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МЕТНОВООСУ OF STATICS AND DYNAMICS MODELING OF SINGLE-CHARGED IONS EXCHANGE IN WATER TREATMENT МЕТОДОЛОГИЯ МОДЕЛИРОВАНИЯ СТАТИКИ И ДИНАМИКИ ОБМЕНА ОДНОЗАРЯДНЫХ ИОНОВ 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 for the exchange of singly charged ions in statics and dynamics conditions are designed and methods of their solution in MathCAD are proposed. Convex isotherms of ion exchange lead to «breakage front» of concentrations (their rapid decrease) distinctly visible at 2D and 3D figures. The proposed model 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, ion charge, 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 однозарядных ионов в статических и динамических условиях и предложены методы их решения в пакете MathCAD. Выпуклые изотермы ионного обмена приводят к «обрывному фронту» концентраций (их быстрому уменьшению), отчетливо видимому на 2D и 3D рисунках. 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, заряд иона, математическая модель, динамика равновесного обмена.

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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. This article is an example of mastering complex ion-exchange calculations in MathCAD. Ion exchange is one of the typical processes of water purification and one of perspective sorption methods. It is carried out by the usage of ion exchange materials. The problem of calculation of filter is conditionally divided on the task of describing static (equilibrium) and the modeling of dynamic of ion exchange, including charges of ions that are capable to exchange. Isotherms of ion exchange determine the movement of ions that are absorbed and are part of the mathematic model of ion-exchange filters – the main technological equipment of heat and atomic electric stations. The stage of the work cycle of the ion-exchange filter is carried out at convex isotherm. Ion exchange at convex isotherm allows increasing the concentration in ion exchanger in comparison with their concentration in solution. Regeneration is realized at concave isotherm. The dynamic model must include the fact that at passing of solution through the filter, different concentration points will move with different rates. Depending on the kind of isotherm – convex or concave – «breakage» or «blurred» concentration front can be observed, respectively.

The goal was to design the mathematic model of static and dynamic of ion exchange for single charge-ions. For reaching this goal 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 single-charged ions.

Ion exchange equilibrium. Ion exchange is a reverse process. The equilibrium is established according to the law of mass action. Rates of direct

and reverse reactions for the reaction of single-charged or same-charged ions $\overline{A} + B \leftrightarrow \overline{B} + A$ (for example, RH + Na⁺ = RNa + H⁺) are equal at equilibrium:

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

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:

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

A solution of the equation (2) relatively Q_B is:

$$Q_{B} = \frac{k_{1} \cdot C_{B}}{k_{2} \cdot (1 - C_{B}) + k_{1} \cdot C_{B}}.$$
(3)

Division of numerator and denominator on k₂ gives:

$$Q_B = \frac{k \cdot C_B}{1 + (k-1) \cdot C_B} \tag{4}$$

where $k=k_1/k_2$ – equilibrium constant. The equation (4) is known as the exchange adsorption equation. At k>>1 it is turned into the equation of convex isotherm of Langmuir:

$$Q_B = \frac{k \cdot C_B}{1 + k \cdot C_B} \tag{5}$$

and at $k \le 1$ – into the equation of concave isotherm:

$$Q_B = \frac{k \cdot C_B}{1 - C_B} \tag{6}$$

The equation k = 1 gives linear isotherm:

$$Q_B = C_B \tag{7}$$

Provided that (1), by the equation:

$$k_1 \cdot Q_A (1 - C_A) = k_2 \cdot (1 - Q_A) \cdot C_A$$

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the equation for component A $(k=k_1/k_2)$ can be taken:

$$Q_A = \frac{C_A}{k + C_A \cdot (1 - C_A)}.$$

The equation, similar to (4), for component A is taken $k^*=k_2/k_1$:

$$Q_A = \frac{k \cdot C_A}{1 + (k \cdot -1) \cdot C_A}.$$
(8)

Equations (4) and (8) are similar and different by equilibrium constants. The case of an exchange of single-valence ions, describing by equations (4), (5) and (8), is the most common form its analysis and attention in the scientific literature [1-4].

Dynamic of ion exchange. The dynamic (sorption at the relative and direct movement of phases) of ion exchange can be described by the model of the dynamic of equilibrium isotherm adsorption [1, 3], including that ion exchange and adsorption are similar. 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 mathematic model of filter operation, working at equilibrium conditions, is a system of equations, consisting of the equation of material balance and static of equilibrium. The equation (4) is used in case of an exchange of single-charged ions, and the equation of material balance in dimensionless form is:

$$\frac{\partial C(Z,t)}{\partial t} + V_{wave}(C)\frac{\partial C(Z,t)}{\partial Z} = 0.$$
(9)

Calculation of wave speed V_{wave} is carried out by the following equation (the first derivative form eq. (4) is included):

$$Vwave(Z,k) = \frac{rat}{\frac{k}{\left[1+C(Z)\cdot(k-1)\right]^2} + p \cdot rat}.$$
(10)

In equations (9) and (10): p – volume fraction of water (porosity of ionite); Z – independent variable – coordinate in dimensionless form Z=z/L; independent variable – time in dimensionless form $t = \tau w/L$; z – the direction of axis of filter; L – height of the layer of ionite; w – rate of movement of solution in free cross-section of the filter; τ – time of filter operation in inter-regeneration filter; rat – dimensionless distribution correlation: $Rat = \frac{c_0}{q_0}$.

The equation (9) (the mathematic model of ionite filter is reduced to it) is a quasi-linear homogeneous equation in partial derivatives of hyperbolic types. Its solution by the method of characteristics in MathCAD for the exchange of single-charged ions is given in [3].

According to assumptions, made above, the process of the dynamic of exchange is described only by the system of two equations, and the mathematic model of filter operation contains the differential equation (9) and equation of isotherm of ion exchange (3). Limit conditions of the system will be the following:

the concentration of ion B in solution before contact with layer $c(0, c) = c_0$;

the concentration of ion \overline{B} in ionite before exchange q(z, 0) = 0.

The first equation points out, that solution with constant concentration c_0 is over the layer of ionite z = 0 at any moment of time τ . The second one – that at an initial period time ($\tau = 0$) on an altitude of the layer of ionite z absorbable ion *B* is absent.

A common model of the dynamic of ion exchange in a non-movement layer is a model of the frontal working out of the ionized layer. The concentration of a component inflow is extremely increased at the passing of the «frontal» layer at an initial period time. The concentration of an ion in the «frontal» layer reaches equilibrium amount and it isn't changed during the process, thanks to the continuous raising of substance with the flow. The operation time of the layer till saturation of the «frontal» area is called the period of formation of the exchange front. The second period is begun then. The constant form of the initial curve is observed for it. The front of concentration is moved with a constant linear rate *w* along with the layer. This is evidenced by the stationary mode of the process. The «working layer» is existed as a zone of a mass movement. The concentration is decreased inflow from initial to practically zero: at Z=0 Z=0 $C=C_0=1$ and Q=0, at Z =1 $C\approx 0$.

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

$$C(Z) = C_0 \cdot exp(-5 \cdot Z) = exp(-5 \cdot Z), \qquad (11)$$

where $C_0 = 1$.

Calculations. The solution of the equation (4), (9), (10) and (11) in MathCAD [3] had been used by us. The initial data were the following:

The porosity of ionite: p=0,6; the concentration of ion B in water, g-eq./m³, $c_0=6$; total exchange capacity of cationite, g-eq./m³, $q_0=2000$; 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 $\tau = 20$ h;

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 = $c_0/q_0 = 6/2000 = 0,003$. Change of dimensionless concentration (matrix): c:=0,0.01..1

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

1 $C(Z) := e^{-(5 \cdot Z)^2}$ $\underbrace{ \underbrace{ \texttt{Wave}(Z,k) \coloneqq}_{k} \coloneqq \frac{\texttt{Rat}}{ \frac{k}{\left[1 + C(Z) \cdot (k-1)\right]^2} + (p \cdot \texttt{Rat}) }$ $Z1(t,Z) := Z + t \cdot V wave(Z,k1)$ $Z2(t,Z) := Z + t \cdot V wave(Z,k2)$ 2 Zmin := 0Zmax := 1Ni := 40 Nj := 80 tmin := 0 tmax := 80 $i:=0 \, . \, Ni \qquad \quad j:=0 \, . \, Nj$ $Z_{\text{Min}} \coloneqq Z \min + (Z \max - Z \min) \cdot \frac{1}{M}$ $t_j := tmin + (tmax - tmin) \cdot \frac{j}{N_i}$ $3 \quad \underbrace{Z1}_{\mathbf{X}_{i},j} := Z1(\mathbf{t}_{j}, Z_{i}) \qquad \qquad \underbrace{T}_{\mathbf{X}_{i},j} := \frac{\mathbf{t}_{j}}{\mathbf{tmax}} \qquad \qquad \underbrace{C}_{\mathbf{X}_{i},j} := C(Z_{i})$ $Z_{i,j} := Z_{i,j} Z_{i,j}$

Fig. 1. Fragment of the program in MathCAD 13

Double- and triple-dimension (spatial-temporal) dependences of concentrations of single-charged (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 single-charged ions (the most applicable value). The front of such hypothetic form, when the concentration of ions in solution is changed jump-like from $c = c_0 (C=1)$ to $c \approx 0 (C \approx 0)$ (fig. 2).



Fig. 2. Double and triple dimension dependence of the concentration of single-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 - eq. (4)

Conclusions. The equations are derived for isotherms of ion exchange relatively single-charged ions. The principle of determination of an equilibrium constant in Excel and calculations for different initial concentrations of single-charged ion 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.

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