Mathematical simulation of wastewater cleanse processes with high content of toxic organic water pollutants

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Abstract. In the study the authors constructed mathematical models of wastewater treatment processes with Fenton's reagent, ozone oxidative purification in the presence of a homogeneous catalyst, ozone oxidative purification in the presence of a heterogeneous catalyst, ozone oxidative purification in the presence of hydrogen peroxide — the Peroxon process. The resulting mathematical models allow the authors to predict the rate of chemical oxygen consumption (COD) at any time during the cleaning process, as well as to plan time expenditures to achieve the required level of this indicator. In addition, in the course of the research the integral coefficient of the models was calculated as a function of time, allowing to compare the cleaning processes and rank them by efficiency. As a result of the analysis of the integral coefficient, it was shown that the most effective is the oxidative purification of waste water with ozone in the presence of a homogeneous catalyst.

1. Introduction

Throughout the history of human development, engineering and all technical advances have been associated with resource consumption and environmental pollution. At present, emissions of industrial enterprises, energy systems and transport to the environment are achieved in such sizes that exceed the maximum permissible sanitary norms. Anthropogenic pollution of surface and groundwater provides global character and access to the operational resources of fresh water on the planet. Anthropogenic pollution of surface and groundwater provides global nature and access to the operational resources of fresh water on the planet.

It should be noted that currently the problem of wastewater cleansing of woodworking enterprises has not been studied enough.

Therefore, the search for fundamentally new environmentally friendly methods for cleansing wastewater containing toxic compounds is timely and relevant.

The most intensively polluted surface water is chemical, oil refining and woodworking industries. The wastewaters of these industries contain various mineral, biogenic, chemical and organic substances many of which are toxic [1].

2. Relevance

A number of works of domestic and foreign scientists are devoted to the issues of wastewater treatment of woodworking enterprises. Moreover, in these studies, the use of ozonation and the use of
Fenton's oxidative system for the treatment of wastewater from toxic pollutants are not considered [2-22].

Therefore, we first investigated the oxidative methods of sewage treatment of wood-slab plants using ozone, hydrogen peroxide and Fenton's reagent. The results obtained are given in this study.

The aim of the study is development of regression models for predicting the COD index at any time during ozone and also ozone purification in the presence of catalysts of the studied wastewater from toxic organic pollutants, identification of the most effective of the investigated methods of cleaning.

3. Experiment
In the study was used industrial wastewater wood-tiled plant. Physical and chemical wastewater treatment was carried out by coagulation and flocculation [23]. As coagulants, 1% solutions of Al₂(SO₄)₃, FeCl₃, FeSO₄ and aluminum oxychloride (OXA) were tested. Determination of the required dose of coagulant was performed without alkalinization and chlorination of water. As flocculants a 0.1% solution of polyacrylamide (PAA), a 0.5% solution of activated silicic acid (ACC) and a 0.1% solution of cationic polyacrylamide of the brand REF FC were used. The following were used as oxidizers for organic water pollutants: Fenton's reagent (a mixture of hydrogen peroxide with iron (II) sulfate and ozone. Ozonation was carried out with or without the presence of catalysts).

Using Fenton's reagent, the concentration of phenol decreased to 0.05 mg / dm³, when ozonized to 0.01 mg / dm³, with homogeneous catalytic ozonation to 0.001 mg / dm³.

As a result of the experiment, encouraging results were obtained on the wastewater treatment of the wood-slab plant using various methods [24]. It is known, for the analysis of data obtained experimentally, it is assumed the use of various statistical methods and techniques of mathematical modeling, among which the most commonly used analysis of a number of distributions and statistical analysis of interrelationships of phenomena, namely, correlation and regression analysis. The results of this analysis make it possible to predict the "behavior" or dynamics of a process.

4. The results of mathematical modeling
In order to summarize, present, analyze and interpret the experimental data, dynamic series of the distribution were considered, i.e. series with numerical indicators of chemical oxygen consumption (COD), presented in time sequence.

So, to determine the development trend of a dynamic COD change process with a change in the series level, a regression model was constructed as a function of time t:

\[ COD_i = f(t) + \varepsilon_i \]

where \( f(t) \) is a certain functional dependence, reflecting the tendency of development of the dynamic process, \( \frac{mgO_2}{l} \); \( \varepsilon_i \) - model error, \( \frac{mgO_2}{l} \); COD₁ empirical value of chemical oxygen consumption, \( \frac{mgO_2}{l} \).

As a result, this model allowed aligning or smoothing the time series, which facilitated their analytical research. It was found that the relationship of the COD from time to time can be represented as:

\[ \overline{COD}_i = f(t) = at^b \]  \hspace{1cm} (1)

where \( \overline{COD}_i \) is the theoretical value of chemical oxygen consumption, \( \frac{mgO_2}{l} \); a - model parameter, \( \frac{mg · O_2}{l · min} \), b - model parameter, dimensionless quantity, t-time of the process.
Model parameters (1) are calculated using the least squares method, after preliminary linearization of the model by logarithmization:

$$\ln(f(t)) = lna + b \cdot \ln(t),$$

(2)

A statistical analysis of the adequacy (reliability) of the regression models (1) according to Fisher's test and Student's criterion at a significance level of $\alpha = 0.05$ was carried out [25]. The results of the statistical analysis of the regression models are presented in Table 1.

| No | The name of the time series | Model parameters * | $R^2$ | $F$ | $t_a$ | $t_b$ | $F_{table}$ | $T_{table}$ |
|----|-----------------------------|--------------------|-------|-----|-------|-------|-------------|-------------|
|    |                             | $a$    | $b$    |     |       |       |             |             |
| 1  | Oxidative wastewater treatment with Fenton's reagent | 23095 | -0.854 | 0.96 | 153.60 | 43.68 | 12.39       |             |
| 2  | oxidative wastewater treatment with ozone | 11852 | -0.706 | 0.99 | 877.53 | 130.93 | 29.62       |             |
| 3  | oxidative wastewater treatment with ozone (in the presence of a homogeneous catalyst) | 5213 | -0.857 | 0.77 | 20.81  | 15.14  | 4.56        |             |
| 4  | oxidative treatment of waste water with ozone (in the presence of a heterogeneous catalyst) | 10091 | -1.03  | 0.91 | 60.35  | 23.12  | 7.76        | 5.99        | 2.45        |
| 5  | oxidative purification of waste water with ozone (in the presence of hydrogen peroxide - the process Peroxon") | 8103 | -0.982 | 0.93 | 80.82  | 27.39  | 8.99        |             |

$R^2$ is the correlation index; $F$-Fisher test; Student's $t_a$-test for parameter $a$; $t_b$-student's $t$ test for parameter $b$; $\alpha$-level of significance; degrees of freedom $k_1$ and $k_2$; $F_{table}$ is the tabular value of the Fisher criterion with $\alpha = 0.05$; $T_{table}$ is the tabular value of student's criterion with $\alpha = 0.05$

As can be seen from the above data, the correlation index is greater than 0.7, which means that there is indeed a close functional relationship between the COD index and time. In addition, the conditions of two statistical criteria are met, namely $t_{tab} < t_a$, $t_{tabl} < t_b$, $F_{tabl} < F_a$, $F_{tabl} < F_b$, which indicates the adequacy (confidence) of the constructed models and their parameters with a probability of 95%.

Thus, we have proved that regression models of type (1) are applicable for predicting the level of COD in oxidative wastewater treatment with ozone, including in the presence of a catalyst. These dependencies (Figure 1) can be used in inverse problems, when it is necessary to estimate the time required for cleaning to the desired value of COD.
Figure 1. Regression model of COD change over time during oxidative purification of waste water with Fenton's reagent.

For a more detailed study of the time series and to identify the most effective of them in this work, the integral efficiency coefficient of the studied methods was also calculated:

$$I = \int_{t_1}^{t_2} f(t) \, dt = \int_{t_1}^{t_2} at^b \, dt = \frac{at^{b+1}}{b+1} - \frac{at_1^{b+1}}{b+1},$$

where a and b are the parameters of the model (1), t1 and t2 are the initial and final time points of the experiment, I is the integral coefficient of the mathematical model (1).

Integral values are most effective in estimating, since while all processes are considered as continuous, i.e. we are able to take into account the change in the COD at each point of the allotted time interval and not at individual points in time at which the experiment was conducted. The meaning of the integral coefficient, as well as any integral indicator, is that it represents the area limited by dependence (1) on the time interval $[t_1; t_2]$. This area is the sum of COD values at each point of a given time interval. This means that the smaller the area, the more intense the process. The calculation results are shown in Figure 2.

Figure 2. The results of calculating the integral coefficient of mathematical models (1) of the studied cleaning processes.
Comparing the obtained values of the integral coefficient, we can conclude that the most effective is the oxidative purification of waste water with ozone in the presence of a homogeneous catalyst.

5. Conclusions

Thus, a regression model for estimating and predicting the COD over time has been constructed using various methods for the oxidation of toxic organic substances contained in the wastewater of woodworking enterprises. It is established that the most effective is the method of oxidative purification of waste water with ozone in the presence of a homogeneous catalyst. In addition, the proposed algorithm for evaluating the effectiveness of the process can be used when choosing a method for treating wastewater with a high content of toxic organic water pollutants.

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