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*Механізм ферментативної кінетики у біо-клітині моделювався багатоканальною системою масового обслуговування. Процес біодеградації з субстратним інгібуванням математично описаний методом динаміки середніх. Отримана система диференціальних рівнянь зі здалегіть не визначеним порядком  $n$ , що відповідає механізмам субстратного інгібування різноманітної інтенсивності. Для питомої швидкості деструкції знайдено повний спектр рішень  $V_n$  системи від мінімального порядку  $n=2$  до граничного  $n \rightarrow \infty$ . Повний спектр рішень необхідний для обгрунтованого вибору єдиної узагальнюючої формули. Встановлено, що параметри форми кривої для рішення з мінімальною інтенсивністю інгібування  $V_2$  суттєво вирізняються із загального ряду формул спектру.*

*У чисельному експерименті фізичне дослідження імітувалося описом методом найменших квадратів даних, які задаються розрахунком за формулами різноманітної структури, з урахуванням несистематичної випадкової помилки. Метод чисельного експерименту дозволив задавати варійовані параметри із заданою точністю та у широкому діапазоні, що є неможливим в умовах фізичного дослідження. Серії чисельних експериментів продемонстрували можливість формули граничного порядку  $V_e$  описувати залежності всього спектру рішень. Для критичного мінімального порядку середня відносна помилка гарантовано не перевищує п'яти відсотків. Збільшення випадкової помилки завжди призводить до статистичної рівності, у точності опису формулами мінімального  $V_2$  та граничного порядків  $V_e$  даних, які задаються розрахунком за залежністю другого порядку.*

*У сукупності важливість результатів чисельного моделювання фізичного експерименту полягає у доведенні можливості використання формули граничного порядку  $V_e$  у якості єдиної при описі процесів біодеградації з різноманітними механізмами субстратного інгібування. Цей висновок підтверджено адекватним описом залежності граничного порядку експериментальних даних за п'ятьма шкідливими речовинами з різноманітним ступенем інгібування*

*Ключові слова: біодеструкція, субстратне інгібування, система масового обслуговування, чисельний експеримент, єдина формула*

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# CONSTRUCTION OF A GENERALIZED MODEL OF THE HARMFUL SUBSTANCES BIOCHEMICAL DESTRUCTION PROCESS KINETICS UNDER CONDITIONS OF SUBSTRATE INHIBITION USING THE METHODS OF SIMULATION MODELING

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## 1. Introduction

Biochemical degradation compared to physical methods of degradation of harmful substances is an environmentally

friendly and relatively inexpensive way of treatment of gaseous exhausts and those dissolved in water. For gaseous exhausts insoluble in water, such as methane, a bioreactor with a washing layer is used. A bioreactor, in which the processes



of absorption and bio-oxidation in irrigation water are combined, is used for water-soluble gaseous hydrogen sulphide, sulphur dioxide, ammonia. Biodegradation of formaldehyde is a periodic aerobic or anaerobic process in tanks with active sludge. The basis for calculation in the design and practical use of biotreatment are adequate mathematical models for processes of biochemical degradation.

The theoretical ideas about the bio-oxidation process resulted in the dependence «biodegradation rate – pollutant concentration» with empirically determined coefficients. The relationship «concentration – time» obtained directly in the physical experiment cannot be used to verify the theoretical formulas either, because of its a priori low sensitivity to estimated effects. That is why the adequacy of mathematical models is verified based on the experimental relationship «biodegradation rate – pollutant concentration», obtained by preliminary processing. Experimental studies of biodegradation of most harmful substances revealed the existence of a maximum on the curve «biodegradation rate – pollutant concentration» [1–11], which proves the existence of the substrate inhibition effect in this process. The implementation of this mechanism during bio-oxidation of gaseous non-soluble (methane), soluble (hydrogen sulfide, sulfur dioxide, ammonia) and dissolved in water substances (formaldehyde) will determine the relevance of the development of the adequate mathematical model of the process of biochemical degradation with substrate inhibition.

## 2. Literature review and problem statement

The models of mathematical description of biodegradation with substrate inhibition, shown in Table 1, can be classified as theoretical, modified and phenomenological.

The theoretical method of research is based on compiling and solving the systems of differential equations of enzyme kinetics. In this case, this system of equations is derived from the scheme of biochemical reaction, including the formation of enzyme–substrate complexes (ESC). The mechanism of substrate inhibition is explained by the emergence of inactive ESC with the number of attached substrate molecules  $n \geq 2$ . In Table 1, theoretical dependences ( $a, b, c$  – empirical coefficients) are represented by models (1)–(6). The research [1] presented a formula that takes into account the substrate inhibition effect in the elementary way. Model (1) is the simplest one because it implies the existence of one inactive ESC with two non-attached substrate molecules  $n=2$ . In paper [12], the applicability of the model (1) for biodegradation of phenol with determination coefficients  $R^2 = 0.948–0.985$ , was demonstrated. Applicability of the model with  $n=2$  in particular cases does not exclude the formation in real processes of the arrays of inactive ESC with higher than minimal order. That is why the desire to obtain theoretical dependences related to the inhibition mechanisms at  $n > 2$  is understandable. In order to take into account inhibition of higher intensity, two formulas (2), (3) were proposed in study [2]. To limit the number of empirically determined coefficients, inactive ESC only with  $n=3$  is laid in the model (2). However, the physical picture of the incomplete solution, at which there is no ESC with  $n=2$ , virtually cannot be implemented.

Model (3) is the generalization of model (2) with previously unspecified  $n \geq 3$ . Both models have not gained a widespread use. Paper [3] virtually represents a final attempt of theoretical research to take into account the effect

of substrate inhibition by the classical method with plotting the diagrams of enzymatic reactions. Two formulas (4), (5) were proposed. Model (4) is the only complete solution for  $n=3$  with four empirically determinable coefficients. The latter naturally increases the capabilities of model (4) compared with three-parameter models. Model (5) is given in the general form and is not practical in character. The properties of the series in the denominator were not studied. However, knowledge of the patterns for changing coefficients  $c_i$  opens up the opportunity to reduce formula (5) to a three-parameter formula with its generalization to an arbitrary order of ESC. Article [4] proposed a specific model, which can be also interpreted as semi-empirical. As a theoretical, a four-parameter model (6) corresponds to the mechanism of inhibition that is less intensive than in model (1). ESC of second order is active, but its activity is lower than that of ESC with  $n=1$  ( $c_2 < c_1$ ). A multiplier in brackets can also be regarded as a correction function. Model (6) was used practically in comparative analysis with other formulas.

Table 1

Dependences of specific biodegradation rate  $V$  on substrate concentration  $\rho$

Model		Source
$V = \frac{a\rho}{b + \rho + c\rho^2}$ ,	(1)	[1]
$V = \frac{a\rho}{b + \rho + c\rho^3}$ ,	(2)	[2]
$V = \frac{a\rho}{b + \rho + c\rho^n}$ ,	(3)	
$V = \frac{a\rho}{b + \rho + c_1\rho^2 + c_2\rho^3}$ ,	(4)	[3]
$V = \frac{a\rho}{b + \rho + \rho \sum_{i=1}^n c_i \rho^i}$ ,	(5)	
$V = \frac{a\rho}{b + \rho + c_1\rho^2} (1 + c_2\rho)$ ,	(6)	[4]
$V = \frac{a\rho}{b + \rho} \exp(-c\rho)$ ,	(7)	[5]
$V = \frac{a\rho}{b + \rho} - c(\rho - \rho_0)$ ,	(8)	[6]
$V = \frac{a\rho}{b + \rho} (1 - c\rho)^n$ ,	(9)	[7]
$V = \frac{a\rho}{b + \rho} \left( \frac{1}{1 + c\rho} \right)$ ,	(10)	[8]
$V = \frac{a\rho}{b(1 - c\rho)^m + \rho} (1 - c\rho)^n$ ,	(11)	[9]
$V = a[\exp(-b\rho) - \exp(-c\rho)]$ ,	(12)	[10]
$V = a\rho^n \exp(-c\rho)$ .	(13)	[11]

The modified or hybrid method for description of biodegradation is presented in Table 1 with models (7)–(11). The essence of the approach is that the known theoretical solution for  $n=1$  (fractional two-parameter dependence without maximum) is corrected by some empirical function,



which phenomenologically takes into account the inhibition effect. Almost all possible types of correction functions were used. In paper [5], the correction exponential function with a negative exponent was applied as a multiplier. The authors of article [6] take into account the inhibition effect by subtraction of linear correction function. In article [7], the phenomenological correction was proposed in the form of power function. In this case, this formula became four-parameter one. In study [8], inhibition effect is empirically taken into account by multiplying by power function. Model (10) will give results similar to those calculated according to formula (7) in the region of small ranges of concentration changes. In paper [9], in addition to the power function in the form of the common multiplier, free term  $b$  of solution with  $n=1$  is additionally corrected by power function in denominator. In this case, the structure of the five-parameter formula (11) is clearly overloaded. The modification method also gives good results when using three empirical coefficients. In this class of models, model (7) is the most flexible and most often used. For example, as it follows from the diagram presented in [13], a good match of experimental values and the values calculated from this formula was achieved.

Fully empirical or phenomenological approach is presented in Table 1 by models (12), (13). The phenomenological method implies the description of two processes – the fading increase in biodegradation rate (dependence  $n=1$ ) and the actual inhibition effect – by empirical functions at the macro-level. In research [10], these two processes are represented in the form of the difference between exponential functions with negative exponents. Formula (12) is flexible enough and also successfully applied in the form of two-parametric ( $b=0$ ) model. In study [14], determination coefficient  $R^2=0.963$  in relation to phenol fermentation was achieved. In research [11], the fading increase in biodegradation rate is represented by power dependence on substrate concentration, while inhibition effect is taken into account by multiplying by exponential dependence like in model (7). Using model (13), the processes of bio-oxidation of five gaseous and water-dissolved harmful substances were successfully described [11]. It is possible to regard the impossibility of closed integration for obtaining the dependence «concentration-time» in the stationary process as the drawback of formula (13), compared to most other models. The kind of empirical dependence with maximum and inflection point characteristic of specific biodegradation rate with substrate inhibition, proposed by reference books, is limited to models (12), (13).

The search for adequate dependences of biodegradation kinetics naturally includes not only the development of new mathematical models, but also comparative analysis of the effectiveness of existing formulas. The task of the critical analysis in this case is clearly solved by comparing the known parameters of assessing the accuracy of description of experimental data. It turned out that a characteristic feature of such research is approximation of results with high determination coefficients, obtained when using different models. This conclusion was made by the authors of [15] when comparing three-parameter models (1), (7), (9), (10). In this case, model (9) was calculated for  $n=0.5; 1$ . In study [16], the capabilities of models (1), (4), (6), (7), (9), (11), (12) were assessed. The best results were achieved for formulas (1), (6), (7), (9), where determination coefficient fluctuated in the narrow range  $R^2=0.909–0.933$ . For models (4), (11), (12),  $R^2=0.730–0.836$ . Research [17] gave assessment of accuracy of description of experimental data by models (1), (4),

(6)–(9), ((11), (12) at  $b=0$ ). Models (1), (4) had the best result with  $R^2=0.97; 0.98$ , respectively. High values of determination coefficients  $R^2=0.89–0.90$  are also characteristic of other formulas. In publication [18], based on the description of three series of experiments, the practical identity of the theoretical model (1)  $R^2=0.924–0.976$  and purely empirical formula (12)  $R^2=0.935–0.976$  were revealed. The indicators of the two-parametric model (12) at  $b=0$  –  $R^2=0.858–0.970$  differ insignificantly. The results, presented in [19], testify to practical match of root mean square deviations of models (1), (2), (7), (12). For models (4), (6), this indicator is lower by 10 %. In paper [20], theoretical (1) and modified (9) formulas were applied as equal with determination coefficient  $R^2=0.95$ . In research [21], high accuracy in the description of biodegradation kinetics by four different models was achieved: (1) –  $R^2=0.9249$ , (4) –  $R^2=0.9237$ , (7) –  $R^2=0.9028$ , (12) –  $R^2=0.9527$ . The authors of [22] showed the adequacy of models (1), (4), (6), (9) with determination coefficients within  $R^2=0.947–0.995$ . The data published in [23] demonstrate very close values of root mean square deviation when using models (1), (4), (7), (9), (2). In paper [24], during comparative evaluation of models (1), (4), (11) determination coefficients ranged within  $R^2=0.9616–0.9877$ . The data of research [25] for two series of experiments on ammonium bio-oxidation show the adequacy of the groups of models (1), (4), (6), (9), (12), and (12) (at  $b=0$ ) –  $R^2=0.91–0.99$ . Extensive testing of formulas was performed by authors of [26]. In models (1), (3), (6), (7), (12), determination coefficient reached high values  $R^2>0.963$ . The results, obtained in [27], demonstrate practical equality of models (1), (4) –  $R^2=0.989; 0.984$ , respectively. Excellent conformity with the experiment was revealed in research [28] for all the studied models – (1), (4), (7), (9), (11), (12) – at  $b=0$ . Multi-variant description of the same experimental data at high determination coefficients testify to the possibility of using the unified generalized solution. Obviously, the quality of generalization for the given kind of a curve with zero point, maximum and inflection point will be determined not only by the magnitude of argument change range, but also by the value of random error of the experiment.

In general, critical analysis of the structures of formulas [1–11] revealed the lack of theoretical dependence for mechanisms of substrate inhibition of high intensity. In addition, a comparison of the accuracy of description of the experimental data [12–28] by various formulas showed their closeness in actual ranges of substrate concentrations. That is why the unresolved problem is finding and substantiation of the unified theoretical dependence, describing different mechanisms of substrate inhibition in the generalized form.

The only region of theoretical solutions requiring further studying is analysis of high-order formulas included in the model of the general form (5). To select the generalizing formula, it is necessary to obtain and analyze the ratio of all possible theoretical solutions. However, when using the classical approach, it is impossible to construct a common scheme for the reaction of undefined order of ESC. To solve the correspondent system of differential equations, it is necessary to accept in advance the maximal number of attached substrate molecules. This difficulty is overcome by the representation of a bio cell with enzymes in the form of a multi-channel queuing system where an enzyme is the channel. The method of dynamics of averages can be a particular implementation of this approach. Statement of the scheme of enzymatic kinetics reaction in terms of probabilistic model of the queuing theory



make it possible to get a whole range of solutions up to the limiting order of ESC  $n \rightarrow \infty$ . Identification of the generalizing model in the spectrum of solutions will require an extensive numerical experiment, including comparison of effectiveness of application of various formulas with consideration of random error in a physical experiment. Construction of probabilistic models of the development of processes in time and the computation experiment are the methods of simulation.

### 3. The aim and objectives of the study

The aim of this study is to search for and to substantiate, using the methods of simulation, a unified calculation dependence «biodegradation rate – concentration of atmosphere pollutant», generally describing the mechanisms of substrate inhibition of various intensity determined by order of inactive ESC from two ad infinitum. Pollutants include gaseous (methane, formaldehyde, hydrogen sulfide, sulfur dioxide and ammonia) non-soluble (methane), soluble (sulfur dioxide, hydrogen sulfide and ammonia) and dissolved in water (formaldehyde) harmful substances.

To accomplish the set aim, it is necessary to solve the following tasks:

- to determine the full range of theoretical formulas for calculating specific biodegradation rate, corresponding the various mechanisms of enzyme kinetics with substrate inhibition, using the method of dynamics of averages. A full range is necessary to identify the patterns of the ratio of forms of curves of calculation dependences as intensity of substrate inhibition increases and structures of formulas change;

- using the method of numerical experiment, to prove the existence in the spectrum of theoretical solutions of the unified generalizing formula, which makes it possible to perform practical calculations of bio-oxidation kinetics with substrate inhibition of any intensity in the actual range of pollutant concentrations with admissible error. The proof should include the evaluation of the influence of random error of the experiment on the conformity of the unified generalizing formula with other dependences of the spectrum.

### 4. Research procedure

To obtain a full range of theoretical formulas for calculating specific biodegradation rate, the probabilistic model was applied. The proposed probabilistic simulation model is based on the representation of a bio cell with enzymes in the form of a multi-channel system of queuing. The events of a substrate molecule meeting an enzyme, as well as the break of their contact, are accepted as random. Formation and decomposition of ESC are considered as the Markovian process. Biodegradation occurs as a result of a basic enzymatic act only at one attached molecule of the substrate. ESC of higher order are inactive.

Mathematical description of the model was performed using the method of dynamics of averages, in which mean numbers of ESC of different orders are determined, rather than probabilities of the state of each enzyme or substrate molecules in a bio cell. The applied method of dynamics of averages is an effective and widely used method of

mathematical modeling of behavior of complex technical and military systems in the study of operations. The admission of the method is the replacement of mathematical expectation of a function with the same function of mathematical expectation. With respect to modeling the kinetics of enzymatic reactions, errors can occur only at the substrate concentration in the vicinity of a bio cell, measured by several molecules. Apparently, this admission corresponds to accepting direct proportionality between the reaction rate and the substrate concentration while compiling the classical schemes of enzymatic reactions. The formula obtained by both methods for orders of one and two are the same. Thus, the method adequately models the kinetics of the process, excluding the non-working region of virtually zero concentrations of removed harmful substances, where due to this, relative error increases dramatically even at an insignificant absolute error.

The substantiation of using the unified generalized formula was proved based on comparative assessment of accuracy of description of the specified estimated values of one function – by the dependence with another mechanism for substrate inhibition.

For comparative evaluation of the effectiveness of theoretical solutions when describing the data, corresponding to different intensity of substrate inhibition, we used the method of numerical experiment. The known merits of the method include the possibility to perform calculations in a wide range of exactly assigned varied parameters, which is virtually not realizable in a physical experiment.

At the first stage, twenty calculation points of the described functions simulated an exact physical experiment without a random error. The coefficients of the describing formula were determined by the least-squares method. The designed programs implement the widely used method of gradient or quickest descent, written down in VBA. Calculation was performed until reaching the relative change in the sum of squares of differences in one iteration step less than  $10^{-16}$ . Relative changes of coefficients  $a, b, c$  in this case made up  $10^{-8}$ – $10^{-10}$ .

At the second stage of the study, the third series of numerical experiments using the random number generator was performed in order to assess the influence of a random error. The unit, in which experimental data were represented taking into account the existing error in a physical experiment, was added to the developed programs. The numerical experiment made it possible to vary an error with a view to assessing its influence, which is not possible when doing experiment.

### 5. Mathematical modeling of enzymatic kinetics with different mechanisms of substrate inhibition

The graph of the states of the elements of the proposed model was represented in Fig. 1, where:  $F_i$  is the mean quantities of ESC with attached  $i$ -th molecules of the substrate;  $\lambda_i$  and  $\nu_i$  are the intensities of formation and decomposition of ESC of  $i$ -th order;  $\nu_p$  is the intensities of product formation;  $S$  and  $P$  are mean quantities of molecules of substrate in the neighborhood of a bio cell.

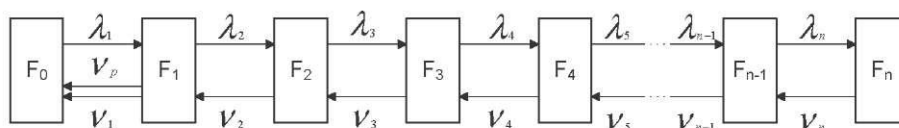


Fig. 1. Graph of possible states of enzyme in a bio cell



The method of dynamics of averages [29] enables writing down the following differential equations for the graph in Fig. 1:

$$\frac{dS}{dt} = -\lambda_1 F_0 + v_1 F_1, \tag{14}$$

$$\frac{dF_0}{dt} = -\lambda_1 F_0 + v_1 F_1 + v_p F_1, \tag{15}$$

$$\frac{dF_1}{dt} = -\lambda_2 F_1 + v_2 F_2 + \lambda_1 F_0 - v_1 F_1 - v_p F_1, \tag{16}$$

$$\frac{dF_2}{dt} = -\lambda_3 F_2 + v_3 F_3 + \lambda_2 F_1 - v_2 F_2, \tag{17}$$

$$\frac{dF_3}{dt} = -\lambda_4 F_3 + v_4 F_4 + \lambda_3 F_2 - v_3 F_3, \tag{18}$$

$$\frac{dF_4}{dt} = -\lambda_5 F_4 + v_5 F_5 + \lambda_4 F_3 - v_4 F_4, \tag{19}$$

.....

$$\frac{dF_{n-1}}{dt} = -\lambda_n F_{n-1} + v_n F_n + \lambda_{n-1} F_{n-2} - v_{n-1} F_{n-1}, \tag{20}$$

$$\frac{dF_n}{dt} = -\lambda_n F_{n-1} + v_n F_n, \tag{21}$$

$$\frac{dP}{dt} = v_p F_1. \tag{22}$$

The existence of stationary phase in the elementary enzymatic act, experimentally proved in enzymology [30], makes it possible to equal to zero the left side of the equations of the system (15)–(21). In terms of the Tikhonov theorem, equation (14) or a slow process is called a degenerate system and equations (15)–(21), or a quick process are called an attached system. It was mathematically proven [31] that the solution of the full system (14)–(21) tends to solve a degenerate system with left parts of the attached system tending to zero in the absence of the self-oscillatory processes. The Tikhonov theorem is virtually successfully used in modern theoretical studies of enzymatic reactions [32]. In a well-grounded way, we accept:

$$\frac{dF_i}{dt} = 0, \tag{23}$$

and obtain the system of ordinary equations:

$$-\lambda_1 F_0 + (v_1 + v_p) F_1 = 0, \tag{24}$$

$$-\lambda_2 F_1 + v_2 F_2 = 0, \tag{25}$$

$$-\lambda_3 F_2 + v_3 F_3 = 0, \tag{26}$$

$$-\lambda_4 F_3 + v_4 F_4 = 0, \tag{27}$$

$$-\lambda_5 F_4 + v_5 F_5 = 0, \tag{28}$$

.....

$$-\lambda_n F_{n-1} + v_n F_n = 0, \tag{29}$$

$$\lambda_n F_{n-1} - v_n F_n = 0. \tag{30}$$

The solution to system (24)–(30) in relations to productive ESC will be:

$$F_1 = \frac{\lambda_1 F}{v_1 + v_p + \lambda_1 \left( 1 + \frac{\lambda_2 + \lambda_2 \lambda_3 + \dots + \lambda_2 \lambda_3 \lambda_4 + \dots + \lambda_2 \lambda_3 \lambda_4 \dots \lambda_n}{v_2 v_3 v_4 \dots v_n} \right)}, \tag{31}$$

where  $F$  is the total quantity of enzymes in a bio cell:

$$\lambda_i = \lambda S. \tag{32}$$

Similarly, we accept intensity of ESC decomposition as proportional to the number of unproductive attachments:

$$v_i = (i-1)v. \tag{33}$$

Condition (23) allows writing down:

$$\frac{dS}{dt} = -\frac{dP}{dt}. \tag{34}$$

With this in mind, we obtain an expression for the rate of change in the number of substrate molecules:

$$\frac{dS}{dt} = \frac{v_p \lambda F S}{v_1 + v_p + \lambda S \left[ 1 + \frac{\lambda S}{v} + \frac{1}{2} \left( \frac{\lambda S}{v} \right)^2 + \frac{1}{6} \left( \frac{\lambda S}{v} \right)^3 + \dots + \frac{1}{24} \left( \frac{\lambda S}{v} \right)^4 + \dots + \frac{1}{(n-1)!} \left( \frac{\lambda S}{v} \right)^{n-1} \right]}. \tag{35}$$

Dependence (35) with accuracy to designations corresponds to the results obtained by the classical method for compiling the scheme of enzymatic reaction for first-order ESC (Monod formula) and second-order ESC (Andrews formula).

For the rate of concentration change specific per biomass unit, expression (35) can be represented as:

$$V = \frac{ap}{b + \rho \left[ 1 + cp + \frac{1}{2} (cp)^2 + \frac{1}{6} (cp)^3 + \dots + \frac{1}{24} (cp)^4 + \dots + \frac{1}{(n-1)!} (cp)^{n-1} \right]}, \tag{36}$$

where  $\rho$  is the substrate concentration;  $a, b, c$  are the experimentally determined coefficients.

Formula (36) includes the range of solutions, the size of which depends on the order  $n$  of the original system (15)–(21). System order corresponds to the order of ESC, that is, the maximal number of attached substrate molecules. In general, the whole range of solutions is represented as a set of formulas:

$$n = 2, V_2 = \frac{ap}{b + \rho [1 + cp]}, \tag{37}$$

$$n = 3, V_3 = \frac{ap}{b + \rho \left[ 1 + cp + \frac{1}{2} (cp)^2 \right]}, \tag{38}$$

$$n = 4, V_4 = \frac{ap}{b + \rho \left[ 1 + cp + \frac{1}{2} (cp)^2 + \frac{1}{6} (cp)^3 \right]}, \tag{39}$$

.....

$$n \rightarrow \infty, V_\infty = \frac{ap}{b + \rho \exp(cp)}. \tag{40}$$



An increase in the order of the system corresponds to the mechanism of substrate inhibition with greater intensity. The formulas obtained, regardless of order  $n$  include three experimentally determined parameters.

Analysis of the spectrum of solutions requires quantitative estimation of the relationship between the shapes of the curves of expressions, belonging to it. To do this, it is convenient to represent formulas (37)–(40) in the dimensionless form:

$$V^* = \frac{V}{a}, \tag{41}$$

$$V_2^* = \frac{cp}{cb + cp[1 + cp]}, \tag{42}$$

$$V_3^* = \frac{cp}{cb + cp \left[ 1 + cp + \frac{1}{2}(cp)^2 \right]}, \tag{43}$$

$$V_4^* = \frac{cp}{cb + cp \left[ 1 + cp + \frac{1}{2}(cp)^2 + \frac{1}{6}(cp)^3 \right]}, \tag{44}$$

$$V_e^* = \frac{cp}{cb + cp \exp(cp)}, \tag{45}$$

where  $V^*$  is the specific bio-oxidation rate, referred to its maximum possible value without the inhibition effect;  $cb$  is the factor of the shape of the curve, corresponding to a definite formula of the spectrum;  $cp$  is the factor of the range of argument, determining the curve length by X-axis.

A dimensionless curve shape factor (SF)  $cb$  unambiguously determines the coordinates of maximum and inflection points for dependences of spectrum with  $n \geq 2$ . At small values of dimensionless argument range factor (RF)  $cp$ , formulas (42)–(45) will give close results by virtue of quick convergence of a series in denominator.

By calculation with the use of the least square method, we found coefficients in statistically significant dependences (46)–(53) of coordinates the maximum on SF  $cb$ . The coordinates, which are the original data for obtaining dependences (46)–(53), were found by the known method of numerical differentiation of calculation curves of the corresponding order. The adequacy of the method is proved by the obtained values of coefficients in expressions (46) and (50), which should be exactly equal to 1; 0.5 and 2; 0.5, respectively:

$$cp_{m_2} = 1.0032 * (cb)^{0.5001}, \quad R^2 = 1, \tag{46}$$

$$cp_{m_3} = 0.7017 * (cb)^{0.4233}, \quad R^2 = 0.9981, \tag{47}$$

$$cp_{m_4} = 0.6356 * (cb)^{0.3984}, \quad R^2 = 0.9953, \tag{48}$$

$$cp_{me} = 0.6034 * (cb)^{0.3839}, \quad R^2 = 0.9919, \tag{49}$$

$$V_{m_2}^* = \frac{1}{1 + 1.9995 * (cb)^{0.4999}}, \quad R^2 = 1, \tag{50}$$

$$V_{m_3}^* = \frac{1}{1 + 2.5419 * (cb)^{0.5539}}, \quad R^2 = 0.9992, \tag{51}$$

$$V_{m_4}^* = \frac{1}{1 + 2.7018 * (cb)^{0.5704}}, \quad R^2 = 0.9984, \tag{52}$$

$$V_{me}^* = \frac{1}{1 + 2.7769 * (cb)^{0.5785}}, \quad R^2 = 0.9977, \tag{53}$$

where  $cp_{mi}$  is the dimensionless coordinate of maximum on X-axis for the curve of the  $i$ -th order;  $V_{mi}^*$  is the dimensionless coordinate of maximum on Y-axis for the curve of the  $i$ -th order;  $R^2$  is the determination coefficient.

Comparison of coefficients in dependences (46)–(53) shows a significant quantitative difference of second-order formulas (46) and (50) from other formulas of the range. In this case, we should note proximity of dependences (48) and (49), as well as (52) and (53). These dependences are also characteristic of the coordinates of inflection points. The above analysis demonstrates the special place of curve shape for  $n=2$  in the general series of the curves of higher orders. With an increase in order  $n \geq 3$ , the difference in curve shape is quickly leveled. Beginning with  $n=4$ , the curve shape parameters quantitatively differ little from shape parameters for  $n \rightarrow \infty$  ( $cp_{me}, V_{me}^*$ ).

Thus, formula (45), the corresponding to the mechanism of limiting order ( $n \rightarrow \infty$ ) with the highest inhibition intensity, is close by the parameters of the curve shape to all dependences of the spectrum, except for expression (42). That is why substantiation for the use of formula (45) as generalizing should be assessment of the possibility of describing with its use the dependences with lower order and, above all, with minimal  $n=2$ . For complete assessment, it is also necessary to verify the quality of description of dependences, corresponding to mechanisms of higher inhibition intensity by formula (42).

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## 6. The rationale for applicability of the unified computational formula for different models of substrate inhibition

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At the first stage, two series of computational experiments were performed: description of model (43) by formula (42), as well as description of models (42)–(44) by dependence (45). Varying values of SF were accepted as overlapping the actual range:  $cb=0.005; 0.01; 0.025; 0.1; 0.5; 2; 10; 25; 50$ . Approximation accuracy was assigned by average relative error (determined by absolute magnitude) from virtually full match to admissible deviation:  $\delta_0=0.005; 0.02; 0.05; 0.1$ . Determination coefficient  $R^2$  and root mean square error  $\sigma_0^*$ , referred to limiting value of destruction rate  $V=a$  were determined.

These calculations make it possible to compare beforehand the capabilities of models (42) and (45) by the description of the intermediate variant with  $n=3$ . In this case, the application of the least-squares method will lead to distortion of original coefficients:

$$V_{23}^* = \frac{k_a(cp)}{k_b(cb) + cp[1 + k_c(cp)]}, \tag{54}$$

$$V_{e3}^* = \frac{k_a(cp)}{k_b(cb) + cp \exp[k_c(cp)]}, \tag{55}$$

where  $V_{23}^*$  – dependence (42) describes (43);  $V_{e3}^*$  – dependence (45) describes (43);  $k_a, k_b, k_c$  are the distortion coefficients  $a, b, c$ , respectively.

For fixed values of  $\delta_0$ , maximal reachable values of SF  $cp_g$  were calculated. Obviously, higher values of  $cp_g$  ceteris paribus must correspond to the best description of the function. Table 2 shows calculation values of  $cp_g$  for models (42) and (45) during description of intermediate ratio (43).



**Table 2**  
Change in maximum achievable range of argument  $cp_g$  depending on shape factor  $cb$  at assigned relative error  $\delta_0=0.005; 0.02; 0.05; 0.1$

$cb$	$V_e$ describes $V_3$				$V_2$ describes $V_3$			
	$cp_{g05}$	$cp_{g2}$	$cp_{g5}$	$cp_{g10}$	$cp_{g05}$	$cp_{g2}$	$cp_{g5}$	$cp_{g10}$
0.005	0.9001	1.648	2.557	3.625	0.5076	1.0645	1.8304	2.82
0.01	0.9235	1.686	2.614	3.705	0.5403	1.1124	1.8963	2.908
0.025	0.9722	1.764	2.727	3.865	0.6039	1.2061	2.0277	3.084
0.1	1.1028	1.986	3.049	4.31	0.6909	1.45	2.3787	3.564
0.5	1.309	2.504	3.842	5.39	0.8839	1.885	3.0855	4.353
2	1.653	3.223	5.151	7.207	1.1971	2.409	3.4107	4.688
10	2.3872	4.718	7.702	11.015	1.8329	2.82	4.2025	6.118
25	3.081	6.005	9.99	14.277	2.1879	3.333	5.0565	7.545
50	3.772	7.331	12.251	17.567	2.492	3.923	6.013	9.042

It follows from the data in Table 2 that formula (45) has significantly more commonality when describing the dependence with order  $n=3$  in all the range of variations in  $cb$  at any specified accuracy  $\delta_0$ . Naturally, formula (45) will also have an advantage over model (42) when describing dependences with higher order  $n>3$ . It is also necessary to note one negative property of model (42): at  $cb>0.5$ , there occurs a catastrophic (up to hundreds of thousands) increase in distortion coefficients and a sharp increase in the number of iterations. These effects arise because of poor expression of a minimum and fractionality of function (42).

Table 3 shows the results of assessment of accuracy of descriptions of function  $V_2$  with the least order by the dependence with limiting order  $V_e$ . At fixed values of  $\delta_0$ , we calculated the maximal achievable values of SF, assigned to the coordinate of a maximum on the X-axis  $cp_g/cp_m$ . These relative values of the range factor (RVRF) make it possible to assess visually the capabilities of model (45) in practice. The magnitude of RVRF in laboratory experiments does not usually exceed 5–6 units, except for the cases for  $cb<0.01$  when  $cp_g/cp_m=8–10$ .

**Table 3**  
Change of relative range of argument  $cp_g/cp_m$  and root mean square error  $\sigma_0^*$ , depending on shape factor  $cb$  at relative error  $\delta_0=0.005; 0.02; 0.05; 0.1$

$cb$	$cp_g/cp_m$				$\sigma_0^*$			
	0.005	0.02	0.05	0.1	0.005	0.02	0.05	0.1
0.005	8.01	18.29	34.82	60.00	0.00433	0.01421	0.02759	0.04109
0.01	6.12	13.75	26.01	44.76	0.00415	0.01367	0.02654	0.03953
0.025	4.38	9.64	18.04	30.97	0.00383	0.0127	0.02465	0.03671
0.1	2.69	6.17	11.37	19.30	0.00301	0.01057	0.02055	0.03048
0.5	1.65	4.25	7.65	12.91	0.00162	0.00731	0.01426	0.02123
2	1.22	3.21	6.11	10.27	0.00081	0.00439	0.0091	0.01361
10	0.97	2.62	5.24	8.76	0.00034	0.00217	0.0048	0.00719
25	0.89	2.42	5.00	8.35	0.0002	0.00139	0.0032	0.00481
50	0.86	2.32	4.89	8.16	0.00014	0.00098	0.00232	0.0035

It follows from the data in Table 3, that at high accuracy  $\delta_0=0.005$ , practical capabilities of model (45) are limited to small values of SF  $cb=0.01$ . However, at a 5 % relative error, formula (45) already describes with guarantee an actual range of changes in SF, which for the dependence with minimal order is focused in the region of  $cb<0.5$ . For models with a higher order, the capabilities of formula (45) are higher by virtue of proximity of curves' shapes.

The values of relative root mean square error  $\sigma_0^*$  decrease to very small values at an increase in  $cb$ , which indicates lesser visibility of the application of this indicator compared to an average relative error. Determination coefficient also is inferior to indicator  $\delta_0$  in sensitivity in relation to varying parameters.

The above analysis was performed in the coordinates of dimensionless parameters  $cp_{gn}$  and  $cb_n$  for the described dependences  $V_n^*$  of the  $n$ -th order. In the framework of the computation experiment, we calculated range factor  $cp_{gen}$  and shape factor  $cb_{en}$ , corresponding to formula  $V_{en}^*$ , that describe dependence  $V_n^*$ . Fig. 2 shows the results of the second series of the computational experiment in calculated coordinates of the describing formula  $V_{en}^*$ .

For each group of curves, the assigned relative error varies from top to bottom:  $\delta_0=0.1; 0.05; 0.02; 0.005$ .

It follows from the data in Fig. 2 that the admissible range of existing calculated parameters  $cp_{gen}$  and  $cb_{en}$  of describing dependence  $V_{en}^*$  corresponds to each described function  $V_n^*$  of the definite order. The regions are inter-crossing and are limited at the top and at the bottom by curves with maximum  $\delta_0=0.1$  and minimum  $\delta_0=0.005$  by average relative errors, respectively. On the left, the regions are limited by the Y-axis, and on the right – by extreme points of curves with different values of  $\delta_0$ . At an increase in order  $n$ , the corresponding region of existence of solutions for the describing dependence expands on both axes and is shifted up Y-axis. This pattern is indicative of a natural increase in capabilities of formula  $V_{en}^*$  at an increase in the order of a described curve at a fixed relative error. The region under the lowest curve ( $V_2^*$ ;  $\delta_0=0.005$ ) in Fig. 2 is the region of practically invariant solutions in relations to the order of describing dependence. In the insensitivity zone, the value of the range factor is so small that experimental points do not contain any significant information about the curve shape.

At the second stage of the study, to assess the influence of a random error, we performed the third series of computational experiments using the random number generator. The developed programs were supplemented with the unit, in which the experimental data  $V_{2s}^*$  were represented in the form:

$$V_{2s}^* = V_2^* + \Delta V_s^*, \tag{56}$$

where  $\Delta V_s^*$  in the non-systematic random error.

The computational series included six implementations on each of the four assigned values of maximal possible random error  $\Delta V_{gs}^* \geq \Delta V_s^*$ . The calculated value of relative root mean square error  $\sigma_s^*$  corresponded to each implementation. The computational series were performed for varying parameters: at  $\delta_0=0.05 - cb=0.05; 0.1; 10$  and at  $cb=0.1 - \delta_0=0.02; 0.05; 0.1$ . Magnitudes of  $cp_g$  were accepted as equal to those calculated before for corresponding  $\delta_0$  and  $cb$ . A certain initial root-mean square deviation  $\sigma_0^*$  also corresponded to value  $\delta_0$ . We assessed the influence of a random error on accuracy of description by formula (45) of dependence (42) –  $V_{e2s}^*$  and by formula (42) of itself –  $V_{22s}^*$ .



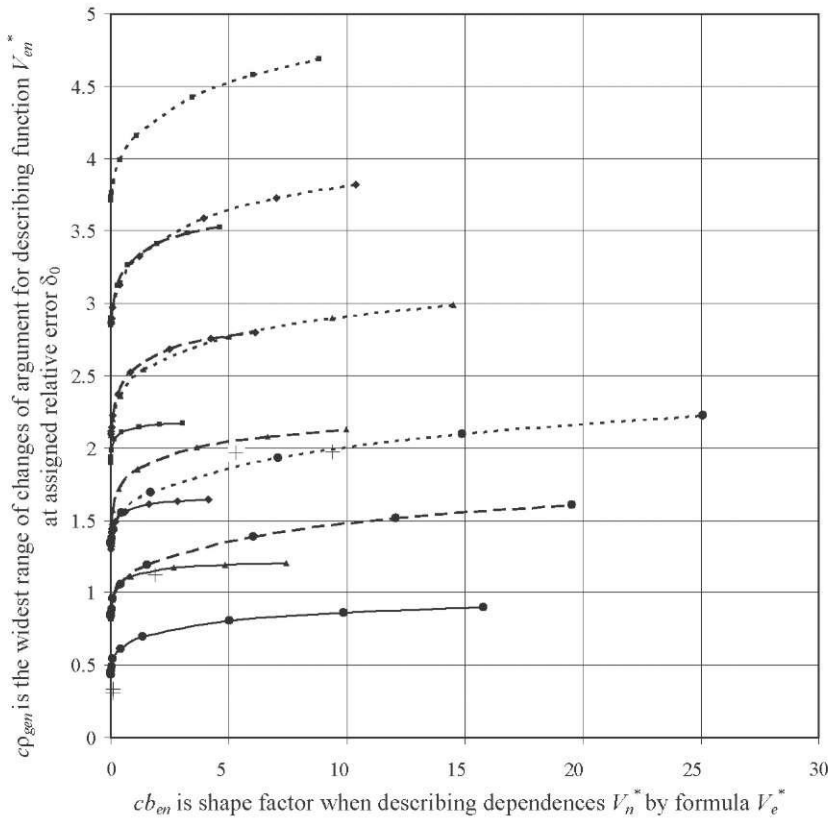


Fig. 2. Dependence of the widest range of argument change  $cp_{gen}$  on shape factor  $cb_{en}$  when describing ratio  $V_n^*$  by formula  $V_e^*$ . Group of continuous curves –  $n=2$ ; dashed curves –  $n=3$ ; dotted curves –  $n=4$

The results of assessment for the data averaged by six implementations are shown in Fig. 3, 4. It follows from the data in Fig. 3, 4 that at an increase in random error, statistical difference between descriptions  $V_{e2s}^*$  and  $V_{22s}^*$  continuously decreases. The corresponding average relative errors  $\delta_e$  and  $\delta_2$  become equal when condition  $\sigma_s^*/\sigma_2^* \geq 2.4$  is met. A random non-systematic error  $\delta_s$  seems to absorb initial error  $\delta_0$  of mismatch of a describing and described functions.

Continuous lines –  $\delta_e$  for model  $V_{e2s}^*$ , dashed lines –  $\delta_2$  for model  $V_{22s}^*$ . For each pair of curves, the assigned shape factor varies from top to bottom:  $cb=10; 0.1; 0.005$ .

Continuous lines –  $\delta_e$  for model  $V_{e2s}^*$ , dashed lines –  $\delta_2$  for model  $V_{22s}^*$ . For each pair of curves, initial relative error varies from top to bottom:  $\delta_0=0.1; 0.05; 0.02$ .

It is obvious that a random error leads to a distortion of numerical values of coefficients when describing a second-order function itself  $V_{22s}^*$ . A relative error in determining coefficients, averaged by six implementations, is limited by  $\delta_k \leq 0.05$  only within  $\delta_s \leq 0.01$  of a relative random error for the describing formula as a whole. At  $\delta_s=0.05-0.1$ , an averaged error in evaluation of coefficients reaches the values of  $\delta_k=0.2-0.35$ . In particular implementations, considerably larger gaps in the assessment of the accuracy of a model as a whole and accuracy of determining its coefficients were detected. To determine reliably the true values of empirical coefficients, it is necessary to perform at least six series of a very accurate physical experiment.

It is possible to argue that obtained formula  $V_{e2s}^*$  describes not original dependence  $V_2^*$ , but rather a new ratio  $V_{22s}^*$  with distorted coefficients and the error of initial mismatch  $\delta_0$  decreasing even to zero. The latter circumstance follows from the evident equality:

$$\delta_e = \delta_0 + \delta_s. \tag{57}$$

That is why when using the graphs from Fig. 2 to assess the order of experimental dependences, we should correlate the points in coordinates « $cp_e-cb_e$ » with the curves corresponding to smaller  $\delta_0$  and larger values of  $n$ .

The points presented in Fig. 2 according to Table 4 indicate that destruction of hydrogen sulfide, sulfur dioxide and methane occurs in a zone of insensitivity to the order of a described function. For ammonia and formaldehyde (anaerobic process), the order is  $n \geq 4$ , for formaldehyde (aerobic process), destruction of hydrogen sulfide, sulfur dioxide, and methane occurs in a zone of insensitivity to the order of a described functions. For ammonia and formaldehyde (anaerobic process), the order is  $n \geq 4$ , for formaldehyde (aerobic process),  $n \geq 3$ .

These conclusions are supported by direct comparative estimate of capabilities of formulas of the range, shown in Table 5.

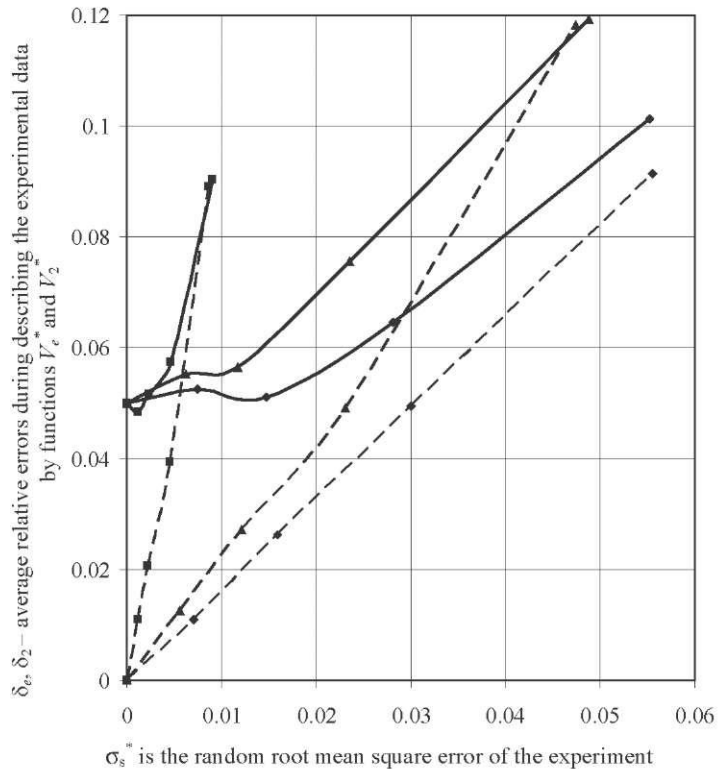


Fig. 3. Dependence of average relative errors  $\delta_e$  and  $\delta_2$  on random root mean square error of experiment  $\sigma_s^*$  and shape factor  $cb$  at  $\delta_0=0.05$



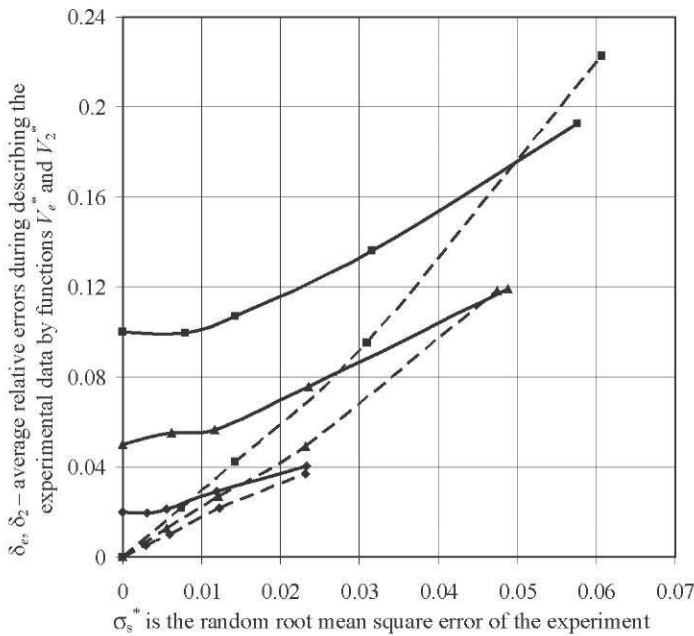


Fig. 4. Dependence of average relative errors  $\delta_e$  and  $\delta_2$  on root mean square error of experiment  $\sigma_s^*$  and initial relative error  $\delta_0$  at  $cb=0.1$

For ammonia and formaldehyde (both kinds of processes), formula  $V_2$  has clearly worse indicators due to the higher order of the described experimental data. For sulphur dioxide and methane, the advantage of formula  $V_2$  is not statistically significant, and for hydrogen sulphide, there is a statistically insignificant advantage of formula  $V_e$ . Increased numerical values of empirical coefficients demonstrate the previously marked negative feature of dependence  $V_2$  when describing the curves of high orders.

Thus, the practical application of model (45) also proves its commonality when describing the kinetics of biodestruction of various harmful substances with substrate inhibition of varying intensity. It should be noted that formula (45) is workable technically for any whatever large ranges of concentrations of environmental pollutants.

**7. Discussion of results of studying the regularities of biodegradation process with substrate inhibition**

The study includes obtaining a full range of theoretical solutions for the dependence of biodestruction rate on substrate concentration and the evidence of the existence in this spectrum of a unified dependence, generally describing the mechanisms of substrate inhibition of varying intensity.

The application of the method of dynamics of averages resulted in obtaining of a full range of theoretical dependences of biodegradation with substrate inhibition. The solution of the spectrum is distinguished by the number of terms of a quickly converging power series in denominators of formulas. The number of terms of the series characterizes the order of the dependence, corresponding to various inhibition intensity, changing from minimal  $n=2$  to limiting  $n=\infty$ . We detected the proximity of shapes of curves for dependences of specific bio-oxidation rate on concentration of harmful substances for orders from  $n=3$  ( $V_3$ ) to  $n=\infty$  ( $V_e$ ), and consequently, the essential difference of the dependence of minimum order  $n=2$  ( $V_2$ ) on other formulas of the range. The value of coordinate of maximum of function  $V_2$  is by 1.42 times higher than in dependence  $V_3$ . The results of analysis of the full spectrum of solutions made it possible to determine formulas  $V_2$  and  $V_e$  for estimation of their application as generalizing ones and state the sequence of necessary calculations.

To prove the possibilities of using the unified formula in describing the processes of bio-oxidation with substrate inhibition, the method of numerical experiment was applied. Mutual description of various functions from the full range was performed using the least squares method until obtaining the maximum range of the change in argument at the assigned relative error.

At the first stage, the accuracy of description of intermediate dependence  $V_3$  by formulas  $V_2$  and  $V_e$  was compared. The obtained data (Table 2) suggests that the range of variation of argument in formula  $V_e$  is by 1.5–2 times more in comparison with dependence  $V_2$ . This result made it possible to exclude formula  $V_2$  from the candidates to being applied as a generalizing dependence. At this stage, the numerical experiment on description of dependences of other orders  $V_2, V_3$

Table 4

Dimensionless parameters of description of experimental data [11] by formula  $V_e$

Coordinates	Hydrogen sulfide	Sulfur dioxide	Methane	Ammonia	Formaldehyde (aerobic process)	Formaldehyde (anaerobic process)
$cb_e$	0.1296	0.06458	0.06493	5.276	1.873	9.373
$cp_e$	0.3362	0.3318	0.3121	1.966	1.124	1.972

Note: the coordinates are shown in Fig. 2 by crosses

Table 5

Comparative estimation of accuracy of description of experimental data [11] by formulas  $V_2, V_3, V_4$  and  $V_e$

Parameter	Hydrogen sulfide	Sulfur dioxide	Methane	Ammonia	Formaldehyde (aerobic process)	Formaldehyde (anaerobic process)	
a	$V_2$	72.539	67.348	416.19	$1.0363 \cdot 10^5$	219.63	3,368.2
	$V_3$	71.509	64.465	402.42	262.20	207.08	3,314.9
	$V_4$	71.350	64.116	400.93	58.392	204.97	3,286.2
	$V_e$	71.406	64.003	400.66	39.683	203.84	3,263.0
b	$V_2$	39.052	25.784	2.4102	$1.1633 \cdot 10^5$	1,496.0	4,803.5
	$V_3$	38.534	24.172	2.2992	336.28	1,489.3	5,138.8
	$V_4$	38.437	23.972	2.2868	71.480	1,499.4	5,219.4
	$V_e$	38.488	23.898	2.2843	47.048	1,499.6	5,229.0
c	$V_2$	0.0041828	0.0037558	0.037996	988.73	0.0026275	0.0061665
	$V_3$	0.0034280	0.0028010	0.029208	0.48316	0.0014410	0.0024675
	$V_4$	0.0033628	0.0027198	0.028514	0.15185	0.0012904	0.0019772
	$V_e$	0.0033662	0.0027023	0.028427	0.11213	0.0012491	0.0017924
$\sigma$	$V_2$	1.663	1.818	5.556	0.3394	1.505	19.85
	$V_3$	1.640	1.838	5.807	0.2457	1.323	14.94
	$V_4$	1.637	1.843	5.839	0.2400	1.318	13.40
	$V_e$	1.636	1.844	5.842	0.2394	1.336	17.27
$\delta$	$V_2$	0.06739	0.06049	0.03469	0.1082	0.02774	0.1827
	$V_3$	0.06628	0.05940	0.03643	0.08236	0.02548	0.1392
	$V_4$	0.06610	0.05926	0.03665	0.08107	0.02564	0.1257
	$V_e$	0.06607	0.05916	0.03669	0.08144	0.02585	0.1192
$R^2$	$V_2$	0.9810	0.9793	0.9957	0.9511	0.9234	0.9747
	$V_3$	0.9815	0.9789	0.9953	0.9744	0.9408	0.9857
	$V_4$	0.9816	0.9788	0.9952	0.9756	0.9412	0.9885
	$V_e$	0.9816	0.9787	0.9953	0.9757	0.9396	0.9897

Note: magnitudes a, b, c and  $\sigma$  are accommodated with dimensionalities in [11]



and  $V_4$  by formula  $V_e$  was performed. It follows from the data of Table 3 that formula  $V_e$  describes dependence  $V_2$  with 5 % accuracy in the actual range of changes in concentrations of harmful substances. The ratio of the range of a change of argument to the position of maximum is  $>5$  even under conditions of its weak expression.

At the second stage of the numerical experiment, the effect of a random error on the possibility of using a unified formula was simulated. The existence of a random error also leads to a distortion of results when describing experimental data with order  $n=2$  by dependence  $V_2$ . That is why the influence of a random error on comparative accuracy of description of experimental data with a minimal order of inhibition by formulas  $V_2$  and  $V_e$  was modeled. The results of the numerical experiment (Fig. 3, 4) indicate that with an increase in a non-systematic error, the statistical difference between the descriptions by  $V_2$  and  $V_e$  continuously decreases up to zero. Convergence is achieved at the ratio of a random error to the initial error that is equal to  $\geq 2.4$ . This result extends the capabilities of formula  $V_e$  when describing actual data of a lower order.

The results of the numerical experiment prove the possibility of using formula  $V_e$  as unified during practical calculations of kinetics of the biodegradation process with substrate inhibition of varying intensity. Dependence  $V_e$  in its pure form describes the stationary bio-oxidation process without changing the reaction zone and additional arrival of a pollutant in it. The proposed model is not a complete model of a non-stationary process in the bioreactor. The development of such a model requires a separate study. The resulting unified formula is a necessary component of a non-stationary model as the scientific basis for the development of calculation methods and substantiation of project solutions for biochemical treatment plants.

Subsequent improvement of calculation methods also involves assessing the impact of a change in biomass concentration in the biodegradation process.

## 8. Conclusions

1. Using the method of dynamics of averages, we found a full range of theoretical solutions for dependences of speci-

fic bio-oxidation rate  $V_n$  on pollutant concentration  $\rho$ . Each solution differs by the inhibition intensity expressed by the number of members of quickly converging power series in denominators of equations. The size of the series is determined by the order of a solution, varying from minimal  $n=2$  ( $V_2$ ) to limiting  $n \rightarrow \infty$  ( $V_e$ ). The formulas with more than minimal order  $n \geq 3$  are characterized by the proximity of the shapes of curves of «specific rate  $V_n$  – concentration  $\rho$ ». The shape of the curve for the solution with minimal order  $V_2$  differs significantly from other dependences of the range. The value of coordinate of the maximum of function  $V_2$  is by 1.42 times higher than that of dependence  $V_3$ .

2. Mathematical modeling of physical experiments proved the possibility of the practical use of the solution of limiting order  $V_e$  as a unified formula enabling to calculate specific biodegradation rate at any intensity of substrate inhibition. In three series of computational experiments we consistently showed:

– the advantage of formula  $V_e$  compared to formula of minimal order  $V_2$  in accuracy of description of experimental data with intermediate intensity of substrate inhibition  $V_3$ . The advantage is that the possible range of a change in concentrations at the same relative error is by 1.5–2 times larger;

– guaranteed ensuring 5 % accuracy during the description by formula  $V_e$  of experimental data with minimal order  $V_2$  in the actual range of changes in pollutant concentration. The ratio of the maximum range to the coordinate of the position of maximum is always  $>5$ ;

– convergence, even up to statistical equivalence, of descriptions by extreme dependences of ranges  $V_2$  and  $V_e$  of experimental data of minimal order at an increase in a random non-systematic error. Convergence is achieved at the ratio of a random error to the initial description error equal to  $\geq 2.4$ .

The versatility of the dependence of limiting order  $V_e$  is proved by the adequate (determination coefficient  $R^2=0.9396-0.9953$ ) description of empirical data on five harmful substances with varying degrees of inhibition. The existence of biodegradation processes with inhibition intensity of more than minimal  $n \geq 3$  was revealed.

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## ABSTRACT AND REFERENCES

## ECOLOGY

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**CONSTRUCTION OF A GENERALIZED MODEL OF THE HARMFUL SUBSTANCES BIOCHEMICAL DESTRUCTION PROCESS KINETICS UNDER CONDITIONS OF SUBSTRATE INHIBITION USING THE METHODS OF SIMULATION MODELING (p. 6–16)**

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For the purpose of obtaining the complete range of solutions for substrate inhibition of varying intensity, the mechanism of enzyme kinetics in a biocell was modeled by a multi-channel queuing system. A full range of solutions is required to make a well-grounded choice of a unified generalizing formula. The process of biodegradation with substrate inhibition was described mathematically using the method of dynamics of averages. For specific destruction rate, a full range of solutions  $V_n$  of the system from minimum  $n=2$  to limiting  $n \rightarrow \infty$  order was found. It was established that the parameters of the curve shape for the solution with minimum inhibition intensity  $V_2$  substantially stand out from the general series of the spectrum formulas. The value of the coordinate of function maximum ( $n=2$ )  $V_2$  is by 1.42 times higher than that of dependence ( $n=3$ )  $V_3$ .

In the numerical experiment, the physical test was simulated by description with the help of the method of the least squares of the data, assigned by the calculation from the formulas of different structures, bearing in mind a sporadic random error. The series of numerical experiments demonstrated the capability of the formula of limiting order formula  $V_e$  to describe the dependences of the whole spectrum of solutions. During describing the intermediate ratio  $V_3$  with the help of formulas  $V_2$  and  $V_e$ , the benefit is the possible range of changing the concentrations, which is by 1.5–2 times larger at the same relative error for dependence  $V_e$ . For critical minimal order, an average relative error is sure not to exceed five percent. An increase

in random error always result in statistical equality, in accuracy of describing by formulas of minimal  $V_2$  and limiting orders  $V_e$  of the data, assigned by calculation of second-order dependences. Statistical equality is achieved at the ratio of a random error to the initial error equal to  $\geq 2.4$ .

Collectively, the importance of the results of numerical modeling of a physical experiment involves proving the possibility of using the formula of limiting order  $V_e$  as unified when describing the biodegradation processes with different mechanisms of substrate inhibition. This conclusion is proved by the adequate ( $R^2=0.9396-0.9953$ ) description with the help of the dependence of limiting order of experimental data on five harmful substances with varying inhibition degrees. A large amount of calculation allowed achieving a definite result – we obtained the unified formula that makes it possible to proceed to scientifically grounded design calculations for bio-treatment plants.

**Keywords:** biodegradation, substrate inhibition, queuing system, numerical experiment, unified formula.

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**USE OF FLY ASH FOR CONDITIONING THE EXCESS ACTIVATED SLUDGE DURING DELIQUFEACTION AT CHAMBER-MEMBRANE FILTER PRESSES (p. 17–23)**

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Results of experimental studies of deliqufeaction of excess activated sludge from municipal wastewater treatment facilities in chamber-membrane filter presses were presented. To condition the sludge, fly ash from thermal power plants was added as a mineral additive. Experimental studies have shown high efficiency of deliqufeaction of the excess activated sludge with addition of fly ash. Increase in the dose of fly ash has led to an overall increase in filtration capacity and a decrease in moisture content in the filter cake. It was found that in the case of adding fly ash in an amount of 2 wt. % of the initial sludge, deliqufeaction efficiency did not increase significantly. In this case, filtering time was reduced only by 15 % and specific capacity increased by 12 %. In the case of increasing the proportion of fly ash to 6 wt. % of initial sludge, a more intensive acceleration of the process was observed. Filtering duration was reduced from 100 to 10 min, specific capacity increased from 87 to 400 l/m<sup>2</sup>-hr.

Experimental studies have shown that addition of fly ash to sediments of municipal wastewater treatment facilities as a mineral component provides the possibility of deliqufeaction of the suspensions obtained using a chamber-membrane filter press. With optimal doses of 4–5 wt. % of the mass of initial sludge, filter capacity is expected to be 350–400 l/m<sup>2</sup>-hr. The resulting filter cake had moisture content of about 60 %, a dense, dry structure making it possible to transport it in bulk.

**Keywords:** chamber-membrane filter press, conditioning, fly ash, deliqufeaction, filtering duration, activated sludge.

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