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PROCESS MODULE OF OIL-CONTAINING WASTEWATER TREATMENT OF LOCAL SEWAGE SYSTEM AND ITS CONTROLLING MATHEMATICAL MODEL

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Abstract.

At contemporary level of development of oil-extracting, oil-processing and oil-chemical industry, with development of car-services' market and growth of number of motor transport establishments, fuel-filling stations, car washes and other similar objects, the issue of purification of such enterprises' waste waters becomes more and more critical; this stipulates the necessity of application of technologies, neutralizing this impact. Application of pure bio-technologies with installation of selected micro-organisms providing high indexes of water purification in manageable mode is the most perspective in the field of oil-contaminated industrial waste waters purification.

The article "Bio-technical module of hydrocarbon containing waste waters of enterprises of individual sewage system" contains the data on optimization of oil and oil products bio-degradation of OJSC "Kazanorgsyntez" with application of jet-settler (JS), specially created for this purpose, and bringing of all bio-technological scheme into the mode of purification and advanced treatment of technological waste waters up to standards of reverse water supply or discharge into open water bodies without damaging of their ecological condition.

A constituent part of biotechnological scheme are mathematic models on lower and upper levels of two-level modeling (the lower level is defined by analytical model of bio-reactor and directed at provision of waste waters purification up to maximum permissible concentration; the upper level is defined by record of network models in Petri's networks, which provides the management of flows in the installation) that are used for management of oil-containing waste waters purification process, developed by authors. Their program realization allows to analyze the condition of bio-purification system in general, forecast the development of emergency situations and manage the bio-purification process.

Keywords: oil, micro-organisms, association, bio-degradation, oil contaminations, mathematic model, modified Petri's network, hydrocarbon-containing waste waters purification, waste waters.

Introduction.

At contemporary level of development of oil-extracting, oil-processing and oil-chemical industry, with development of car-services' market and growth of number of motor transport establishments, fuel-filling stations, car washes and other similar objects, the issue of purification of such enterprises' waste waters becomes more and more critical; this stipulates the necessity of application of technologies, neutralizing this impact[7]. At present time there is a sufficient quantity of diverse technical means of such profile presented at Russian market, but in most cases the dimensional proportion, productivity, operating costs and the need of hydrocarbon-containing waste waters deep purification degree with achievement of sanitary (0.1-0.3 mg/L) and commercial fishing (0.05 mg/L) standards are not meeting the requests of small and equivalent enterprises.

Application of pure bio-technologies with installation of selected micro-organisms providing high indexes of water purification in manageable mode is the most perspective in the field of oil-contaminated industrial waste waters purification [2, 3, 4].

The module principle laid in the basis of biotechnological scheme allows to form the flexible automated technological modules (FATM) of variable structure from typical equipment of chemical productions. The main constituent of FATM system of deep purification and advanced treatment of oil- and hydrocarbon-containing waste waters of diverse enterprises of individual sewage system can be a mathematic model of process realized in bio-purification apparatus – jet-settler (JS) [1, 5, 6] and modified Petri's network [8, 9]. Materials and methods of research. In course of solution of tasks established in research, methods of system analysis, computer modeling, theory of Petri's networks were used.

Results.

We've checked the of complex of newly created bacterial consortium of hydrocarbon oxidizing micro-organisms (HOM), including nine strains of *Alcaligenes*, *Micrococcus*, *Brevibacterium*, *Pseudomonas*, *Bacillus*, *Flavobacterium* and *Clostridium* genuses to purify combined hydrocarbon-containing industrial waste waters of OJSC "Kazanorgsyntez" in technological scheme (Fig. 1), represented by: initial preparation of waste waters concentrated by hydrocarbons by filtration from gross impurities; settling and removal of grossly- and fine dispersed substances from oil film, deep bio-destruction of suspended and dissolved in water oil products in jet-settler (JS) created anew (JS) with set parameters of HOM quantity, concentration of bio-genes and inducting substances, secondary stabilization of purified waters by settling and with removal of adnate bacteria biomass in manageable mode.

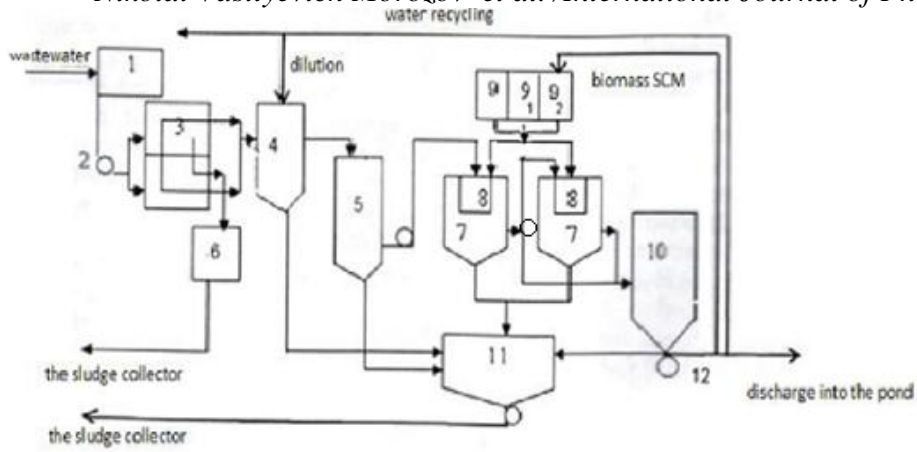


Figure 1. Flow diagram of block plant for purifying and fining of mixed oil-containing wastewater.

1 – the receiver of sewage water with separation of coarse impurities; 2 – pumping station for feeding waste water from the collection in oil separator; 3 – oil separator; 4 – balancing reservoir; 5 – preliminary settling tank; 6 – gathering center; 7 – jet settler; 8 – jet units; 9 – dosing tank of biogenic elements; 9.1 – dosing tank of inducing compounds; 9.2 – dosing tank of oil-oxidizing microorganisms; 10 – storage of the treated water with pumping station (12) of turnover water supply and supply of HOM biomass formed to 9.2; 11 – slurry reservoir; 12 – the pump of turnover water supply.

We used a system approach of two-level modeling, consisting of models on lower and upper levels, which logically characterizes conditions of structurally complicated management objects functioning dynamics analysis.

According to model at the lower level, the waste liquid, balances on preparation stage by salts, biogene elements, bio-catalyst compounds, pH, temperature etc., with oil-oxidizing micro-organisms, is fed into jet-settler of column type through the jet element (pos. 8), where the process of oil-containing waste waters (OWW) biological purification is conducted. For purposes of construction of mathematic description of JS flow structure, all volume of apparatus was conditionally divided into three zones. I – column's upper part, zone of mixing, in which the major process of hydrocarbons degradation is realized. II – middle part of apparatus, the settling zone where further process of waste water purification from contaminations takes place. III – lower part of the apparatus, sump zone, where the hydrocarbons degradation process ends. The course of process in upper part of the apparatus, considered by us as a model of perfect mixing reactor [2], is described by system of common differential equations. For stationary modes of process the given system was brought to the form:

$$\begin{aligned}
 B^{(0)} - B^{(1)} + t_{sr1}q_B^{(1)} &= 0 \\
 S^{(0)} - S^{(1)} + t_{sr1}q_S^{(1)} &= 0
 \end{aligned}
 \tag{1}$$

that has an analytic solution. Here, $t_{sr1} = V / v$ is an average time of flow's element staying in the spraying zone; V_1 – spraying zone volume, m³; v – volume speed of incoming flow m³/s; $B(0)$, $B(1)$ and $S(0)$, $S(1)$ – quantity of micro-organisms and concentration of oil products in flow in spraying zone, respectively; $q_B(1)$, $q_S(1)$ – growth rate of oil-oxidizing micro-organisms and bio-oxidizing of hydrocarbons, respectively.

Sprayed particles of the flow at continuing oxidizing of oil products in medium part are gradually settling by height of apparatus. Processes in upper part of the apparatus, considered by us as a model of perfect displacement reactor [2], are modeled by system of common differential equations:

$$\frac{dB^{(2)}}{dt} = q_B^{(2)}$$

$$\frac{dS^{(2)}}{dt} = q_S^{(2)}, \tag{2}$$

$$B^{(2)} \Big|_{t=t_{sr1}} = B^{(1)}$$

$$S^{(2)} \Big|_{t=t_{sr1}} = S^{(1)}, \quad (t_{sr1} < t < t_{sr1} + t_{sr2})$$

where $t_{sr2} = S_c h_2 / v$ is an average time of flow's element staying in displacement zone; h_2 – height of displacement zone.

Rate of microbiological processes is described by equations [3]:

$$q_B = \frac{dB}{dt} = mB - K_d B; \tag{3}$$

$$q_S = \frac{dS}{dt} = -\frac{1}{Y_s} mB. \tag{4}$$

Here m is a specific bacteria growth rate; K_d – constant of micro-organisms die-away rate; Y_s – economic coefficient connecting the amount of formed bio-mass with the amount of substrate.

Specific oil-oxidizing micro-organisms development rate is determined bit by micro-organisms' type and medium parameters:

$$m = m_{max} f_1(S) f_2(H^+) f_3(t^0) f_4(C_{cat}) B, \tag{5}$$

where

$$f_1 = S / (K_s + S),$$

$$f_2 = 1 / (1 + H^+ / K_1 + K_2 / H^+),$$

$$f_3 = 1 / \exp\left[\frac{(t_{opt}^0 - t^0)^2}{d}\right],$$

$$- f_4 = 1 / (1 + C_{cat} / K_{cat1} + K_{cat2} / C_{cat}),$$

here mmax – maximum specific rate, defined by peculiarities of micro-organisms; H+ - concentration of hydrogen ions; K1 and K2 – constants of inhibition; t0opt – optimal, and t0 – current temperature of waste waters; d – temperature range; Ccat. – concentration of bio-catalyst compounds; Kcat.1 and Kcat.2 – constants of activation.

Kinetic characteristics (parameters) of process qB and qS are determined (calculated) by empiric proportions:

$$q_B = \frac{m_{max}SB}{(1 + H^+ / K_1 + K_2 / H^+)(K_S + S) \exp\left[\frac{(t_{opt}^0 - t^0)^2}{d}\right] (1 + C_{kam} / K_{kam1} + K_{kam2} / C_{kam})} - K_d B$$

$$q_S = - \frac{1}{Y_S} \frac{m_{max}SB}{(1 + H^+ / K_1 + K_2 / H^+)(K_S + S) \exp\left[\frac{(t_{opt}^0 - t^0)^2}{d}\right] (1 + C_{kam} / K_{kam1} + K_{kam2} / C_{kam})} \quad (6)$$

where mmax – maximum specific micro-organisms' growth rate; Kd – constant of micro-organisms die-away rate; Ys – coefficient by substrate, connecting the amount of biomass and the amount of substrate (hydrocarbons) its growing took; Ks – constant of semi-saturation (affinity constant to substrate); K1 и K2 – constants of inhibition by hydrogen ions; K1 describes the inhibition in acid area (H+>>K1); K2 describes the inhibition in alkaline area (K2>>H+); H+ - concentration of hydrogen ions; t0opt – value of temperature, optimal for micro-organisms development; t0 – current temperature; d – temperature range; Ccat – concentration of bio-catalyst compounds; Kcat1 and Kcat2 – effective constants of inhibition – activation in respective areas, pK1 and pK2 – constants of dissociation. Identification of kinetic parameters of reaction rate qB and qS was conducted on basis of processing of data received in laboratory of bio-technology of KFPU under the guidance of this work's co-author (3): mmax = 0,7; KS = 10; pK1 = 4; K1 = -lg(pK1); pK2 = 9; K2 = -lg(pK2); Kcat1 = 5; Kcat2 = 50; t0opt = 280C; d = от 140C до 300C; Kd = 0,02; YS = 1. Equation system (2) is solved conjointly with equations of biochemical transformation kinetics (6) by method of Runge-Kutta.

Calculation results by model are presented in Fig. 2, 3.

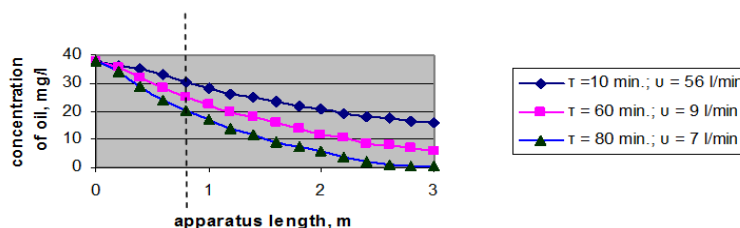


Figure 2. The change in the concentration of petroleum products along the length of the apparatus.

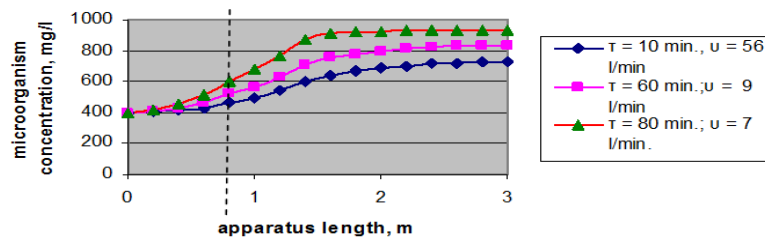


Figure 3. The change in the concentration of microorganisms along the length of the apparatus.

In Fig. 2 are presented calculation data of kinetics of oil-containing waste waters biochemical purification process at different flow rates. Calculation show that permissible degree of purification is achieved at flow rates in limits of 7 L/min. Oxidizing of oil hydrocarbons goes maximally in zone of jet element and external recycle, and goes further at all length of JS, weakening by degree of lowering of oil products concentration to zone of settling.

In general, the integrity of bio-purification is also provided by correction of biogene elements and inducing substances. Maintaining of these elements in waste liquid (flow) in concentrations of 2 to 20 mg/L increases the quantity of hydrocarbon oxidizing micro-organisms in limits of 2 times (fig. 3), which increases the bio-oxidizing effectiveness in JS up to 72-78%. Additional purification in the second stage of JS for 0.5 to 1 hour period allows to achieve the destruction of residual concentrations in waste liquid to standards of reverse water supply.

By semi-industrial experiments on pilot bio-technological scheme the following purification parameters were established: 1) at concentration of oil products of 20 – 186 mg/dm³, flow rate 0.015-0.03 m/sec the time of staying is 1.0 to 1.5 hours; 2) at concentration, exceeding 200 mg/dm³ or load by COD 1000 mg/L and more, the rate of liquid in pilot installation approaches 0.031-0.045 m/sec, at time of staying of 1.3-3.0 hours [3, 4, 6].

For purposes of management of oil-containing waste waters purification process by accepted technological scheme was developed mathematic model and its program realization.

The latter is presented in form of modifies Petri's network, which fulfillment allows to research system connections and laws of installation's functioning in general. In natural form, the network of Petri developed by us takes the

following form: $C = \langle P, T, I, O, M, \tau_1, \tau_2 \rangle$ [8, 9, 10, 11],

where $T = \{t_j\}$ is a finite non-vacuous aggregate of symbols called transgressions; they are estimated on basis of amount of quantity of production condition portions at continuous feeding in apparatuses of technological scheme.

$P = \{p_i\}$ - is a finite non-vacuous aggregate of symbols, called positions. In our case it is a aggregate of technological scheme apparatuses;

$I: P \times T \rightarrow \{0, 1\}$ – input function that sets for every transgression t_i the aggregate of its positions $p_i \in I(t_j)$.

O: $P \times T \rightarrow \{0, 1\}$ – output function that reflects the transgression into aggregate of output positions $p_i \in O(t_j)$.

M: $P \rightarrow \{1, 2, 3, \dots\}$ - function of marking (formatting) of the network that sets in correspondence of each position a non-negative integral number, equal to number of marks in the given position that changes in process of network's operation. Transgression's actuation immediately changes the formatting $M(p) = (M(p_1), M(p_2), M(p_3) \dots M(p_n))$ into formatting $M'(p)$ according to the following rule:

$$M'(p) = M(p) - I(t_j) + O(t_j) \tag{7}$$

Record of equation (7) means that transgression t_j extracts one mark from each of its input position and adds one mark into each of output one.

$\tau_1 : T \rightarrow N$ and $\tau_2 : P \rightarrow N$ function, determining the time of delay at actuation of transgression and the time of delay in position [8, 9,10].

Dynamics of MSP conduction is defined by motion of marks, modeling the motion of discrete flows of semi-products.

Therefore, the considered modification of Petri's networks allows to solve the following tasks:

1. Analysis if system apparatuses' functioning in emergency situations conditions;
2. Analysis of management switching on network level;
3. Analysis of discrete-continuous productions technological schemes for provision of stable condition [8, 9, 10].

With the aid of automated modeling system (AMS) were constructed models of major apparatuses that are realizing the bio-purification technological process [12]. From the system of program (SP) modules of typical apparatuses was synthesized the model of complete installation, its graph is presented in Fig. 4.

With application of SP-model we developed the program complex of system of oil-containing waste waters bio-purification technological module, imitating the functioning of bio-purification in virtual time [8, 9].

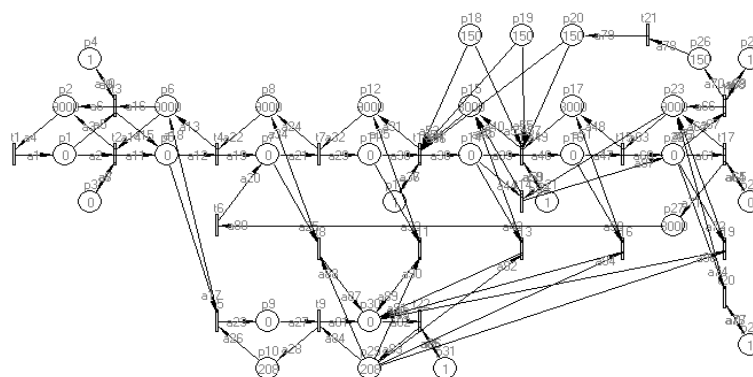


Figure 4. Model of process module as MPN.

By means of SCADA-technology TRACE MODE was developed the program complex of management system of oil-containing waste waters biological purification technological process [13]. A substantial peculiarity of developed program complex of technological process management system is its ability to adapt to technological module of bio-purification of any capacity, both for installation in frames of a separate purification station, transport means wash or small motor transport establishments or motor tractor stations, and a water purification system of large oil-chemical productions [14].

The system of technological process management allows to perform the following actions:

1. Supervisory control of management system major elements (waste waters level, length of process of oil products bio-destruction in waste waters etc.);
2. Stop of bio-purification system, if necessary;
3. Analysis of condition of bio-purification system on disposal or deactivation of contaminations in general and forecasting of emergency situations development [9, 14].

Conclusions:

1. The method of two-level system modeling of oil-containing waste waters bio-chemical purification technological process, determining the ability to conduct the analysis of industrial bio-purification installations functioning in conditions of dynamically changing process parameters is proposed.
2. The mathematic model of oil-containing waste waters bio-purification process in jet-settler, determining the functioning of oil-containing waste waters purification installation with effectiveness of oil products deactivation up to maximum permissible concentration in 1.2 hours of purification that allows to intensify the process by temporal parameter is developed.
3. Mathematic model of oil-containing waste waters bio-purification system functioning, realized in form of modified Petri's network, allowing to research system connections and laws of installation's functioning in general is constructed. The model is used for development of program means that allow to analyze bio-purification processes of the given production in order to provide the stable functioning of waste waters purification installation.
4. The program complex of waste waters bio-chemical purification systems of considered production, allowing to analyze conditions of bio-purification system condition in general and forecast the development of emergency situations is developed.
5. Effectiveness of proposed method is tested in pilot installation at industrial waste waters neutralization and

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purification facility of OKSc "Kazanorhsyntez", which performance shown the ability of provision of waste waters purification up to standards of reverse water supply and discharge into water bodies without any damage of their ecological condition.

Summary.

In order to solve practical tasks in achievement of more substantial effect in purification and treatment of hydrocarbon-containing waste waters of productions, in composition of which are present: benzol, isopropylbenzol, toluol, acetone, mono-, di- and triethylene glycoles, formaldehyde, surface active substances, phenol and other oil products, the application of bio-technological scheme with inclusion of two consequently positioned jet-settlers (JS) is more rational. This allows to inactivate the waste waters with initial hydrocarbons concentration up to sanitary standards (0.1 – 0.3 mg/L), and, therefore, up to standards of reverse water supply.

In conditions of deficit of fresh water used in production process, the developed bio-technological scheme provides the completeness of recuperation of exhaust waters in establishments of both individual sewage system, and bulk facilities. In traditional purification facilities, the 80-85% effect is achieved by biological oxidizing of oil contaminations in 16 to 20 hours, and with application of HOM consortium, and with two stages of purification in JS the effect is 92-96% in 2.0-2.5 hours. By this opens the way of use of waters, purified up to standards of reverse water supply.

The constructed mathematic model of oil-containing waste waters bio-purification system functioning, realized in form of modified Petri's network, allows to research system connections and laws of installation's functioning in general. The model is used for development of program means that allow to analyze bio-purification processes of the given production in order to provide the stable functioning of waste waters purification installation.

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