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Dynamic linear adsorption with solid adsorbent material

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A mathematical problem of linear physical adsorption of a dissolved impurity is formulated, by consider-ing its diffusion transfer during the filtration of an aqueous suspension through a uniform adsorbent bed at a constant rate. By averaging the impurity concentrations in the free and bound states over an arbi-trary time period, an approximate solution of the problem is obtained, which is only expressed in terms of the elementary functions. On its basis, it is proposed to calculate the rational duration of the filter run. The solution is discussed and illustrated with a number of examples with typical input data.

Keywords: *physical adsorption, filtration, adsorbent, suspension, filter, approximate solution*

Adsorption devices are widely used in chemical technologies and, in particular, when removing the dissolved contaminants from waste and natural waters. Therefore, the extensive literature is devoted to the study of the adsorption process under static and dynamic conditions, including numerous books (e. g. [1, 2]). Naturally, one has to limit oneself to only mentioning small number of papers directly related to this development. Additionally, the formulations and solutions of some basic problems of adsorption are presented, for example, in [3-6]. For the practical imp-lementation of the results of theoretical studies, the reliable initial information is required. The potential and current absorption capacities of many adsorbents have been studied in detail by experimental methods [7-11]. Just based on the published empirical data on isotherms and ki-netics of adsorption, the dynamic adsorption is modeled using analytical methods below.

It is assumed that a weakly concentrated aqueous solution is filtered at a constant rate V (downward filtration) through a uniform layer of grains with a height L. The kinetics of rever-sible adsorption is linear, and mechanisms of mass transfer are comparable in importance. Then, taking the diffusion transfer into account, the dynamics of an impurity in the free (C) and bound (S) states is described by the following system of linear equations:

$$D_l \frac{\partial^2 C}{\partial z^2} - V \frac{\partial C}{\partial z} + n_0 \frac{\partial C}{\partial t} + \rho_s \frac{\partial S}{\partial t} = 0, \qquad (1)$$

$$\frac{\partial S}{\partial t} = \lambda_s (K_{ad} C - S).$$ (2)

The following boundary and initial conditions are joined to system (1), (2)

$$z = 0, \quad C = C_0; \quad z = L, \quad \frac{\partial C}{\partial z} = 0;$$ (3)

$$t = 0, \quad S = C = 0.$$ (4)

Here, D_l is the (effective) diffusion coefficient, n_0 is the porosity of the adsorbent layer, ρ_s is the bulk density, λ_s is the rate coefficient of the impurity adsorption, K_{ad} is the adsorption coefficient.

As a result of the dimensionless representation, the mathematical model (1)-(4) takes the form

$$\frac{1}{Pe} \frac{\partial^2 \bar{C}}{\partial \bar{z}^2} - \frac{\partial \bar{C}}{\partial \bar{z}} - \frac{\partial \bar{C}}{\partial \bar{t}} - \frac{\partial \bar{S}}{\partial \bar{t}} = 0,$$ (5)

$$\frac{\partial \bar{S}}{\partial \bar{t}} = \bar{\lambda}_s (\bar{K}_{ad} \bar{C} - \bar{S});$$ (6)

$$\bar{z} = 0, \quad \bar{C} = 1; \quad \bar{z} = 1, \quad \frac{\partial \bar{C}}{\partial \bar{z}} = 0;$$ (7)

$$\bar{t} = 0, \quad \bar{S} = \bar{C} = 0.$$ (8)

where $\bar{C} = C/C_0$, $\bar{S} = \rho_s S/C_0$, $\bar{t} = Vt/(n_0 L)$, $\bar{z} = z/L$, $Pe = VL/D_e$, $\bar{\lambda}_s = n_0 L \lambda_s / V$, $\bar{K}_{ad} = \rho_s K_{ad}$.

When deriving the approximate dependences for the concentrations being calculated, the following procedure was used for their averaging over the calculation period $[0, T]$

$$\bar{C}_{av}(\bar{z}, T) = \frac{1}{T} \int_0^T \bar{C}(\bar{z}, \bar{t}) d\bar{t}, \quad \bar{S}_{av}(\bar{z}, T) = \frac{1}{T} \int_0^T \bar{S}(\bar{z}, \bar{t}) d\bar{t}.$$ (9)

Previously, it was successfully implemented for the suspension filtration [12].

A rigorous solution to the linear problem (5)-(8) was found by an operational method in the form of an improper integral. In view of the strong oscillation of the integrand at large values of the integration variable, the concentrations $\bar{C}, \bar{S}$ can be calculated over time and by height only by numerical methods, but the well-known software packages for the mathematical analysis are ineffective here [13]. Naturally, the approximate analytical methods are clearly preferable for predictive, technological, and constructive calculations. As a result of the application of an averaging operation in accordance with (5) to the kinetic equation (7) the following relations between $\bar{C}_{av}$ and $\bar{S}_{av}$ were found:

$$\bar{S}_{av}(\bar{z}, T) = \frac{\bar{\lambda}_s \bar{K}_{ad} T}{2 + \bar{\lambda}_s T} \bar{C}_{av}(\bar{z}, T), \qquad \bar{C}_{av}(\bar{z}, T) = \frac{2 + \bar{\lambda}_s T}{\bar{\lambda}_s \bar{K}_{ad} T} \bar{S}_{av}(\bar{z}, T).$$ (10)

At the high adsorption capacity of an adsorbent and the prolonged filtration, as well as in the problems of the clarification of suspensions, the value $\partial C / \partial t$ is called small in comparison with $\partial S / \partial t$ and is not considered in what follows. By averaging all the terms in Eq. (6) and taking (10) into account, the following equation is derived for $\bar{C}_{av}$

$$\frac{1}{Pe}\frac{d^2\overline{C}_{av}}{d\overline{z}^2} - \frac{d\overline{C}_{av}}{d\overline{z}} - \frac{2\overline{\lambda}_s\overline{K}_{ad}}{2+\overline{\lambda}_sT}\overline{C}_{av} = 0. \tag{11}$$

The corresponding boundary conditions follow from (8), namely,

$$\overline{t} = 0, \quad \overline{C}_{av} = 1; \qquad \overline{z} = 1, \quad \frac{d\overline{C}_{av}}{d\overline{z}} = 0. \tag{12}$$

Then the average concentration $\overline{C}_{av}$ changes over the bed height by the end of the calculation period as follows

$$\overline{C}_{av}(\overline{z}, T) = \frac{\delta_2(T)e^{-\delta_1(T)(1-\overline{z})} - \delta_1(T)e^{-\delta_2(T)(1-\overline{z})}}{\delta_2(T)e^{-\delta_1(T)} - \delta_1(T)e^{-\delta_2(T)}}, \tag{13}$$

where $\delta_{1,2}(T) = \dfrac{Pe}{2}\left[1 \pm \sqrt{1 + \dfrac{8\overline{\lambda}_s\overline{K}_{ad}}{Pe(2+\overline{\lambda}_sT)}}\right]$. For the simplification of calculations at large values

Pe, it is expedient to transform the formula (13) to the form

$$\overline{C}_{av}(\overline{z}, \mathrm{T}) = \frac{[1-\delta(T)]e^{-Pe\delta(\overline{t})}e^{\frac{Pe\overline{z}}{2}[1+\delta(\overline{t})]} - [1+\delta(T)]e^{\frac{Pe\overline{z}}{2}[1-\delta(\overline{t})]}}{[1-\delta(\overline{t})]e^{-Pe\delta(\overline{t})} - 1 - \delta(\overline{t})}, \tag{14}$$

where $\delta(T) = \sqrt{1 + \dfrac{8\overline{\lambda}_s\overline{K}_{ad}}{Pe(2+\overline{\lambda}_sT)}}$. On the basis of representation (13) or (14), the characteristic $\overline{C}_e$

(equal to $\overline{C}(1, \overline{t})$) as a key for the technological and construction analyses can be calculated in two ways. A simple and, nevertheless, rather reliable method is based on the fact of an almost linear increase in the impurity content in the filtrate. It has been repeatedly confirmed by the results of experimental and theoretical studies of the filtration of aqueous suspensions and solutions. Thus, it is easy to derive the dependence $\overline{C}_e(\overline{t})$, that is convenient for engineering calculations and takes the following form for an arbitrary relative duration of the calculation period $\overline{t}$

$$\overline{C}_e(\overline{t}) \approx \frac{4\delta(\overline{t})e^{\frac{Pe}{2}[1+\delta(\overline{t})]}}{[1+\delta(\overline{t})]e^{Pe\,\delta(\overline{t})} + \delta(\overline{t}) - 1}. \tag{15}$$

Certainly, it is more reliable to calculate the filtration characteristics (first of all, $\overline{C}_e$) on the basis of a solution of the problem with respect to the function $\overline{C}(\overline{z}, \overline{t})$. This problem is based on Eq. (6), which is substituted with the approximate expression for the function

$$\overline{S}(\overline{z}, \overline{t}) = \frac{\overline{\lambda}_s\overline{K}_{ad}\overline{t}}{2+\overline{\lambda}_s\overline{t}}\overline{C}_{av}(\overline{z}, \overline{t}). \tag{16}$$

Expression (16) was obtained by applying again the averaging procedure to Eq. (7). Then the basic equation takes the form

$$\frac{1}{Pe}\frac{\partial^2\overline{C}}{\partial\overline{z}^2} - \frac{\partial\overline{C}}{d\overline{z}} - \overline{\lambda}_s\overline{K}_{ad}\overline{C} = -\frac{\overline{\lambda}_s^2\overline{K}_{ad}\overline{t}}{2+\overline{\lambda}_s\overline{t}}\overline{C}_{av}(\overline{z}, \overline{t}), \tag{17}$$

being solved under the boundary conditions (8). After cumbersome calculations, the representation for the concentration under study is obtained in the integral form

$$\overline{C}(\overline{z},\overline{t}) = \frac{\delta_4 e^{\delta_4+\delta_3\overline{z}} - \delta_3 e^{\delta_3+\delta_4\overline{z}}}{\delta_4 e^{\delta_4} - \delta_3 e^{\delta_3}} - \psi_d(\overline{t})\left\{\frac{e^{\delta_3\overline{z}} - e^{\delta_4\overline{z}}}{\delta_4 e^{\delta_4} - \delta_3 e^{\delta_3}}\int_0^1 [\delta_4 e^{\delta_4(1-\eta)} - \right.$$

$$\left. -\delta_3(\overline{t}) e^{\delta_3(1-\eta)}]\overline{C}_{av}(\eta,\overline{t})d\eta + \int_0^{\overline{z}} [e^{\delta_4(\overline{z}-\eta)} - e^{\delta_3(\overline{z}-\eta)}]\overline{C}_{av}(\eta,\overline{t})d\eta. \right. \tag{18}$$

Thus, the relative content of the dissolved substance at the filter exit increases with time in accordance with the following relation:

$$\overline{C}_e(\overline{t})\frac{\delta_4 - \delta_3}{\delta_4 e^{-\delta_3} - \delta_3 e^{-\delta_4}}\{1 - \psi_d(\overline{t})\int_0^1 [e^{-\delta_4\eta} - e^{-\delta_3\eta}]\overline{C}_{av}(\eta,t)d\eta\}. \tag{19}$$

Here, $\delta_{3,4} = \dfrac{Pe}{2}\left(1 \pm \sqrt{1 + \dfrac{4\overline{\lambda}_s\overline{K}_{ad}}{Pe}}\right)$, $\psi_d(\overline{t}) = \dfrac{2\overline{\lambda}_s^2\overline{K}_{ad}Pe\overline{t}}{(2 + \overline{\lambda}_s\overline{t})\sqrt{Pe^2 + 4\overline{\lambda}_s\overline{K}_{ad}Pe}}$. To exclude the integrals

in formulae (18), (19), they must be substituted with expression (13) and integrated within specified limits. Then the basic calculation formula relative to $\overline{C}_e$ taces a more complicated form, but contains only elementary functions, namely,

$$\overline{C}_e(\overline{t}) = \frac{\delta_4 - \delta_3}{\delta_4 e^{-\delta_3} - \delta_3 e^{-\delta_4}}\left\{1 + \frac{\psi_d(\overline{t})}{\delta_2(\overline{t})e^{-\delta_1(\overline{t})} - \delta_1(\overline{t})e^{-\delta_2(\overline{t})}}\left[\left(\frac{\delta_2(\overline{t})}{\delta_1(\overline{t}) - \delta_4} - \frac{\delta_1(\overline{t})}{\delta_2(\overline{t}) - \delta_4}\right)e^{-\delta_4} - \right.\right.$$

$$\left.\left. -\left(\frac{\delta_2(\overline{t})}{\delta_1(\overline{t}) - \delta_3} - \frac{\delta_1(\overline{t})}{\delta_2(\overline{t}) - \delta_3}\right)e^{-\delta_3} - \frac{\delta_2(\overline{t})(\delta_4 - \delta_3)}{[\delta_1(\overline{t}) - \delta_4][\delta_1(\overline{t}) - \delta_3]}e^{-\delta_1(\overline{t})} + \frac{\delta_1(\overline{t})(\delta_4 - \delta_3)}{[\delta_2(\overline{t}) - \delta_4][\delta_2(\overline{t}) - \delta_3]}e^{-\delta_2(\overline{t})}\right]\right\}. \tag{20}$$

It follows from (18) that, immediately after the contamination front passage through the adsorbent layer, the profile $\overline{C}^0(z)$ will be formed inside. Therefore, it can be interpreted as the initial profile for the subsequent calculations of the technological process,

$$\overline{C}^0(\overline{z}) = \frac{\delta_4 e^{-\delta_3(1-\overline{z})} - \delta_3 e^{-\delta_4(1-\overline{z})}}{\delta_4 e^{-\delta_3} - \delta_3 e^{-\delta_4}} . \tag{21}$$

The formulae represented above to calculate the relative concentration of the adsorptive within the adsorbent bed actually generalize the effective formula [12]. This formula is justified in the case of significant adsorptive diffusion transfer and formally derived at $\overline{S}^0 = 0$ from (18) by a limiting transfer $\overline{t} \to \infty$.
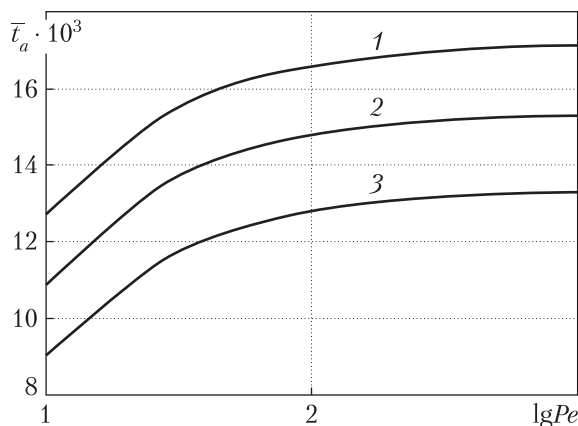
The main purpose of technological calculations in relation to adsorption filters is to establish the duration of the operation period (filter run) t_a, during which the outlet impurity concentration C_e will not exceed the maximum permissible value C_* [14, 15]. The relative value
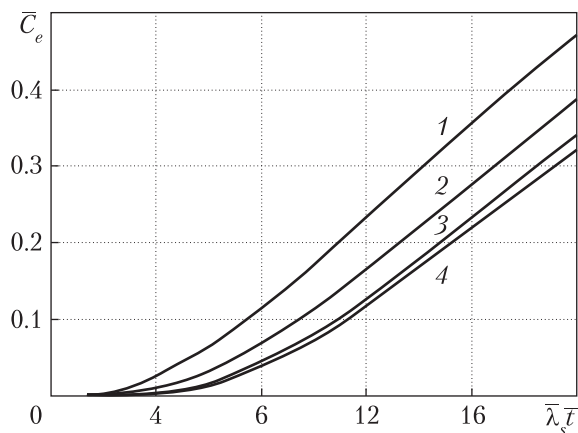
Fig. 1. An increase in the relative concentration of the adsorptive in the filtrate in time: $1 - Pe = 10$; $2 - Pe = 25$; $3 - Pe = 100$; $4 - Pe \to \infty$
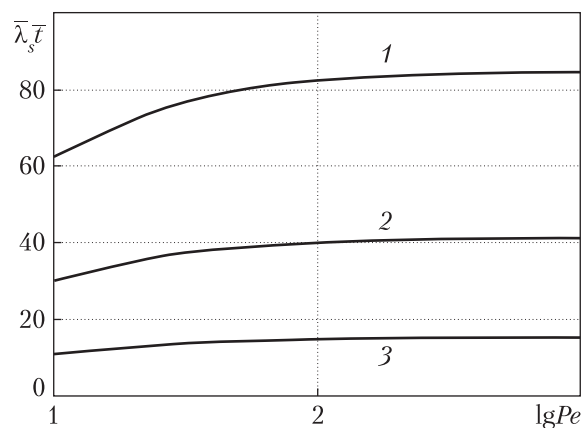
Fig. 2. Dependence $\bar{\lambda}_s \bar{t}_a(\lg Pe)$: $1 - \bar{K}_{ad} = 10^4$; $2 - \bar{K}_{ad} = 5 \cdot 10^3$; $3 - \bar{K}_{ad} = 2 \cdot 10^3$

Fig. 3. Dependence $\bar{t}_a(\lg Pe)$: $1 - \bar{\lambda}_s = 0.01$; $2 - \bar{\lambda}_s = 0.001$; $3 - \bar{\lambda}_s = 0.0005$

$\bar{t}_a$ is recommended to determine on the basis of the more compact formula (19). Then, it is necessary to satisfy the equation (by a simple scanning of values $\bar{t}_a$)

$$\psi_d(\bar{t}_a) \int\limits_0^1 (e^{-\delta_4 \eta} - e^{-\delta_3 \eta}) \bar{C}_{av}(\eta, \bar{t}_a) d\eta =$$

$$= 1 - \frac{\delta_4 e^{-\delta_3} - \delta_3 e^{-\delta_4}}{\delta_4 - \delta_3} \bar{C}_*. \tag{22}$$

The above expressions for the relative concentration of the adsorptive in the adsorbent bed are illustrated by examples of calculating its output value $\bar{C}_e(\bar{t})$ and the technological time $\bar{t}_a$. At the same time, the attention was focused on the importance of the diffusion transfer of a dissolved impurity for the operation of adsorption filters and the Peclet number for the calculation characteristics. The input data varied widely to cover both normal and extreme process conditions.

First of all, the dynamics of contamination in the filtrate was determined using formulae (15) and (20) in order to assess the suitability of the simpler first formula for predicting the quality of the adsorption water treatment. Pre-recorded values $\bar{\lambda}_s$ (0.001 *or* 0.01), $\bar{K}_{ad}$ ($2 \cdot 10^4$). A set of the $\bar{C}_e(\bar{\lambda}_s \bar{t})$ curves corresponding to four values Pe is shown in Fig.1. The reference curve for identifying the role of the above-mentioned mass transfer mechanism in the removal of the substance is the limiting curve 4 calculated at $Pe \to \infty$. The results of calculating $\bar{C}_e$ using the two indicated formulae turned out to be so close that the corresponding pairs of curves for all accepted values Pe practically are merged together. The noted fact testifies to the legitimacy of accepting the hypothesis about the linear nature of the increase in the contamination

content in the filtrate and, which is more important, about the actual equivalence of both calculation formulae.

The results of three series of calculation of the technological time $\bar{t}_a$ allow us to get a more complete understanding of the impact of physical and chemical properties of the adsorbent and adsorptive on the performance of the adsorption filter. First of all, the parameter Pe was changed continuously by two orders of magnitude or more. The values of $\bar{t}_a$ were calculated by making adjustment on the basis of Eq. (22) with a single value of $\bar{C}_*$ (0.2), and the values of the parameters $\bar{K}_{ad}, \bar{\lambda}_s$ were either fixed in turn (respectively, 10^4, 0.01, and 0.001) or discretely changed. Differences in the position and shapes of the calculated curves are due to different absorption capacities (Fig. 2) and the kinetics of mass transfer (Fig. 3). With the maximum possible enhancement of the diffusion transfer according to the accepted initial data, which is formally expressed in a decrease of Pe to 10, the estimated time was reduced by 25 ... 33 %. If we restrict ourselves to the values of Pe, which are characteristic of the adsorption filters, then the analogous changes were half as much. Thus, the cost of water treatment can increase significantly. In addition, a high sensitivity of $\bar{t}_a$ to $\bar{\lambda}_s$ and especially to $\bar{K}_{ad}$ follows from Fig. 2 and 3. Thus, a reduction in the second coefficient by 5 leads to almost the same reduction in the time of calculations. At the same time, with a 2-fold $\bar{\lambda}_s$ change, $\bar{t}_a$ changed by about 15%.

To summarize, first of all, we note the application efficiency and the simplicity of the developed technique for calculating the dynamic linear adsorption. Bearing in mind the subsequent analytical studies of nonlinear dynamic adsorption, the reality and justification of a significant simplification of the modeling and calculations should be emphasized. Indeed, if we rely on models with respect to the averaged characteristics, being studied, then the additional calculation errors will be negligible.

REFERENCES

1. Koganovsky, A. M., Klimenko, N. A. & Levchenko, T. M. (1990). Adsorption of organic substances from water. Leningrad : Himiya (in Russian).
2. Zapolsky, A. K., Mishkova-Klimenko, N. A., Astrelin, I. M., Brik, M. G., Gvozdyak, P. I. & Knyazkova, T. V. (2000). Physico-chemical foundations of water treatment technology. Kyiv: Libra (in Ukrainian).
3. Poliakov, V. L. (2012). Modeling of water treatment in adsorber medium. Dopov. Nac. akad. nauk Ukr., No. 5, pp. 63-71 (in Russian).
4. Chaudhary, D. S., Vigneswaran, S., Jegatheesan, V., Ngo, H. H., Moon, H., Shim, V. G. & Kim, S. H. (2002). Granular activated carbon (GAC) adsorption in tertiary wastewater treatment: experiments and models. Water Sci. Tech., 47, No. 1, pp. 113-120.
5. Crittenden, J. C., Hutzler, N. J., Geyer, D. G., Oravitz, J. L. & Friedman, G. (1986). Transport of organic compounds with saturated groundwater flow: model development and parameter sensitivity. Water Resour. Res., 22, pp.271-284.
6. Sorial, G. A., Suidan, M. T., Vidic, R. D. & Maloney, S. W. (1993). Competitive adsorption of phenols on GAC. I. Adsorption equilibrium. J. Environ. Eng., 119, pp. 1026-1043.
7. Khan, A. R., Al-Bahri, T. A. & Al-Haddad, A. (1997). Adsorption of phenol based organic pollutants on activated carbon from multi-component dilute aqueous solutions. Water Res., 31, No. 8, pp. 2102-2112.
8. Ko, D. C. K., Porter, J. F. & McKay, G. (2001). Film-pore diffusion model for the fixed-bed sorption of copper and cadmium ions onto bone char. Water Res., 35, pp. 3876-3886.
9. Meshko, V., Markovska, L., Mincheva, M. & Rodrigues, A. E. (2001). Adsorption of basic dyes on granular activated carbon and natural zeolite. Water Res., 14, pp. 3357-3366.
10. Mollah, A. H. & Robinson, C. W. (1996). Pentachlorophenol adsorption and desorption characteristics of granular activated carbon. Water Res., 30(12), I. Isotherms, pp. 2901-2906, II. Kinetics, pp. 2907-2913.

11. Sotelo, J. L., Ovejero, G., Delgado, J. A. & Martinez, I. (2002). Comparison of adsorption equilibrium and kinetics of four chlorinated organics from water onto GAC. Water Res., 36, pp. 599-608.

12. Poliakov, V. L. (2011). Engineering calculation of suspension filtration through two-layer filter medium at linear kinetics of mass-exchange. J. Water Chemistry and Technology, 33, No. 4, pp. 367-380 (in Russian).

13. Lindstrom, F. T. & Boersma, L. (1973). A theory of the mass transport of previously distributed chemicals in a water-saturated sorbing porous medium: III. Exact solution for first-order kinetic sorption. Soil Science., 115, No. 1, pp. 5-10.

14. Imboden, D. M. (1993). Environmental organic chemistry. New-York: Wiley Interscience.

15. Walker, G. M. & Weatherley, L. R. (1997). Adsorption of acid dyes on to granular activated carbon in fixed beds. Water Res., 31, No. 8, pp. 2093-2101.

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ДИНАМІЧНА ЛІНІЙНА АДСОРБЦІЯ
ПРИ АДСОРБЕНТІ ІЗ СУЦІЛЬНОГО МАТЕРІАЛУ

Сформульовано математичну задачу лінійної фізичної адсорбції розчиненого домішку з урахуванням його дифузійного переносу разом з фільтрацією водної суспензії через однорідний шар адсорбенту з постійною швидкістю. Завдяки осередненню концентрацій домішків у вільному і фіксованому зв'язаному станах протягом довільного періоду часу одержано наближений розв'язок задачі, який виражається тільки через елементарні функції. На його основі пропонується розраховувати раціональну тривалість фільтроциклу. Розв'язок обговорюється і ілюструється рядом прикладів з типовими вихідними даними.

Ключові слова: *фізична адсорбція, фільтрування, адсорбент, суспензія, фільтр, наближений розв'язок.*