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CALCULATING MAIN PARAMETERS OF POLLUTANTS REMOVAL CREATED ON BASIS OF MATHEMATICAL MODEL OF BIOCHEMICAL WASTEWATER TREATMENT PROCESS

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Purpose. Article is devoted to developing of methodology of determining parametres of wastewater biochemical treatment, that allows to control the quality of treated water and to insure ecological safety of environment in general. **Methodology** is based on Monod-Iyerusalymsky model taking into account modern mathematical models of active sludge behavior. **Results.** The model includes the parameters, which can be controlled, requires no additional experiments, describes with a reasonable degree of accuracy the oxidation capacity of treatment plants from which a conclusion can be drawn that the model meets the requirements set forth in scientific and technical literature. The developed methodology of determining oxidation capacity of bioreactor depending on effect of main parameters of the biochemical process and calculation of required content of nitrogen, phosphorus and oxygen includes counting of substrate concentration, amount of biomass formed, loading on active sludge, rate of biomass increase, oxidation capacity of treatment plants, demand for nitrogen and phosphorus and amount of oxygen required. **Originality.** The model recommended for the use to calculate the oxidation capacity is a hybrid model created on the basis of the Monod-Iyerusalymsky model, Mozer equation of pressure selection and active sludge model. **Practical value.** Calculating parameters make it possible to regulate the sludge dose in the bioreactor, the oxidation capacity of biological treatment plants, the rate of biomass increase in the bioreactor, and also to control in the process of operation treatment plants the necessity to add certain microelements and predict behavior of active sludge ability to biodegradation of pollutants. **Conclusions.** The model will make it possible to avoid the changes unforeseen by the project in activity of active sludge and correspondingly in efficiency of purification of wastewater from organic pollutants. References 12, table 1.

Key words: biochemical treatment, wastewater, calculating methodology, active sludge, oxidation capacity, nitrogen, phosphorus.

РАСЧЕТ ОСНОВНЫХ ПАРАМЕТРОВ УДАЛЕНИЯ ПОЛЛЮТАНТОВ, ОСНОВАННЫЙ НА МАТЕМАТИЧЕСКОЙ МОДЕЛИ ПРОЦЕССА БИОХИМИЧЕСКОЙ ОЧИСТКИ СТОЧНЫХ ВОД

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В результате анализа научно-технической литературы и проведенных экспериментов определены основные параметры процесса биотрансформации загрязнителей сточных вод и факторы, влияющие на качество очистки стоков в биореакторе. Полученная математическая модель процесса позволила разработать методику расчета основных параметров работы биохимических очистных сооружений, необходимых для контроля эффективности их работы и качества очищенных сточных вод, сбрасываемых в поверхностные водоемы. В целях управления природными и инженерными сооружениями водоотведения и повышения экологической безопасности окружающей среды предлагается определение концентрации субстрата (количества органических веществ в стоках), скорости роста и количества образующейся биомассы, нагрузки на активный ил биореакторов, окислительной способности сооружений, потребности в азоте и фосфоре для поддержания нормальной жизнедеятельности микроорганизмов активного ила.

Ключевые слова: биохимическая очистка, сточные воды, методика расчета, активный ил.

ACTUALITY. The ecological safety insurance is impossible without sufficient management of quality of wastewater treatment. Biotransformation of organic pollutants, present in watewater, is effective method for its treatment, but the main agent of the process – active sludge – is a biological system, which is very sensual for any changes of concentration and values of chemical matters in wastewater, and also for external parameters [1, 2].

PURPOSE. The use of mathematical models describing the process of biochemical treatment considerably facilitates and improves operation of treatment plants. This is because they enable to select the optimum conditions of the functioning of microorganisms in facilities, assess the behavior of treatment plants in response to a certain scenario of the development (characteristics of wastewater fed for treatment, active sludge, loading on the treatment plants, etc.), predict possible consequences after certain changes during the treatment process, increase the efficiency of the removal of pollutants, reduce the consumption of energy, chemical reagents and funds for servicing treatment plants, etc.

When the introduction of biological wastewater treatment technologies only started in our country, it was necessary, first of all, to ensure the efficient removal of organic and suspended matters from effluents. However, as early as the beginning of the 90s years the efficient removal of nitrogen and phosphorus came to the fore. Therefore, by the end of the 90s years the need arose for new mathematical models describing the process of biochemical treatment of municipal wastewater. This was caused, on the one part, by the necessity for optimization of operation of treatment plants and, on the other part, by the necessity for their reconstruction by means of the development of the nitrification/denitrification and biological phosphorus removal technologies in Ukraine.

METHODOLOGY. Among the models existing today the most known and recognized ones are “Active Sludge Models” (ASM1, ASM2 and ASM3) developed by the International Association on Water Pollution Research and Control (IAWPRC) [3-5]. These models describe the processes of removal of organic matters and nitrogen compounds from wastewaters, and versions 2 and 3 describe also the phosphorus removal. Many calculations for the abovementioned purposes are made by these models. However, as detected through practice, even these most complete models have essential drawbacks. In the models nearly half of all constants and parameters used in them (8 of 19), according to data of authors, require further clarification in laboratory experiments for adaptation to the conditions of a particular object. For facilitating the description of the processes taking place in bioreactors, one can also use the model on the basis of the Monod-Iyerusalymsky model [2] with the help of which the oxidation capacity of the bioreactor can be determined depending on the parameters of wastewaters such as temperature, *pH*, total nitrogen, oxygen concentration in the bioreactor, concentrations of NH_4^+ and PO_4^{3-} (as one of the most significant pollutants in wastewater, that influence on the process of biochemical treatment).

On the basis of the analysis of scientific literature and pooling of the existing experience the following requirements were developed which the mathematical model [6] should meet:

1. The model should describe the oxidation capacity of treatment plants with a reasonable degree of accuracy depending on the main parameters affecting the process of biological treatment of wastewaters of malting enterprises and similar-in-content wastewaters and allow the calculation of the oxidation capacity depending on the concentrations of main factors, process flow sheet and mode of the treatment plant operation.
2. All parameters of the model should be determined on the basis of operational data or taken as constants, i.e. the model should not include the parameters the determination of which requires special experiments.
3. The model should include all manageable parameters for ease of its use at the stage of the optimization of process conditions.
4. The model should include all main processes influencing the treatment efficiency in the bioreactor-membrane module system.

RESULTS. As a result of the analysis of experimental data obtained and existing research methods, the method of carrying out analysis with and without the time factor allowed to investigate the correlation dependences between the efficiency of wastewater biochemical treatment and values of the relevant indicators of wastewaters: temperature, pH, chemical oxygen demand (COD) value at the inlet in the bioreactor, concentration of oxygen, nitrogen and phosphorus in the bioreactor [2]. As a result of the dynamical analysis of experimental data obtained, it was determined that the concentrations of phosphorus and nitrogen had a considerable impact on the biomass increase in the bioreactor. The statistical analysis showed that in the starting period there was a shortage of organic substrate (which resulted in the insufficient concentration of active sludge). The analysis of correlation dependencies shows that the second by value is the factor of temperature [2].

To increase the effectiveness of pollutants removal authors propose the use of methods of biochemical process intensification: increase fermentation temperature, two- and several stages fermentation, in which the second and subsequent stages are used for the separation of excess water and reduction the volume of the fermented substrate, increase the concentration of biomass of microorganisms in bioreactors, and technologies of prior mechanical, chemical and thermal processing of biomass. The last methods allows not only to increase effectivity of treatment process, but also to decrease biomass amount and energy need for bioreactors.

The processes of biological treatment of wastewaters that proceeds in the voidage or on the carrier surface are the result of metabolic activity of microorganisms the basis of which is composed of reactions catalyzed by enzymes both inside and outside the cell.

The mathematical description of the kinetics of enzymatic reactions is based on the assumption of the existence of the enzyme substrate complex and dependence of the reaction rate on the decomposition rate of this complex with formation of the reaction product and free enzyme [3, 6]. According to this hypothesis for the enzymatic reactions proceeding by the scheme

$$E + S \Leftrightarrow E\ S \Leftrightarrow E + P$$

where S – the substrate concentration, E - the enzyme concentration, ES – the enzyme-substrate concentration, P – the concentration of reaction products.

Michaelis and Menten derived a well known equation [3, 6]:

$$V = \frac{V_{\max} S}{S + K_m},$$

where V – the rate of biochemical substrate destruction referred to a unit of active biomass of microorganisms, mg/g·h; V_{max} – the maximum specific rate of biochemical substrate destruction referred to a unit of active biomass of microorganisms or the reaction rate without limiting by substrate, mg/g·h; S – the substrate concentration (the amount of organic matters in the treated water, mg/l); K_m – the Michaelis constant characterizing the affinity of the substrate enzyme, mg/l.

According to this equation the dependence of the reaction rate on the concentration of an organic matter is expressed by the hyperbolic function.

Kinetics of oxidation of organic pollutants of wastewaters estimated by BOD, as well as oxidation of specific ingredients and oxidation of ammonium nitrogen (nitrification) are considered by many authors similarly to kinetics of the enzymic analysis and described by the Michaelis-Menten equation [2, 7–8]. The complex structure of organic matters in the wastewater in this case is approximated by a simple source of carbon nutrition.

In order to describe more complex enzyme reactions a great number of relevant modifications of this equation was developed which reflect the mechanisms of the interaction of the enzyme, substrate, inhibitors and other components of the reaction.

The use equations of enzymatic reactions and the Michaelis-Menten equation is convenient in processing of experimental data for the purpose of determining the kinetic constants in order to assess and compare the biological oxidation capacity and calculate the processes of treatment of different organic matters and types of wastewaters.

The most important characteristic of biological treatment is the rate of the growth of microorganisms. The studies of Monod and Iyerusalymsky showed that the biomass growth rate (μ) is described by the equation similar to the Michaelis-Menten equation:

$$\mu = \frac{\mu_{\max} S}{S + K_m},$$

where the growth rate (μ) is expressed by the equation:

$$\mu = \frac{1}{X}\frac{dX}{dt}$$

and the rate of biomass buildup is equal to

$$\frac{dX}{dt} = \mu X,$$

where X is the concentration of microorganisms. Then the rate at which organisms are washed out from the reactor will be determined by formula:

$$-\frac{dX}{dt} = \frac{XQ}{W} = XT.$$

Therefore, the total increase will be:

$$\mu X - \frac{X}{T} = X\left(1 - \frac{1}{T}\right).$$

The relationship between the rate of the substrate consumption and the rate of the biomass growth is expressed by the approximation by using a coefficient of proportionality Y, the so called "economic coefficient", which characterizes the biomass yield per unit of the substrate consumed:

$$\frac{dX}{dt} = Y\frac{dS}{dt}, \dots.. \frac{dX}{dS} = Y.$$

The rate of the substrate consumption is determined by the following equation:

$$-\frac{dS}{dt} = -\frac{dS}{dX}\frac{dX}{dt}.$$

It is obvious that any change in the substrate concentration in the culture (dS/dt) is equal to the input of the substance minus yield of the substance plus its consumption, or

$$\frac{dS}{dt} = \frac{S_0}{T} - \frac{S_1}{T} - \frac{X}{YT},$$

However, in a steady state the rate of substrate concentration (dS/dt) is equal to zero. Then

$$\frac{S_0}{T} = \frac{S_1}{T} - \frac{X}{YT},$$

or

$$X = Y(S_0 - S_1).$$

Bacteria that carry out the deep removal of heavily oxidizable and bio-resistant organic matters possess an efficient metabolism and low growth rates. The removal of heavily oxidizable organic matters in the biological treatment facilities with free-floating activated sludge often fails to give a proper result in consequence of washing out from the system the microorganisms that oxidize these matters since they have low growth rates. The retention of such microorganisms in the biological treatment facilities in the voidage is practically impossible.

Actually, at an insignificant sludge increase, e.g. 0,1 mg/mg of the removed BOD, the retention of sufficient amount of free-floating activated sludge in the aerotank is impossible [9]. In oxidation of wastewater with BOD=75 mg/l (15 mg/l at outlet) the increase will be 6 mg/l, the washout of activated sludge from the secondary sedimentation tanks for a well flocculating sludge at the best case is 10…12 mg/l, which exceeds the increase of microorganisms. Therefore, in this case the advanced and reliable water treatment can be achieved only by using the immobilized microorganisms not washed out with the water flow.

The population of the sludge microorganisms has the entire spectrum of species that slowly grow. Except the latter the species can appear that grow in these conditions faster than initial ones. The substitution of initial forms by them results in the population alteration. According to the Mozer analysis [8], one species (A) replaces the other (B) provided that

$$\mu_a > \mu_b.$$

The larger difference between the specific rates of growth the faster this replacement takes place and selection in favor of the fast-growing species acts more efficient.

Mozer characterizes the pressure of selection as a difference in specific rates of growth of the given species [8]:

$$\sigma = \mu_a - \mu_в.$$

In the absence of the process limitation by the substrate concentration the growth rates and oxidation rates are close to maximum ones and selection is carried out in favor of the microorganisms that grow with the maximum rate $\mu_{\max}$.

Considering that the change in the concentration of biomass of both species of microorganisms (X_a, $X_в$) at flow-through cultivation is determined not only by the increase, but also by the allocation of a part of biomass, the expression may be written as:

$$dX_a / dt = \mu_a X_a - X_a / T,$$
$$dX_в / dt = \mu_в X_a - X_в / T,$$

where T – time of residence or aeration in reactor,h.

At a steady state at which dX/dt = 0:

$$\left(\frac{\mu_{a\max} S}{(K_{am} + S)} - \frac{1}{T} \right) Y (S_0 - S_1) = 0,$$

$$\left(\frac{\mu_{B\max} S}{(K_{Bm} + S)} - \frac{1}{T} \right) Y (S_0 - S_1) = 0,$$

At substrate concentrations not limiting the growth when $S>>K_{am}=S_o$ and $S>>K_{Bm} =S_0$, we can conceder that $K_{am}+S =S$ and $K_{Bm}+S=S$. In this case and if $S_1=S_o$:

$\mu_a \cong \mu_{a\max}$ and $\mu_b \cong \mu_{b\max}$,

$$\left(\mu_{a\max} - \frac{1}{T} \right) Y_a = 0$$

$$\left(\mu_{B\max} - \frac{1}{T} \right) Y_B = 0$$
.

The obtained equations show that the main parameter determining the species in the reactor at constant effluent discharge (at the same T) and oxidation of easily oxidable organic matters which are characterized by sufficiently high economic coefficient (Ya$\cong$YB) is the value of the maximum growth rate. The pressure of selection is generally determined by the difference of the maximum growth rates:

$$\sigma = \mu_{a\max} - \mu_{в\max}.$$

So, in active sludge biocenosis during oxidation of easily oxidable organic substrate with high economic coefficient the most fast-growing species, which have the highest maximum rates of growth and oxidation, are automatically separated.

In the reactor in the integrated treatment when the substrate concentration is usually low, So>>S, ($S<<K_{am}$ i $S<<K_{вm}$), one can conceder that $K_{am}+S\cong Kam$ and $K_{em}+S\cong K$*вт*. In this case the rates of growth of the species under consideration are lower than maximum ones ($\mu_a >> \mu_b$ i $\mu_b << \mu_{b\max}$) and their values are generally determined by the value of parameter K_m:

$$\mu_a \cong \frac{\mu_{a\max} S}{K_{am}}, \quad \mu_B \cong \frac{\mu_{B\max} S}{K_{Bm}}.$$

$$\left(\frac{\mu_{a\max} S}{K_{am} - \frac{1}{T}} \right) Y_a S_0 = 0,$$

$$\left(\frac{\mu_{B\max} S}{K_{Bm} - \frac{1}{T}} \right) Y_B S_0 = 0$$
.

- the change in the concentration of biomass of both species of microorganisms at a steady state.

In oxidation of heavily oxidizable organic pollutants when Y_a and Y_B => 0, it follows that in the reactor operating in the mode of integrated treatment, at low substrate concentration, the species are selected not by the maximum growth rate, but by the minimum value of constant $K_т$, and it is this value that determines, under conditions of substrate limitation, the value of growth rate of the basic active species.

The selected model of biochemical wastewater treatment meets the above requirements. The model adapted for the bioreactor contains 4 constants and 4 parameters versus 8 ones in the models developed by IAWPRC. At the same time the detection of these constants is carried out in the model not by means of additional laboratory experiments, but through the use of operational data of the object. All processes in the model are described on the basis of manageable parameters. Such parameters include in this case the following:

1. The nitrogen concentration in wastewater.
2. The temperature of wastewater fed into treatment plants.
3. The concentration of total nitrogen at inlet into biological treatment plants.
4. The PO_4^{3-} concentration in wastewater.

The above manageable parameters make it possible to regulate:

– the sludge dose in the bioreactor,
– the oxidation capacity of biological treatment plants,
– the rate of biomass increase in the bioreactor,

and also control in the process of operation treatment plants the necessity to add certain microelements since contrary to municipal wastewaters which have, as a rule, sufficient amount of microelements required for nutrition of microorganisms the wastewaters of malting enterprises very often have insufficient amount of microelements [10]. Consequently, the unforeseen changes in activity of the biocenosis of active sludge can take place in the absence of special addition to the bioreactor of those microelements which are lacking for activity of microorganisms.

The developed methodology of determining oxidation capacity of bioreactor depending on effect of main parameters of the biochemical process and calculation of required content of nitrogen, phosphorus and oxygen includes counting of substrate concentration, amount of biomass formed, loading on active sludge, rate of biomass increase, oxidation capacity of treatment plants, demand for nitrogen and phosphorus and amount of oxygen required.

The necessary information for calculating should include the following data:

– biological oxygen demand (S_{BOD}), mg/l;
– chemical oxygen demand (S_{COD}), mg O_2/l;
– concentration of suspended matters, mg/l;
– concentration of active sludge (X), mg/l;
– concentration of total nitrogen (TKN), mg/l;
– concentration of NH_4-N (S_{NH4}), mg/l;
– *pH*,
– total phosphorus (P), mg/l;
– concentration of orthophosphates (S_{PO4}), mg/l;

– retention time of wastewater in construction (SRT), days;
– coefficient of biomass growth, kg COD / kg COD added;
– capacity of treatment plants, m^3/day.

Initial data for calculation of parameters of the model are presented in Table 1.

Table 1 – Paremeters for determining process demends

Coefficients of heterotrophic biodegradation reaction			
Parameter	Desig-nation	Limits	
Maximum biomass increase	μ_m	3,00	13,2
Half-rate constant	K_m	5,00	40
Biomass increase	Y	0,30	0,5
Endogenous respiration coefficient	k_d	0,06	0,2
Fraction of dead cells	f_d	0,08	0,2
θ -values			
Temperature constant	θ_T	1,03	1,08
Constant of substrate dissociation	k_d (θ_d)	1,03	1,08
Constant of saturation by COD	K_s(θ_S)	1,00	1,00
Oxygen dissociation constant	C_{02}	-	-
PO_4^{3-} dissociation constant	S_{PO4}	-	-
NH_4^+ dissociation constant	S_{NH4}	-	-
Coefficient of inhibition by active sludge degradation products	φ (l/g)	-	-

By the developed methodology the substrate concentration (amount of organic matters in treated water, mg/l) is calculated by formula:

$$S = \frac{K_S(1 + k_d \cdot SRT)}{SRT(\mu_m - k_d)}.$$

Amount of biomass formed (kg):

$$P_{X,VSS} = \frac{QY(S_0 - S) + f_d \cdot k_d \cdot Q \cdot Y \cdot (S_0 - S)SRT}{(1 + k_d)},$$

where Q – wastewater flow rate, S_0 – value of substrate (amount of organic matters in treated water, mg/l) at the plant inlet.

Loading on active sludge:

$$F/M = QS_0/VX,$$

$$K_T = k_d \cdot \theta_T^{(T-20)},$$

where F – organic substrate concentration; M – biomass amount, V - rate of chemical degradation of substrate per unit of active microbial biomass.

Rate of biomass increase (g/l):

$$\mu_{max} = \mu_m S_{NH_4}/(S_{NH_4} + K_{S,NH_4})) \cdot (S_{PO_4}/(S_{PO_4} + K_{PO_4})$$

Oxidation capacity of treatment plants (g/g):

$$OC = \frac{\mu_{max} S C_{0_2} X}{(K_m C_0 + K_0 S + C_0 S)(1/(1 + \varphi X))} K_T,$$

where S – substrate concentration; C_{02} – the concentration of dissolved oxygen, mg/l; K_m – the Michaelis constant equal to the substrate concentration at which the reaction rate is half of the maximum rate, mg/l; C_{O_2} – the oxygen dissociation constant, mg/l; φ – the coefficient of inhibition by active sludge degradation products, l/g.

Demand for nitrogen and phosphorus will be equal, respectively:

$$D_N = f_{X,N} F_{SP},$$

$$D_P = f_{X,P} F_{SP},$$

$$F_{SP} = S_0 Y_{demand},$$

where $f_{X,N}$, $f_{X,P}$ – respectively, the content of nitrogen and phosphorus in active sludge, Y_{demand} – the coefficient of biomass increase observed for the given conditions (kg COD/kg of COD added).

Amount of oxygen required for aeration (kg/day or kg/h):

$$Ro = Q\ (S_0 - S) - 1.42\ P_{X,VSS},$$

where $P_{X,VSS}$ – the mass of active sludge in the bioreactor.

On the basis methodology the computer program for calculating parameters of wastewater biochemical treatment in a visual programming environment Delphi was developed.

CONCLUSIONS.

1. As a result of the analysis of scientific and technical literature and patents a conclusion was drawn on the necessity to use the mathematical model for determining the efficiency of treatment of wastewaters in the membrane bioreactor.
2. The model recommended for the use to calculate the oxidation capacity is a hybrid model created on the basis of the Monod-Iyerusalymsky model, Mozer equation of pressure selection and active sludge model ASM3.
3. The selected model will make it possible to avoid the changes unforeseen by the project in activity of active sludge and correspondingly in the efficiency of purification of wastewater from organic pollutants.
4. The model includes the parameters which can be controlled, requires no additional experiments, describes with a reasonable degree of accuracy the oxidation capacity of treatment plants from which a conclusion can be drawn that the model meets the requirements set forth in scientific and technical literature.

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РОЗРАХУНОК ОСНОВНИХ ПАРАМЕТРІВ ВИДАЛЕННЯ ПОЛЮТАНТІВ, ЩО БАЗУЄТЬСЯ НА МАТЕМАТИЧНІЙ МОДЕЛІ ПРОЦЕСУ БІОХІМІЧНОГО ОЧИЩЕННЯ СТІЧНИХ ВОД

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В результаті аналізу науково-технічної літератури та проведених експериментів визначені основні параметри процесу біотрансформації полютантів стічних вод і фактори, що впливають на якість очищення стоків у біореакторі. Отримана математична модель процесу дозволила розробити методику розрахунку основних параметрів роботи біохімічних очисних споруд, що необхідні для контролю ефективності їх роботи і якості очищених стічних вод, що скидаються у поверхневі водойми. З метою управління природними та інженерними спорудами водовідведення та підвищення екологічної безпеки довкілля пропонується визначення концентрації субстрату (кількість органічних речовин в стоках), швидкість росту і кількість утвореної біомаси, навантаження на активний мул біореакторів, окисну здатність споруд, потребу у нітрогені та фосфорі для підтримки нормальної життєдіяльності мікроорганізмів активного мулу.

Ключові слова: біохімічне очищення, стічні води, методика розрахунку, активний мул.

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