Statistically distributed characteristics of wastewater discharged from Kamskiy Kabel, LTD and containing organic phenolic compounds

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Abstract. A method of drawing up a statistically distributed characteristics of wastewater with the specified accuracy has been considered, which allows to study the patterns of fluctuation in the concentrations of organic phenolic substances in wastewater, on the example of the water discharged from Kamskiy Kabel, LTD. Based on the performed research, a model of the expected value and of mean square deviation of the fluctuation in the concentrations of organic phenolic substances has been built. It has been found that the fluctuation in the concentration of organic solvents in wastewater is seasonal, and the statistically distributed curve of the concentrations fluctuation has three extremum points.

1. Introduction
At present, big industrial enterprises generate considerable amounts of surface run-offs, which are polluted with substances of various nature. Besides the surface run-offs, which in their composition are similar to those of residential areas, industrial sites, where it is impossible to completely eliminate the negative effects from production, generate surface run-offs, which contain toxic organic substances dramatically increasing the values of COD and BOD20.

Among the measures on ensuring the decrease of the hazardous impact on the environment, the issues of treating wastewater off hazardous toxic pollutants are of special importance [1,2], as well as the use of the surface run-offs from industrial enterprise in the system of water recycling, what would allow to eliminate the negative impact on water bodies and to save the water being used. Especially urgent are the issues of treatment of phenolic wastewater, which is a big source of water bodies pollution and large amounts of which are generated at the enterprises manufacturing and using phenolic products [3,4].

According to the data available, the phenolic products at these enterprises are stored in special tanks; so, during the pump over of organic solvents spillages and leakages may occur for a number of reasons [5,6]. Rain water and melt water contribute to the generation of the surface run-offs, which contain organic phenolic compounds.

For the purpose of determining the characteristics and quantity of the wastewater being generated by Kamskiy Kabel, LTD, the conditions of its generation have been studied. In its production process, Kamskiy Kabel, LTD uses tricresol, naphtha, xylenol, and xylene as solvents. The yearly average volume of the wastewater generated by the enterprise amounts to approximately 24 thou. m³/year.
The conducted research has revealed that the wastewater contains all the four types of solvents, as well as their combinations, what has allowed us to conclude that this wastewater has a complex multi-component composition.

The data show that all the solvents under consideration contain phenol and its higher homologues (cresols and dimethylphenols), what has made it possible and reasonable to perform a revised estimation of the quantitative content of phenolic solvents in the wastewater [7].

Having analyzed the conditions of the phenolic flow generation at Kamskiy Kabel, LTD, we can conclude that the properties of this wastewater depend on the changes in the content and ratio of the components constituting the system.

The performed research has demonstrated that the nature of the wastewater generation and the pollutants concentrations are of strongly pronounced statistical character. The necessity to obtain averaged-out analytical characteristics of the wastewater containing phenolic solvents in order to further develop the methods of its treatment, makes relevant the task on elaborating the statistically distributed characteristics of the wastewater under consideration.

2. Drawing up a Statistically Distributed Characteristics of the Wastewater

The variety of technological processes at Kamskiy Kabel, LTD explains the need for organizing the disposal of the surface run-offs, different in the composition of impurities, at different drainage area sites, what would allow to develop an optimal treatment scheme in the future.

The changes in the content of solvents in wastewater is a stochastic value, which depends on the occurrence and the number of spillages of the solvents, as well as on their possible dilution by rain water and melt water [8-10].

The statistical nature of atmospheric precipitation, its intensity, as well as the snow cover depth determining the duration of the melt water generation, along with the instability of outflow during one raining period, explain the complex character of the surface run-offs generation, what may considerably complicate the designing of, and later, the operation of the treatment facilities.

In order to obtain the averaged-out analytical indices for the wastewater, and to solve the issue of selecting the method of its treatment, there has arisen a necessity to elaborate a statistically distributed characteristics to the specified accuracy [11-13].

For that purpose, the research has been performed to study the patterns of seasonal fluctuations in the concentrations of organic pollutants in the wastewater from the solvents warehouse of Kamskiy Kabel, LTD.

The wastewater has been analyzed for their content of organic solvents. The research results were evaluated as per the calculations with regard to phenol, using the method [14-16].

Each function f(\(t\)) has further on been taken into account as a “possible fulfilment” of random process X(t) complying with the reference outcome of the observations.

The total of all possible fulfilments obtained at various outcomes of the observations forms the random process X(t). Meanwhile, the probability measure known for various events at the same time allows to determine the probability that the process fulfilment will feature this or that peculiarity, or meet certain conditions.

Figure 1 shows the dependence of the change in the solvents content, with regard to phenol, in the wastewater from the solvents warehouse of Kamskiy Kabel, LTD, as per the seasons, over the recent 7 years.
Figure 1. Expected value and mean square deviation of the fluctuation in the concentrations of organic phenolic substances.

In order to establish the statistically distributed characteristics of wastewater under study to the specified accuracy, it has been required to describe the random process using a certain number of brief characteristics [17-19]. The expected value has been accepted as one of such stochastic value’s characteristics, which is a certain averaged function around which the fulfillment is scattered, that is the certain seasonal constant values of the organic solvents concentrations in the wastewater \( C(t) \), as well as the “correlation function” characterizing the connection between two stochastic values (solvents concentrations in the wastewater), complying with different values of the non-stochastic parameter. The expected value of the random process \( X(t) \) is the nonrandom function \( M_X(t) \), the value of which at each value \( t=t_0 \) of the \( t \) parameter equals the expected value \( M_X(t_0) \) of the very stochastic value \( X(t_0) \), which complies with this value of the parameter. The mean square deviation of the random process is described by this equation:

\[
\omega_x(t) = +\sqrt{D_x(t)}
\]  

(1)

\( \omega_x(t) \) is the mean square deviation of the process; \( D_x(t) \) is the random process dispersion \( X(t) \), which is an unstable function, the values of which at each value \( t=t_0 \) of the \( t \) parameter equal dispersion \( D_x(t_0) \) of the very stochastic value \( X(t_0) \), which complies with this value of the parameter.

To assess the degree of dependence of two cross sections, the “correlation function” has been considered, expressed as follows:

\[
K_x(t_1; t_2) = M[X(t_1)X(t_2)]
\]  

(2)

\( K_x(t_1; t_2) \) is the correlation function of random function \( x(t) \); \( t_1, t_2 \) are the independent arguments; \( M[x(t_1)x(t_2)] \) is the correlation cross section moment complying with the independent fixed values of arguments.
A tolerable error of the expected value of the random function has been evaluated as per the upper boundary $\delta$ of the tolerable error with the specified probability $\gamma = 0.95$

$$P\left(\left| x - a \right| \leq \delta \right) = \gamma$$  \hspace{1cm} (3)

$x$ is the sample mean of the stochastic value; $a$ is the expected value; $\delta$ is the upper boundary of the tolerable error; $\gamma$ is the specified probability.

The upper boundary of the error can be considered in three cases [19, 20]. When the stochastic value $x$ is distributed as per normal law and the known mean square deviation $\sigma$, the upper boundary of the error is calculated as follows:

$$\delta = t_{\gamma} \sigma / \sqrt{n}$$  \hspace{1cm} (4)

$n$ is the number of tests; $t$ is the value of the Laplace’s function argument; $\sigma$ is the known mean square deviation $x$.

In case of normal distribution of the stochastic value $x$ and its unknown mean square deviation $\sigma$, the upper boundary of the error with the reliability $\gamma$ is calculated as follows [20, 21]:

$$\delta = t_{\gamma} S / \sqrt{n}$$  \hspace{1cm} (5)

$n$ is the number of tests; $S$ is the “corrected” mean square deviation; $t_{\gamma}$ is the coefficient determined using a table.

In our case, with the specified reliability level $\gamma = 0.95$, the upper boundary of the error equals 0.098 and 0.099 as calculated using the equations (4) and (5), what allows to assume that the expected value of the random function with the specified probability $\gamma = 0.95$ is the statistical characteristics of the wastewater under consideration.

According to data in Figure 1, the statistically distributed curve of the fluctuation of the organic solvents mix concentrations has three extremum points. In the time interval $t_5<t<t_{6.5}$ the fluctuation of the solvents concentrations in the wastewater reaches 600 mg/l with regard to phenol, and in the time interval $t_8<t<t_{9.5}$ they reach the maximum and amount to 1200 mg/l, while in the remaining time intervals the concentrations of organic solvents in the wastewater fluctuates within the value of 300 mg/l.

The obtained experimental data allow to characterize the wastewater from the solvents warehouse of Kamskiy Kabel, LTD as dramatically varying in its seasonal content of organic solvents. It is important to note that the sharp increase in the concentrations of organic solvents in the surface run-offs is observed after a preceding durable dry weather period.

The highest concentrations have been registered in the beginning of the run-offs till the maximum outflow is reached, and then they sharply decrease. It has been found that the melt water run-offs are the most polluted ones, and the value of their BOD$_{20}$ parameter can be compared to untreated household effluents.

The results obtained have determined the necessity and reasonability to further on take into consideration all the three levels of the peak concentrations, when solving the issue of the technological and instrumentation support of the process of treatment of such wastewater.

3. Conclusion
In order to determine the characteristics and amount of the phenolic wastewater discharged from Kamskiy Kabel, LTD, the conditions of its generation have been studied. It has been found that the properties of such wastewater depend on the change in the content and ratio of the components constituting the system.

The conducted research has demonstrated that the nature of generation of the wastewater and the concentration of pollutants are of strongly pronounced statistical character, and the change in the solvents concentration in the wastewater is a stochastic value.
The performed studies of the patterns of seasonal fluctuation in the concentrations of organic phenolic solvents in the wastewater from Kamskiy Kabel, LTD over the recent 7 years have allowed to establish a statistically distributed characteristics of the wastewater under consideration with the specified accuracy, what has allowed to characterize it as dramatically varying in its seasonal content of organic solvents.

This work helps take into account the stochastic character of the generation of this type of wastewater, when solving the issue of the technological and instrumentation support of the treatment process with consideration to the peak concentrations; and since according to [22] the whole average annual volume of the wastewater must go to the treatment facilities, this work is quite relevant. However, with the difficulty of performing the calculations for the treatment facilities based on the statistically distributed characteristics of the wastewater under study, it is necessary to pay special attention to the measures on improving the engineering level of the operation of the production equipment, localization of the territory’s sites where spillages of raw materials and intermediate products are inevitable, and regulation of storing and transportation of the toxic organic substances.

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