Combined technology of field research and modeling in the development of the rationing method pulp mill wastewater in the conditions of deep water outlets

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Abstract. The algorithm and the structure of information support for the model of implementation of the method of normalization of pulp mill wastewaters for deep dispersing water outlets, taking into account the hydrological regime, are determined. The combined technology is based on a geoinformation model of a natural-technogenic complex with identification parameters based on natural data of various hydrological regimes, wind unidirectional and multidirectional currents in depth. The characteristics of the jet zone and the main dilution are evaluated in accordance with the situational water use plan of the pulp mill. The hydraulic solution of the problem of transformation of nonconservative pollutants is implemented using the model of convective-diffusion transport, based on the equation of V. M. Makkaveev, and the transformation of substances using linear mono- and nonlinear bimolecular schemes. To determine the specificity of biochemical processes, the intensity of oxygen uptake and decomposition of organic substances was estimated by direct and indirect indicators. The proposed nonlinear model allowed us to determine the degree of uniformity of water masses in the jet zone of deep water discharge in the main dilution section up to the control gate. The algorithm of identification of parameters of the estimated model the convective-diffusive transport and transformation of substances on observed data taking into account specificity of the studied processes, and used types of models of transfer and transformation of organic compounds. The main measured parameters are temperature, electrical conductivity, turbidity of water, dissolved oxygen content, $\text{BOD}_5$, $\text{BOD}_{20}$, suspended substances, nitrite ion, phenols, phosphates, lignosulfonates. Laboratory studies were carried out at various dilution multiplicities with the determination of biochemical oxidation constants used in modeling various sites in a water object.

1. Introduction
The main goal of the work is a developing the combined technology of field research and modeling for the development of a method for regulating the flow of pulp mill. The object of research was a deep dispersing water outlet of waste water from a pulp mill. The city-forming enterprise is located in Pitkyaranta, Republic of Karelia. The pulp mill belongs to the first category of danger; it uses the method of sulphate cooking of pulp. The work was carried out in a team with researchers from Saint Petersburg State University of Industrial Technologies and Design, Karelian scientific center of the Russian Academy of Sciences, from the pulp mill, group of divers from Petrozavodsk. Based on a
number of experimental field data, the processes of biochemical oxidation of specific organic compounds in wastewater were modeled and the dilution of treated wastewater was modeled in the "pulp mill – water facility" system under deep water discharge conditions. The water outlet of the pulp mill under study is located in lake Ladoga at a distance of 800 meters from the shore. The design of the considered deep water outlet consists of 7 vertical pipes, the heads of which are located at a depth of 18-21 meters.

2. Method and materials
Echolocation shooting in the framework of combined technology was performed by the Garmin EchoMAP 50s echo sounder. Hydrophysical measurements were performed in vertical sensing mode at three-ray and cross-section stations using multi-parameter CTD90m Sea & Sun Technology and RBRconcertoC.T.D.DO.PAR|fast6 probes. Current observations are made by the Nortek Aquadopp HR Current Profiler 2.0 MHz acoustic flow profiler.

3. Modeling of processes of biochemical oxidation of specific substances of pulp mill waste water
The processes of oxygen consumption for the oxidation of organic matter and reaeration through the water-air interface are described by the system of Phelps-Streeter equations. The system has a limited range of applicability: for large oxygen deficits under anaerobic conditions, the oxygen deflection curve constructed using the Phelps-Streeter equations gives a quantitatively improbable picture – a negative value of the oxygen concentration in water, which cannot be. It follows that at high concentrations of organic matter, the monomolecular model cannot be used. In this case, you can use a non-linear bimolecular model, which is based on two parameters, or a trimolecular model, which also includes a third parameter - bacteria.

The monomolecular model is written as [1]:

\[
\begin{align*}
\frac{dC_{\text{BOD}}}{dt} &= -k_1 \cdot C_{\text{BOD}}^0 \\
\frac{dC_{\text{O}_2}}{dt} &= -k_1 \cdot C_{\text{BOD}}^0 \cdot k_2 \cdot C_{\text{O}_2}^{\text{lim}} + k_2 \cdot C_{\text{O}_2}^0
\end{align*}
\]

(1)

where \( C_{\text{BOD}} \) is the concentration of organic compounds characterized by BOD, mg/l; \( C_{\text{O}_2} \) is the concentration of oxygen dissolved in water, mg/l; \( C_{\text{O}_2}^{\text{lim}} \) is the limiting content of oxygen dissolved in water at preset temperature, mg/l; \( k_1 \) is the coefficient of biochemical oxidation, 1/day; \( k_2 \) is the coefficient of reaeration, 1/day; \( t \) is time, day.

The bimolecular model is written as the following system of equations [1]:

\[
\begin{align*}
\frac{dC_{\text{BOD}}}{dt} &= -\alpha \cdot C_{\text{BOD}} \cdot C_{\text{O}_2} \\
\frac{dC_{\text{O}_2}}{dt} &= -\alpha \cdot C_{\text{BOD}} \cdot C_{\text{O}_2} + \beta \cdot C_{\text{O}_2}^{\text{lim}} \cdot C_{\text{O}_2}
\end{align*}
\]

(2)

where \( \alpha \) is the coefficient of biochemical oxidation for the bimolecular model, (\( \alpha \) depends on \( T^\circ \), characteristics of substances, oxygen concentration); \( \beta \) is the reaeration coefficient for the bimolecular model, \( \beta = k_2 \).

The experiment was conducted on the example of water discharge into lake Ladoga of treated waste water from a pulp mill for August 2019 data.

To conduct a numerical experiment for modeling the oxygen regime and determining the constants of biochemical oxidation and reaeration, the case of water quality formation presented in table 1 is considered. The following values were used as input data: initial and limit concentrations of dissolved oxygen, values of \( \text{BOD}_5 \), lignosulfonates (LS), water temperature at the time of analysis, and coefficients of biochemical oxidation and reaeration.

The results of modeling the processes of biochemical oxidation of specific organic substances of pulp mill wastewater were performed in the MathCad 15 program and are shown in figure 1.
It should be noted that the result of modeling is a parameter of the time for complete oxidation of organic substances. According to figure 1, a small amount of time is required for complete oxidation of BOD$_5$ and phenols, since these parameters are characterized by biologically soft organic compounds of effluents – up to 20 days. For complete oxidation of lignosulfonates (LS) in the waste water of a pulp mill, it takes about 100 days according to the built model.

**Table 1.** Initial data of the experiment for modeling the oxygen regime and determining the constants of biochemical oxidation and reaeration using a mono- and bimolecular model.

| Parameter | $C_0$, mg/l | TLV, mg/l [2] | $T$, $^\circ$C | $k_1$, 1/day [5] | $k_2$, 1/day [1] |
|-----------|-------------|---------------|----------------|----------------|----------------|
| O$_2$     | 10.0        |               | 3.5            |                |                |
| BOD$_5$   | 3.0         | 2.0           | 3.5            | 0.04           | 0.05           |
| LS        | 9.6         | 3.0           | 3.5            | 0.02           | 0.05           |
| Phenols   | 0.003       | 0.001         | 3.5            | 0.056          | 0.05           |

**Figure 1.** Dependences of changes in the values of BOD$_5$, LS and dissolved oxygen over time at the outlet from the pulp mill treatment facilities during discharge to a water body. $Z_{i,1}$ – monomolecular model of BOD$_5$, LS, $Z_{i,2}$ – monomolecular model of O$_2$, $Z_{i,3}$ – bimolecular model of BOD$_5$, LS, $Z_{i,4}$ – bimolecular model of O$_2$.

4. Simulation of dilution of pulp mill waste water based on convective-diffusion transfer and transformation of substances

In Russian legislation, when wastewater is discharged into a water body outside of an urban area, the pollutants concentration must not exceed the standards in the control line at a distance of 500 meters from the discharge point. Thus, a section of a water body is used for diluting wastewater. The existing guidelines for calculating discharge standards and dilution multiplicities do not provide for the case when the discharge is deeper than 20 meters.

Mathematical models of wastewater dilution are used to solve this problem. The staff of the scientific and pedagogical school "Forecasting and environmental regulation of natural ecosystems" under the guidance of professor. Shishkin A. has been developing methods and tools for modeling the processes of convective-diffusion transfer and transformation of substances for many decades.

Within the framework of this task, the calculation of the distribution of pollutants in lake Ladoga is performed by computer modeling in the program Waste 4.5 Final, which used the differential equation of a homogeneous isotropic stationary two-dimensional model [6]:

$$Vx \,*(dC/dx) = Dy \,(dC/dy_2) - k_1 \,C,$$

where Vx is the average flow velocity along the flow; C is the concentration of the substance; x, y are the coordinates along and across the flow axis; Dy is the coefficient of turbulent transport or diffusion; $k_1$ is the coefficient of impurity self - purification.
This experiment was carried out on the example of a deep water discharge into lake Ladoga of the company's treated wastewater in April 2020. Water samples were taken at the site of the dispersing water outlet between the pipes at a depth of 15 m and laboratory analysis was performed for the main target indicators of the pulp mill waste water.

In the course of laboratory analysis, it was determined that the majority of concentrations in wastewater exceed the MPC, while such indicators as BPC5, nitrites, suspended solids, phosphates and lignin have the highest excess. When analyzing background concentrations, it is observed that for suspended substances, lignosulfonate and phenol, there is a small margin for diluting wastewater.

At the first stage, model A was calculated based on actual and averaged initial data, while the flow direction was taken along the pipes, which coincides with the prevailing North wind direction. The simulation results showed that no excess concentrations were observed in the control range, and the dilution ratio was equal to 30.

The second stage was to build model B with the original data of model A, but the flow direction was perpendicular to the pipes. The comparison of simulation results is shown in the diagrams below (Figure 2).

![Model A](image1)

![Model B](image2)

**Figure 2.** Distribution of concentration plots over the flow width for calculating the coefficients of transverse and vertical diffusion.
The concentrations of target indicators in the control gates for model A and B do not exceed the MPC, while due to the summation of contamination during the flow along the pipes, the concentrations for the first model are slightly higher than for the second. The flow across the pipes creates a wider spot of contamination, which is confirmed by the diagrams. In the future, the model A was used as the basis for modeling.

The third stage of the simulation was to change the flow rate in lake Ladoga from 0.02 to 0.2 m/s in increments of 0.02 m/s. The results of calculations showed that concentrations decrease with increasing flow rate.

To simulate dilution processes at the last stage, the model changed the wastewater flow rate from 0.1 - 1.0 m$^3$/s in increments of 0.01 m$^3$/s, while increasing the concentrations of controlled substances in lake Ladoga.

In a detailed analysis of the graph in the figure, it is worth noting that at a flow rate of more than 0.7 m$^3$/s, the control range shows an excess of the threshold limit value for suspended substances and lignosulfonate.

As a result of modeling, the most unfavorable conditions for dilution of wastewater were determined, and the maximum concentrations in the control line were calculated under various loads.

5. Conclusion
On the basis of reconnaissance field studies in the area of the depth of the outlet of the pulp mill produced by complex hydrological and hydrochemical surveys using modern Garmin echoMAP 50s echo sounder and multi parameter probes: CTD90m Sea & Sun Technology and RBR concertoC.T.D.DO.PAR|fast6 and acoustic profiler Nortek Aquadopp HR Current Profiler 2.0 MHz.

A large amount of real information was obtained for various hydrological conditions and modes. The constructed flow profiles and concentration distribution made it possible to identify the parameters of the transport and transformation model of substances. Recommendations have been prepared for achieving acceptable waste water discharge standards for a pulp mill, taking into account current legislation.

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