1], which describes a methodology for simulating the exchange of singly charged ions.

The aim was to design the mathematic model of static and dynamic of ion exchange for bi-charged ions. For reaching this aim it was necessary to bring out the equation of isotherm of ion exchange, basing on the law of mass action, to adapt the mathematic apparatus and software solutions for bi-charged ions.

Ion exchange equilibrium. The equilibrium is established according to the law of mass action. Reactions of exchange $2RNa + Ca^{2+} = R_2Ca + 2Na^+$ between, for example, exchange of Mg²⁺, Ca²⁺ - (then labelled as B) for H⁺ (desalination of water) or Na⁺ (softening of water) – (then labelled as A) – the most common cases at treatment of water; the part of ions \overline{A} in ionite is replaced by ions $\overline{B}: 2\overline{A} + B \leftrightarrow \overline{B} + 2A$.

Rates of direct and reverse reactions are equal according to the law of mass action at equilibrium:

$$k_1 \cdot Q_A^2 \cdot C_B = k_2 \cdot Q_B \cdot C_A^2, \tag{1}$$

where k₁, k₂ – rate constants for direct and reverse reaction, $Q_A = \frac{q_A}{q_0}$, $Q_B = \frac{q_B}{q_0}$ relative concentrations of exchangeable ions A and B in phase of ion exchanger; $C_A = \frac{c_A}{c_0}$, $C_B = \frac{c_B}{c_0}$ – relative concentrations of ions A and B in phase of solution, at these conditions concentrations of A and B in solution $c_A + c_B = c_0$, and an

anion exchanger $q_A + q_B = q_0$ (q₀ responds of total exchange capacity). If taking into account that $Q_A + Q_B = 1$; $C_A + C_B = 1$, the equation (1) can be written as:

$$k_1 \cdot (1 - Q_B)^2 \cdot C_B = k_2 \cdot Q_B \cdot (1 - C_B)^2 .$$
⁽²⁾

The solution of (2) relatively Q_B (equilibrium constant of exchange $k = k_1/k_2$) is:

$$Q_{B} = 1 + \frac{\left(1 - C_{B}\right)^{2}}{2kC_{B}} - \sqrt{\left(1 + \frac{\left(1 - C_{B}\right)^{2}}{2kC_{B}}\right)^{2} - 1}.$$
(3)

From the equation:

$$k_1 \cdot Q_A^2 \cdot (1 - C_A) = k_2 \cdot (1 - Q_A) \cdot C_A^2,$$
(4)

The similar equation for component A can be taken:

$$Q_{A} = \frac{-C_{A}^{2} + C_{A}\sqrt{C_{A}^{2} + 4k \cdot (1 - C_{A})}}{2k \cdot (1 - C_{A})}.$$
(5)

So, equations (3) and (5) are, respectively, equations of convex (doublevalence) and concave (single-valence) ions. The same amount of constant $k = k_1/k_2$ had been used in both equations. It can be noted, that the equation, similar to (5), had taken by authors of [2] for regeneration of the filter. The equation (3), took by us, establishes the connection between of dimensionless concentration of a bi-charged ion in an ionite from its dimensionless concentration in water. It is important for practice aim and conditions. The equation (3) is firstly used for analysis ion exchange's dynamic [3].

The possible option of usage of the equation of concave isotherm by equation (4) and new equilibrium constant of exchange $k^* = k_2/k_1$:

$$Q_A = \frac{-k^* C_A^2}{2(1 - C_A)} + \sqrt{\left(\frac{k^* C_A^2}{2(1 - C_A)}\right)^2 + \frac{k^* C_A^2}{1 - C_A}}.$$
(6)

This corresponds to the usual approach -k > 1 for convex isotherm according to (3), $k^* < 1$ for concave isotherm according to (6), i.e. $k^* = 1/k$.

We calculated the constant k of equation (3) by the data of exchange isotherm Cu²⁺/Na⁺ on cation exchanger Dowex-50X8 (fig. 40 of monograph [4]). The dependence of exchange constant from normality of solution N is approximated by the equation: $ln \ k = 0.9436 - 1.1783 \cdot lnN$. So, at N = 1 constant k=2.56.

Dynamic of ion exchange. At designing a mathematic model of ion exchange filter, working at equilibrium conditions, it can be considered, that at passing the solution of ion through the infinitely small layer of ion exchanger, the equilibrium is established instantly. This allows ignoring rates of transferring ions in absorbable solution because concentrations in solution and on the surface of ion exchanger are equal. The front of concentration is moved with constant linear rate *w* along the layer. This is evidenced about stationary mode of the process. The «working layer» is existed as zone of mass movement. The concentration is decreased in flow from initial to practically zero: at Z=0 Z=0 $C=C_0=1$ and Q=0, at Z=1 $C\approx0$.

The static equation is eq. (3), the equation of material balance in dimensionless form is [5]:

$$\frac{\partial q}{\partial \tau_z} + \mathbf{p} \cdot \frac{\partial c}{\partial \tau_z} + \frac{\partial (w \cdot c)}{\partial z} = 0.$$
(7)

If to consider change in concentration of the exchangeable front as function from the time, the equation (7) will be:

$$\frac{\partial q}{\partial \tau_z} + \mathbf{p} \cdot \frac{\partial c}{\partial \tau_z} = 0$$
, where $\frac{\partial q}{\partial \tau} = -\mathbf{p} \cdot \frac{\partial c}{\partial \tau}$.

Including the equation of outside diffusion kinetics:

$$\frac{\partial q}{\partial \tau_z} = -\mathbf{p} \cdot \frac{\partial c}{\partial \tau_z} = \beta \cdot (c - c') \quad , \tag{8}$$

where τ_z – contact time of the solution with determined area of ionite, s; β – coefficient of mass transfer in solution, m³/(m³·s); c' – equilibrium concentration of the component in solution (bordering on the surface of the ionite), g-eq./m³. The equilibrium concentration c'=0 before the beginning of ion exchange. The following equation is finally taken: $-p \cdot \frac{\partial c}{\partial \tau_z} = \beta \cdot c$. After integration in limits from c_0 to c and from 0 to τ_z : $c = c_0 \cdot exp(-\beta \cdot \tau_z/p)$.

Including the contact time with determined area of the ionite layer $\tau_z = z/w$ ($\tau_L = L/w$ – residence time of the solution in filter), the last equation will be:

$$c = c_0 \cdot exp(-\beta \cdot z/(p \cdot w)). \tag{9}$$

The initial distribution of relative concentrations along the filter:

$$C = C_0 \cdot exp(-K \cdot Z), \tag{10}$$

where $C_0 = 1$ i $K = \beta / (p \cdot w)$.

We ask the initial distribution of concentration along the filter C(Z) as:

$$C(Z) = 0.9999 \cdot exp(-K \cdot Z), \tag{11}$$

including impossibility of usage amount of $C_0 = 1$ in eq. (12): C(Z)=1 at Z=0.

Calculation of wave speed V_{wave} is carried out by the following equation (the first derivative form eq. (3) is included):

$$Vwave(Z,k) \coloneqq \frac{rat}{\frac{-(1-C(Z))}{k \cdot C(Z)} - \frac{1}{2} \cdot \frac{(1-C(Z))^2}{k \cdot C(Z)^2} - \frac{1}{\left[\left[1 + \frac{1}{2} \cdot \frac{(1-C(Z))^2}{k \cdot C(Z)}\right]^2 - 1\right]^{\frac{1}{2}}} \cdot \left[1 + \frac{1}{2} \cdot \frac{(1-C(Z))^2}{k \cdot C(Z)}\right] \cdot \left[\frac{-(1-C(Z))}{k \cdot C(Z)} - \frac{1}{2} \cdot \frac{(1-C(Z))^2}{k \cdot C(Z)^2}\right] + p \cdot rat}$$
(12)

Calculations. The characteristic method [6] is adapted for analysing the propagation of bi-charged ions in a filter. The initial data were the following: the porosity of ionite: p=0,6; the concentration of ion B in water, g-eq./m³, c₀=6; total exchange capacity of cationite, g-eq./m³, q₀=2000; the linear speed of water w=10 m/h; the height of the layer of ionite L=2,5 m; operation time of filter during inter-regeneration period $\tau = 20$ hour.

Limit amounts of coordinates of points Z: $Z_{min}=0$; $Z_{max}=1$. According to initial data in dimensionless form $t_{min}=0$; $t_{max}=\tau \cdot w/L=20\cdot 10/2, 5=80$; dimensionless distribution ratio Rat (in eq. (12) rat) = $c_0/q_0 = 6/2000 = 0,003$. Change of dimensionless concentration (matrix): c:=0,0.001..0.9999

The determination of β is problematic. The amount of it depends on many factors: type and size of ionite, construction parameters and mode of filter

working, ion type etc. So, for bi-charged cobalt ions $\beta^* = 0,000026$ m/s [7]. In this case, the specific outer surface of grains of the ionite, m²/m³ (including dimension of β^* , $K = \beta^* \cdot S_{spec}/(p \cdot w)$), will be: $S_{spec} = 6 \cdot (1-p)/d$, where d – equivalent diameter of grains of the ionite, m. The specific area of grains of the ionite, m²/m³: $S_{spec} = 6 \cdot (1-0,6)/0,002 = 1200$.

The constant K in (11) equals:

$$K = \beta \cdot S_{\text{spec}} / (p \cdot w) = 0,000026 \cdot 1200 \cdot 3600 / (0,6 \cdot 10) = 18,72$$

To facilitate the self-realization of the above material, a fragment of the program in MathCAD is provided in Figure 1.



Fig. 1. Fragment of the program in MathCAD 13

Programming result: double- and triple-dimension (spatial-temporal) dependences of concentrations of bi-charged ions (fig. 2) along the axis of the filter had built. Digits 0, 40 and 80 respond to the dimensionless time t.

«Breakage» front is observed for convex isotherms of ion exchange of bicharged ions. The front of such hypothetic form, when the concentration of ions in solution is changed jump-like from $c = c_0$ (C=1) to $c \approx 0$ (C ≈ 0) (fig. 2).



Fig. 2. Double and triple dimension dependence of the concentration of bi-charged ion along the axis of the filter $C_{i,0}$, $C_{i,40}$, $C_{i,80}$ from $Z1_{i,0}$, $Z1_{i,40}$, $Z1_{i,80}$ for exchange constant k=2,56

Conclusions. The equations are derived for isotherms of ion exchange relatively bi-charged ions. The principle of determination of an equilibrium constant in Excel and calculations for different initial concentrations of bicharged ions in solution had given. The algorithm and program had creatively adapted in Mathcad for calculations of filtration and designing of double- and triple-dimension dependences of concentration of ion along the axis of the filter. The features of complex calculations, which are revealed, will help teachers and students implement the proposed methodology in the educational process.

References

- Kontsevoi A., Kontsevoi S. Methodology of statics and dynamics modeling of single-charged ions exchange in water treatment. International scientific journal "Internauka". 2019. №16
- Gromoglasov A .A. Vodopodgotovka: proczessy` i apparaty` / A. A. Gromoglasov, A. S. Kopy`lov, A. P. Pil`shhikov. M. : E`nergoatomizdat, 1990. 272 s. [in Russian]
- Kontsevoi A.L., Kontsevoi S.A., Tarhons"ka O.O. Analiz statyky i dynamiky obminu ioniv riznoho zaryadu. Voda i vodoochysni texnolohiyi. Naukovo-texnichni visti. №2(8), 2012. S. 50-58. [in Ukrainian]
- 4. Gel`ferikh F. Ionity`. Osnovy` ionnogo obmena / F. Gel`ferikh. M. : Izd-vo inostrannoj literatury`, 1962. 491 s. [in Russian]
- Serpyonova E. N. Promy'shlennaya adsorbcyya hazov y parov / E. N. Serpyonova. M.: Vy'sshaya shkola, 1969. 416 s. [in Russian]
- Ochkov V. F. Analiz izoterm ionnogo obmena v srede Mathcad / V. F. Ochkov, A. P. Pil`shhikov, A.P. Solodov, Yu.V. Chudova // Teploenergetika. 2003. #7 S. 13-18. [in Russian]
- 7. Gressier F. Etude de la rétention des radionucléides dans les résines échangeuses d'ions de circuits d'une centrale nucléaire à eau sous pression / F. Gressier. Paris : Mines Tech, 2008. 198 p.