

*У результаті лабораторних експериментів показана можливість біоочистки розчинних у воді газоподібних сірководню, діоксиду сірки та аміаку. На основі отриманих емпіричних залежностей та теоретичних уявлень щодо нестационарності процесу розроблено математичну модель біодеструкції газоподібних водорозчинних забруднювачів. Алгоритм враховує стан динамічної рівноваги між безперервною абсорбцією забруднювачів та їх біоокисненням у воді шару біореактору, що омивається. Отримані залежності дозволяють адекватно описувати процес біоочистки та розраховувати його параметри*

*Ключові слова: очистка викидів, процес біоочистки, сірководень, діоксид сірки, біореактор*

*В результате лабораторных экспериментов показана возможность биоочистки растворимых в воде газообразных сероводорода, диоксида серы и аммиака. На основании полученных эмпирических зависимостей и теоретических представлений о нестационарности процесса разработана математическая модель биодеструкции газообразных водорастворимых загрязнений. Алгоритм учитывает состояние динамического равновесия между непрерывной абсорбцией загрязнений и их биоокислением в воде омываемого слоя биореактора. Полученные зависимости позволяют адекватно описывать процесс биоочистки и рассчитывать его параметры*

*Ключевые слова: очистка выбросов, процесс биоочистки, сероводород, диоксид серы, биореактор*

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# DEVELOPMENT OF THE MATHEMATICAL MODEL OF THE BIOTREATMENT PROCESS OF WATER-SOLUBLE GASEOUS EMISSIONS

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## 1. Introduction

Environmental protection against gaseous pollutants takes a leading place in ensuring the environmental safety of cities. A special position in this class of pollutants belongs to hydrogen sulfide, sulfur dioxide and ammonia, which are foul-smelling degradation products of organic matter. Their sources are utilities in general and sewer networks, in particular. The low concentration of these pollutants makes traditional physicochemical or thermal treatment methods ineffective and economically unsound.

An effective and environmentally friendly method of treatment of low-concentration gaseous emissions is biodegradation. Sizing and design of industrial plants require

the study and mathematical description of processes in a bioreactor. The biotreatment process of hydrogen sulfide, sulfur dioxide and ammonia, due to their good water solubility, occurs in the trickling water layer. Data on the kinetics of such a stationary process can be obtained only experimentally. The combination of continuous absorption and biooxidation in a water layer causes non-stationarity of the biotreatment process of the specified pollutants. The process non-stationarity complicates pollution control equipment sizing and requires additional empirical data. The foregoing shows the urgency of experimental studies and the need to develop an adequate mathematical model of the biotreatment process of water-soluble gaseous substances. Development of a mathematical model of the biodegradation process of

gaseous emissions is an important stage of sizing and design of biotreatment plants.

## 2. Literature review and problem statement

Biological methods are based on the ability of microorganisms to degrade a huge amount of harmful substances to harmless products like water and carbon dioxide under aerobic conditions [1]. Their feature is that biochemical processes do not require expensive reagents and proceed at ambient temperature and pressure, which makes them economically viable. At present, biofilters, bioscrubbers and trickle-bed bioreactors are used for biotreatment [2]. These units are based on the following principle: gaseous harmful substances, absorbed by the aqueous medium, are absorbed by microorganisms and then undergo biodegradation. Microorganisms utilize water-dissolved pollutants as a nutritious substrate to meet their energy needs and for biomass build-up [3].

The biotreatment method of gaseous emissions is commonly used for air deodorization from a mixture of organic matter [4], and also the accompanying inorganic odorants, such as hydrogen sulfide  $H_2S$  on livestock farms [5]. At the same time, biotreatment is also applied to specific emissions that contain benzene, toluene, ethylene benzene [6], carbon disulfide  $CS_2$  [7], methyl- and dimethyl mercaptans [8], styrene [9], and organochlorine pollutants, for example, dichloromethane [10].

Application of the biotreatment method of gaseous emissions is particularly effective at low concentrations of pollutants and relatively low performance, typical for sewage networks [11].

Among modern gas treatment units, biofilters [12, 13] and trickle-bed bioreactors are in general use [14]. Many modern studies are devoted to the determination of kinetic parameters and mathematical description of the biotreatment process. The paper [15] considers the kinetic characteristics of the degradation process in biofilms of gas treatment units. According to the production data [16], the hydrogen sulfide removal kinetics have been determined. Mathematical descriptions of processes in the trickle-bed biofilter based on statistical evaluation of experimental data [17] and understanding of mass transfer [18] have been performed. The mathematical description of the laboratory stationary biodegradation process adequate for a wide class of pollutants has been proposed in the research [19]. The mathematical models of biotreatment of water-soluble methane [20] and water-dissolved formaldehyde [21], considering the non-stationarity of processes in real industrial plants have been developed.

Literature review confirms both the development of biotreatment methods, and insufficient research of specific biotreatment processes of gaseous hydrogen sulfide, sulfur dioxide and ammonia that are well absorbed by water. This class of pollutants requires a comprehensive experimental and theoretical study with the aim of developing a mathematical model to describe biotreatment of water-soluble gaseous pollutants in the trickle-bed bioreactor.

## 3. Goal and objectives

The goal of the paper is to develop a mathematical model of the non-stationary biotreatment process of gaseous

emissions, including water-soluble hydrogen sulfide, sulfur dioxide and ammonia.

To achieve this goal, it is necessary to accomplish the following objectives:

- to determine experimentally the kinetic parameters of the stationary biodegradation process of water-dissolved hydrogen sulfide, sulfur dioxide and ammonia;
- to develop a mathematical model of biooxidation of water-soluble gaseous emissions, taking into account the real non-stationarity of processes in the bioreactor.

## 4. Materials and methods of the research of the biotreatment process of water-soluble gaseous pollutants

### 4.1. Experimental materials and equipment

The biooxidation process parameters of water-dissolved  $H_2S$ ,  $NH_3$  and  $SO_2$  were studied in a 5 dm<sup>3</sup> acrylic glass column installation (Fig. 1).

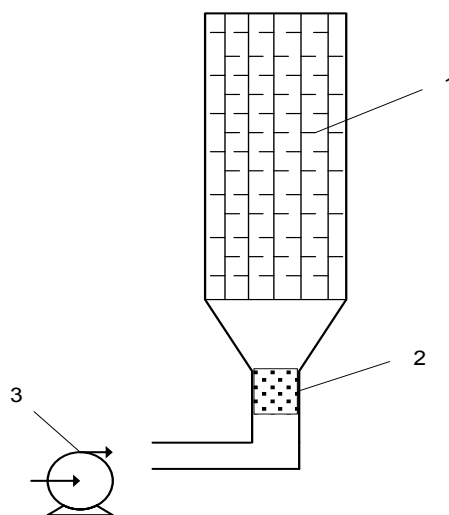


Fig. 1. Schematic diagram of a laboratory installation for biotreatment of an aqueous medium from dissolved  $H_2S$ ,  $NH_3$  and  $SO_2$ ; 1 – lavsan brush attachment with immobilized specialized microbiocenosis; 2 – dispersant; 3 – compressor

The vessel was filled with the water, containing nutrient salts, as well as sulfur and nitrogen compounds, simulating the  $H_2S$ ,  $NH_3$  and  $SO_2$  water dissolution products. The installation included the system of air supply through the dispersant providing fine-bubble dispersion. The attachment (lavsan brushes) with the packaging density of 150–200 mm/dm<sup>3</sup>, at which specialized immobilized microbiocenosis was formed by autoselection, was placed in the installation. The bioreactor was inoculated with an enrichment culture of ammonium-oxidizing and thionic bacteria. The biomass concentration was 1.0 g/dm<sup>3</sup> of the installation volume. The enrichment culture was prepared in the Soriano and Walker nutrient medium with the addition of 5 g/dm<sup>3</sup> of  $Na_2S_2O_3$  (the compound used in elective media for isolation of  $S^{2-}$ -oxidizing thiobacilli). The material for accumulation of thiobacilli and ammonium-oxidizing bacteria was concrete of the crest part of the sewers. After the bioreactor was inoculated, nutrient salts at the concentrations used in the Soriano and Walker medium with 400 mg/dm<sup>3</sup> of  $Na_2S_2O_3$  were added to the aqueous medium. After the biofilm formed

on the bed (about 0.06 g/g of the bed) and oxidation of  $\text{NH}_4^+$  and  $\text{S}_2\text{O}_3^{2-}$  stabilized, experiments were performed to determine the removal process parameters of dissolved  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and  $\text{SO}_2$ : specific oxidation rate of  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$  and  $\text{NH}_4^+$ ; the bacteria microbiocenosis mass; the half-saturation concentration of oxidized substrates; the mass of the feed material. The experiments were carried out in the aqueous medium with the addition of phosphorus, magnesium, and iron salts according to the composition of the Soriano and Walker medium and, depending on experimental purposes, compounds simulating the dissolution products of any of  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  or  $\text{SO}_2$  gases –  $\text{Na}_2\text{S}$ ,  $\text{Na}_2\text{SO}_3$  and  $\text{NH}_4\text{OH}$  respectively. The concentrations of  $\text{S}^{2-}$ ,  $\text{SO}_3^{2-}$  and  $\text{NH}_4^+$  in the aqueous medium were determined:  $\text{S}^{2-}$  – by the methylene blue formation reaction,  $\text{SO}_3^{2-}$  – by the iodine solution titration in the presence of formaldehyde,  $\text{NH}_4^+$  – with the Nessler's reagent.

Since  $\text{S}^{2-}$  and  $\text{SO}_3^{2-}$  are oxidized by bacteria of the same ecological-trophic group, it can be assumed that  $\text{H}_2\text{S}$  and  $\text{SO}_2$  in an aqueous medium may compete for thiobacilli oxidases. Therefore, water, in which these two S-containing substrates were in equal concentrations, was treated in a special experiment.

#### 4. 2. Assumptions of the model of the non-stationary biotreatment process of water-absorbed pollutants

The bioreactor that purifies air from water-soluble gaseous compounds can be called countercurrent. Removal of harmful matter in such a bioreactor occurs in the water absorbing it, moving in the direction opposite to the movement of the gas-air mixture to be purified.

As a result of continuous spraying of water into the bioreactor, according to the laws of adhesion, surface tension and gravity, it will be on the bed while moving along it. The combined effect of these laws should obviously lead to dynamic balance, that is, the constancy of water on the bed at any time. This is also required by the condition of balance of supplied and discharged water.

The bioreactor of this type combines the functions of an absorber and the trickle-bed bioreactor. Simultaneously with absorption, the harmful matter biodegradation process takes place in water.

The attached gas-air mixture layers of infinitesimal thickness  $dy$ , moving upward the bioreactor from its inlet to the outlet, transferring pollution to the water trickling the bed are considered. In turn, the attached water layers of infinitesimal thickness  $dy$  move downward the bioreactor from the outlet to the inlet and absorb pollution. The idea of a moving conditional horizontal water layer of infinitesimal thickness is equivalent to the assumption that the rate of movement of any infinitesimal volume of water in the considered horizontal section of the bioreactor is constant.

The horizontal section of the bioreactor is not solid. Most of its area is occupied by the gas-air mixture, against the background of which there are separate regions, including lavalan filaments in the section, biomass and water, constantly residing on the bed. Pollution absorption and biodegradation occur horizontally, successively from the gas-air mixture to water, and then from water to biomass.

Each upwardly moving gas-air mixture can have the initial concentration of pollution equal to its time-varying concentration in the sewer. Harmful matter continuously flows from the gas-air mixture to the downwards-moving infinitesimal water layer due to absorption. Besides, in case

of water reuse for the bioreactor trickling and given incomplete treatment, variation of initial pollution concentration in water with time is possible. Thus, a process in the countercurrent bioreactor is always non-stationary.

Processes in the bioreactor include:

- upward movement of the gas-air mixture in the bioreactor, partially filled with the water-trickled bed;
- downward movement of water held on the bed;
- pollution arrival from the gas-air mixture into water as a result of absorption;
- biochemical destructuring of harmful matter in water.

In the calculations, complete absorption of the pollution entering the bioreactor and the specific pollution transfer rate, constant by the bioreactor height were assumed. Then, the background concentration  $\rho_{rt}$  – pollution concentration in the downward moving conditional infinitesimal water layer without considering the biotreatment process, is determined as:

$$\rho_{rt} = \rho_0 + \frac{\rho_{rm}}{t_d} t, \quad (1)$$

where  $\rho_{rm}$  is the maximum background pollution concentration in the water layer at the initial value equal to zero,  $\text{g}/\text{m}^3$ ;  $\rho_0$  is the initial harmful matter concentration in the water layer,  $\text{g}/\text{m}^3$ ;  $t_d$  is the biotreatment duration (time of water residence in the bioreactor), h.

#### 5. Results of the research of kinetic characteristics of biodegradation of water-soluble gaseous pollutants

Experimental data [19] show that the oxidation rate changed from 12  $\text{mg}/\text{g}\cdot\text{h}$  to 40  $\text{mg}/\text{g}\cdot\text{h}$  in the range of  $\text{H}_2\text{S}$  concentrations in water of 15–120  $\text{mg}/\text{dm}^3$ . Similar results of concentration changes were also obtained for the rate of  $\text{SO}_2$  oxidation in water. In the range of  $\text{NH}_3$  concentrations in water of 2.5–20  $\text{mg}/\text{dm}^3$ , the oxidation rate varied from about 1.5  $\text{mg}/\text{g}\cdot\text{h}$  at the minimum concentrations to the maximum value of 5  $\text{mg}/\text{g}\cdot\text{h}$ .

It follows from the experimental research data that the maximum specific oxidation rate of S-containing substrates of 80  $\text{mg}/\text{g}\cdot\text{h}$  is almost twice the specific oxidation rates of  $\text{H}_2\text{S}$  and  $\text{SO}_2$ . It can be argued that the oxidation of  $\text{H}_2\text{S}$  and  $\text{SO}_2$  is made by various thiobacilli, which do not compete with each other for sulfur-containing substrates. Otherwise, the specific oxidation rate of S-containing substrates would be about 40  $\text{mg}/\text{g}\cdot\text{h}$ .

The analysis of experimental data indicates that the dependences of specific biochemical oxidation rate of  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and  $\text{NH}_3$  in water on their concentrations exist and have the form of a peaked curve. The developed macrokinetic mathematical model of the stationary process [22] quantifies the relation between the specific oxidation rate  $V_p$  and the concentration of the removed matter  $\rho$  for the considered pollutants:

$$V_p = a \cdot \rho^b \cdot e^{-c\rho}, \quad (2)$$

where  $a$ ,  $b$ ,  $c$  are the empirical coefficients determined in the course of statistical processing of the experimental data.

The considered bioreactor combines the processes of absorption and biodegradation of harmful matter. Therefore, a continuous change of the full pollution mass balance in time

in a moving conditional water layer of infinitesimal thickness can be written as:

$$G_{t+1} = G_0 + \delta G_{rt} - \delta G_{vt}, \quad (3)$$

where  $G_t$  is the pollution mass in the water layer at the time  $t$ , g;  $\delta G_{vt}$  is the change in the pollution mass in the water layer at the time  $t$  due to biodegradation, g;  $G_0$  is the pollution mass in the water layer at the time  $t=0$ , g;  $\delta G_{rt}$  is the pollution mass increase in the water layer at the time  $t$  due to absorption, g.

The components of (3) are:

$$G_t = \rho_t \cdot dR_w, \quad (4)$$

$$\delta G_{vt} = -m_b \cdot \frac{dy}{H} \int_0^t V_{pt} dt, \quad (5)$$

$$dR_w = F_w \cdot dy, \quad (6)$$

$$\delta G_{rt} = -m_b \cdot \frac{dy}{H} \int_0^t v \cdot dy \cdot dt, \quad (7)$$

where  $\rho_t$  is the harmful matter time-varying concentration in the water layer, g/m<sup>3</sup>;  $m_b$  is the amount of biomass, g;  $V_{pt}$  is the specific biooxidation rate calculated by (2) for the variable concentration  $\rho_t$  of the non-stationary process, g/g<sub>0</sub>·h;  $dR_w$  is the volume of the moving infinitesimal water layer, m<sup>3</sup>;  $H$  is the bioreactor height, m;  $F_w$  is the water layer area, m<sup>2</sup>;  $v$  is the specific absorption rate per unit height of the bioreactor, g/m h.

In (5), uniform biomass distribution along the bioreactor is assumed.

Upon proceeding to concentrations, (3) can be transformed to the following form:

$$\rho_t = \rho_{rt} - \mu \int_0^t V_{pt} dt, \quad (8)$$

where  $\mu$  is the biomass concentration in the volume of the space occupied by water, g<sub>0</sub>/m<sup>3</sup>.

By differentiating (8) in time, we get:

$$\frac{d\rho_t}{dt} = \frac{d\rho_{rt}}{dt} - \mu V_{pt}. \quad (9)$$

The expression (9) is the basic differential equation of the non-stationary biotreatment process in the bioreactor of the considered type. In comparison with the basic differential equation of a stationary process, there is an additional term, which considers non-stationarity as a result of the continuous absorption process. In the form of total differentials, Eq. (9) can be represented as:

$$d\rho_t = d\rho_{rt} + d\rho_{vt}, \quad (10)$$

where  $d\rho_{vt}$  is the differential of the concentration change due to the biooxidation process, g/m<sup>3</sup>.

The relation (10) shows that the differentially small change in the harmful matter concentration in water at each time-point is equal to the algebraic sum of the differentially small concentration changes due to absorption and biodegradation processes. The expression (10) is, in fact, a differential analog of the mass balance of the given non-stationary process.

The structure of the formula for  $V_{pt}$  does not make it possible to get a closed analytical solution of Eq. (9). Therefore, we apply the numerical integration algorithm, proceeding from differentials to finite increments:

$$\Delta\rho_i = \Delta\rho_{ri} + \Delta\rho_{vi}, \quad (11)$$

$$\rho_{i+1} = \rho_i + \Delta\rho_i, \quad (12)$$

$$t_{i+1} = t_i + \Delta t, \quad (13)$$

$$\Delta\rho_{ri} = \frac{\rho_{rm}}{t_{\Pi}} \Delta t, \quad (14)$$

$$\Delta\rho_{vi} = \frac{1}{\phi_{pi}} (e^{-\phi_i \mu_0 V_i \Delta t} - 1), \quad (15)$$

$$\phi_i = \frac{b}{\rho_i} - c, \quad (16)$$

$$V_{pi} = a \cdot \rho_i^b \cdot e^{-c\rho_i}. \quad (17)$$

Due to resizing, in comparison with the experiment, recalculation of the coefficient is necessary:

$$a = 10^{-3} \cdot a^*, \quad (18)$$

where  $a^*$  is the empirical coefficient, determined directly from the experimental data.

The numerical integration algorithm (11)–(17) is convergent, but requires a much smaller integration step ( $\Delta t=0.0002$  h) to achieve high accuracy in comparison with a stationary process [1].

The results of calculations of the hydrogen sulfide biotreatment process depending on the initial pollution concentration in the trickling water  $\rho_0$ , the maximum background concentration  $\rho_{rm}$  and the initial biomass concentration  $\mu_0$  are shown in Fig. 2, 3.

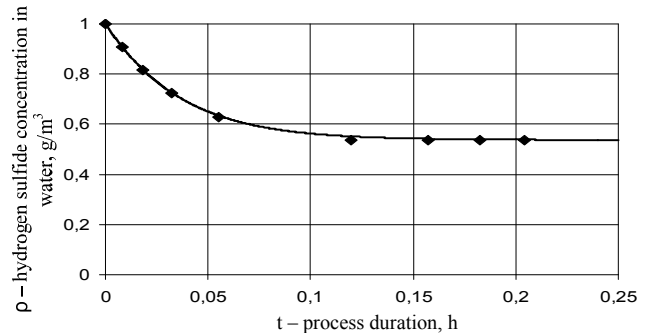


Fig. 2. Process duration effect on the hydrogen sulfide concentration in the moving water: water movement time in the bioreactor  $t_m=0.2$  h; initial hydrogen sulfide concentration in the trickling water  $\rho_0=1$  g/m<sup>3</sup>; initial biomass concentration in the bioreactor  $\mu_0=1000$  g/m<sup>3</sup>; the maximum background hydrogen sulfide concentration in water  $\rho_{rm}=5$  g/m<sup>3</sup>; curve – numerical integration results; points – calculations by the approximate formula

The obtained data confirm the achievement of a final stage of the non-stationary process after a certain period of time, characterized by constant pollution concentration in water. Let's call it equilibrium concentration  $\rho_e$  since it

corresponds to the onset of dynamic balance in the non-stationary process. The value of equilibrium concentration does not depend on the initial pollution concentration, increases with the pollution volume increase and decreases with the biomass concentration increase. In the examples, the dynamic balance was reached approximately at the water layer outflow from the bioreactor ( $t_m=0.2$  h).

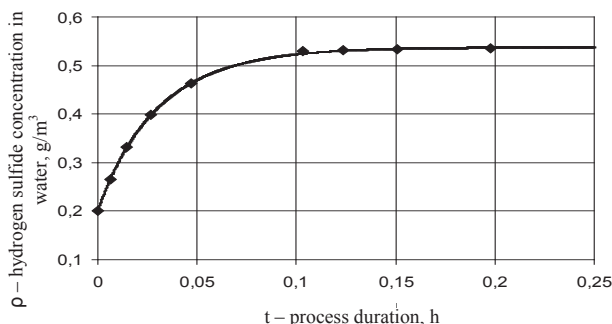


Fig. 3. Process duration effect on the hydrogen sulfide concentration in the moving water: water movement time in the bioreactor  $t_m=0.2$  h; initial hydrogen sulfide concentration in the trickling water  $\rho_0=0.2$  g/m<sup>3</sup>; initial biomass concentration in the bioreactor  $\mu_0=1000$  g/m<sup>3</sup>; the maximum background hydrogen sulfide concentration in water  $\rho_{rm}=5$  g/m<sup>3</sup>; curve – numerical integration results; points – calculations by the approximate formula

Dynamic balance is determined by the condition:

$$d\rho_{rt} + d\rho_{vt} = 0 \tag{19}$$

or in the finite increments:

$$d\rho_{ri} + d\rho_{vi} = 0. \tag{20}$$

Let the mass of harmful matter, absorbed by water per unit of time per unit of biomass be called the specific rate of pollution arrival to the bioreactor  $V_g$ :

$$V_g = \frac{g_0}{m_b}, \tag{21}$$

where  $g_0$  is the intensity of pollution arrival to the bioreactor, g/h, or

$$V_g = \frac{\rho_{rm}}{\mu \cdot t_d}. \tag{22}$$

Given  $\Delta t \rightarrow 0$ , we assume:

$$\Delta\rho_{vi} = -\mu V_{pi} \Delta t \tag{23}$$

and then from (14), (20) and (23), we get the relation for calculating the equilibrium pollution concentration:

$$V_{pp} = V_g, \tag{24}$$

where  $V_{pp}$  is the specific biooxidation rate determined by (2) for the equilibrium harmful matter concentration, g/g<sub>b</sub>·h.

Fig. 4 presents the phase diagram of hydrogen sulfide, sulfur dioxide and ammonia biotreatment. It should be noted

that dynamic balance is achieved at lower specific rates of pollution arrival into the bioreactor than the maximum specific biooxidation rates, that is, under the condition:

$$V_g \leq \frac{b}{c}. \tag{25}$$

Failure to comply with (25) leads to an unlimited increase in the harmful matter concentration in the water withdrawn from the bioreactor. We can state that (25) determines the boundary of implementation of effective biotreatment process. As for hydrogen sulfide and sulfur dioxide, this boundary virtually corresponds to the specific pollution arrival rate  $V_g=0.04$  g/g<sub>b</sub>·h. Thus, equilibrium concentrations do not reach the values of 90 and 60 g/g<sub>b</sub>·h, respectively (Fig. 4). The ammonia curve correlates with the hydrogen sulfide and sulfur dioxide curves on a scale of about one to ten.

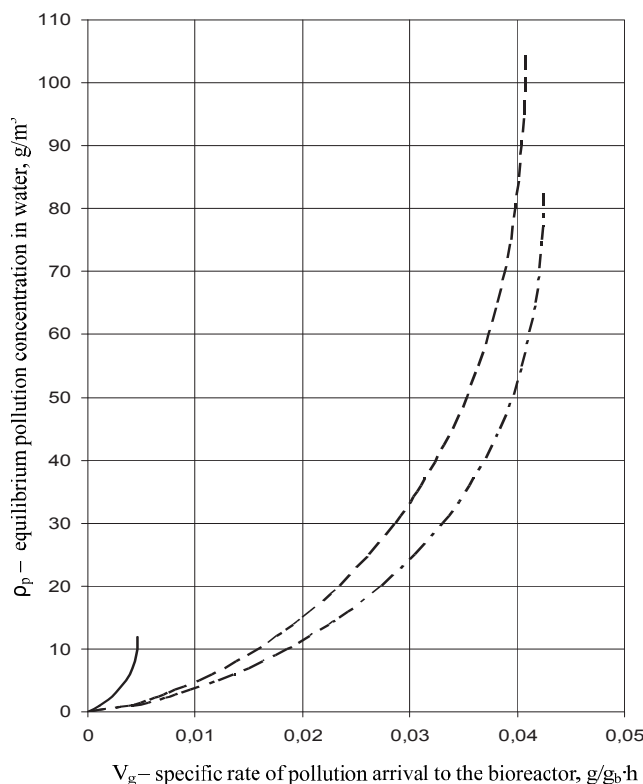


Fig. 4. Phase diagram of the process, characterized by simultaneous pollution degradation and dissolution in water: solid curve – ammonia; dotted – hydrogen sulfide; dash-dotted – sulfur dioxide

In case the dynamic balance is achieved, the desired process characteristic – the harmful matter concentration at the bioreactor outlet  $\rho_1$ , is obviously equal to:

$$\rho_1 = \rho_p \tag{26}$$

and  $\rho_p$  is calculated by (24).

However, if the biotreatment process duration (the residence time of water in the bioreactor) is insufficient to achieve the dynamic balance, its final state can be determined only by designing the course of the entire process.



## 6. Discussion of the research results and mathematical modeling of the biotreatment process

The above approach (11)–(17) is a mathematical solution that allows designing the course of the entire biotreatment process, including the equilibrium state. However, as shown above, the equilibrium state can be calculated precisely and much easier by (24).

Therefore, we consider the possibility of biotreatment process design without attempting to determine the equilibrium state simultaneously. To do this, we present a discrete change in the mass balance of pollution in the water layer of finite thickness  $\delta H$  and area  $F_w$  as it moves for a finite time interval  $\delta t_i$  and given the concentration change equal to  $\delta \rho_i$ . Then, by determining the subsequent values of time  $t_{i+1}$  and concentration  $\rho_{i+1}$  from their previous values as:

$$t_{i+1} = t_i + \delta t_i, \quad (27)$$

$$\rho_{i+1} = \rho_i + \delta \rho_i, \quad (28)$$

we can, by analogy with the previously stated, write down:

$$G_{i+1} = G_i + \delta G_{ri} - \delta G_{Ri}, \quad (29)$$

$$G_{i+1} = \rho_{i+1} \cdot F_w \delta H, \quad (30)$$

$$G_i = \rho_i \cdot F_w \delta H, \quad (31)$$

$$\delta G_{ri} = v \cdot \delta H \cdot \delta t_i, \quad (32)$$

$$\delta G_{Vi} = m_b \cdot V_{ci} \delta t_i \frac{\delta H}{H}. \quad (33)$$

The expression (33) assumes uniform biomass distribution along the bioreactor height and averaged specific biooxidation rate:

$$V_{ci} = \frac{V_{i+1} + V_i}{2}, \quad (34)$$

where  $V_{i+1}$  and  $V_i$  are specific biooxidation rates, determined from the concentrations  $\rho_{i+1}$  and  $\rho_i$ , respectively,  $g/g_b \cdot h$ .

After the transformations, we get an approximate formula for calculating the time interval  $\delta t_i$  needed to change the concentration in the water layer by the value of  $\delta \rho_i$ :

$$\delta t_i = \frac{\delta \rho_i}{\mu \cdot (V_g - V_{ci})}. \quad (35)$$

The formula (35) does not give a solution directly for the equilibrium concentration since when (24) is satisfied, the

calculation by (35) leads to  $\delta t_i \rightarrow \infty$ . However, according to the calculation results in Fig. 2, 3, (35) describes well the concentration change over the period of time preceding the achievement of dynamic balance.

The accuracy, sufficient for engineering calculations, is achieved by dividing the possible concentration change from the initial value  $\rho_0$  to almost equilibrium value  $\rho_e$  into eight intervals. Moreover,  $\rho_0$  is zero in the absence of water reuse. Note that in order to get a uniform distribution of calculated points, the latter three intervals should amount to about a tenth of a percentage point of the indicated maximum concentration range.

Thus, if the biotreatment process duration  $t_d$  is insufficient to achieve the equilibrium state, the desired pollution concentration in water at the bioreactor outlet  $\rho_i$  can be determined using the approximate formula (35). Thus, given a certain number of intervals (5–8), for which in the sequential calculation by (35) the following condition is satisfied:

$$t_i = \sum \delta t_i, \quad (36)$$

we get

$$\rho_j = \sum \delta \rho_i. \quad (37)$$

The proposed mathematical model of the kinetics of the considered non-stationary biotreatment process, based on the approximate formula (35), can be recommended for practical calculations, as combining the desired accuracy and sufficient simplicity.

## 7. Conclusions

1. It was found that experimental dependences of the specific biooxidation rate on the pollution concentration have a maximum. Changes in the specific degradation rate as for hydrogen sulfide and sulfur dioxide are within 12–40 mg/g of biomass per hour, and for ammonia 1.5–5 mg/g, respectively. It was revealed that the nature, as well as qualitative and quantitative parameters of the dependencies, prove the technological possibility of biotreatment of the water-soluble gaseous harmful matter.

2. The mathematical model of biotreatment of gaseous pollutants, which considers the process non-stationarity due to continuous absorption of pollutants by the water of the trickling layer of the bioreactor was developed. It is the algorithm based on the mass balance and empirical dependence of the specific oxidation rate on the hydrogen sulfide, sulfur dioxide and ammonia concentrations. Its feature is an accounting of the state of dynamic balance, which determines the boundary of implementation of effective biotreatment process.

## References

1. Kennes, C. Bioprocesses for air pollution control [Text] / C. Kennes, E. R. Rene, M. C. Veiga // Journal of Chemical Technology & Biotechnology. – 2009. – Vol. 84, Issue 10. – P. 1419–1436. doi: 10.1002/jctb.2216
2. Shestopalov, O. V. Analysis of existent processes and devices of bioscrubbing gas emissions [Text] / O. V. Shestopalov, I. V. Pitak // Technology audit and production reserves. – 2014. – Vol. 3, Issue 5 (17). – P. 49–52. doi: 10.15587/2312-8372.2014.25373
3. Chan, W.-C. Biodegradation of Methyl Ethyl Ketone and Methyl Isopropyl Ketone in a Composite Bead Biofilter [Text] / W.-C. Chan, K.-H. Peng // Engineering in Life Sciences. – 2008. – Vol. 8, Issue 2. – P. 167–174. doi: 10.1002/elsc.200720231
4. Seedorf, J. Biological exhaust air treatment systems as a potential microbial risk for farm animals assessed with a computer simulation [Text] / J. Seedorf // Journal of the Science of Food and Agriculture. – 2013. – Vol. 93, Issue 12. – P. 3129–3132. doi: 10.1002/jsfa.6106

5. Iranpour, R. Literature review of air pollution control biofilters and biotrickling filters for odor and volatile organic compound removal [Text] / R. Iranpour, H. H. J. Cox, M. A. Deshusses, E. D. Schroeder // *Environmental Progress*. – 2005. – Vol. 24, Issue 3. – P. 254–267. doi: 10.1002/ep.10077
6. Mohammad, B. T. Mesophilic and thermophilic biotreatment of BTEX-polluted air in reactors [Text] / B. T. Mohammad, M. C. Veiga, C. Kennes // *Biotechnology and Bioengineering*. – 2007. – Vol. 97, Issue 6. – P. 1423–1438. doi: 10.1002/bit.21350
7. Rojo, N. Carbon disulfide biofiltration: Influence of the accumulation of biodegradation products on biomass development [Text] / N. Rojo, R. Munoz, G. Gallastegui, A. Barona, L. Gurtubay, F. X. Prenafeta-Boldu, A. Elias // *Journal of Chemical Technology & Biotechnology*. – 2012. – Vol. 87, Issue 6. – P. 764–771. doi: 10.1002/jctb.3743
8. Malhautier, L. Treatment of complex gaseous emissions emitted by a rendering facility using a semi-industrial biofilter [Text] / L. Malhautier, S. Cariou, P. Legrand, E. Touraud, P. Geiger, J. L. Fanlo // *Journal of Chemical Technology & Biotechnology*. – 2014. – Vol. 91, Issue 2. – P. 426–430. doi: 10.1002/jctb.4593
9. Song, T. Effect of surfactant on styrene removal from waste gas streams in biotrickling filters [Text] / T. Song, C. Yang, G. Zeng, G. Yu, C. Xu // *Journal of Chemical Technology & Biotechnology*. – 2012. – Vol. 87, Issue 6. – P. 785–790. doi: 10.1002/jctb.3717
10. Engesser, K.-H. Microbiological Aspects of Biological Waste Gas Purification [Text] / K.-H. Engesser, T. Plaggemeier // *Biotechnology Set.* – 2008. – P. 275–302. doi: 10.1002/9783527620999.ch12n
11. Nelson, M. Soil-Based Biofiltration for Air Purification: Potentials for Environmental and Space Life Support Application [Text] / M. Nelson, H. L. Bohn // *Journal of Environmental Protection*. – 2011. – Vol. 02, Issue 08. – P. 1084–1094. doi: 10.4236/jep.2011.28125
12. Rizzolo, J. A. Biofiltration of increasing concentration gasoline vapors with different ethanol proportions [Text] / J. A. Rizzolo, A. L. Woiciechowski, V. C. C. dos Santos, M. Soares, J. Paca, C. R. Soccol // *Journal of Chemical Technology & Biotechnology*. – 2012. – Vol. 87, Issue 6. – P. 791–796. doi: 10.1002/jctb.3780
13. Zagorskis, A. An Investigation on the Efficiency of Air Purification Using a Biofilter with Activated Bed of Different Origin [Text] / A. Zagorskis, R. Vaiskunaite // *Chemical and Process Engineering*. – 2014. – Vol. 35, Issue 4. doi: 10.2478/cpe-2014-0033
14. Gonzalez-Sanchez, A. Kinetic Characterization by Respirometry of Volatile Organic Compound-Degrading Biofilms from Gas-Phase Biological Filters [Text] / A. Gonzalez-Sanchez, L. Arellano-Garcia, W. Bonilla-Blancas, G. Baquerizo, S. Hernandez, D. Gabriel, S. Revah // *Industrial & Engineering Chemistry Research*. – 2014. – Vol. 53, Issue 50. – P. 19405–19415. doi: 10.1021/ie503327f
15. Shareefdeen, Z. Hydrogen Sulphide Removal Using a Novel Biofilter Media [Text] / Z. Shareefdeen, A. Aidan, W. Ahmed, M. B. Khatri, M. Islam, R. Lecheheb, F. Shams // *World Academy of Science, Engineering and Technology*. – 2010. – Vol. 62. – P. 13–16.
16. Shareefdeen, Z. M. Kinetics and Modeling of H<sub>2</sub>S Removal in a Novel Biofilter [Text] / Z. M. Shareefdeen, W. Ahmed, A. Aidan // *Advances in Chemical Engineering and Science*. – 2011. – Vol. 01, Issue 02. – P. 72–76. doi: 10.4236/aces.2011.12012
17. Bonilla-Blancas, W. Application of a novel respirometric methodology to characterize mass transfer and activity of H<sub>2</sub>S-oxidizing biofilms in biotrickling filter beds [Text] / W. Bonilla-Blancas, M. Mora, S. Revah, J. A. Baeza, J. Lafuente, X. Gamisans et. al. // *Biochemical Engineering Journal*. – 2015. – Vol. 99. – P. 24–34. doi: 10.1016/j.bej.2015.02.030
18. Bakhareva, A. Development of universal model of kinetics of bioremediation stationary process with substrate inhibition [Text] / A. Bakhareva, O. Shestopalov, O. Filenko, B. Kobilyansky // *Eastern-European Journal of Enterprise Technologies*. – 2016. – Vol. 2, Issue 10 (80). – P. 19–26. doi: 10.15587/1729-4061.2016.65036
19. Bakhareva, A. Development of a mathematical model of the process of biological treatment of gaseous emissions [Text] / A. Bakhareva, O. Shestopalov, O. Filenko, T. Tykhomyrova // *Eastern-European Journal of Enterprise Technologies*. – 2015. – Vol. 6, Issue 6 (78). – P. 53–61. doi: 10.15587/1729-4061.2015.56220
20. Bakhareva, A. Development of a mathematical model of the process of biological treatment of gaseous emissions [Text] / A. Bakhareva, O. Shestopalov, O. Filenko, T. Tykhomyrova // *Eastern-European Journal of Enterprise Technologies*. – 2016. – Vol. 1, Issue 10 (79). – P. 4–10. doi: 10.15587/1729-4061.2016.59508
21. Bahareva, A. Yu. Macrokinetic mathematical model development of biological treatment process of gasiform emissions [Text] / A. Yu. Bahareva, O. V. Shestopalov, E. O. Semenov, N. O. Bukatenko // *ScienceRise*. – 2015. – Vol. 2, Issue 2 (7). – P. 12–15. doi: 10.15587/2313-8416.2015.37057