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DEPENDENCE OF BIOCHEMICAL TREATMENT OF WASTEWATER FROM PROCESS FACTORS

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Purpose. Biochemical treatment is effective way of pollution decrease in wastewaters, but it has its specific caused by biological origin of active sludge. Article is devoted to research of factors that effect on active sludge and its ability to biodegradation and waste water treatment process. The aim of research is to establish dependences of biochemical treatment of wastewater from factors effected on pollution decrease. **Methodology.** In order to determine the dependence, the statistical analysis was carried out, i.e. the analysis of data was carried out with the neglect of time factors. **Results.** In result of experiments the biggest correlation dependences between efficiency of effluent treatment by basic problematic parameter was obtained for oxidation capacity. This fact indicates the adaptation of microorganisms to values of organic pollutions and constant shortage of organic substrate in wastewater. There were also established correlation dependences between the efficiency of wastewater treatment and values of temperature, acidity level, concentrations of oxygen, nitrogen and phosphorus in the bioreactor. Stable statistic linkage of treatment efficiency with the concentration of activated sludge may be explained by change of relationship of anabolism and catabolism processes in biocenosis of activated sludge, accumulation of heavily oxidizable high-molecular colloids of wastewaters, products of metabolism or degradation of bacterial cells at high concentrations of activated sludge and low loading on sludge. **Originality.** The research describes dependences between treatment efficiency and treatment parameters without considering time factor. **Practical value.** Determined parameters of biochemical treatment of wastewater allow to model and predict behavior of active sludge ability to biodegradation of pollutants. **Conclusions.** Method of carrying out analysis without the time factor was selected with a view to investigate the correlation dependences between the efficiency of wastewater treatment and values of the relevant indicators of wastewaters at the inlet in the bioreactor, concentration of oxygen, nitrogen and phosphorus in the bioreactor. Experimental data showed that in the starting period there was a shortage of organic substrate (which resulted in the insufficient concentration of activated sludge). The analysis of correlation dependencies shows that the second by value is the factor of temperature (optimum values are +20…30 ˚C). References 10, table 1, figures 4.

Key words: biochemical treatment, wastewater, correlation, oxidation capacity, temperature, nitrogen, phosphorus.

ЗАВИСИМОСТЬ БИОХИМИЧЕСКОЙ ОЧИСТКИ СТОЧНЫХ ВОД ОТ ФАКТОРОВ ПРОЦЕССА

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В результате проведенных экспериментов наибольшая корреляционная зависимость получена между эффективностью очистки сточных вод и способностью ила к окислению. Также установлены корреляционные зависимости между эффективностью очистки сточных вод и значениями температуры, уровнем кислотности, концентрациями кислорода, азота и фосфора в биореакторе. Стабильная статистическая зависимость эффективности очистки от концентрации активного ила может быть объяснена изменением отношения процессов анаболизма и катаболизма в биоценозе активного ила, накопление сильно окисляющихся высокомолекулярных коллоидов сточных вод, продуктов метаболизма или деградацией бактериальных клеток при высоких концентрациях активного ила и низкой нагрузке на ил.

Ключевые слова: биохимическая очистка, сточные воды, корреляция, способность к окислению, температура, азот, фосфор.

ACTUALITY. The main causes of decrease of the quality of biochemical wastewater treatment are high concentration of pollutants in wastewater, sharp fluctuations of quantitative indicators and quality of effluents, suboptimal content of nutrients etc. More over, the old treatment equipment is unable to cope with the continuing increase in wastewater certain chemicals, including phosphates [1]. Therefore, it is important to consider factors of treatment effect in order to manage with the treatment process effectively.

PURPOSE. In order to determine the dependence of biotic and abiotic factors and efficiency of biochemical treatment of wastewaters, the statistical analysis was carried out, i.e. the analysis of data was carried out with the neglect of time factors.

METHODOLOGY. The correlation analysis was carried out with a view to determine the significance of the factors affecting the functioning of biochemical process. The comparison of correlation dependences between the efficiency of effluent treatment by the basic problematic parameter, i.e. chemical oxygen demand (COD), and change in the relevant parameters:

- COD of wastewaters - COD_{inlet},
- PO_4 concentration,
- total nitrogen,
- oxygen concentration in the bioreactor,
- pH level,
- temperature,
- NH_4 concentration,
- active sludge concentration C_{as}.

That made it possible to determine the effect of fluctuations of the above biotic and abiotic factors on the biochemical treatment of wastewaters.

In order to simplify the calculations, the analysis of correlations of relevant data was carried out with the use of software, i.e. MathCad v.14 for facilitating the calculations of functions of mathematical statistics and improving accuracy of calculations, i.e. the calculation of correlations.

RESULTS. Obtained correlations and standard deviations (S) are presented in Table 1.

Table 1 – Values of correlations

	ΔХСК	S
$ХСК_{inlet}$	0,905	21,02
PO_4	0,468	176,685
N_{total}	0,361	233,21
O_2	0,401	199,55
pH	0,374	205,20
T	0,801	151,278
NH_4	0,442	2,43
C_{as}	0,468	166,483

The largest value of the correlation of the oxidation capacity (ΔCOD) and COD_{inlet} (R=0.905) is indicative of the adaptation of microorganisms to the values of COD in wastewater. Also, this is connected with the fact that a constant shortage of the organic substrate was observed in wastewater.

The literature also gives the high values of correlation dependence between the COD gradient and oxidation capacity of the system (R=0.84) and efficiency of the COD decrease in the bioreactor (R=0.9) [2, 3].

The second one by value is the correlation between the efficiency of wastewater treatment and temperature. In consequence of further analysis the following dependence between these values was obtained:

$$\Delta COD = \frac{T - 43{,}169}{43{,}255} \quad (1)$$

where ΔCOD - difference in the values of COD at inlet and outlet of the treatment plants, mgO_2/l; T - temperature, ºC.

The above obtained dependence has a linear character in contrast to that given in the scientific and technical literature and has an exponential character, but while using any dependence, it is necessary to bear in mind that the efficient functioning of activated sludge is possible only at temperatures being in the range of 5–32 °C.

For enzymatic reactions taking place during biological treatment as for any chemical and biochemical reactions, the impact of temperature on reactions is expressed by a reaction rate constant. The reaction rate constant is a general parameter allowing many parameters of external medium to be taken into account, specifically: pH; oxygen concentration; concentration of microorganisms; and light intensity in case of photosynthesis. One of the most important parameters is temperature affecting the rate of both chemical and biochemical reactions. Van't Hoff studied that the reaction rate doubled for every 10 ^{o}C increase in temperature [4]. The dependence of the reaction rate on the temperature is most often described with the help of the Arrhenius equation:

$$k = Ae^{-\frac{E_A}{RT}}, \quad (2)$$

where T – absolute temperature or Kelvin thermodynamic temperature; E_A – activation energy to be acquired by reactants so that the reaction should take place; R is the gas constant (R = 8.314 K^{-1} $mole^{-1}$); A – the pre-exponential factor of the frequency connected with the frequency of collision of reactant molecules.

The Arrhenius equation is commonly used in the wastewater treatment systems for modeling the effect of the temperature on the reaction [4].

Let us take a derivative from expression (2) and then integrate the result in the temporary limits of T_0 and T_f for the reaction rate constant is the function dependent on time. As a result we will obtain the following expression:

$$\frac{k_f}{k_0} = \left(\frac{E_A}{RT_f T_0}\right)^{(T_f - T_0)}, \quad (3)$$

where k_0 and k_f are the reaction rate constants at temperatures T_0 and T_f.

Equation (3) allows the time factor to be taken into account in calculation of the reaction rate constant.

Equation (3) has sense at temperatures of +5–25 °C since beyond these limits the expression will have no sense because in this case considerable changes are observed in microbiological composition [4]. High and low temperatures have different effect on microorganisms [5]. High temperatures cause irreversible colloid changes in plasma (folding and disorder in enzyme activity) which results in the stoppage of activity of microorganisms. Low (to -2°C) temperatures do not result in bacterial die-off, but decrease their activity for a certain time.

The microorganisms do not have the thermoregulation capacity and therefore the temperature of the cell content meets the external environment. The normal growth of microorganisms is possible only in a certain interval of temperatures. High and low temperatures have different effect on microorganisms [5].

Henze M. [5] gives another interpretation of this dependence of the biological process rate on the temperature:

$$\mu_{\max}(T) = \mu_{\max}(20^o C) \cdot \exp(\iota(T - 20)), \quad (4)$$

where $\mu_{\max}$ is the maximum increase in activated sludge.

This expression for aerobic processes has sense in the interval of temperatures from 0 to 32ºC. At 32–40 ºC the rate of substrate consumption practically does not change. If the temperature increases above this limit, i.e. at a temperature increase to 45ºC, the rate, as a rule, rapidly decreases almost to zero. The heterotrophic conversion may also take place under thermophilic conditions (50–60ºC), the rate values being higher approximately by 50 % than at 35ºC [5].

The excess pressure causes insignificant effect on microorganisms. They are able to withstand pressure up to 300 MPa and above [4].

The effect of pH on the treatment efficiency, proceeding from the value of correlation R_{pH}=0.374 also exists through the chemical reactions taking place in the process of nitrification. In consequence of the relevant analysis of the obtained data the following dependence describing the effect of pH on the biological treatment of wastewaters was obtained:

$$\Delta COD = e^{\frac{8.426-pH}{0.056}} \qquad (5)$$

The obtained dependence has an exponential character as the dependence given in the literature [5]. On the assumption of standard characteristics of wastewaters under conditions of the absence of violations, pH will be within the range of 6.5-8.5 for which this expression is valid.

The averaged indicators of operation of the treatment plants (fig. 1) confirm the existence of certain dependence between the efficiency of wastewater treatment from organic matters, temperature and pH change due to the relevant enzyme reactions.

The biogenic elements and trace elements are required for successful biochemical reactions in waste water. These include N, S, P, Mg, Ca, Na, Cl, Fe, Mn, Mo, Ni, Co, Zn, C etc.

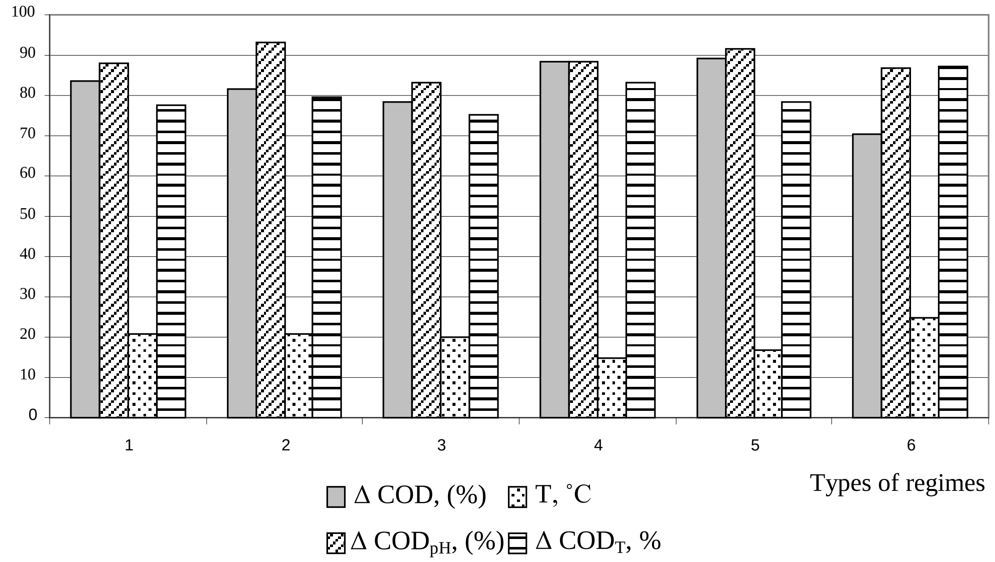

Figure 1 – Dependence between efficiency of wastewater treatment from organic matters (ΔCOD), temperature (Δ COD_T) and pH (Δ COD_{pH}) change

Among them the main elements are N, P and K. The lack of nitrogen slows down the oxidation of organic pollutants in wastewaters and results in the formation of hard- settling sludge. The lack of phosphorus leads to the growth of filamentous bacteria and, as a result, to the activated sludge swelling.

The content of biogenic elements depends on the content of wastewaters and should be determined by experiment. The approximate ratio of BOD: N: P at the treatment duration of 3 days is 100:5:1. At the treatment duration of 20 days this ratio should be maintained at the level of 200:5:1 [4].

The effect of nitrogen and phosphorus on the aerobic degradation process can be described by the double Monod equation [4]:

$$\mu_{спост} = \mu_{макс}(S_2/(S_2+K_2)), \qquad (6)$$

but it does not reflect that at the low concentrations of nitrogen and phosphorus the bacterial growth is inhibited.

$$\mu_{спост} = \mu_{\max} S_{NH_4}/(S_{NH_4}+K_{S,NH_4}))\cdot(S_{PO_4}/(S_{PO_4}+K_{PO_4}), \qquad (7)$$

where S_{NH_4} is the ammonium concentration, S_{PO_4} is the phosphorus (orthophosphate) concentration, K_{S,NH_4} is the saturation constant for nitrogen, K_{PO_4} is the saturation constant for phosphorus [4, 5].

The equation (7) makes it possible to take into account the effect of phosphates and NH_4 concentrations on the biomass growth in the bioreactor, which can be used as an indicator of the state of activated sludge and correspondingly on the efficiency of biodegradation of organic substrate in the bioreactor.

There is some dependence between the value of the wastewater treatment efficiency and content of phosphorus and nitrogen ($R_{N,COD=}$0,361, $R_{PO4,COD}$=0,368).

As is seen from fig. 2 (curve of dependence of the treatment efficiency for COD on the NH_4 concentration in wastewaters), NH_4 concentration in the bioreactor is within a certain range and varies from 5.7 to 14 for the given type of wastewaters at the efficiency of wastewater treatment varying from 650 to 1550 ΔCOD.

The effect of nitrogen and phosphorus on the process of wastewater biochemical treatment plays a

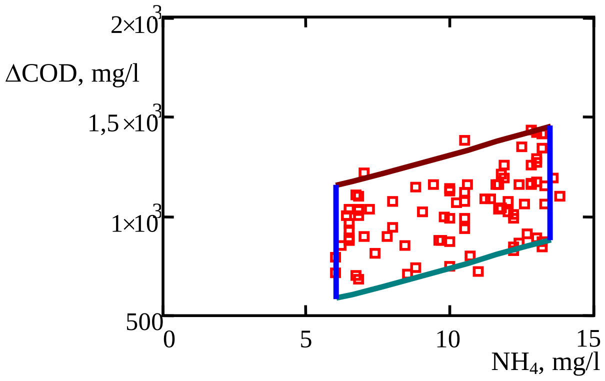

Figure 2 – Curve of dependence of treatment efficiency for COD on NH_4 concentration in bioreactor, $R_{N,COD}$=0.361

rather important role taking into account data obtained in consequence of the dynamical analysis, particularly for production effluents since, as a rule, the content of these matters in production wastewaters is insufficient in contrast to municipal wastewaters [5, 6]. Besides, at an insufficient amount of N or P the inhibition of the biological treatment process takes place.

There is also the correlation dependence ($R_{PO4,COD}$=0.368) between the PO_4 concentration and efficiency of treatment due to the fact that for heterotrophic conversion the microorganisms need also microelements without which the process of biochemical treatment will be inhibited. It was also detected that with the increase of the PO_4 concentration the efficiency of the removal of heavily oxidizable organic compounds in wastewater increased (fig. 3).

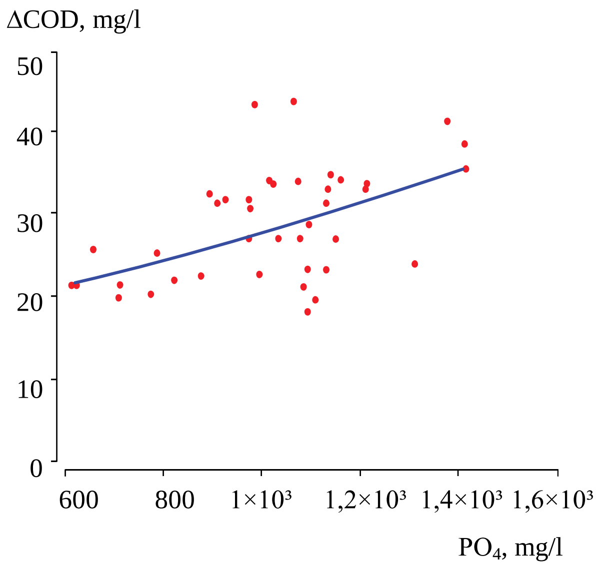

Figure 3 – Curve of dependence of treatment efficiency for COD on PO_4 concentration in wastewaters, $R_{PO4,COD}$=0,368

One of the factors connected with the content of inorganic matters in the bioreactor that affect the efficiency of the biochemical treatment of wastewaters is the oxygen concentration in the bioreactor since oxygen is a vital element required for activity of microorganisms and correspondingly for oxidation of organic compounds by them, which affect the decrease in the level of COD and BOD.

The rate of the whole treatment process is limited by the diffusion resistance of water in the absorption of oxygen [5].

The most reliable method to increase the amount of absorbed oxygen is to increase the volume factor of mass transfer. This is achieved by breaking down the gas bubbles and increasing the gas content of the wastewater flow.

The rate of consumption of oxygen by microorganisms does not exceed the rate of its absorption. The oxygen consumption rate increases with the increase of its content in water, but only to a certain limit. The concentration of oxygen in water at which the rate of its consumption becomes constant and does not depend on the further increase of the concentration is called critical. The critical concentration is less than equilibrium concentration and depends on the nature of microorganisms and temperature [5].

The dependence of the aerobic process rate on the oxygen concentration can be written by the Monod equation [4]:

$$\mu_{cons} = \mu_{\max}(S_{O_2,2}/(S_{O_2,2}+K_{O_2,2})), \quad (8)$$

where $S_{O_2,2}$ is the oxygen concentration in reactor, $K_{O_2,2}$ is the oxygenation constant, $\mu_{\max}$ is the rate of activated sludge growth.

Combining this equation with the equation of Monod growth kinetics:

$$\mu_{спост} = \mu_{макс}(S_2/(S_2+K_2)), \quad (9)$$

We obtain:

$$\mu_{cons} = \mu_{\max}(S_2/(S_2+K_2))\cdot(S_{O_2}/(S_{O_2}+K_{O_2,2})), \quad (10)$$

where S_2 is the concentration of organic substrate in wastewater, K_S is the oxygenation constant for COD. The oxygenation constant K_{O_2} depends on the size of flocs (biofilm thickness) and temperature since the temperature imposes restrictions on the oxygen diffusion into the flocs (biofilm) [7].

In consequence of the analysis of experimental data the dependence was obtained (fig. 4) according to which it is seen that the oxygen concentration in the bioreactor should be within the range 7-7.8 mg/l for more efficient biodegradation of heavily oxidizable compounds of wastewater.

Generally, the oxygen concentration in bioreactors is within the range of 8–9,5 mg/l, but due to the insufficient amount of organic substrate in the bioreactor volume and shortage of some microelements, which was determined in the dynamical analysis, the efficiency of biochemical treatment of wastewaters for COD has the maximum value at decreased values of oxygen.

At the oxygen concentration exceeding 7.8 mg/l the endogenous respiration is accelerated, which results in the decrease in the amount of activated sludge in the

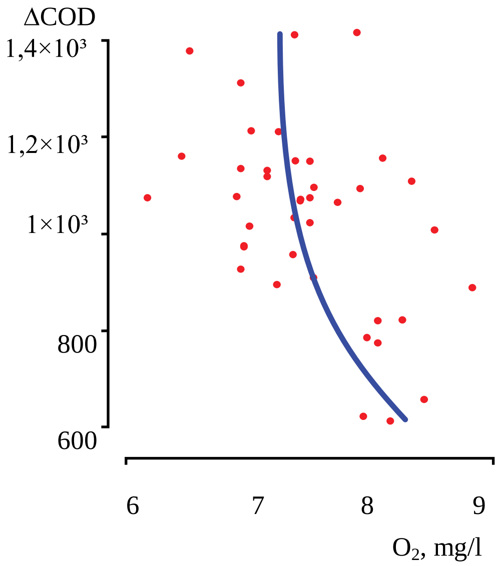

Figure 4 – Dependence of wastewater treatment efficiency on oxygen concentration, R_{O2}=0,468

reactor volume and correspondingly results in the decrease in the efficiency of biochemical processes.

From research [2] it is known that the gradient (as a difference in the values of COD in the bioreactor and at the outlet of the system) considerably increases at the reduction of the aeration time (R= -0,51), which is connected with the imbalance between the rate of incoming of pollutants and the rate of their biological degradation. There was also a stable statistic linkage of ΔCOD with the concentration of activated sludge (R_{O2}=0,468) in the bioreactor. This can be explained by the change of the relationship of the anabolism and catabolism processes in the biocenosis of activated sludge, accumulation of the heavily oxidizable high-molecular colloids of wastewaters, products of metabolism or degradation of bacterial cells at high concentrations of activated sludge and low loading on sludge.

For determining the efficiency of treatment of wastewaters in the bioreactor there is the necessity to use the mathematical model. Among the models existing today the most known and recognized ones are "Activated Sludge Models" (ASM1, ASM2 and ASM3) developed by the International Association on Water Pollution Research and Control (IAWPRC) [6, 8, 9]. 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. Taking into consideration that standard models include the processes taking place in standard aerotanks, it will be more correct to use the model that is adapted to the membrane bioreactors, but makes allowance for the effect of the main important factors in calculation of the oxidation capacity.

For facilitating the description of the processes taking place in membrane bioreactors, one can also use the model on the basis of the Monod-Iyerusalymsky model with the help of which the oxidation capacity of the membrane bioreactor can be determined depending on the parameters of wastewaters such as T, pH, total nitrogen, oxygen concentration in the bioreactor, concentration of NH_4, PO_4.

On the basis of the analysis of scientific literature and pooling of the existing experience the following requirements were developed which the mathematical model [10] 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.

The selected model meets the above requirements. The model adapted for the membrane 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 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 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 [2]. Consequently, the unforeseen changes in activity of the biocenosis of activated sludge can take place in the absence of special addition to the bioreactor of those microelements which are lacking for activity of microorganisms.

Conclusions

As a result of the analysis of the existing research methods, the method of carrying out analysis without the time factor was selected with a view to investigate the correlation dependences between the efficiency of wastewater treatment and values of the relevant indicators of wastewaters: T, pH, COD value at the inlet in the bioreactor, concentration of oxygen, nitrogen and phosphorus in the bioreactor.

Experimental data showed that in the starting period there was a shortage of organic substrate (which resulted in the insufficient concentration of activated sludge). The analysis of correlation dependencies shows that the second by value is the factor of temperature (optimum values are +20…30 ˚С).

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ЗАЛЕЖНІСТЬ БІОХІМІЧНОГО ОЧИЩЕННЯ СТІЧНИХ ВОД ВІД ФАКТОРІВ ПРОЦЕСУ

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В результаті проведених експериментів найбільша кореляційна залежність отримана між ефективністю очищення стічних вод і здатністю мулу до окислення. Також встановлено кореляційні залежності між ефективністю очищення стічних вод і значеннями температури, рівнем кислотності, концентраціями кисню, азоту та фосфору в біореакторі. Стабільна статистична залежність ефективності очищення від концентрації активного мулу може бути пояснена зміною відношення процесів анаболізму і катаболізму в біоценозі активного мулу, накопичення високомолекулярних колоїдів стічних вод, продуктів метаболізму або деградацією бактеріальних клітин при високих концентраціях активного мулу і низькому навантаженні на мул.

Ключові слова: біохімічне очищення, стічні води, здатність до окислення, температура, азот, фосфор.

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