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MODEL OF BIOLOGICALLY ACTIVE FILTER WITH GRANULAR ACTIVATED CARBON IN WATER TREATMENT SYSTEM

A mathematical model of phenomena occurring in the water treatment system in biologically active bed consisting of granular activated carbon has been presented. The model is designed to simulate activated carbon column as the series of batch reactors. Adsorption process in each reactor has been described by the equation of the concentration field in the internal structure of the adsorbent taking into consideration the fact that the mass transfer process is limited by external diffusion as well as pore and surface diffusion, the mass balance equation in the whole system and isotherm equation of the Langmuir type.

Kinetic and diffusion parameters of the model for the multicomponent solution have been determined analytically using empirically estimated equivalent molecular weight, which in average way characterizes the adsorption quality of the system.

The next parameter of the model, which is determined empirically, is part of biodegradable compounds in whole mass of adsorbable compounds.

The principal assumption of the model is that particles, which are biodegradable in biofilm, have to be adsorbed first. This condition is not essential for the process description because the efficiency of adsorbate oxidation in biofilm does not depend on the direction of substrate inflow.

The model was verified by the comparison of simulated breakthrough curve of adsorption bed with that obtained in direct measurement. Such a verification allows the statement that the model proposed approximates the process consisting in great extent in simultaneous adsorption and biodegradation.

NOTATIONS

b – parameter of adsorption isotherm equation of the Langmuir type,
c_e – adsorbate concentration in effluent from batch reactor (g/m^3),
c_i – internal adsorbate concentration (in carbon pores) (g/m^3),
c_0 – initial adsorbate concentration (g/m^3),
c_p – adsorbate concentration (g/m^3),
D – external diffusion coefficient (m^2/h),
D_p – pore diffusion coefficient (m^2/h),
D_s – surface diffusion coefficient (m^2/h),

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D_e – equivalent diffusion coefficient   (m^2/h),

ρ_c – carbon density   (g/m^3),

ε_g – porosity of carbon grain,

ε – bed porosity,

x – efficiency of adsorption   (g/kg),

x_m – quantity adsorbed in the monolayer   (g/kg),

$x_0 = f(c_0)$ – maximal efficiency of adsorption   (g/kg),

t – contact time   (h),

t_r – time of batch reactor operation   (h),

t_e – time of carbon column exhaustion   (h),

t_b – time of carbon column breakthrough   (h),

d – diameter of carbon grain   (m),

d_a – diameter of adsorbate particle   (m),

W – amount of carbon   (kg),

V – volume of solution   (m^3),

k_e – coefficient of external mass transfer   (m/h),

L – direction of diffusion,

Sh – Sherwood number,

Fo – Fourier number,

N – Avogadro number   ($6.024 \cdot 10^{23}$),

γ – parameter of concentration field equation in solution,

F – cross-section of carbon bed   (m^2),

z – adsorption zone   (m),

H – depth of activated carbon bed   (m),

U_f – rate of filtration   (m/h),

η – viscosity of water   (Pa·s),

K – Boltzman constant   ($1.38 \cdot 10^{-16}$ erg/K),

T – temperature   (K),

ρ_a – adsorbate density   (g/m^3),

M_e – equivalent molecular weight   (g/mol),

γ_e – parameter of equivalent molecular weight equation,

δ_e – parameter of equivalent molecular weight equation,

$\varkappa$ – part of biodegradable compounds in whole mass of adsorbate compounds.

1. INTRODUCTION

Trends towards development of water treatment technology for drinking purposes are created by the state of water resources which are easy to obtain. In many countries, there are regional deficits of water which could be simply treated. More often the heavily polluted rivers are the only source of water. That is why the investment in water management ought to be directed to water source protection and development of water treatment technologies based on natural processes.

Natural biological processes take place during infiltration which can be treated as a unit process in water treatment systems. Heavily polluted surface water must be treated by adsorption, which is essential in the improvement of water composition. Apart from typical adsorption process on GAC bed, in water treatment system one can observe concomitant processes. These processes are the result of both biological

activity which is generated spontaneously and chemical reactions between carbon and free chlorine, chloramine, chlorine dioxide as well as other oxidants like oxygen and potassium permanganate present in water to be treated [1]–[4].

Adsorption of dissolved organic compounds as well as reactions of oxidants with carbon can be described quantitatively and qualitatively, but biological activity of the GAC bed has hitherto been described qualitatively and to some extent only [5], [6]. When full activity of spontaneously generated microbiological process is reached earlier than the breakthrought point of adsorption bed, then biological activity must be taken into consideration in system designing. This phenomenon is always observed in water treatment systems. That is why functions of the BAF–GAC have never been recognized quantitatively and simulated in a proper way.

2. THE MODEL ASSUMPTIONS

Both proper oxygen concentration and temperature in the system allow an intensive reproduction of heterotrophic bacteria after several weeks of carbon bed work. Compounds adsorbed on the surface of activated carbon particles are subject to biodegradation due to activity of these bacteria and in this way carbon is bioregenerated. Bacteria are reproduced in a film layer which is called a biofilm. In the biofilm which is fully active, the state of dynamic equilibrium between the adsorbed mass, oxidized mass with concentration gradient oriented towards the carbon particles, desorbed mass and oxidized mass with gradient oriented towards the bulk solution is obtained [5].

The principle assumption of the model is that all the adsorbate particles, before their biochemical destruction, have to be adsorbed. This fact is not important in the process description, because certain bacteria population reproduced in biofilm is able to oxidize particular mass of organic compounds, and it does not matter from which direction it inflows to the biofilm. The model is valid for the bed porosity higher than 0.5, so it approximates adsorption–biodegradation process in fluidized bed. The product of complete oxidation, carbon dioxide, when releasing in fixed bed can disturb hydrodynamic conditions of flow. In upflow filtration this disturbance is eliminated.

3. THE MODEL DEVELOPMENT

The adsorption column has been arranged in series of batch reactors. The description of adsorption process in single reactor is based on equation of the concentration field of adsorbate the internal structure of adsorbent particles

$$\varepsilon_g \left(\frac{\partial c_i}{\partial t}\right)_L + \rho_c \left(\frac{\partial x}{\partial t}\right)_L = \varepsilon_g D_p \frac{\partial^2 c_i}{\partial L^2} + \rho_c D_s \frac{\partial^2 x}{\partial L^2}. \tag{1}$$

Combining the above equation with the boundary and initial conditions necessary to solve it and the mass balance and adsorption isotherm equations, one obtains the mathematical model for adsorption process in batch reactor. For the system, in which all possible factors limiting the mass transfer, i.e., external, pore and surface diffusions, are essential, the initial and boundary conditions can be defined as follows:

$$t = 0 \quad \text{and} \quad 0 \leqslant L \leqslant \frac{d}{2}; \quad c_i = x = 0, \tag{2}$$

$$t > 0 \quad \text{and} \quad L = 0; \quad c_i = c_0, \tag{3}$$

$$D_e \frac{\partial c_i}{\partial L} = -k_e c_i \quad \text{for} \quad L = \frac{d}{2}. \tag{4}$$

In order to solve the concentration field equation with conditions (2)–(4), it is necessary to assume an equivalent coefficient of diffusion which may be defined as

$$D_e = \varepsilon_g D_p + \rho_c D_c \frac{dx}{dc_i}. \tag{5}$$

Assuming that the equivalent coefficient of diffusion for a system characterized by a nonlinear adsorption isotherm is independent of concentration, one can anticipate that the coefficient of surface diffusion D_s must depend on concentration. The dynamic equilibrium of the system under study is described by the convex adsorption isotherm of the Langmuir type:

$$x = \frac{x_m b c_i}{1 + b c_i}. \tag{6}$$

Making use of the equation defining the coefficient of surface diffusion [7]

$$D_s = f\left(D; \exp\frac{x}{x_0}\right), \tag{7}$$

one can see that as the value of x increases, so does the value of D_s at the decreasing value of the dx/dc_i ratio for a system having a convex adsorption isotherm. Under extreme conditions, when D_s increases and dx/dc_i decreases, their product may take a constant value.

If D_e fails to depend on c_i and x, it may also be independent of the interior of adsorbent particle L and of the duration of the process t. Thus, equation (1) takes the form

$$\varepsilon_g \left(\frac{\partial c_i}{\partial t}\right)_L + \rho_c \left(\frac{\partial x}{\partial t}\right)_L = D_e \frac{\partial^2 c_i}{\partial L^2} \tag{8}$$

and the mass balance is

$$\frac{\Delta c_e}{\Delta t} = -\frac{24 W}{\rho_c \cdot V \cdot d^2} D_e \Delta c_i. \tag{9}$$

The adsorption isotherm was analyzed for four concentration intervals. In each of them the isotherm was a straight line.

Analysis of the adsorption isotherm in the first concentration interval involves the simplified Langmuir equation

$$x = x_m b c_i; \; c_i \in \left(0; \; c_p^{\mathrm{I}} = \frac{c_0}{4 + 3bc_0} \right). \tag{10}$$

In the second interval, we arrive at the following equation of the isotherm:

$$x = \frac{x_m b (2 + bc_0)^2}{4(1 + bc_0)^2} c_i + \frac{x_m b^2 c_0^2}{4(1 + bc_0)^2},$$

$$c_i \in \left(c_p^{\mathrm{I}}; \; c_p^{\mathrm{II}} = \frac{c_0(12 + 13bc_0)}{16 + 24bc_0 + 7b^2 c_0^2} \right). \tag{11}$$

The equation for the third interval takes the form

$$x = \frac{x_m b (4 + bc_0)^2}{(4 + 5bc_0)^2} c_i + \frac{16 x_m b^2 c_0^2}{4 + 5bc_0},$$

$$c_i \in \left(c_p^{\mathrm{II}}; \; c_p^{\mathrm{III}} = \frac{c_0(8 + 9bc_0)}{8 + 10bc_0 + b^2 c_0^2} \right). \tag{12}$$

And the equation for the fourth concentration interval is

$$x = \frac{x_m b}{(1 + bc_0)^2} c_i + \frac{x_m b^2 c_0^2}{(1 + bc_0)^2},$$

$$c_i \in (c_p^{\mathrm{III}}; \; c_0). \tag{13}$$

The solution of the equation of the concentration field (8) has the form

$$c_i(L, t) = c_0 \left\{ 1 - \frac{k_e/D_e}{Sh} L - \frac{2}{\gamma \left(1 - \dfrac{\sin 2\gamma}{2\gamma} \right)} \sin \frac{2\gamma}{d} L \exp(-\gamma^2 \, Fo) \right\} \tag{14}$$

in which the Sherwood number is described as

$$Sh = \frac{k_e \dfrac{d}{2}}{D_e}, \tag{15}$$

the value of γ as:

$$\gamma \, \mathrm{ctg}\, \gamma = -Sh, \tag{16}$$

and the coefficient of external mass transfer for the bed simulated by series of batch reactors is defined by equation

$$k_e = 2D \left\{ d \left[\left(\frac{\varepsilon}{1-\varepsilon} \right)^{1/3} - 1 \right] \right\}^{-1}. \tag{17}$$

The Fourier number described by formula

$$Fo = \frac{D_e \cdot t}{(d/2)^2} \tag{18}$$

changes because of the change of the D_e value in each concentration interval

$$D_e^{I} = \frac{D_e \cdot \rho_c}{\varepsilon_g + \rho_c \cdot x_m \cdot b}, \tag{19}$$

$$D_e^{II} = \frac{4\rho_c \cdot D_e (1 + bc_0)^2}{4\varepsilon_g (1 + bc_0)^2 + \rho_c \cdot x_m b(2 + bc_0)^2}, \tag{20}$$

$$D_e^{III} = \frac{\varepsilon_g \cdot D_e (4 + 5bc_0)^2}{\varepsilon_g (4 + 5bc_0)^2 + \rho_c x_m b(4 + bc_0)^2}, \tag{21}$$

$$D_e^{IV} = \frac{\varepsilon_g D_e (1 + bc_0)^2}{\varepsilon_g (1 + bc_0)^2 + \rho_c x_m b}. \tag{22}$$

The value of equivalent diffusion coefficient can be analytically determined by the formula

$$D_e = D \left(0.5\varepsilon_g^2 + 0.196\rho_c \frac{x_m b}{1 + bc_0} \right). \tag{23}$$

The volume of reactor is the product of the cross-section area of the bed (F) and the adsorption zone depth (Z). So the amount of carbon in the reactor is

$$W = F \cdot z \cdot \rho_c (1 - \varepsilon), \tag{24}$$

and the volume of solution in the reactor

$$V = F \cdot z \cdot \varepsilon. \tag{25}$$

Taking into account equations (24) and (25), the mass balance equation (9) can be simplified

$$c_e = c_0 - \frac{24(1 - \varepsilon)}{\varepsilon \cdot d^2} D_e \cdot c_i \cdot t. \tag{26}$$

The time of batch reactor operation with fully active biofilm and empirically determined part of biodegradable compounds in the whole mass of adsorbate $\varkappa$ is described by:

$$t_r = \frac{z}{v_f} \frac{x_m b c_e (1 - \varepsilon) \rho_c}{(1 + bc_e)(c_0 - c_e)\varepsilon(1 - \varkappa)}. \tag{27}$$

4. DETERMINATION OF THE MODEL PARAMETERS

The kinetic and diffusion parameters in the model were determined as a function of the external diffusion coefficient D. It may be established by use of the Stokes–Einstein formula

$$D = \frac{KT}{3\pi\eta d_a},$$ (28)

provided that the adsorbate particle size (d_a) is known. Unfortunately, there is no possibility to determine the adsorbate particle diameter by a direct method.

Keeping these in mind and taking into account the relation involved in the adsorption process, the notion of the equivalent molecular weight of the adsorbate was derived and determined empirically. The term was used to denote the mass of such a model adsorbate (with concentration measured as TOC) whose sorbing parameters were similar to the adsorption parameters of the analysed mixture displaying initial TOC concentration identical to that of the model solution [8], [9].

The equivalent molecular weight can be expressed in the following form

$$M_e = \left(\gamma_e \frac{x_m}{c_0}\right)^{\delta_e} + 80.$$ (29)

Assuming that the approximation

$$(\rho_a)^{1/3} = \sim 1$$ (30)

is erroneous in a negligibly small degree [10], the average adsorbate particle size may be determined as:

$$d_a = \left(\frac{6M_e}{\pi N}\right)^{1/3},$$ (31)

and finally the external diffusion coefficient can be described by the equation

$$D = 9.97 \cdot 10^{-12} T \left[\left(\gamma_e \frac{x_m}{c_0}\right)^{\delta_e} + 80\right]^{-1/3}.$$ (32)

Therefore the laboratory research, necessary for determination of the model parameters for a defined solution and activated carbon, is limited to the determination of the parameters of the adsorption isotherm equation of the Langmuir type (x_m; b). At the same time, the part of biodegradable compounds (x) in all adsorbable compounds ought to be established.

5. ALGORITHM OF MODEL APPLICATION

The basic data necessary for BAF–GAC operation description are as follows: influent adsorbate concentration measured as TOC (c_0),

parameters of isotherm equation of the Langmuir type $(x_m; b)$,

carbon grain diameter representative of the whole sample (d),

carbon grain porosity (ε_g),

bed porosity (ε),

carbon density (ρ_c),

empirical parameters of the equivalent molecular weight equation $(\gamma_e; \delta_e)$,

part of biodegradable compounds in adsorbable compounds $(\varkappa)$,

acceptable adsorbate concentration in effluent determination (ε_{TOC}).

The next steps are:

assumption of required adsorbate concentration in effluent (c_{en}),

assumption of filtration rate (U_f),

choice of design parameters, i.e., a) bed depth (H) and bed operation time (t_e), b) bed operation time (t_e) and necessary bed depth (H).

Next, the diffusion and kinetic parameters are determined $(D; k_e; D_e$ and $D_e = f(c_p); Sh; \gamma)$; contact time in reactor (t) and step of its change $(\varDelta t)$ are assumed.

For the contact time (t), the Fourier number is determined, provided that the D_e value is changed for each concentration interval

$$Fo = f[D_e = f(c_p)]. \tag{33}$$

The internal adsorbate concentration (c_i) and concentration of effluent from batch reactor (c_e) are determined using equations (14) and (26), respectively.

When the concentration obtained (c_e) is higher than required (c_{en}), it can be assumed that the new value of t is higher than the old one $(t + \varDelta t)$. And *vice versa*. When c_e is smaller than c_{en}, it is necessary to decrease the t value $(t - \varDelta t)$.

Time correction is made until the absolute value of the difference between c_{en} and c_e is smaller than ε_{TOC}. Determination of the value t allows establishing the mass transfer zone (z), i.e., reactor height and reactor operation time (t_r), from the equation (27). Next, having definite bed depth value (H) we can calculate the time of bed operation (t_e) until effluent concentration reaches the c_{en} value

$$t_e = t_r \frac{H}{z}, \tag{34}$$

or the time assumed for regeneration (t_e) of bed height

$$H = \frac{t_e}{t_r} z. \tag{35}$$

In last step of algorithm, the characteristic points of breakthrough curve coordinates are determined:

$$\frac{c_{e1}}{c_0}; t_1 = H v_f^{-1},$$

$$\frac{c_{e_n}}{c_0}; \ t_e,$$

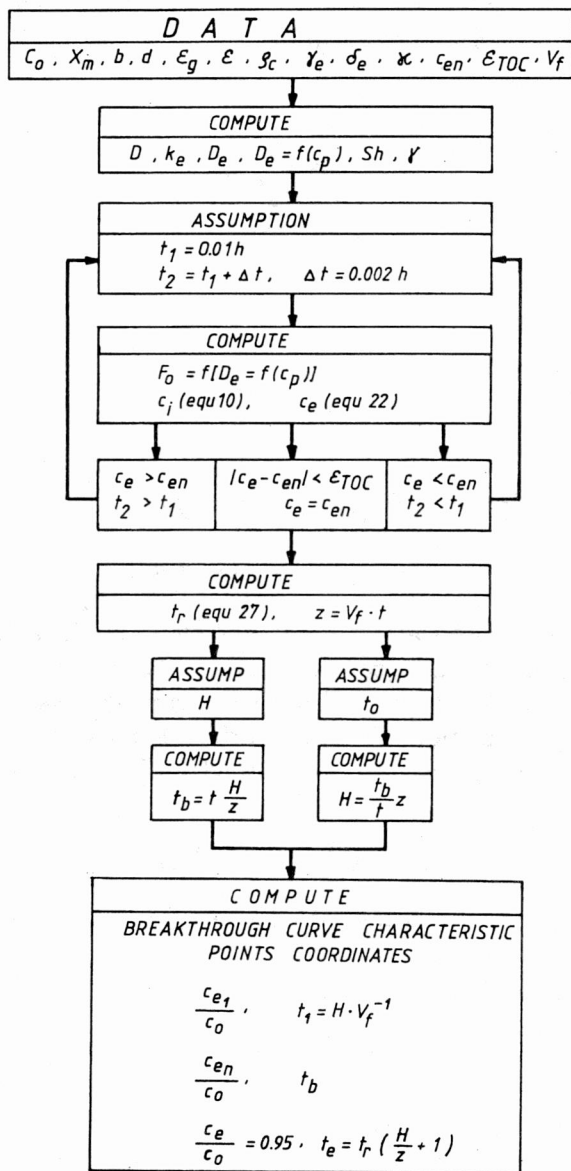$$\frac{c_e}{c_0} = 0.95; \qquad t_e = t_r\left(\frac{H}{z} + 1\right).$$

Fig. 1. Algorithm of BAF–GAC calculation

In figure 1, a block diagram of algorithm for the BAF–GAC calculation when the bed is treated as a series of batch reactors is presented.

6. MODEL VERIFICATION

The BAF–GAC model has been verified for the system whose parameters obtained in laboratory tests are as follows: $x_m = 18$, $b = 0.75$, $\gamma_e = 10$, $\delta_e = 2.65$, $\varkappa = 0.85$, $d = 0.002$, $\varepsilon_g = 0.18$, $\varepsilon = 0.6$ and $T = 288$ K.
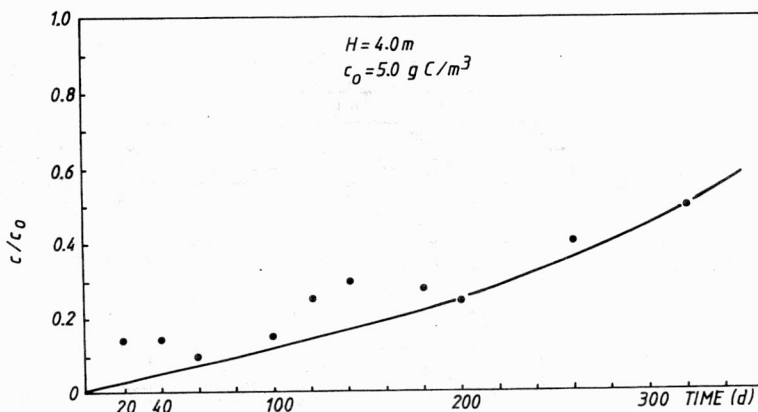

Fig. 2. Breakthrough curve of BAF–GAC

Filtration of the surfare water through one meter GAC bed at the filtration rate of 7.5 m/h was preceded by its coagulation at TOC concentration equal to 5 g of carbon/m^3. The model has been verified by similarity analyses of the breakthrough curves obtained by direct measurement and those simulated by the model (figure 2). The breakthrough point has been established for $c_{e_n}/c_0 = 2/5 = 0.4$.

7. CONCLUSIONS

The model presented describes the adsorption and biodegradation processes which occur simultaneously. Its application, in simple and not time-consuming laboratory tests, requires the determination of the parameters which allow analytical determination of diffusion and kinetic parameters. These parameters in average way characterize the adsorption quality of the multicomponent system.

The part of biodegradable compounds in the whole mass of adsorbable compounds measured as TOC has to be evaluated. The model can be used in fluized activated carbon beds with the porosity higher than 0.5. The model takes into consideration all elementary phenomena in BAF–GAC and enables such a modification of the parameters which guarantees the required final effects.

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MODEL BIOLOGICZNIE AKTYWNEGO ZŁOŻA WĘGLA AKTYWNEGO PRACUJĄCEGO W TECHNOLOGICZNYM UKŁADZIE UZDATNIANIA WODY

Przedstawiono matematyczny model symulacji pracy biologicznie aktywnego złoża węgla aktywnego pracującego w technologicznym układzie oczyszczania wody. Kolumnę modelowano za pomocą serii reaktorów porcjowych. Modelem adsorpcji w każdym reaktorze jest układ równań: pole stężeń w wewnętrznej strukturze węgla przy założeniu, że czynnikami limitującymi process adsorpcji są dyfuzja zewnętrzna, porowa i powierzchniowa; równanie bilansu masy w całym układzie oraz równanie izotermy adsorpcji Langmuira.

Parametry dyfuzyjne i kinetyczne modelu dla roztworu wieloskładnikowego określono, wykorzystując empirycznie wyznaczoną równoważną masę cząsteczkową adsorbatu, która w sposób uśredniony charakteryzuje właściwości adsorpcyjne systemu. Wyznaczono doświadczalnie udział związków ulegających biodegradacji w całej masie adsorbatu (mierzonego poziomem OWO). Model zweryfikowano, porównując przebieg krzywej przebicia symulowanej modelem z krzywą uzyskaną w bezpośrednim pomiarze, co potwierdziło dużą zgodność modelu z rzeczywistością.

МОДЕЛЬ БИОЛОГИЧЕСКИ АКТИВНОГО СЛОЯ АКТИВНОГО УГЛЯ, РАБОТАЮЩЕГО В ТЕХНОЛОГИЧЕСКОЙ СИСТЕМЕ ВОДОПОДГОТОВКИ

Представлена математическая модель имитации работы биологически активного слоя активного угля, работающего в технологической системе водоподготовки. Колонку моделировали при помощи серии порциальных реакторов. Моделью адсорбции в каждом реакторе является система уравнений: поле концентраций во внутренней структуре угля при предположении, что агентами,

лимитирующими процесс адсорбции являются: внешняя диффузия, диффузия в порах и поверх-ностная диффузия; уравнение баланса массы во всей системе, а также уравнение изотермы адсорбции Лангмуара.

Диффузионные и кинетические параметры модели для многокомпонентного раствора опреде-лили, используя эмпирически определенную эквивалентную молекулярную массу адсорбата, которая усредненным способом характеризует адсорбционные свойства системы. Эксперимен-тально определено участие соединений, подвергающихся биодеградации во всей массе адсорбата (измеряемого уровнем ОВО). Модель проверили, сравнивая протекание кривой пробоя, имитируе-мой моделью с кривой, полученной в непосредственном измерении, что подтвердило большое согласование модели с действительностью.