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PHENOMENOLOGICAL MODELLING OF BIODEGRADATION OF MULTICOMPONENT SUBSTRATES

The paper attempts to systematize the mathematical models for processes of biochemical oxidation of organic pollutants in water bodies. Several generalized models have been offered. All models have been relatively divided into three groups: empirical, formal and simulation ones. In fact, all these groups of models are phenomenological.

It is shown that coefficients in the traditional formal models are, as a rule, of imaginary nature likewise the collective variables such as the total organic matter concentration, bacterial biomass etc.

The simplicity of models and the minimum number of their parameters are an important criteria of their feasibility. The paper compares the best of such models and discusses some of their properties common to all of them.

1. INTRODUCTION

The classical STREETER and PHELPS's model [28] describes the biooxidation processes in rivers assuming the monomolecular nature of organic matter decay as measured by an integral index such as the biochemical oxygen demand (BOD). The best known models employed today describe aerobic biological treatment processes in aeration tanks and biological filters by means of the first order equations [6]. The STREETER and PHELPS's supposition that the decay constant is a natural and only temperature-dependent has been proved as incorrect since the oxidation process depends both on the microorganism concentration in water and on the organic pollutant composition.

TISCHLER and ECKENFELDER [31] have shown that the first order of the summary oxidation reaction for the total organic matter may be obtained from overlapping of kinetic oxidation curves for individual components. Some of the recently published papers demonstrate that there can be a better agreement between experimental data on kinetic equations of an order exceeding the first one for the total organic pollutant expressed in such values as BOD, COD and TOC.

On the basis of a thorough analysis of the models and their most noted modifications the present paper asserts that the most adequate models of the processes of biochemical

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oxidation of multicomponent pollutants in somewhat "oblique" way contain time. They are inevitably of phenomenological nature.

2. GROWTH DYNAMICS OF PURE CULTURE OF MICROORGANISMS AND OF SUBSTRATE CONSUMPTION

It is known that in a wide range of cultivation conditions the microorganisms growth rate is proportional to their biomass (X):

$$dX/dt = \mu X, \quad (1)$$

where μ is the specific growth rate.

The μ value can be regarded constant only in case of accelerated growth because, in general, it depends on the concentration of the limiting substrate S , as proposed by MONOD [21]:

$$\mu = \frac{\mu_m S}{K_s + S}, \quad (2)$$

where μ_m is the maximum specific growth rate, K_s is the constant of half-saturation. Monod's formula is similar to the Michaelis-Menten's equation for enzymatic reaction rates.

Simultaneously with an increase in the biomass the substrate concentration changes at a rate

$$dS/dt = -\frac{\mu}{Y} X, \quad (3)$$

where $Y = |dX/dS|$ is the coefficient of substrate transformation into the microorganism biomass.

Let us present (1) to (3) as a system known as Monod's model

$$\begin{aligned} dX/dt &= \frac{\mu_m X S}{K_s + S}, \\ dS/dt &= -\frac{1}{Y} \frac{\mu_m X S}{K_s + S}. \end{aligned} \quad (4)$$

The characteristic values of Monod's model constants are as follows: $\mu_m = 0.1-0.5 \text{ h}^{-1}$, $K_s = 1-30 \text{ mg/dm}^3$, $Y = 0.4-0.6$.

Monod's model is a formal description and, naturally, approximates the genuine enzymatic processes occurring in a cell. On the basis of the respective kinetic equations [34] one can derive Monod's formal model.

TEISSIER's dependence [29] is sometimes employed instead of Monod's formula (2)

$$\mu = \mu_m (1 - e^{-KS}). \quad (5)$$

Some other formulas are also used.

The oxygen demand process occurring during substance oxidation can be described by the following equation:

$$dC/dt = (1-Y) dS/dt, \quad (6)$$

where C is the dissolved oxygen concentration and S is measured in oxygen units.

Assuming Y to be a constant value (in some cases it is not true) the following equation was derived in paper [3]:

$$t = \frac{1}{\mu_m} \left\{ \frac{YK_s}{X_0 + YS_0} \ln \frac{S_0}{S} + \frac{X_0 + Y(S_0 + K_s)}{X_0 + YS_0} \ln \frac{X_0 + Y(S_0 - S)}{X_0} \right\}. \quad (7)$$

In case when $S_0 < K_s$ using (4) one shall obtain

$$dS/dt \approx -\frac{\mu_m}{K_s} S(X_0/Y + S_0 - S) = -aS(b-S), \quad (8)$$

wherefrom

$$S = \frac{S_0(1+\gamma)e^{-\beta t}}{1+\gamma e^{-\beta t}}, \quad (9)$$

where $\gamma = YS_0/X_0$, $\beta = \mu_m(S_0 + X_0/Y)/K_s$.

For the biological oxygen demand we shall have

$$Y = -\int_0^t \frac{dC}{dt} dt = -(1-Y) \int_{S_0}^S dS = (1-Y)S_0 \left\{ \frac{1-e^{-\beta t}}{1+\gamma e^{-\beta t}} \right\}. \quad (10)$$

SIMPSON [27] derived formula (10) in a somewhat different way. Assuming that $S_0(1-Y) = S_0^*$, we can have three parameters S_0^* , β , γ in formula (10), where Y is oxygen utilized (BOD).

Fig. 1 shows dependence (10) for *Pseudomonas fluorescens* growing on glucose.

Moser's function [22] occasionally used for pure cultures is an interesting generalisation for Monod's formula:

$$\mu = \frac{\mu_m(S/S_k)^n}{1+(S/S_k)^n}, \quad (11)$$

where $S_k^n = K_s$.

For $(S_0/S_k)^n \ll 1$ instead of (8) the equation will be of more general type

$$dS/dt = -\frac{\mu_m}{S_k^n} S^n(X_0/Y + S_0 - S) = a_1 S^n(b-S). \quad (12)$$

This equation contains a new parameter n which helps to change the inflection point position. In a general case equation (12) is integrated numerically.

It should be emphasized again that models of Monod's type can only approximate (with or without success) the real processes occurring within a bacterial cell.

Equation (10) and the like can fairly well describe only the initial phase of the biochemical oxygen demand which ends when the substrate practically disappears. However, the cell can store some amount of reserved substrate which is utilized when the amount of external substrate is insufficient. A number of models is offered to describe this phenomenon [39, 7].

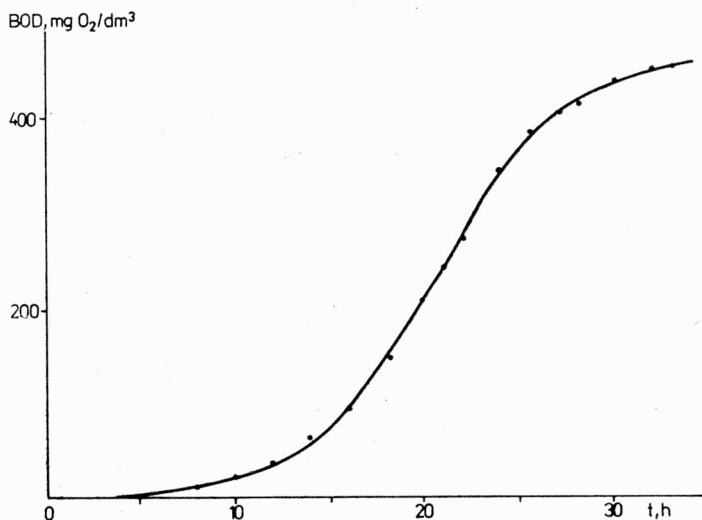


Fig. 1. BOD of the glucose-grown culture of *Pseudomonas fluorescens* (from [27])
Rys. 1. BZT rosnącej na glukozie kultury *Pseudomonas fluorescens* (według [27])

3. BIOCHEMICAL OXIDATION OF MONOSUBSTRATE BY A COMPLEX OF MICROORGANISMS

Processes of biochemical oxidation of organic substances occur most intensively in man-made biological reactors such as aeration tanks and biological filters. The latter maintain high concentrations of microorganisms (activated sludge and biological film) while the dissolved oxygen content is sufficiently high.

Activated sludge and biofilms are complexes of microorganisms which can oxidize substrates both simultaneously and in succession rendering either stimulating or inhibiting mutual effects. At the same time, it is quite possible to describe the oxidation process by the same models which were offered for pure cultures (fig. 2). With sufficiently high microorganism concentration in such models it may be considered constant.

Since the activated sludge particles and the biofilm fragment are rather large formations, mass transfer processes when substrate gets from the solution into the sludge particle or the biofilm become particularly important in the oxidation of individual substrate-pollutants. Papers [2, 33] have offered some respective stable diffusion models permitting determination of the substrate concentration distribution within a sludge particles and biofilms.

According to diffusion models for high substrate concentrations activated sludge and biofilms prove to be "saturated". Due to this the oxidation rate becomes independent of any further increase in the substrate concentration. Such property is quite typical of Monod's and of Teissier's functions [2, 5] as well as of their extensions, for example, Moser's

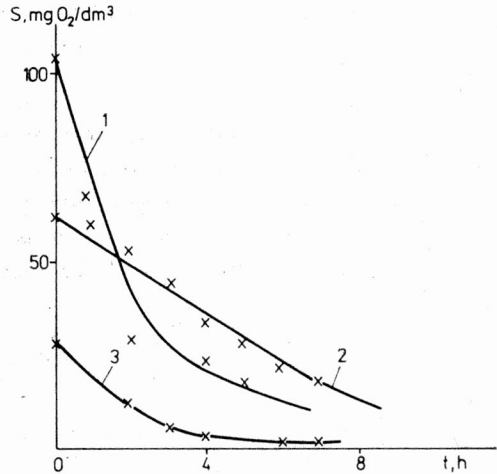


Fig. 2. Kinetics of activated sludge oxidation of glucose (1), phenol (2) and aniline (3)

× - experimental points from [31], solid lines - dynamic curves following from the models of: 1 - Moser ($\mu_m X/Y = 63$ mg/dm³/h, $S_k = 72$ mg/dm³, $n = 1.75$), 2 - Monod ($\mu_m X/Y = 8$ mg/dm³/h, $K_s = 10$ mg/dm³), 3 - Teissier ($\mu_m X/Y = 27$ mg/dm³/h, $K = 0.02$ dm³/mg)

Rys. 2. Kinetyka utleniania glukozy (1), fenolu (2) i aniliny (3) w osadzie aktywnym

× - punkty doświadczalne według [31], linie ciągłe - krzywe dynamiczne wynikające z modeli: 1 - Mosera ($\mu_m X/Y = 63$ mg/dm³/h, $S_k = 72$ mg/dm³, $n = 1,75$), 2 - Monoda ($\mu_m X/Y = 8$ mg/dm³/h, $K_s = 10$ mg/dm³), 3 - Teissiera ($\mu_m X/Y = 27$ mg/dm³/h, $K = 0,02$ dm³/mg)

function [11]. Hereby the coefficients of formal models are, in turn, determined by characteristics of activated sludge particles or of biofilms. In this way VAVILIN et al. [35] have presented the following assessment of the activated sludge particles under the given conditions

$$\alpha = \sqrt{\frac{\rho d^2 \mu_m}{Y D_i S_c}} \gg \frac{1}{\zeta_c},$$

$$K_s \approx S_c \left\{ \left(1/3 - 1/(2)^{5/3} + \frac{1}{6} \frac{\delta}{\zeta} \frac{D_i}{D_e} \right) (\alpha R)^2 + 1/2 \right\}, \quad (13)$$

where ρ is the density of dry biomass of the respective microorganisms in a sludge particle, S_c is a certain critical substrate concentration at which the reaction order gets changed (from the zero order to the first one), ζ_c is the respective value of the radius, D_e and D_i are coefficients of the substrate diffusion in water and within the sludge particle, δ is the thickness of the diffusion layer, and R is the floc's radius.

Similarly, in case of a biofilm with the thickness h we shall have

$$K_s \approx S_c \frac{(0.25 + \delta \alpha D_i / D_e) (\alpha)^2 + 1}{2}. \quad (14)$$

Hereby we have received quite reasonable half-saturation constants K_s : glucose—

20 mg/dm³ (flocs), 200 mg/dm³ (biofilm), ammonium — 0.15 mg/dm³ (flocs), 1 mg/dm³ (biofilm).

According to HARREMOES [13], under certain conditions a kinetic equation of the 1/2 order seems to be adequate for biofilms.

4. BIOCHEMICAL OXIDATION OF MULTICOMPONENT POLLUTANT IN A BATCH AERATION TANK

Wastewaters, as a rule, are multicomponent substrates. Describing their kinetic experiments some authors were in favour of Monod's and of Teissier's models while some others preferred as more adequate those of the first order and even of higher ones. TISCHLER and ECKENFELDER [31] have shown that individual components of a multicomponent substrate get oxidized simultaneously. Let us consider Teissier's function for individual components. With its help we shall see that

$$S(t) = \sum_1^e S_i(t) = \sum_1^e \frac{1}{K_i} \ln \{1 + (e^{K_i S_{0i}} - 1) e^{-K_{0i} K_i X t}\}, \quad (15)$$

$$\begin{aligned} dS/dt &= \sum_1^e dS_i/dt = \sum_1^e \varrho(S_i) = \psi(t) \\ &= \sum_1^e K_{0i} X \left\{ \frac{(e^{K_i S_{0i}} - 1) e^{-K_{0i} K_i X t}}{1 + (e^{K_i S_{0i}} - 1) e^{-K_{0i} K_i X t}} \right\}, \end{aligned} \quad (16)$$

where $K_{0i} = \mu_m i / Y_i$, S_{0i} is the initial concentration of an i -component.

Functions (15) and (16) have $3l$ parameters (S_{0i} , K_i , K_{0i} , $i = 1, 2, \dots, l$). Instead of (16) we can use a series of approximations, say, Moser's function (10) which contains three parameters (K_0 , S_k , n).

If the components $i = 1, 2, \dots, l$ are innumerated according to their "disappearance" in the aeration tank (in reality S_i becomes smaller than a certain value S_i^*) by the moment $t = t_i$, then the case $n > 1$ in Moser's function employed for the multicomponent substrate S will correspond to $S_{0i} < S_{0i+1}$, $K_{0i} > K_{0i+1}$.

Moser's model with n capable of assuming any positive value can fairly well describe the oxidation dynamics for municipal wastewaters (fig. 3).

Considering (15) and (16) one can notice that for a multicomponent substrate the time t is a real variable while the variable S is "imaginary" as well as the reaction rate constant K_0 , the reaction order n and the value S_k .

Dynamic oxidation curves for multicomponent pollutants may be well described by some extensions of Fair's and Grau's models [9, 12]:

$$\varrho(X, S) = K' X S (S/S_0)^{n-1}, \quad (17)$$

$$\varrho(X, S) = K'' X (S/S_0)^n, \quad (18)$$

$$\varrho(X, S) = K''' X S^n / S_0, \quad (19)$$

where $\rho(X, S)$ is the oxidation rate in the basic equation describing the process of aerobic biological treatment in a batch aeration tank

$$dS/dt = -\rho(X, S). \quad (20)$$

In relationships (17) to (19) the reaction order n is fixed while in Moser's function (11) it can change from the zero to a n -one with the substrate concentration decrease. It is obvious that with small value of

$$S \ll \sqrt[n]{K_s} = S_k \text{ and } K_0 = \mu_m/Y = K'''/S_0 = K''/S_0^n = K'/S_0^{n-1}$$

Moser's model becomes identical to those of Fair and Grau.

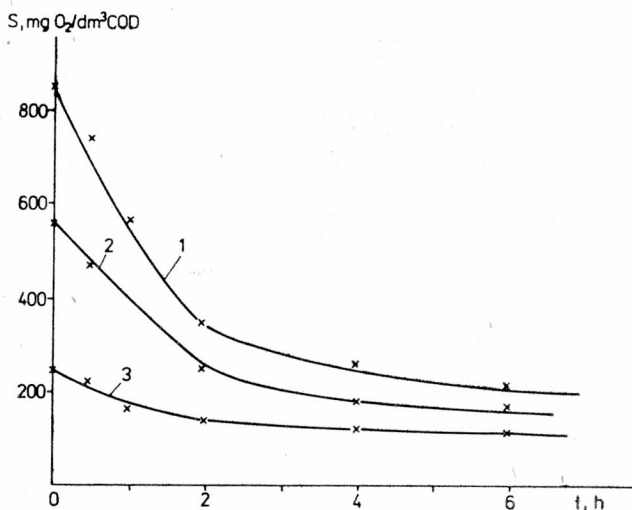


Fig. 3. Municipal wastewater oxidation kinetics

x - experimental points from [4], $X = 2.92 \text{ g/dm}^3$ (1), $X = 1.56 \text{ g/dm}^3$ (2), $X = 1.25 \text{ g/dm}^3$ (3)

$$\text{Moser's model} \begin{cases} \mu_m/Y = 0.11 \text{ h}^{-1}, S_k = 0.4 \text{ g/dm}^3, n = 5 \\ \mu_m/Y = 0.11 \text{ h}^{-1}, S_k = 0.27 \text{ g/dm}^3, n = 6 \\ \mu_m/Y = 0.06 \text{ h}^{-1}, S_k = 0.165 \text{ g/dm}^3, n = 8 \end{cases}$$

Rys. 3. Krzywe kinetyczne utleniania ścieków bytowo-gospodarczych

x - punkty eksperymentalne według [4], $X = 2,92 \text{ g/dm}^3$ (1), $X = 1,56 \text{ g/dm}^3$ (2), $X = 1,25 \text{ g/dm}^3$ (3)

$$\text{model Mosera} \begin{cases} \mu_m/Y = 0,11 \text{ h}^{-1}, S_k = 0,4 \text{ g/dm}^3, n = 5 \\ \mu_m/Y = 0,11 \text{ h}^{-1}, S_k = 0,27 \text{ g/dm}^3, n = 6 \\ \mu_m/Y = 0,06 \text{ h}^{-1}, S_k = 0,165 \text{ g/dm}^3, n = 8 \end{cases}$$

The solutions to equation (20) with functions (17) to (19) and that of Moser's will be respectively as follows

$$S = S_0 / \sqrt[n-1]{1 + (n-1)K'Xt}, \quad (21)$$

$$S = S_0 / \sqrt[n-1]{1 + (n-1)K''Xt/S_0}, \quad (22)$$

$$S = S_0 / \sqrt[n-1]{1 + (n-1)K'''S_0^{n-2}Xt}, \quad (23)$$

$$t = \frac{S_k}{K_0X} \left\{ \frac{1}{1-n} [(S_0/S_k)^{1-n} - (S_e/S_k)^{1-n}] + S_0/S_k - S/S_k \right\}. \quad (24)$$

Taking into account (21) to (23), the dynamic equation can be written as

$$dS/dt = -K'XS(S/S_0)^{n-1} = -\frac{K'X}{1 + (n-1)K'Xt} S, \quad (25)$$

$$dS/dt = -K''X(S/S_0)^n = -\frac{K''X}{S_0 + (n-1)K''Xt} S, \quad (26)$$

$$dS/dt = -K'''XS^n/S_0 = -\frac{K'''X}{S_0^{2-n} + (n-1)K'''Xt} S. \quad (27)$$

As seen from (25) to (27), the rate constant of the quasi-first order is a diminishing function of time and with the increasing reaction order this dependence becomes more profound.

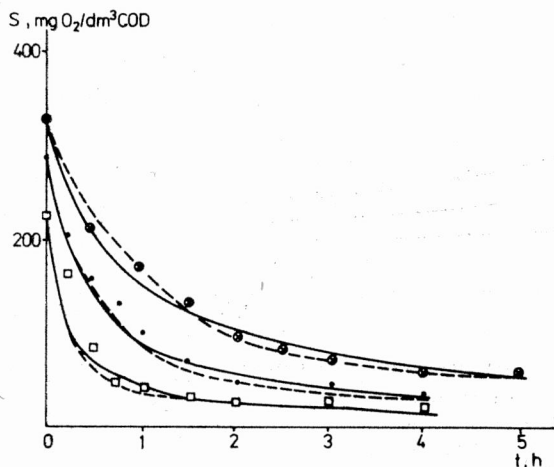


Fig. 4. Multicomponent substrate oxidation kinetics (peptone-starch)

Experimental points from [11]: \circ - $X = 428$ mg/dm³, \bullet - $X = 815$ mg/dm³, \square - $X = 1586$ mg/dm³

Theoretical curves: model (27) - $K = 0.0024$ dm³/mg/h, $n = 2$; model (28) - $K = 0.5$ h⁻¹,

$$K'_s = 150 \text{ mg/dm}^3/\text{h}$$

Rys. 4. Krzywe kinetyczne utleniania wieloskładnikowego substratu (pepton - skrobia)

Punkty doświadczalne według [11]: \circ - $X = 428$ mg/dm³, \bullet - $X = 815$ mg/dm³, \square - $X = 1586$ mg/dm³

Teoretyczne krzywe: model (27) - $K = 0.0024$ dm³/mg/h, $n = 2$; model (28) - $K = 0,5$ h⁻¹,

$$K'_s = 150 \text{ mg/dm}^3/\text{h}$$

Instead of Moser's model one can successfully employ the following extension (modification) of Mond's function (fig. 4)

$$dS/dt = -q(X, S) = -\frac{KXS}{K'_s \frac{Xt}{S_0} + S}. \quad (28)$$

Here the half-saturation constant is a function of the value called loading $F/M = Xt/S_0$ which, in its turn, is time-dependent. Model (28) should be solved numerically.

It is interesting to note that with sufficiently large values of time and $KS_0/X'_s = 1/n-1$ models (25) to (28) prove to be identical.

So, the reaction rate constant for the quasi-first order which follows from the best models of the multicomponent pollutant oxidation is a diminishing function of time. It is logical to interpret this fact by suggesting a gradual disappearance of pollutants in the course of oxidation and the survival of those which are harder to oxidize. With larger microorganism concentrations this process occurs faster.

5. BIOCHEMICAL OXIDATION OF MULTICOMPONENT POLLUTANTS IN AERATION TANKS

The basic equation for a completely mixing aeration tank is

$$S_0 - S_e - T\varrho(X, S_e) = 0, \quad (29)$$

where S_0 , S_e are the pollutant concentrations in the influent and in the effluent of the aeration tank, $T = V/q$ is the retention time of the mixed liquor in the aeration tank (V is the aeration tank volume, q is the sewage flow).

ADAMS et al. [1] have suggested the following modification of Grau's model:

$$\varrho(X, S) = KX \left(\frac{S_e - y}{S_0} \right), \quad (30)$$

where y is the correction for nonbiodegradable compounds.

Substituting (30) into (29) one obtains

$$\frac{S_0(S_0 - S_e)}{XT} = K(S_e - y). \quad (31)$$

Relationship (31) fairly well meets the experimental data of [1]. It is considered, however, that Grau's and Adams's model is only one of the many possible approximations of the real oxidation processes. The following can be considered as some generalization of (31)

$$\frac{S_0(S_0 - S_e)}{XT} = K(S_e - y)^n \quad (32)$$

which meets the experimental data much better than (31).

Making use of a modified Monod's model (28) and of equation (29) we can derive the following equation

$$\frac{XT}{S_0 - S_e} = \frac{1}{K} + \frac{K'_s}{K} \frac{XT}{S_0} \cdot \frac{1}{S_e} \quad (33)$$

which is presented in fig. 5. It is obvious to see that this dependence can fairly well describe the experiment. It should be noted that with $XT/S_0 = F/M - \text{const}$, i.e. with constant loading, the classical Monod's function describes the experimental data pretty well. Formula (33) can be generalized as

$$\frac{XT}{S_0 - S_e} = \frac{1}{K} + \frac{K'_s}{K} \left(\frac{XT}{S_0} \right)^n \cdot \frac{1}{S_e}. \quad (34)$$

When designing an aeration tank one must pay special attention to the value of [34]

$$\theta = \frac{XT}{Y(S_0 - S_e)} \quad (35)$$

which is called the sludge age. According to model (10), the maximal specific growth rate of activated sludge can be presented as follows:

$$\mu_m = \frac{v_m}{1 + d\theta} \approx \frac{v_m}{1 + d^*XT/S_0}, \quad (36)$$

where $d^* = d/Y$, v_m are constant values. Then Monod's function will give us the following:

$$\varrho(X, S) = \frac{\mu_m XS}{K_s + S} \frac{v_m}{Y} \frac{X}{1 + d^*XT/S_0} \frac{S}{K_s + S}. \quad (37)$$

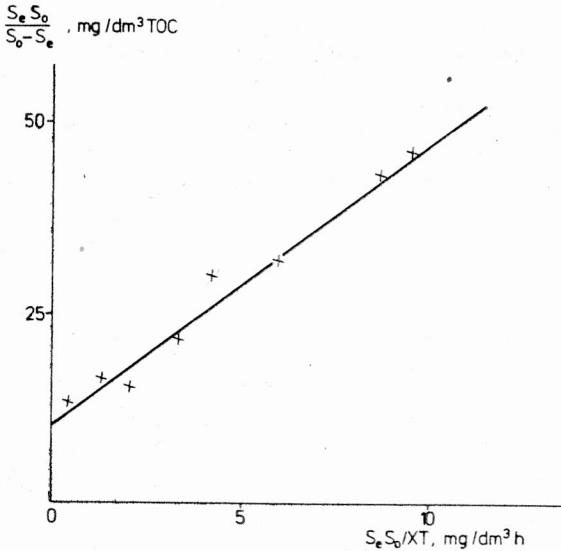


Fig. 5. Equation (33) for a completely mixed aeration tank

× - experimental points from [11], $K = 0.26$ h^{-1} , $K'_s = 2.5$ $mg/dm^3/h$, correlation coefficient $r = 0.99$. Peptone was used as substrate

Rys. 5. Zależność (33) dla komory napowietrzania z całkowitym mieszaniem

× - punkty doświadczalne według [11], $K = 0,2$ h^{-1} , $K'_s = 2,5$ $mg/dm^3/h$, współczynnik korelacji $r = 0,99$. Jako substratu użyto peptonu

With sufficiently high values of T and low values of S relationships (37) and (28) are identical.

Thus, our correction for the sludge activity decrease in respect of its increasing age, as a matter of fact, is equivalent to the rate constant decrease of the quasi-first order as function of time, in full accordance with the gradual disappearance of biodegradable substrates.

The following equation is the basic one for ideal plug-flow aeration tank

$$dS/d\xi = -T\varrho(X, S), \quad (38)$$

where $\xi = X/L$ is the dimensionless coordinate along the axis of the aeration tank (L is its length).

The dependences $\varrho(X, S)$ mentioned-above can be well used to describe oxidation processes in an ideal plug-flow aeration tank; the solutions in this case will be similar to (21) to (24).

When designing an aeration tank it is necessary to establish the interrelation between the pollutants concentration on the inlet S_0 and exit S_e of the aeration tank, the aeration period T and activated sludge concentration

$$S_e = f(X, T, S_0, t^0, \alpha_1, \alpha_2 \dots \alpha_k), \quad (39)$$

where $\alpha_1, \alpha_2 \dots \alpha_k$ are the constants of the mathematical model used to describe the dependence $\varrho(X, S)$. The temperature correction t^0 is also frequently considered. As follows from the above, the type of the function f is determined by that of the aeration tank (an ideal mixing tank or an ideal plug-flow one). Paper [38] gives a summary of mathematical models and their modifications most frequently used (tab. 1).

It is evident that a good mathematical model should provide for a minimum deviations of the design concentration value S_e from the experimental S_e^{ex} in a wide range of changing parameters T, S_0, X, t^0 . In this way, given series of experimental points $T_i, S_{0i}, S_{ei}, X_i, t_i^0$ in which $i = 1, 2, \dots, N$ being the serial number of the experiment, this model will have the following value

$$\varphi = \sum_{i=1}^N (S_{ei}^{ex} - S_{ei})^2 \quad (40)$$

which must be minimal. It will be so at certain values of the constants $\alpha = \alpha_1^*, \alpha_2 = \alpha_2^*, \dots, \alpha_k = \alpha_k^*$ found in calculations.

There are two models giving the same error in calculating the concentration S_e but the preference should be given to the one which is more simple and which contains fewer constants. In view of this the adequacy degree of a model is usually determined by the value $\bar{\varphi} = \varphi/(N-K)$ or $\sigma = \sqrt{\bar{\varphi}}$, where k is the number of constants. The value $\bar{\varphi}$ is called the root-mean-square deviation, and σ is the dispersion which shows the absolute error at a certain determination of the concentration S_e .

Tables 2 to 3 present sets of experimental values T_i, X_i, S_{0i}, S_{ei} obtained during investigations of biological treatment processes in large municipal wastewater treatment plants [15, 18, 43]. One can see that the deviation range of T, X, S_0, S_e is rather wide.

Employing these experimental data for each of the models presented in tab. 1, paper [38] tries to describe the numerical minimum of the dispersion value σ . The results of such numerical processing are given in tab. 4*. For some of the best models the calculated values S_e are presented in tabs. 2 and 3.

Let us now consider the design of a completely mixed flow (CMF) aeration tank. In this case most of the models make almost the same mistake in calculating the concentration S_e ($\sigma \approx 7 \text{ mg/dm}^3$). The model with function (19) has shown the best agreement with the experiment ($\sigma \approx 4.55 \text{ mg/dm}^3$).

* The temperature correction was neglected.

Table 1

Basic types of models used for design of aeration tanks
 Podstawowe typy modeli użytych do projektowania zbiorników napowietrzających

Name of the model	Oxidation rate $q(X, S)$	Equation for pollutant concentrations on the aeration tank exit S_0 — initial pollutant concentration, X — activated sludge concentration, T — aeration period, $a = KXT$, $b = KXT/S_0$	
		CMF aeration tank	PF aeration tank
1	2	3	4
1. Zero order	$K_0 X$	$S_e = S_0 - K_0 XT$	$S_e = S_0 - K_0 XT$
2. 1st order	$K_1 XS$	$S_e = \frac{S_0}{1+a}$	$S_e = S_0 e^{-a}$
3. n -order	$K_n X S^n$	$(S_0 - S_e)/S_e^n - a = 0$	$S_e = \{S_0^{1-n} - a(1-n)\}^{1/1-n}$
4. Grau's 1st order	$K_1^* X S/S_0$	$S_e = \frac{S_0}{1+b}$	$S_e = S_0 e^{-b}$
5. Grau's 2nd order	$K_2 X (S/S_0)^2$	$S_e = \frac{S_0}{2b} (\sqrt{1+4b}-1)$	$S_e = \frac{S_0}{1+b}$
6. Grau's n -order generalized*	$K_n^* X (S/S_0)^n$	$(S_0 - S_e)(S_0/S_e)^n - a = 0$	$S_e = \left\{ S_0^{1-n} - \frac{a(1-n)}{S_0^n} \right\}^{1/1-n}$
7. Grau's n -order generalized**	$K_n^{**} X S^n/S_0$	$S_0(S_0 - S_e)/S_e^n - a = 0$	$S_e = \{S_0^{n-1} - b(1-n)\}^{1/1-n}$
8. Grau's 1st order with correction	$K_1^* X \left(\frac{S-y}{S_0} \right)$	$S_e = \frac{S_0 + yb}{1+b}$	$S_e = y + (S_0 - y)e^{-b}$
9. Grau's 2nd order with correction for nonbiodegra- dable compounds	$K_2^{**} X \left(\frac{S-y}{S_0} \right)^2$	$S_e = y + \frac{S_0}{2b} \left(\sqrt{1+4b \left(1 - \frac{y}{S_0} \right)} - 1 \right)$	$S_e = \frac{S_0^2 + by(S_0 - y)}{S_0 + b(S_0 - y)}$

	1	2	3	4
10. Monod's	$K_v X S / (K_s + S)$	$P = (S_0 - K_s - a) / 2$ $S_e = P + \sqrt{P^2 + K_s S_0}$	$P = (S_0 - K_s - a) / 2$ $S_e = P + \sqrt{P^2 + K_s S_0}$	$S_e - S_0 + K_s \ln \frac{S_0}{S_e} - a = 0$
11. Moser's	$\frac{K_v X (S/S_k)^n}{1 + (S/S_k)^n}$	$\frac{(S_0 - S_e)[1 + (S_e/S_k)^n]}{(S_e/S_k)^n} - a = 0$	$\frac{(S_0 - S_e)[1 + (S_e/S_k)^n]}{(S_e/S_k)^n} - a = 0$	$\frac{S_k}{1-n} \{(S_0/S_k)^{1-n} - (S_e/S_k)^{1-n}\} + S_0 - S_e - a = 0$
12. Moser's modified	$\frac{K_v X (S/S_k)^n}{1 + (S/S_k)^m}$	$\frac{(S_0 - S_e)[1 + (S_e/S_k)^m]}{(S_e/S_k)^n} - a = 0$	$\frac{(S_0 - S_e)[1 + (S_e/S_k)^m]}{(S_e/S_k)^n} - a = 0$	$\frac{1-n}{1+m-n} \{(S_0/S_k)^{1-n+m} - (S_e/S_k)^{1-n+m}\} + (S_0/S_k)^{1-n} + (S_e/S_k)^{1-n} - \frac{a(1-n)}{S_k} = 0$
13. Haldane's	$\frac{K_v X S}{K_s + S + S^2/K_1}$	$\frac{(S_0 - S_e)(K_s + S_e + S_e^2/K_1)}{S_e} - a = 0$	$\frac{(S_0 - S_e)(K_s + S_e + S_e^2/K_1)}{S_e} - a = 0$	$(S_0 - S_e) \left(1 + \frac{S_0 + S_e}{2K_1} \right) + K_s \ln \frac{S_0}{S_e} - a = 0$
14. Ierusalimsky's	$\frac{K_v X S}{(K_s + S)(K_x + K)}$	$P = \left(S_0 - K_s - \frac{a}{K_x + X} \right) / 2$ $S_e = P + \sqrt{P^2 + K_s S_0}$	$P = \left(S_0 - K_s - \frac{a}{K_x + X} \right) / 2$ $S_e = P + \sqrt{P^2 + K_s S_0}$	$S_0 - S_e + K_s \ln S_0 / S_e - \frac{a}{K_x + X} = 0$
15. Teissier's	$K_v X (1 - e^{-S/S_k})$	$(S_0 - S_e) / (1 - e^{-S_e/S_k}) - a = 0$	$(S_0 - S_e) / (1 - e^{-S_e/S_k}) - a = 0$	$S_e = S_k \ln \{ 1 + (e^{S_0/S_k} - 1) e^{-a/S_k} \}$
16.		$S_e = \frac{S_0}{1 + a^n}$	$S_e = \frac{S_0}{1 + a^n}$	$S_e = S_k \ln \{ 1 + (e^{S_0/S_k} - 1) e^{-a/S_k} \}$
17.		$S_e = \frac{S_0}{1 + b^n}$	$S_e = \frac{S_0}{1 + b^n}$	$S_e = S_k \ln \{ 1 + (e^{S_0/S_k} - 1) e^{-a/S_k} \}$
18.		$S_e = S_0 e^{-a^n}$	$S_e = S_0 e^{-a^n}$	$S_e = S_k \ln \{ 1 + (e^{S_0/S_k} - 1) e^{-a/S_k} \}$
19.		$S_e = S_0 e^{-b^n}$	$S_e = S_0 e^{-b^n}$	$S_e = S_k \ln \{ 1 + (e^{S_0/S_k} - 1) e^{-a/S_k} \}$
20. Tuček's		$S_e^2 + \rho S_e + q = 0$ ρ and q are determined by the parameters of the system and by 4 constants	$S_e^2 + \rho S_e + q = 0$ ρ and q are determined by the parameters of the system and by 4 constants	$S_e = S_k \ln \{ 1 + (e^{S_0/S_k} - 1) e^{-a/S_k} \}$

Table 2

Experimental data on domestic wastewater treatment in completely mixed aeration tanks and calculated S_e values for model (19) (after [18, 43])

Dane doświadczalne oczyszczania ścieków bytowo-gospodarczych w komorach napowietrzania z całkowitym mieszaniem oraz obliczone wartości S_e dla modelu (18) (według [18, 43])

T [hours]	X [mg/dm ³]	S_0 [mg O ₂ /dm ³] BOD ₅	S_e — effluent BOD ₅ [mg O ₂ /dm ³]	
			experiment.	model (19)
2.13	3930	123	13.5	13.3
9.0	2830	123	6.2	7.55
2.38	3440	167	15.0	18.6
2.38	3100	167	15.0	19.6
2.38	3360	142	17.0	15.8
2.38	3200	142	9.9	16.2
1.08	3460	139	23.6	22.5
1.08	3510	139	25.0	22.2
1.07	3460	115	24.2	18.5
1.09	7900	204	18.4	22.4
1.08	7700	161	17.7	17.8
1.05	7900	345	27.6	39.9
0.89	8800	379	53.0	45.4
0.84	5900	242	33.9	35.3
0.83	10200	167	21.7	18.3
0.73	8900	224	31.4	28.5
0.71	11200	147	23.5	16.5
0.65	8900	141	22.6	18.5
0.89	4200	141	18.3	22.9
0.60	3900	141	25.4	28.6
0.67	4800	84	11.8	14.2
0.43	3600	138	34.5	33.8
0.43	3900	99	22.8	22.9
0.39	4200	141	38.0	18.4
0.31	6000	84	21.0	33.7
0.30	4200	141	35.3	37.9
0.26	5100	141	40.9	37.1

$$K_n^{**} = 0.0125 \text{ h}^{-1}, \quad n = 1.88, \quad \sigma = 4.55 \text{ mg/dm}^3.$$

The processed experimental data for a plug-flow (PF) aeration tank have shown the accuracy of the calculated S_e value to be greatly dependent of the type of the model used. Thus, the values σ for different models can differ by 2 to 3 times. The empirical model (fig. 6) has proved to be the best one ($\sigma \simeq 4.9 \text{ mg/dm}^3$)

$$S_e = \frac{S_0}{1 + (KXT)^n} \quad (41)$$

Table 3

Experimental data on domestic wastewater treatment in plug-flow aeration tanks and calculated S_e values for model (18) (after [15])

Dane doświadczalne oczyszczania ścieków bytowo-gospodarczych w komorach napowietrzania z przepływem tłokowym oraz obliczone wartości S_e dla modelu (18) (według [15])

T [hours]	X [mg/dm ³]	S_0 [mg O ₂ /dm ³] BOD ₅	S_e [mg O ₂ /dm ³] experiment.	as BOD ₅ model
5.3	1844	142.6	19.0	17.5
4.1	1850	132.4	13.0	17.8
9.27	937	181.4	14.0	26.9
5.9	1930	91.1	11.0	8.0
3.3	2330	71.8	8.0	6.8
5.3	2400	79.5	6.0	6.7
4.9	2000	64.0	6.0	5.0
5.2	2190	76.7	9.0	6.1
4.9	2230	72.0	11.0	5.66
6.2	2180	75.7	12.0	5.43
7.7	2420	127.4	14.5	10.2
4.4	1325	59.9	8.0	6.0
6.7	1808	201.2	33.0	26.3
7.2	2196	93.1	11.5	6.9
8.28	2400	145.4	9.0	12.1
7.9	2600	112.1	14.0	7.9
8.9	2800	110.5	12.0	7.0
5.9	2800	103.0	6.0	7.9
4.34	2625	105.4	14.0	10.0
8.45	3000	269.4	18.0	27.6
7.88	3000	276.5	17.0	30.0
4.77	1200	105.9	12.5	14.8
6.4	1680	89.3	6.0	8.0
5.5	1580	55.8	8.0	4.32
6.6	1863	106.0	13.0	9.7
6.0	2218	193.8	32.0	23.7
8.44	1500	80.2	10.0	6.2
2.3	360	164.0	71.4	75.3
1.6	850	95.9	26.2	27.1
1.6	990	101.1	37.8	27.2
4.88	384	135.4	35.2	38.6
2.56	626	129.2	44.8	39.0
4.82	580	113.3	32.0	24.0
2.35	634	94.1	32.2	25.2
2.28	365	95.0	31.7	34.0
2.5	505	85.5	24.0	23.7

$$K_n^* = 0.32 \text{ h}^{-1}, \quad n = 2.77, \quad \sigma = 5.77 \text{ mg/dm}^3.$$

Table 4

Minimum values of dispersion σ for models from tab. 1 and for experimental data from tabs. 2 and 3
 Minimalne wartości dyspersji σ dla modeli z tab. 1 i dla danych doświadczalnych z tab. 2 i 3

Name of the model	Values of constants		Units	σ [mg/dm ³]	
	CMF ¹	PF ¹		CMF	PF
1	2	3	4	5	6
Zero order	$K_0 = 0.0157$	$K_0 = 0.0522$	h^{-1}	95	17
1st order	$K_1 = 0.0014$	$K_1 = 0.000796$	dm ³ /mg/h	7.6	13.9
<i>n</i> -order	$K_n = 0.00012$ $n = 1.73$	$K_n = 0.000002$ $n = 2.43$	(dm ³ /mg) ^{<i>n</i>} h ⁻¹	6.26	8.8
Grau's 1st order	$K_1^* = 0.265$	$K_1^* = 0.11$	h^{-1}	7.5	15.2
Grau's 2nd order	$K_2 = 1.17$	$K_2 = 0.18$	h^{-1}	7	8.6
Grau's <i>n</i> -order extended*	$K_n^* = 0.757$ $n = 1.57$	$K_n^* = 0.32$ $n = 2.77$	h^{-1}	7	5.77
Grau's <i>n</i> -order extended**	$K_n^{**} = 0.0125$ $n = 1.88$	$K_n^{**} = 0.00189$ $n = 1.914$	(dm ³ /mg) ^{<i>n</i>} h ⁻¹	4.55	8.7
Grau's 1st order with correction	$K_1^* = 0.3$ $y = 6$	$K_1^* = 0.126$ $y = 9.4$	h^{-1} mg/dm ³	7.4	8.98
Grau's 2nd order with correction	$K_2^* = 3.41$ $y = 8.34$	$K_2^* = 0.236$ $y = 6.88$	h^{-1} mg/dm ³	6	5.3
Monod's	$K_v = 0.34$ $K_s = 200$	$K_v = 0.4$ $K_s = 405$	h^{-1}	8.55	14.3
Moser's	$K_v = 0.69$ $S_k = 128$ $n = 1.85$	$K_v = 0.0122$ $S_k = 57$ $n = 3.92$	h^{-1} mg/dm ³	6.42	7.45
Moser's modified	$K_v = 0.67$ $S_k = 139$ $n = 1.75$ $m = 3.05$	$K_v = 0.215$ $S_k = 74$ $n = 3.6$ $m = 4.68$	h^{-1} mg/dm ³	5.54	7.54
Haldane's	$K_v = 0.236$ $K_s = 129$ $K_i = 3.9 \times 10^7$	$K_v = 0.148$ $K_s = 120$ $K_i = 10^8$	h^{-1} mg/dm ³ mg/dm ³	9.17	15.2
Ierusalimsky's	$K_v = 15500$ $K_s = 1470$ $K_x = 1950$	$K_v = 10$ $K_s = 250$ $K_x = 41000$	h^{-1} mg/dm ³ mg/dm ³	5.51	14.7

¹ CMF and PF are, respectively, completely mixed flow and plug flow aeration tanks.

1	2	3	4	5	6
Teissier's	$K_v = 0.117$ $S_k = 65$ $K = 0.00165$ $n = 0.864$ $K = 0.253$ $n = 1.012$ $K = 0.00174$ $n = 0.366$ $K = 0.43$ $n = 0.28$	$K_v = 0.169$ $S_k = 169$ $K = 0.0023$ $n = 0.614$ $K = 0.234$ $n = 0.718$ $K = 0.00086$ $n = 0.33$ $K = 0.109$ $n = 0.375$	h^{-1} mg/dm^3 $dm^3/mg/h$ h^{-1} $dm^3/mg/h$ h^{-1}	9.2 6.29 7.76 5.51 7.26	14.47 4.91 5.8 5.14 6.27
Tuček's				7.2	5.3

It should be noted that a model similar to that of Grau's of the second order with only one constant can agree with the experimental results much better than the classical microbiological models of Monod's type.

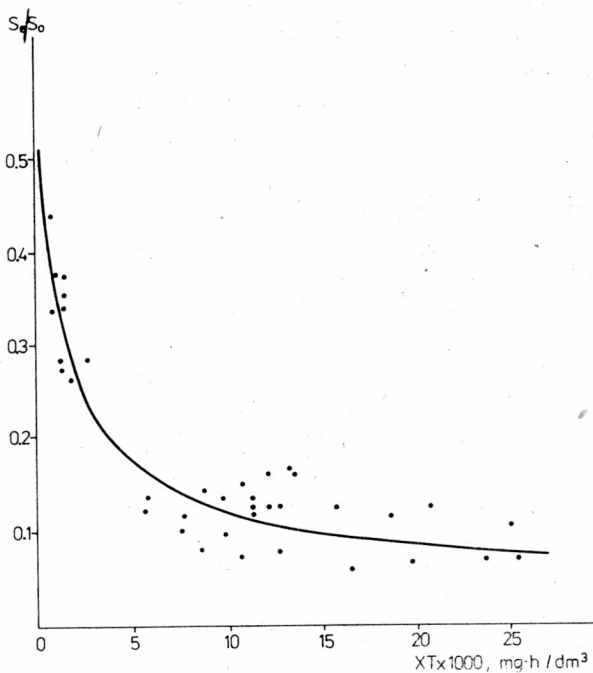


Fig. 6. Relationship (41) for a plug-flow aeration tank treating municipal wastewater

● - experimental points from [15], $K = 2.33$ $dm^3/g/h$, $n = 0.62$

Rys. 6. Zależność (41) dla komory napowietrzania z przepływem tłokowym, w której zachodzi oczyszczanie ścieków bytowo-gospodarczych

● - punkty doświadczalne według [15], $K = 2,33$ $dm^3/g/h$, $n = 0,62$

When compared, the processed results showed that the "sludge activity" (the respective values of rate constants) was about twice as high in the CMF tank as that in the PF one. That is why the efficiency of a CMF aeration tank can be practically higher than that of

a PF one even though the latter may have a very high rate due to great current concentrations of pollutants.

6. BIOCHEMICAL OXIDATION OF MULTICOMPONENT POLLUTANT IN A BIOLOGICAL FILTER

The hydraulic regime in a biological filter is close to that in an ideal PF aeration tank. Therefore equation (38) can be used for a biological filter in which the contact time T is proportional to [26]:

$$T \sim \frac{\alpha H}{(q/A)^m} = \frac{\alpha H}{Q^m}, \quad (42)$$

where H is the biological filter height, A is the cross-section area, α is the filter media specific surface area (m^2/m^3).

In an ordinary 1st order equation with $\rho(S) = K_1 S$ we shall have the well-known model

$$S_e = S_0 e^{-K_1^* \alpha H / Q^m}. \quad (43)$$

Solutions to the basic equation which are similar to (21) to (24) and obtained through the functions discussed above can describe the biological wastewater treatment process in a biological filter much better than the first order model does. It can be attributed to the fact that these functions reflect the decrease of the reaction rate constant of the quasi-first order in respect of time and, consequently, in respect of the biological filter depth.

In some cases the experimental results can be better described by the modifications of OLESZKIEWICZ's and ECKENFELDER's models [24]

$$S_e = S_0 e^{-(K\alpha/L)^n} \quad (44)$$

and

$$S_e = \frac{S_0}{1 + (K\alpha/L)^n}, \quad (45)$$

where $L = S_0 H / Q$ is the organic loading and n is any positive number.

OLESZKIEWICZ and ECKENFELDER considered relationships (44) and (45) at $n = 1$. It is easy to see that in such case formulas (44) and (45) follow from Grau's model (22) of the 1st and 2nd orders, respectively, at $T = H/Q$.

In designing a biological filter the general task will involve the definition of the interrelation

$$S_e = f(\alpha, H, Q, S_0, t^0, a_1, a_2 \dots a_k) \quad (46)$$

which is similar to (39). Selection of coefficients is made with the dispersion numerically minimized

$$\sigma = \sqrt{\frac{\sum_1^N (S_e^{\text{exp}} - S_e)^2}{N - K}}$$

Table 5 presents the values obtained for some models while processing the experimental data of KEEFER and MEISEL [17].

The empirical model of the type of (41)

$$S_e = \frac{S_0}{1 + [KaH/Q]^n} \quad (47)$$

has proved to be the best ($\sigma \simeq 6.1 \text{ mg/dm}^3$).

Table 5

Processed experimental data for biological filter (after [17])
Przetworzone dane doświadczalne dla złoża biologicznego (według [17])

Name of the model	Oxidation rate	Equation for S_e	Value σ	Values of constants
1. 1st order	$K_1 S$	$S_e = S_0 e^{-K_1 aH/Q}$	16.8 mg/dm ³	$K_1 a = 12.9 \text{ days}^{-1}$
2. 1st order*	—	$S_e = S_0 e^{K_1^* aH/Q^m}$	13.5 mg/dm ³	$K_1^* a = 2.38 \text{ l/m} \times (\text{m/day})^m$ $m = 0.31$
3. Oleszkiewicz's, Eckenfelder's	$K_1' S/S_0$	$S_e = S_0 e^{-K_1' aH/QS_0}$	17.1 mg/dm ³	$K_1' a = 1600 \text{ mg}/(\text{dm}^3 \cdot \text{d})$
4. Modification of model 3	—	$S_e = S_0 e^{-K_1'^* aH/S_0 Q^m}$	13.9 mg/dm ³	$K_1'^* a = 355 \text{ mg}/(\text{dm}^3 \cdot \text{d}) (\text{m/day})^m$ $m = 0.4$
5. Fair's and Geyer's	$K_2 S^2/S_0$	$S_e = \frac{S_0}{1 + K_2 aH/Q}$	9.6 mg/dm ³	$K_2 a = 27.9 \text{ l/day}$
6. Modification of model 5	—	$S_e = \frac{S_0}{1 + K_2^* aH/Q^m}$	7.7 mg/dm ³	$K_2^* a = 7.69 \text{ l/m} \times (\text{m/day})^m$ $m = 0.46$
7. Empirical model	—	$S_e = \frac{S_0}{1 + (KaH/Q)^n}$	6.1 mg/dm ³	$Ka = 26 \text{ l/m} \times (\text{m/day})^m$ $n = 0.6$ $m = 0.7$

Total number of data points are 48.

Transforming (44) we shall have the following (fig. 7):

$$\lg \left\{ \frac{S_0 - S_e}{S_e} \right\} = \lg (KaH)^n - mn \lg Q = a - b \lg Q. \quad (48)$$

According to KORNEGAY [19] the classical Monod's model can be also used to describe the oxidation process in a biological filter if the constant K_s is regarded as inversely proportional to the specific sewage flow Q , i.e. as proportional to the contact time T .

The models discussed above can account for the temperature effects upon the biochemical oxidation rate by a dependence for the reaction rate constant suggested already by STREETER and PHELPS [28]

$$K = K_{20^\circ} (\kappa)^{t^\circ - 20^\circ} \quad (49)$$

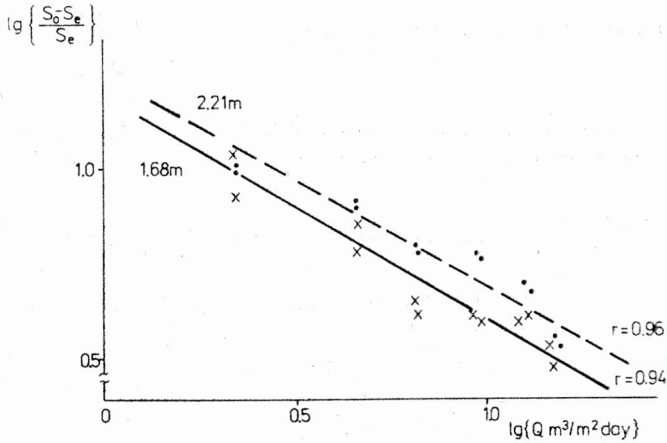


Fig. 7. Relationship (48) for a biological filter treating municipal wastewater experimental points from [17]: ● - ($H = 2.21$ m, $a = (KaH)^n = 18$ ($m^2/d \cdot m^3$) b , $b = mn = 0.55$); × - ($H = 1.68$ m, $a = (KaH)^n = 15.6$ (m^2/m^3) b , $b = mn = 0.58$)

Rys. 7. Zależność (48) dla złoża biologicznego, na którym zachodzi oczyszczanie ścieków bytowo-gospodarczych

punkty doświadczalne według [17]: ● - ($H = 2,21$ m, $a = (KaH)^n = 18$ ($m^2/d \cdot m^3$) b , $b = mn = 0,55$); × - ($H = 1,68$ m, $a = (KaH)^n = 15,6$ (m^2/m^3) b , $b = mn = 0,58$)

Those authors chose $\kappa = 1.047$. This value is very often used to account for the temperature correction but it is not legitimate. In reality, κ is an additional parameter and its value can be found within the minimization of σ described above. Depending upon the wastewater composition and on other parameters, the value κ may vary from 1.01 to 1.2. In this way, while processing the data on the biological filter cited above, we observed $\kappa \simeq 1.1$. With the value κ inaccurately selected the dispersion σ may increase.

On the whole, to account the temperature correction is not as important as the proper selection of the function $\varrho(X, S)$.

7. BIOLOGICAL OXIDATION OF POLLUTANTS IN RIVERS

Wastewaters entering rivers usually contain considerable quantities of various components which can be oxidized by different types of microorganisms present in river water. The summary process is traditionally measured in the dynamics of the BOD (consumption).

As a rule, two stages in the BOD curves are identified (fig. 8). At the initial stage of the process the BOD curve practically repeats the one of the microorganism growth.

By the moment at which biomass reaches its maximal value practically the entire substrate proves to have been utilized for its growth and the further BOD increase is due to the endogenous oxidation of the cellular matter (the end of the 1st stage).

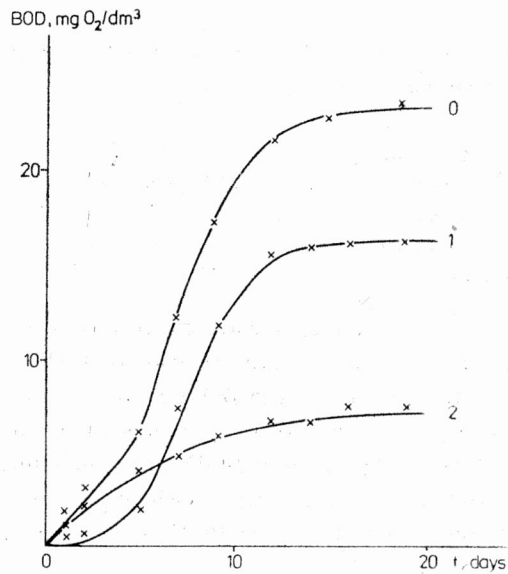


Fig. 8. Relationship (19) for a typical BOD curve

× - experimental points from [5]: 0 - total BOD, 1 - nitrogen BOD (nitrification processes), 2 - carbon BOD (with inhibited nitrification); 1 - $\{(1-Y) S_0 = 16.2 \text{ mg/dm}^3, \beta = 0.65 \text{ day}^{-1}, \gamma = 130\}$, 2 - $\{(1-Y) S_0 = 7.4 \text{ mg/dm}^3, \beta = 0.16 \text{ day}^{-1}, \gamma = 0\}$

Rys. 8. Zależność (19) dla typowej krzywej BZT

× - punkty doświadczalne według [5]: 0 - całkowite BZT, 1 - azotowe BZT (procesy nityfikacji), 2 - węglowe BZT (z zahamowaną nityfikacją); 1 - $\{(1-Y) S_0 = 16,2 \text{ mg/dm}^3, \beta = 0,65 \text{ dzień}^{-1}, \gamma = 130\}$, 2 - $\{(1-Y) S_0 = 7,4 \text{ mg/dm}^3, \beta = 0,16 \text{ dzień}^{-1}, \gamma = 0\}$

The further rise of the BOD curve can be attributed to the oxidation of ammonium nitrogen salts by nitrifying bacteria (the 2nd stage). BOD changes may be also due to the activity of protozoa.

The 1st stage is usually correlated to the decay of biodegradable organic compounds, and the BOD is called carbon BOD in such cases. Table 6 presents the basic types of equations describing the 1st stage.

Traditionally the BOD curves are expressed as

$$y = L_0(1 - e^{-Kt}) \quad (50)$$

with two coefficients L_0 and K . Equation (50) follows from (16) at $(1-y)S_0 = L_0$ and $\gamma = 0$, i.e. with an ordinary 1st order equation.

PHELPS offered equation (50) at the beginning of our century [25]. Later on equation (50) was found to disagree with experimental data and instead a 2nd order and a n -order equations were proposed (tab. 6). HEWITT et al. [16] have shown that those could best agree with the experimental data at larger values of n and L_0 (tab. 6), i.e. in cases when L_0 lost its usual physical interpretation as the ultimate BOD.

The n -order equation does not describe the auto-acceleration of the oxidation process which is usually related to the increase in the microorganism biomass. The traditional growth models of microorganisms discussed in section 1 permit deriving more adequate equations. Relationships (10) employed for a heterogeneous population of microorganisms

Formal models of BOD dynamics
Formalny model dynamiki BZT

Models of fixed reaction order	$dS/dt = -K_n S^n$; $y = L_0 - [(n-1)K_n t + L_0^{1-n}]^{1/(1-n)}$ $S = L_0 - y$	$n = 1$ [25] $n = 2$ [42, 44] $n \geq 0$ (any) [16]
Modified models of 1st order	$y = L_0(1 - e^{-K^*(t-t_0)})$ [30]; $y = L_0(1 - e^{-K^*t}) + y_0 e^{-K^*t}$	[40]
Models with variable rate constant	$dS/dt = \frac{-K_1}{1+at} S$; $S = L_0 - y$; $y = L_0[1 + (1+at)^{-K_1/a}]$	[8]

growing on a mixed substrate can fairly well describe the 1st stage of the BOD curve [3]. Some other models can be also used [27].

The 2nd stage in the BOD curve (fig. 8) is usually correlated to nitrification processes which can be also formally expressed by function (10) or by some others.

Describing the total BOD curve including both the 1st and the 2nd stages one takes down the sum of the functions which were mentioned above. In this way under consideration happen to be multistage BOD models [20, 23]. For example,

$$y = L_0 (1 - e^{-Kt}) + (1 - e^{-k(t-t_0)}). \quad (51)$$

carbon nitrogen

Hereby the 2nd function is accounted beginning with the moment $t = t_0$. More complicated functions of individual stages can be also included but in such cases the number of parameters increases.

An interesting model for nitrification processes has been proposed by HARLEMAN [14].

8. DISCUSSION

Mathematical models describing processes of biochemical oxidation of organic pollutants can be fairly relatively divided into three groups [37]: empirical, formal and simulation ones.

An empirical model does not claim at getting too deeply into the "black box". It describes the outlet (exit) variables as functions of the inlet ones and, as much as possible, minimizes the number of empirical coefficients.

A formal model is written as differential equations with their right parts chosen in such a way that the solutions could be presented as elementary functions. It considerably limits the number of possible models. In such models the number of variables likewise that of coefficients is usually selected to be small. Formal models already claim, in a way, to describe the "mechanism" of the phenomenon. These models originate from the respective equations of formal chemical kinetics.

A simulation model involves a great quantity of presumable links and considerable numbers of variables and coefficients. It is numerically solved by computers.

As a matter of fact, all three groups are phenomenological. They are approximations of the real processes occurring in nature.

Several levels of biochemical oxidation processes have been discussed above, namely: some pure bacterial culture growing on a monosubstrate, a heterogeneous population of microorganisms growing on a monosubstrate, a complex of microorganisms growing on a mixed substrate, such as wastewater. As a rule, the traditional formal models offered for the growth dynamics of pure cultures can be also employed for a complex of microorganisms. As indicated by BRAUN [3] the classic Monod's model utilized for self-purification processes in rivers has some coefficients of fictitious nature. This model cannot be interpreted in the way it is for pure microorganism cultures.

It has already been noted before, that the genuine (real) variable within the limits of schemes available for describing processes of biochemical oxidation of multicomponent pollutants is time. All other variables, such as the total concentration of the organic matter, the microorganism biomass and the like are only collective notions. Solutions to differential equation systems for extended variables are usually adapted to the respective experimental points. In selecting the models one should primarily consider their simplicity and the minimal number of their parameters.

As already shown above, the better agreement between the experimental data and the formal n -order models can be attributed to the fact that the quasi-first order rate constant derived from such models is a diminishing time function. In this way, time, somewhat obliquely, is included in the right parts of these models.

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FENOMENOLOGICZNE MODELOWANIE BIODEGRADACJI WIELOSKŁADNIKOWYCH SUBSTRATÓW

Praca podejmuje próby usystematyzowania modeli matematycznych dla procesu biochemicznego utleniania zanieczyszczeń organicznych w masie wodnej. Zaproponowano kilka modeli uogólnionych. Wszystkie modele podzielono w sposób relatywny na 3 grupy: empiryczną, formalną i symulacyjną. W rzeczywistości wszystkie te grupy modeli są fenomenologiczne.

Wykazano, że w tradycyjnych modelach formalnych współczynniki mają z reguły charakter imaginacyjny, podobnie jak zbiorcze zmienne takie jak ogólne stężenie substancji organicznej, biomasa bakteryjna etc.

Prostota modeli i minimalna liczba ich parametrów są ważnymi kryteriami ich wykonalności. Praca porównuje najlepsze z takich modeli i omawia ich pewne właściwości wspólne dla wszystkich.

PHÄNOMENOLOGISCHE MODELLIERUNG DER BIODEGRADATION MEHRSTOFFSUBSTRATE

In der vorliegenden Arbeit wird eine Systematik für mathematische Modelle vorgestellt, die die biochemische Umsetzung organischer Inhaltsstoffe im Wasser beschreiben.

Im Laufe der Zeit wurden verschiedene generelle Modelle entwickelt, und diese wurden in drei Gruppen unterteilt: empirische Modelle, formale Modelle und Simulationsmodelle.

Es lässt sich zeigen dass die in den traditionellen formalen Modellen enthaltenen Koeffizienten, genauso wie die summarischen Messgrößen für die gesamte organische Verschmutzung, die vorhandene Trocensubstanz als indirektes Mass für die biochemische Aktivität und anderes mehr, die Wirklichkeit nur unvollständig wiedergeben.

Da in der Handhabung der Modelle ihre einfache Struktur als wesentlich erscheint, zielen wir in der vorliegenden Arbeit darauf ab, sozusagen „die geringste Zahl von Parametern“ bei Ausschöpfung des (ex post) vorhandenen Informationsgehaltes abzuschätzen damit (ex ante) auch eine verlässliche Vorhersage gewährleistet ist. In der vorliegenden Arbeit wird dabei der Versuch unternommen, gemeinsame Eigenschaften verschiedener Modelle herauszuarbeiten und sozusagen „das beste Modell“ unter den jeweils gegebenen Bedingungen zu beschreiben.

ХАРАКТЕРНОЕ ВРЕМЯ И ФЕНОМЕНОЛОГИЧЕСКАЯ ПРИРОДА МАТЕМАТИЧЕСКИХ МОДЕЛЕЙ ПРОЦЕССОВ БИОХИМИЧЕСКОГО ОКИСЛЕНИЯ МНОГОКОМПОНЕНТНЫХ ЗАГРЯЗНИТЕЛЕЙ

В статье дается систематизация математических моделей процессов биохимического окисления органических загрязнителей водоемов. Предлагаются некоторые обобщенные модели.

Все модели могут быть условно разделены на три группы: эмпирические, формальные и имитационные. По сути, все модели являются феноменологическими.

Показывается, что коэффициенты традиционных формальных моделей, как правило, имеют фиктивный характер, также как и такие обобщенные переменные как общая концентрация органического вещества, биомасса бактерий и т. п.

Простота моделей и минимальное число параметров являются важными критериями их практической пользы. В статье дается сравнение моделей и обсуждаются некоторые общие свойства лучших моделей.