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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

ECOLOGICAL ASSESSMENT OF VARIOUS ENVIRONMENTAL POLLUTIONS AND THE DEVELOPMENT OF OPTİMAL REMEDIAL METHODS

Speciality: 2426.01 - Ecology

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GENERAL CHARACTERISTICS OF WORK

Relevance of the topic and degree of elabration. One of the important issues of spatial analysis in the study of the temporal dynamics of environmental pollution is the interpolation of a continuous surface using the values of individual spatial samples as base points. A sufficient number of interpolation methods are known, including the spline method, the polynomial regression trend surface method, the radial basis function (RBF) method, etc. At the same time, the requirements for the assessment and extrapolation of environmental pollution pose the need to increase the accuracy of interpolation values of the pollution decomposition process over time.

It is known that the development of special economic zones and technoparks is carried out in the form of an industrial cluster. A cluster is a group of production enterprises located in close geographical proximity. The most important meteorological factors affecting the concentration of aerosol in the atmosphere over the industrial enterprises of the cluster are relative humidity, wind speed and air temperature. In this regard, taking into account the possibility of "washing" aerosol in the lower layers of the atmosphere through the formation of artificial precipitation, the issue of synthesizing optimal meteorological conditions to ensure minimum total aerosol pollution of the atmosphere is relevant. Atmospheric aerosol has a number of negative effects on human life, including contributing to the deterioration of the climate, reducing visibility and poses a threat to human health by entering the body through the respiratory tract. Exposure of the atmosphere to aerosol is accompanied by the possibility of the formation of noise-like signals in spectrometric measurements of its various components.

Taking these into account, the development of the foundations of a combined three-wavelength method of ground-space sun-photometric measurements to compensate for the impact of atmospheric aerosol is an urgent issue. In recent years, an ecological analysis of persistent organic pollutants (POPs) has been carried out, which have a sufficiently low impact on the environment. This includes the class of organochlorine compounds, which have properties such as bioconcentration, global distribution, resistance to physical, chemical and biological changes, and toxic effects on organisms. The class of toxic organochlorine compounds also includes polychlorinated biphenyls (PCBs). Being global environmental pollutants, PCBs enter the body through the lungs, gastrointestinal tract and skin. After these pollutants enter the body with food or air, they accumulate in organs such as the liver, kidneys, lungs, adrenal glands, brain, heart and skin. PCBs can pose significant threats to human health in industrial and nearby areas. The global distribution of PCBs contributes to land, water, and air pollution, requiring remediation procedures to address the resulting contaminants. Incineration is considered the most efficient method for disposing of PCB materials.

However, the incineration method for PCBs disposal is expensive and an alternative is the burial of hazardous waste in underground layers. The incineration method of PCBs disposal has fundamental drawbacks, such as contamination of the surface and groundwater. The most effective way to reduce the concentration of PCBs in water and air is to expose them to ultraviolet rays.

Known methods of soil oil removal, including burning, extraction, biological methods, are considered ineffective, as they lead to secondary pollution of the environment. Depending on factors such as the size of soil particles, the thickness of the irradiated layer, light intensity, and the amount of humus in the soil, photodegradation of organic pollutants in the soil is considered a promising method. In the photocatalytic method, increasing the concentration of TiO_2 in the reactor can lead to an increase in the rate of decomposition of crude oil, and the maximum rate of oil degradation is observed at a concentration of 2% added TiO_2.

It is known that mineral oils and used engine oils have carcinogenic or mutagenic properties. In addition, used engine oils are harmful to marine life. Therefore, it is necessary to protect the environment from the effects of used engine oils. Therefore, infrared spectral analysis of the sample is widely used to assess its toxicity.

Similarly, it is known that since many petroleum hydrocarbons are toxic in nature, oil-contaminated soils pose serious ecological threats to the environment. Biodegradation of petroleum hydrocarbons involves catalytic reactions with microbial and chemical materials in the natural environment. The rate of decomposition of such hydrocarbons depends on factors such as temperature, pH, etc.

Additionally, the development of an optimized kinetic model for the joint biodegradation of oil hydrocarbon components is emerging as an urgent issue, where the optimal kinetic relationship of the components should ensure the achievement of the minimum value of the remaining amount of hydrocarbons. The application of kinetic models of photocatalytic purification of water pollutants allows for the interpretation of experimental data, optimization of the system and increasing the efficiency of the remediation process.

Simple kinetic models are widely used to describe and model the process of photomineralization of organic compounds. Therefore, the issue of further improvement of the photocatalytic method for cleaning water bodies from organic pollutants poses the need to improve the relevant kinetic models as the main problem.

At the same time, modelling studies on the transformation processes of oil spills in aquatic environments remain important and highly relevant. It is known that oil spills on the sea surface undergo degradation to different degrees under the influence of various factors. Therefore, the study of oil degradation processes is one of the important issues for taking countermeasures and planning restoration measures in areas where man-made disasters occur.

Object and subject of the research. The **objects** of research were urban atmospheric pollution, polychlorinated biphenyl emissions, additive Weibull function, soil remediation processes, pseudo-first-order kinetic processes, two-component desorption model, and factors affecting the degradation of hydrocarbons.

The **subject** of the research includes modeling of degraded oil components, optimization of soil desorption regime, serial remediation processes of PCB-contaminated soil, assessment of general aerosol pollution of industrial enterprises and urban atmosphere, and catalytic methods of water purification.

Research purpose and objectives. The **purpose** of the research is to develop highly effective methods for monitoring, assessing, and remediating pollution in various environmental components caused by aerosols, polychlorinated biphenyls, and petroleum hydrocarbons to ensure ecological stability

To achieve the main goal, the following **issues** were raised and resolved in the dissertation work:

1. Development of a conditional spatial interpolation method to identify minimally polluted areas resulting from point aerosol emissions in the urban atmosphere.

2. Solving the problem of optimizing the total aerosol pollution of industrial enterprises of the same cluster, which allows determining the optimal relationship between the height of the aerosol pollution layer and the size of a drop of artificially induced precipitation.

3. Assessment of the risk of human exposure to polychlorinated biphenyl emissions emitted into the atmosphere

4. Development of sequential remediation procedures for soil contaminated with polychlorinated biphenyls at multiple sites, using microwave irradiation and MnO_2 as remediation agents.

5. Development of a two-component desorption model to optimize the desorption process during sequential treatment of soil samples from heterogeneous environments contaminated with varying levels of hydrocarbons

6. Solution to the problem of optimized modelling of degraded oil components in a hydrocarbon mixture, considering the inhibition of one component's degradation by another.

7. Development of a relative logarithmic indicator with extreme properties as an additional feature for assessing the viscosity of degraded oil, and the creation of an optimized simple model for the oil degradation process on the sea surface.

8. Development of highly efficient photocatalytic methods for cleaning soil from petroleum hydrocarbons and water bodies from organic pollutants.

Research methods. In solving the posed problems, elements of adsorption theory, aerosol theory, and relevant principles of mathematical analysis and optimization theory were used. Experimental data obtained from known experiences in the field of environmental monitoring and the results of specific model studies based on established mathematical models were taken as a basis for confirming and verifying the theoretically obtained results.

The main provisions submitted for defense:

1. The proposed method of conditional spatial interpolation for detecting minimally polluted zones during point aerosol emissions into the urban atmosphere.

2. Formulation and solution of the problem of optimizing the total aerosol pollution of industrial enterprises of a single cluster by determining the optimal relationship between the height of the aerosol pollution layer and the size of a drop of artificially induced precipitation.

3. Formulation and solution of the problem of identifying the condition that ensures the minimum integral value of the additional Weibull function, which determines the proportion of a product or substance containing PCBs in use, under the condition of a directly proportional relationship between the half-life and service life of PCBs.

4. Analytical expression of the interdependence between the indicators of pseudo-first-order kinetic processes for microwave radiation and MnO_2 factors used in sequential soil remediation, aimed at achieving the optimal purification.

5. A two-component desorption model that allows synthesizing the optimal regime during the sequential processing of soil samples exposed to varying degrees of hydrocarbon contamination in a heterogeneous space.

6. A model for optimizing the degradation of oil components, based on the known fact that the degradation of one component in a hydrocarbon mixture can inhibit the degradation of others.

7. A new logarithmic relative indicator proposed as an additional informative sign of the viscosity of degraded oil. A simplified model of the process of oil degradation on the sea surface.

8. Methods for optimizing reactions and catalytic processes in the purification of various water bodies with different pollutant concentrations, based on the proposed three-dimensional representation of the photocatalytic reaction results.

Scientific novelty of the research.

1. A spatial interpolation method has been proposed to identify the least polluted areas in cities exposed to point aerosol emissions. In this approach, it is assumed that the spatial base points used for interpolation are influenced by a single strong aerosol source. The distance-dependent relationship that ensures minimal pollution at the interpolation point is determined as a function of the distance from the strong source to the base point and from the base point to the interpolation point.

2. Solving the optimization problem to minimize total aerosol pollution in the surface atmosphere of industrial enterprises of the same class allowed for the determination of the optimal interaction between the height of the aerosol pollution layer and the size of artificially induced rain droplets.

3. It has been shown for the first time that the risk of human exposure to polychlorinated biphenyls emitted into the atmosphere is minimal when the attenuation coefficient of the pollutant's effect is directly proportional to the population of the area under consideration. By evaluating the integral value of the additional Weibull function, the relationship between the half-life of the set of PCB isomers that provides the minimum of polychlorinated biphenyl products in use and the launch indicators of the products in use was determined.

4. A new analytical expression for the relationship between the pseudo-first-order kinetic process indicators of microwave radiation used in sequential soil remediation at multiple points and MnO_2 factors added to the soil, which ensures remediation efficiency, was obtained.

5. A new two-component model has been proposed to optimize the desorption regime during the sequential processing of soils contaminated with hydrocarbons to varying degrees in a heterogeneous environment, based on the growth rate of rapidly desorbing fractions.

6. Based on the known fact that the degradation of one component in a hydrocarbon mixture can inhibit the degradation of another, the problem of modelling degraded oil components has been addressed. The condition has been determined under which the average integral value of residual concentrations reaches its minimum when the geometric mean of the initial concentrations increases.

7. As an additional informative indicator for assessing the viscosity of degraded oil, a new logarithmic relative indicator has been proposed that takes a minimum value in a certain dynamics of changes in the shares of oil fractions.

8. A simplified optimization model of the oil degradation process on the sea surface has been developed, determining the interaction between wind speed over time and the oil evaporation fraction to minimize the fraction of oil dissolved in water.

Theoretical and practical significance of the research.

1. The proposed conditional spatial interpolation method for detecting minimally polluted zones during point aerosol emissions into the urban atmosphere can also be applied to identify areas affected by gases with low toxicity in a mathematically generalized form, which holds particular theoretical significance.

2. The analytical relationship between the height of the aerosol pollution layer and the size of an artificial rain droplet, derived from solving the optimization problem to minimize aerosol pollution in the surface atmosphere of industrial enterprises within the same cluster, is of significant theoretical and practical importance. This finding contributes to the scientific foundations for using artificial rain to purify the air in industrial zones and aids in the design work for engineers and planners.

3. When there is a direct proportional relationship between the pollutant attenuation coefficient and the local population size in a given area, minimizing the risk of human exposure to PCBs emitted into the atmosphere becomes a condition of significant scientific and practical importance. This insight is particularly relevant in designing population settlement plans and constructing residential buildings in former industrial zones.

4. The result of evaluating the integral of the additional Weibull function to determine the proportion of PCB-containing products in use is of significant practical importance for planning environmental remediation measures in areas where such products are distributed

5. In general, other results from the dissertation research, including the method for assessing the viscosity of degraded oil, a simplified model for determining oil degradation on the sea surface, and development of 2-component desorption model for heterogeneous soil environments, hold significant theoretical and practical value. These findings contribute to determining the optimal conditions for cleaning various environments contaminated with petroleum hydrocarbons and improving efficiency of remediation efforts.

Approbation and implementation. The results of the dissertation work were discussed at the meetings of the Joint Scientific and Technical Council of the National Aerospace Agency (NAA) and the Scientific and Technical Council of the Scientific and Research Institute of Aerospace Informatics of NAA, as well as at the following scientific and technical conferences and forums:

1. XII Международная научно-практическая конференция «Актуальные проблемы экологии и охраны труда», Россия, Курск, 20 мая 2020 г.
2. XIII Международная научно-практическая конференция «Актуальные проблемы экологии и охраны труда», Россия, Курск, 28 мая 2021 г.
3. Общероссийская научно-техническая конференция «Автоматизированные системы управления и информационные технологии», Россия, Пермь, 9-11 июня 2021 г.
4. Azərbaycan Texniki Universitetində "Radiotexnika" ixtisası üzrə mühəndis kadrların hazırlanmasının 60 illiyinə həsr olunmuş "Radiotexnikanın müasir problemləri" mövzusunda Respublika elmi - texniki konfransı, Azərbaycan, Bakı, 20-22 oktyabr 2021.

Name of the organization where the dissertation work was carried out. The dissertation work was carried out at the Scientific Research Institute of Aerospace Informatics of the National Aerospace Agency (NAA) of the Ministry of Defense Industry.

The total volume of the dissertation is expressed in characters, with the volume of each structural section of the dissertation indicated separately. The dissertation is presented in a text of 163712 characters in total, with the introduction consisting of 20101 characters, Chapter I consisting of 43231 characters, Chapter II consisting of 30549 characters, Chapter III consisting of 35860 characters, Chapter IV consisting of 31221 characters and conclusions consisting of 2750 characters.

MAIN CONTENTS OF THE WORK

The introduction presents the general state of the problem, justifies the relevance of the topic of the dissertation work, and specifies the goals and objectives of the study, notes the scientific novelty and practical significance of the work. The main provisions to be defended are formulated.

In first chapter of the dissertation, the characteristics of deterministic and statistical interpolation methods used in world practice to assess various pollutions of the natural environment were investigated, and the advantages of the IDW (inverse distance weighting) method were identified. A conditional interpolation method was proposed using the IDW method, and procedures for detecting areas exposed to minimal pollution during point aerosol emissions of the urban atmosphere by solving the variation optimization problem were explained [8].

The solution to the problem is based on the well-known[1] interpolation estimation of the IDW method.

$$Z(x_0) = \sum_{i=1}^{n} w_i Z(x_i) \tag{1}$$

Here w_i are the weighting factors, $Z(x_i)$ is the quantitative indicator of the choice at point x_i. It is assumed that the attenuation of $Z(x_i)$ along the L_i path occurs with an exponential regularity.

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[1] Apaydin, H., Sonmez, F.K., Yildirim, Y.E. Spatial interpolation techniques for climate data in the GAP region in Turkey// Climate Research, - 2004, Vol. 28., - p.31-40.

An optimization function is constructed for the function *L=L(l),* which depends on the distance between the interpolation point and point x_i within the constraint condition $\int_0^{\ell_{max}} L(\ell) d\ell = C$=*const*.

It has been shown that the equality of this function must hold for it to attain an extremum.

$$L(\ell) = \frac{1}{b} ln \frac{bZ(x)}{\lambda_0 \, \gamma \, \ell^p} \tag{2}$$

Here b = *const*, ρ- numerical indicator specific to the IDW method, $\gamma = \int_0^{l_{\max}} (\frac{1}{l^p}) dl$.

To verify the performance of the proposed simplified model, experimental calculations were performed using 3 base points, and the geometric interpretation of the results is given in Figure 1.

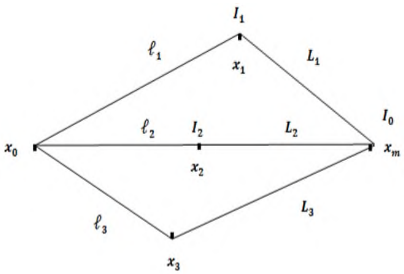

Figure 1. Geometric interpretation of the simplified model of experimental interpolation: $x_i (i = \overline{1,3})$- base points, x_0 - strong source of air pollution, I_0 - initial concentration of the pollutant at point x_0, I - concentration of the pollutant at point x_i

It is shown that there exists an optimal relationship between the distance l from the i-th selection point to the interpolation point and the distance L from the i-th selection point to the strong source, such that the total impact of the strong source on the interpolated point is minimized.

The same chapter also addresses the synthesis of optimal meteorological conditions that ensure minimal total aerosol pollution in the atmosphere of enterprise clusters [7]. In this regard, the well-known model[2], which characterizes aerosol pollution in the atmosphere of enterprise clusters while accounting for the potential formation of artificial precipitation through active influence on rain clouds and aerosol "washing" in the lower layers of the atmosphere, was used as a basis to solve the optimization problem. In this case, the urban air domain is assumed to be a rectangular area with sides h_i, and a regular set of n industrial zones is considered.

$$H = \{h_i\};\; i = \overline{1,n};\; h_i = h_{i-1} + \Delta h\;;\; \Delta h = const \quad (3)$$

Thus, a practical method was developed to simulate rain with droplet sizes ranging from r_{min} to r_{max}. The task was to determine the optimal form of the function $h=h(r)$ such that the objective functional attained an extremum.

$$\delta_n = \int_0^{r_{max}} \left\{ \frac{\left[\frac{a_1}{h(r)} + a_2\right]}{a_3 + \frac{a_4}{r}} + \frac{a_5\left[1 - e^{-\left(a_3 + \frac{a_4}{r}\right)86\cdot 10^3}\right]}{a_3 + \frac{a_4}{r}} \right\} dr \quad (4)$$

Here $a_1 = \sigma;\; a_2 = \frac{v}{d}\delta_{ext}\;;\; a_3 = \frac{v}{d}\;;\; a_4 = \rho\;;\; a_5 = \frac{\delta(0)}{86\cdot 10^3}\;;$ δ - average aerosol emission per unit area of the city; v - average wind speed; d - average horizontal size of the city area; ρ - average rainfall intensity; δ_{ext} - average concentration of pollutants entering the city; δ *(0)*- surface aerosol concentration.

For an analytical solution to the problem, the dependence between the height of the contamination layer *(h)* and the size of the droplet *(r)* is used.

$$\int_0^{r_{max}} h(r)dr = C;\quad C = const \quad (5)$$

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[2] Tiwari, S. Variations in mass of the PM10, PM2,5 and PM1 during the monsoon and the winter at New Delhi/ S.Tiwari, D.M.Chate, P.Pragya [et al.] // Aerosol and Air Quality Research, - 2012. Feb: - p. 20-29. DOİ:10.4209/aaqr.2011.06.0075

As a result, by solving the optimization problem (4), the following values were obtained.

$$h(r)_{opt} = \frac{C\cdot\sqrt{\frac{a_1}{\left(a_3+\frac{a_4}{2}\right)}}}{\int_0^{r_m}\sqrt{\frac{a_1}{\left(a_3+\frac{a_4}{r}\right)}}dr}$$

Thereby showing that the inverse relationship between h and r is satisfied to achieve maximum removal of pollutants in industrial zones.

In the same chapter, a new method for compensating for the effect of atmospheric aerosol in three-wave sun photometers was also proposed, in which the total optical thickness of the aerosol for any wavelength was presented as the sum of $PM_{2.5} + PM_{10}$. In this method, the wavelengths of the three onboard spectroradiometers were taken as the basis for the wavelengths of the sun photometer, and regression equations were established between the PM indicators and the output signals of the spectroradiometer. It was shown that it is possible to calculate the correction factors of the three-wave photometer by solving the system of equations [14].

The **second chapter** of the dissertation is devoted to the investigation of the characteristics of polychlorinated biphenyls (PCB) emissions into the environment and the development of optimized remediation procedures. First of all, the physical and chemical properties of PCB, the consequences they cause, the volume of production in the world, and the main sources were interpreted, and the issue of assessing the risk of harm to human health was considered. For this, the risk (*Ri*) of harmful substances emitted with probability *Pi* in the *i*-th area was calculated, taking into account the grouping of PCB isomers in separate settlements.

$$R_i = P_i P_{1i} \exp\left[-k\Delta_t\right] \quad (6)$$

Here P_{1i} is the probability of emission of harmful substances; k is the attenuation coefficient; Δ_t is the time for the harmful substance to reduce its effect.

Considering the diversity of settlement areas, two variants of the relationship between the R_i and k_j indicators were considered, and by assuming the functional dependence $k_j=f(P_i)$, the solution of the unconditional optimization problem within the constraint condition

$$\int_0^{P_m} f(P)dP_i = C_1; \quad C_1 = \text{const}$$

was obtained as follows

$$f(P) = \frac{1}{\Delta_t} \ln \frac{\Delta_t P R_1}{\lambda_0} \tag{7}$$

Here λ_0 is the calculated value of the Lagrangian multiplier within the considered constraint condition. It is thus shown that when the solution (7) is satisfied, the total risk of harm to human health will be minimized. The second optimization problem proposed is based on the Weibull distribution, which determines the probability of self-destruction of a substance after a certain period of use. In this case, the integral quantity of the additional Weibull function was estimated to determine the fraction of the substance used, and it was shown that if the half-life of any set of isomers is directly proportional to the time of the start of use of polychlorinated biphenyls, the risk of their impact on organisms will be minimized.

The impact of PCBs on the ecological state of the environment, as well as the kinetics of leaching and remediation procedures of contaminated soils, were also investigated here [10]. In order to optimize the remediation process of contaminated environments, the amount of PCBs initially sorbed by soil materials was determined based on the well-known formula[3].

$$x = m \cdot K \cdot C \tag{8}$$

[3] Wang, M. Removal of polychlorinated biphenyls by desulfurization and emissions of polychlorinated biphenyls from sintering plants / M.Wang, M.Hou, K.Zhao [et al.] // Environmental Science and Pollution Research, - 2016. Apr: Vol. 23 (8). - p. 7369–7375. DOI: 10.1007/s11356-015-5903-7.

Here x is the amount of adsorbed substances (μg), m is the weight of the adsorbent (g), C is the equilibrium concentration of PXB in the mixture ($\mu g/ml$), and k is the sorption constant (ml/g).

Thus, a three-dimensional model of a real soil surface was considered using the regression equations shown in that source between total organic carbon (TOC), surface area (SA), and sorption constant.

In this case, the sorption coefficient was taken as a multiple $K = \{k_1, k_2, k_3\}$ and the following system of inequalities was formulated.

$$\left.\begin{array}{l} k_1 \geq 188 + 3{,}36SA + 11{,}4TOC, \\ k_2 \geq 255 + 18{,}5TOC, \\ k_3 \geq 230 + 6{,}64SA, \end{array}\right\} \quad (9)$$

In order to find the optimal value of SA and TOC at given values of k_i ($i = \overline{1,3}$) an objective functional was formulated based on (8). Finally, the total amount of PCB sorbed in the three-dimensional area was calculated as (X_0).

$$X_0 = m_1 k_1 C + m_2 k_2 C + m_3 k_3 C \quad (10)$$

Thus, the objective function of the linear programming problem within the constraint condition (9) is defined as follows

$$C_1 = \frac{X_0}{C} - d_1 = SA \cdot d_2 + TOC \cdot d_3 \quad (11)$$

Here

$$\left.\begin{array}{l} d_1 = m_1 \cdot 188 + m_2 \cdot 255 + m_3 \cdot 230 \\ d_2 = m_1 \cdot 3{,}36 + m_3 \cdot 6{,}64 \\ d_3 = m_1 \cdot 11{,}4 + m_2 \cdot 18{,}5 \end{array}\right\},$$

m_1, m_2, m_3 are the weights of the adsorbents for the three-dimensional case.

Thus, the objective function is presented as follows

$$C_1 = 10 \cdot 10^3 \cdot SA + 29,9 \cdot 10^3 \cdot TOC \qquad (12)$$

The optimal values of SA and TOC quantities were determined based on a practical example, taking m_1, m_2, m_3 = 1000 g, and the geometric solution of the linear programming problem with k_1 = 995; k_2 = 1030; and k_3 = 800 is shown in Figure 2.

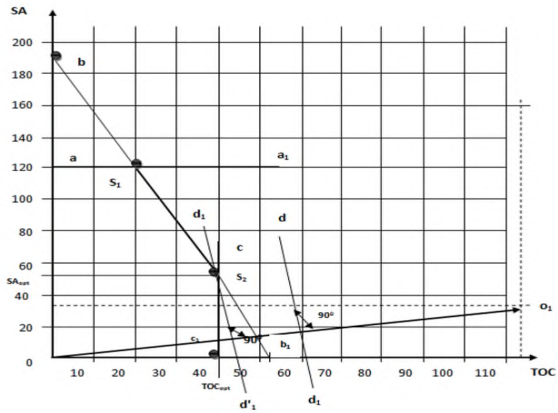

Figure 2. Geometric solution for determining the optimal values of SA and TOC quantities: aa_1, bb_1 and cc_1- constraint lines corresponding to inequalities (9); 00_1 - center line formed based on the objective function (12); dd_1 and dd_1' - base of the support plane; SA_{opt} and TOC - nodal points; S_1, S_2 - calculated optimal values for SA_{opt} and TOC.

Thus, two issues of the remediation process of land areas contaminated with PCBs were considered, in the first case, only the achievement of the efficiency of the process was set as the main goal. The second issue was additionally devoted to achieving the maximum efficiency of PCB adsorption by various components of the soil. It was shown that the application of the linear programming method at given values of the sorption coefficient allows calculating the total amount of organic matter in the soil and the area of the adjacent surface. The obtained optimal values can be used in the selection of land areas for the creation of purification production [10]. This chapter also proposes a method for the degradation of PCBs in atmospheric air and groundwater using TiO_2 nanoparticles and ultraviolet radiation, based on the exponential dependence between the concentration of PCBs in the atmosphere and the distance from the pollution source.

Here, the dependence of the PCB processing time (*t*) on the distance from the pollution source (*L*) is expressed as follows:

$$t(L) = \frac{1}{k_1} ln \frac{k_1 C(L_0)}{\lambda_0} - \frac{kL}{k_1} \quad . \tag{12}$$

Here k_1 is the reaction rate; $C(L_0)$ - PCB concentration at time $t = 0$; λ_0 is the value of the Lagrange constant (λ) calculated within the given constraint condition.

Thus, the use of ultraviolet and microwave radiation for air purification from PCBs, and ultraviolet radiation and TiO_2 nanoparticles for water purification were recommended. At the end of the chapter, a general kinetic model for the removal of PCBs by microwave irradiation and the addition of MnO_2 in the implementation of the soil remediation process is presented as follows

$$ln\left(\frac{C}{C_0}\right) = -(k_1 + k_2)t \tag{13}$$

Here, C_0 and C are the concentrations of PCBs in the soil at $t=0$ and $t=t$, respectively, and K_1 and K_2 are the effects of MnO_2 and microwave radiation on the kinetics of the process, respectively. For the remediation process, the functional dependence $K_2 = f\,(K_1)$ was considered and optimization procedures were carried out within certain constraints, resulting in following solution

$$f(K_1) = \frac{1}{t} ln \frac{C_0 t}{\lambda_0} - K_1$$

Here λ_0 is the calculated value of the Lagrangian multiplier. It is shown that when serial remediation operations are carried out, MnO_2 can be used as a remediation factor by finding the relationship between K_1 and K_2 indicators in the case of limited microwave radiation resources.

Thus, by solving the variational optimization problem, it was determined that the residual concentration of PCBs in the soil reaches a minimum when the obtained condition is met.

The third chapter discusses the issues of cleaning up land contaminated with various hydrocarbons. First of all, the methods of accelerating the photocatalytic process were considered, based on the dependence of the degradation rate of crude oil on the concentration of TiO_2 and the intensity of external radiation [11].

In this regard, the *Langmuir – Hinkelwood* model[4], which determines the rate of catalysis in the photodegradation process of aromatic hydrocarbons, was used and the rate of photodegradation was determined as follows

$$-\ln\left(\frac{C_R}{C_{R_0}}\right) = k_0 \cdot t \tag{14}$$

Here C_R is the reactant concentration, C_{R0} is the value of the reactant concentration at the time $t=t_0$, k_0 is the apparent rate of photodegradation. Thus, in order to accelerate the photodegradation process, it was required to find the optimal value of $k_{op}(t)$ that ensures that C = $C_{R_{(t)}}$ reaches a maximum for the kinetic model (14) by changing soil moisture content over time, that is, assuming $k_0=k_0(t)$.

Thus, by solving the variational optimization problem, it was determined that the residual concentration of PCBs in the soil reaches a minimum when

$$k(t) = \frac{1}{t}\ln\frac{(t \cdot C_{R_0})}{\lambda_0} \tag{15}$$

Therefore, for small values of C_{R_0}, the optimal solution that ensures the maximum of the objective functional in solutions that are inverse to the solution of (15) with the linearized optimization method is obtained as follows.

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[4] Zhao, X. Different effects of humid substance on photodegradation of p, p, - DDT on soil surfaces in the presence of TiO2 under UV and visible light / X.Zhao, X.Quan, H.Zhao [et al.] // Journal of Photochemistry and Photobiology A: Chemistry, - 2004. Vol. 167, - p. 177-183.

$$k(t)_{opt} = A - \frac{1}{t}\ln\frac{(t \cdot C_{R_0})}{\lambda_0} \quad (16)$$

Here, A-linearized optimization threshold, λ_0 –the calculated value of the Lagrangian multiplier. So, the problem of optimizing the cleaning of soil contaminated with aromatic hydrocarbons was solved.

The change in the rate of the photocatalysis process depending on the soil moisture was taken as a basis, and the time dependence of the rate of the photocatalysis process, which provides the extreme amount of cleaned soil, was calculated using the known kinetic equation. This chapter also proposed a two-parameter method for determining the toxicity of used engine oils [3]. For this purpose, the dynamics of changes in the peak points of the absorption spectra of used and untreated oils was investigated. It was found that during the use of engine oil, the peak formed as a result of oxidation increases and exceeds the peak formed due to nitration.

Thus, it was proposed to find the extremum of the scalar convolution of two Gaussian functions by approximating the peak impulses with Gaussian curves. The mathematical justification of the method for determining the degree of decomposition of engine oil is given by selecting the point on the x-axis where the scalar convolution reaches the extreme value and the value of the normalized weight coefficient. The block diagram of the algorithm that determines the degree of degradation based on the value of the parameter on the x-axis given by the automatic measuring device by sequentially changing the value of the weight coefficient is shown in Figure 3.

Thus, the possibility of automatically determining the degree of degradation of engine oil by using the extremum property of a linear scalar convolution with specific criteria has been demonstrated.

Chapter III also examines the issue of constructing a two-component optimal desorption model for heterogeneous soil samples. For this purpose, the possibilities of applying stimulating factors in heterogeneous geospace to increase the efficiency of the desorption process were investigated, and for this purpose, the two-component desorption model[5] was used.

$$\frac{S_t}{S_0} = F_{rap} e^{-k_{tap} \cdot t} + F_{slow} e^{-k_{slow} \cdot t} \qquad (17)$$

Here, S_t and S_0 are the amount of polycyclic aromatic hydrocarbons (PAH) in the soil at time *t* and at the beginning of the experiment; F_{rap} and F_{slow} are the rapidly and slowly desorbed PAH fractions; k_{rap} and k_{slow} ($k_{rap} >> k_{slow}$) are the desorption rates of PAH components.

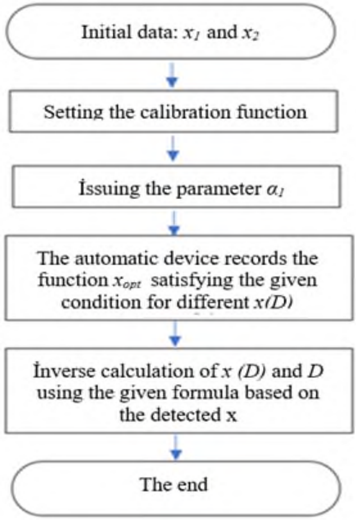

Figure 3. Block diagram of the algorithm for implementing the proposed two-parameter method for automatically determining the degree of engine oil degradation: x_1, x_2 - initial data; $\chi(D) = U_0(D)/U_N(D)$- calibration function; U_0 and U_N- oxidation and nitration amplitudes, respectively; D - degree of oil degradation; α_1 -weighting coefficient of the scalar convolution; $x_{opt} = f\left(\alpha_{1,} D\right)$ - is the optimal value that ensures that the scalar convolution function reaches an extremum.

[5] Bezza, A.F., Chirwa-Nkhalambayausi, M.E. Desorption kinetics of polycyclic aromatic hydrocarbons (PAHs) from contaminated soil and the effect of biosurfactant supplementation on the rapidly desorbing fraction// Biotechnology & Biotechnological Equipment, - 2015. Vol. 29 (4), - p. 680-688.

In order to achieve an increase in desorbed PAH in the remediation of hydrocarbon-contaminated soils, the functional dependencies $k_{rap} = d \cdot k_{slow}$, d = const and $k_{rap} = \varphi(F_{rap})$ are accepted, in the interval $\left(0 \div F_{rap}^{\max}\right)$ the objective functional is constructed as follows:

$$F_0 = \int_0^{F_{rap.\max}} \frac{S_t}{S_a} dF_{rap} = \int_0^{F_{rap.\max}} \left[F_{rap} \left(e^{-\varphi(F_{rap})t} - e^{\frac{-\varphi(F_{rap})t}{d}} \right) + e^{\frac{-\varphi(F_{rap})}{d}t} \right] dF_{rap} \ . \quad (18)$$

For that F_0 could reach an extreme value, the value of the function $k_{rap} = \varphi(F_{rap})$ was calculated as

$$\varphi(F_{rap}) = \frac{\ln\left[\dfrac{1}{1/F_{rap} - 1}\right]}{1 - \dfrac{1}{d}} \quad (19)$$

It was shown that the objective functional (18) reached a maximum when this solution was satisfied.

Thus, an optimal desorption regime was synthesized during sequential processing of soil samples contaminated with hydrocarbons in a heterogeneous space by increasing the proportion of the rapidly desorbed fraction [5].

At the end of the chapter, the issue of constructing a first-order kinetic model of the biodegradation process of petroleum compounds was resolved. In this case, it was required to construct a model such that the kinetic relationship of petroleum components would ensure that the minimum amount of residual undegraded hydrocarbons was achieved.

First, a double averaging method was applied using a simple kinetics model of the first order

$$C = C_0 \cdot e^{-kt_k} \quad (20)$$

In formula (20), C is the current concentration of the degraded substance; C_0 is the initial concentration of the substance; k is a constant characterizing the concentration of the substance; t_k is the degradation time.

Based on this method, a geometric interpretation of the operations of calculating the geometric mean value (A) of $C_i\ (i=\overline{1,n})$ for several hydrocarbon components and selecting a function that inhibits biodegradation and can also be accelerated is given (Fig. 4).

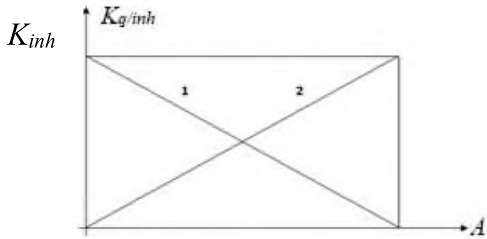

Figure 4. Geometric representation of the relationship between the biodegradation rates of hydrocarbon components of oil: 1- rate of inhibited components; 2- rate of uninhibited components

Thus the limiting conditions $K_1=\varphi_1(A)$ and $K_2=\varphi_2(A)$ are accepted, that is, the degradation rate of the inhibited components is shown to depend on A. So it is defined that $A=C_{01}^{m_1}\cdot C_{02}^{m_2}$, the unconditional variational optimization functional is formulated as

$$F_2=\int_0^{A_{\max}} A\exp\left[-(m_1\phi_1(A)t+m_2\phi_2(A)t)\right]A+\lambda\left[\int_0^{A_{\max}}\left[d_1\varphi_1(A)+d_2\varphi_2(A)\right]dA\right] \quad (21)$$

Here m_1, m_2; d_1, d_2 - experimental weight ratios, λ- Lagrangian multiplier.

Assuming that $\varphi_2(A)$ is known, the optimal relationship between $\varphi_1(A)$ and $\varphi_2(A)$ for F_2 to reach an extreme value is calculated as follows

$$\varphi_1(A)=\frac{\ln\dfrac{A\cdot m_1 t}{\lambda d_1}}{m_1 t}-\frac{m_2\varphi_2(A)}{m_1} \quad (22)$$

Thus, when the solution (22) is satisfied, it is shown that the concentration of the hydrocarbon mixture under study reaches a minimum by calculating the second derivative in expression (21). Thus, based on the fact that the degradation of one component in a hydrocarbon mixture can inhibit the degradation of another component, an optimized mathematical model of the kinetics of the process was constructed, and the condition for the residual concentration to reach a minimum was calculated.

The fourth chapter of the dissertation focuses on the cleaning of water bodies polluted by petroleum hydrocarbons. Here, the kinetic models of photocatalytic cleaning proposed by various authors were investigated, and a three-dimensional geometric representation of the photocatalytic reaction was given on their basis (Fig. 5).

The optimization problem was solved to reduce the dimensions of the photocatalysis process, and integral constraint conditions were formulated for all three cases, taking the reaction rate K, the concentration of pollutants N_0 and the duration of irradiation T as independent variables [13].

A model solution of one of the problems formulated in the sense of finding the rate of the photocatalytic process in water bodies was given by compiling an unconditional variational optimization functional for all three cases.

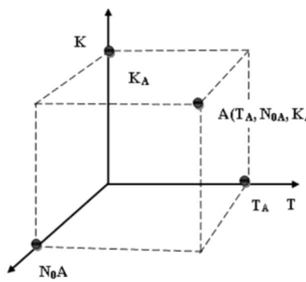

Figure 5. Three-dimensional representation of the photocatalytic reaction: *A* – characteristic point, whose coordinates are T_A (irradiation time); N_{0A} (initial concentration of the pollutant), *K* (reaction rate).

Chapter IV also examines a number of linear and nonlinear kinetic models of photocatalytic degradation of water pollutants, and identifies their advantages and disadvantages depending on the application conditions. Thus, a generalized model of the photocatalytic water purification process is proposed as follows:

$$\ln\frac{N}{N_0} = -k' \cdot f(t) \ . \tag{23}$$

Here N is the number of bacteria in water at time t, N_0 is the initial number of bacteria, k' is an empirical constant, $f(t)$ is a nonlinear function of the irradiation time t. To optimize the photocatalytic group purification of water in a heterogeneous environment, equation (23) is presented as

$$N = N_0 \cdot exp[-k' \cdot f(t)] \tag{24}$$

Thü initial number of bacteria for each of the n ($i = \overline{1, n}$) water areas is determined as

$$N_{0i} = N_{0,i} + \Delta N_0; \qquad \Delta N_0 = \text{const} \tag{25}$$

Taking the N_0 indicator k' as the argument of the constant, equation (24) is found to be continuously obtained after summing over all i values. The solution that ensures that the functional

$$N_{\Sigma} = \frac{1}{N_{0max}} \int_0^{N_{0max}} N_{0i} \cdot exp[-k'\tau(N_{0i})] dN_0 \tag{26}$$

reaches its minimum is determined as follows:.

$$k'(N_0) = \ln\frac{N_0}{N_{0max} \cdot \lambda_0} \tag{27}$$

Here λ_0 is the calculated value of the Lagrangian multiplier. Thus, it was shown that if the condition (27) is satisfied, the total amount of pollution remaining after a certain time t_0 will reach a minimum. Thus, the problem of optimizing the implementation of the photocatalytic process in a group at an arbitrary time t_0, assuming that the pollution level in the areas where water samples are taken is a regular multiple, was solved.

Then, in the same chapter, the evaporation and emulsification processes characterizing the degradation of oil in connection with its spill on the sea surface were investigated as the main factors affecting the viscosity of oil [9].

For this purpose, following formula was used to calculate the density (ρ_e) of the evaporated and emulsified oil.

$$\rho_e = y \cdot \rho_{sw} + \rho_{ref}\left(1 - C_M F_{ev}\right) \tag{28}$$

Here, ρ_{sw} is the density of seawater; ρ_{ref} is the density of the oil before dispersion; C_M is a constant; y is the quantitative indicator of the water fraction in the oil; F_{ev} is the fraction of the evaporated part of the oil given in parts of a unit.

Based on these studies, taking into account that the share of the evaporated part of the oil in the absence of emulsification is sufficiently reduced, the $F_{ev}(t)$ indicator characterizing this process over time t is presented in the following form:

$$F_{ev}(t) = F_{ev}(t)_0\left[1 - k \cdot F_{em}(t)\right] \tag{29}$$

Here, $F_{ev}(t)_0$ is the indicator of the change in the share of the evaporated oil over time t in the absence of emulsification; $F_{ev}(t)$ is the same indicator in the presence of emulsification; k is the proportionality coefficient.

Thus, based on the Mooney equation and expression (29), which characterizes the change in the viscosity η of the degraded oil on the water surface over time t, following relative indicator was introduced:

$$\gamma = ln\frac{\eta(t)}{\eta_0} \tag{30}$$

Here η_0 is the value of the viscosity at the initial moment.

As a result, the relative viscosity

$$\gamma = \left[\frac{C_V \cdot F_{em}}{1 - C_M \cdot F_{em}} + C_E \cdot F_{ev}(1 - kF_{em}(t))\right] \quad (31)$$

was calculated as a function of the fraction of evaporated oil, ensuring that the value reaches its extremum. Using derivative analysis, it was shown that the solution satisfying this condition is given by:

$$F_{\text{em}} = \frac{1}{C_M} - \frac{1}{C_M}\sqrt{\frac{C_V}{C_E \cdot k \cdot F_{\text{ev}}}} \quad (32)$$

At this point, the γ indicator reaches its minimum. Here C_M , C_V, C_E are empirical coefficients.

Thus, the proposed index of relative viscosity γ was calculated by determining the time-dependent change in the viscosity of degraded oil. The calculations showed that if the minimum of γ is detected, evaporation and emulsification processes occur together, and if the minimum is not detected, only evaporation occurs. It was substantiated that the indicator characterizing the dynamics of evaporating oil fractions in the marine environment can serve as an additional informative indicator in assessing the viscosity of degraded oil [8].

At the end of Chapter IV, the issues of transformation of oil spilled into the aquatic environment were investigated, and the development of a simplified model of oil degradation was set as the main goal. For this, it was assumed that the set X of processes characterizing oil degradation consists of interconnected special processes x_i (t); $(i = \overline{1,3})$.

Here x_1 (t) = $F_d(t)$ - fractional volume of oil dissolved in seawater; $x_2(t) = F_e(t)$ - fractional volume of evaporated oil; $x_3(t) = W(t)$ - wind speed.

Thus,it was required to find the optimal relationship between the processes $x_2(t)$ and $x_3(t)$ in order to minimize following integral indicator

$$X_{1int} = \int_{T_0}^{T_f} x_1(t)\,dt \quad (33)$$

Here T_0 - the moment of recording the oil flow, T_f - the moment of evaluation. Based on the increase in toxicity when oil is dissolved in seawater, the amount of dissolved oil is determined by following well-known formula[6]

$$\frac{dF_d}{dt} = K_{diss} A \left(\frac{S}{1000\rho_{oil}}\right) \ ; \quad S = S_0 \cdot exp(-12{,}0 \cdot F_e) \tag{34}$$

Here, K_{diss} is the mass transfer coefficient of the dissolution process (m/s); S is the solubility of oil at time t (g/m^3); S_0 is the initial solubility of oil in water (g/m^3); ρ_{oil} is the initial density of oil (kg/m^3); A is the area of the oil slick (m^2).

Here, taking into account $F_e = F_e(t)$, $\mathrm{A} = \mathrm{A}(t)$, the spread area of the oil slick is determined by calculating the integral from expression (34).

$$F_d = \int_0^{T_f} \frac{K_{diss} A \cdot S_0 \exp(-12{,}0 \cdot F_e)}{1000\rho_{oil}} dt \tag{35}$$

Taking into account the random nature of the change in wind speed over time, the condition $\int_0^{T_f} W(t)\ dt = \mathrm{C}; \ \ \mathrm{C} = const$ was adopted.

Subsequently, the unconditional variational optimization functional is formulated as

$$F_d = \int_0^{T_f} \frac{D\left(F_e(t), \frac{dF_e}{dt}\right)}{2{,}5 \cdot 10^{-3} W(t)^{0{,}78}}\ dt + \lambda \left[\int_0^{T_f} W(t)\ dt - \mathrm{C}\right] \tag{36}$$

and the value of the function $W(t)$ that ensures the minimum of F_d is calculated as follows:

$$W(t) = \frac{D\left(F_e(t), \frac{dF_e}{dt}\right)}{\int_0^{T_f} D\left(F_e(t), \frac{dF_e}{dt}\right) d(t)} . \tag{37}$$

[6] A mathematical model for oil slick transport and mixing in rivers / H.T. Shen, P.D.Yapa, D.S.Wang [et.al.] // Hanover, NH, USA: Cold Regions Research and Engineering Laboratory (CRREL), - 1993, - SR 93-21, - 71 p.

The following notation is adopted here

$$D\left(F_e(t), \frac{dF_e}{dt}\right) = \frac{K_{diss} \cdot S_0 \cdot V_0 \cdot \left(\frac{dF_e}{dt}\right) \cdot \exp(-12{,}6 \cdot F_e(t))}{1000\rho_{oil} \cdot K_{evp}\left[a - \frac{b(T_0 + T_g \cdot F_e)}{T_{oil}}\right]} \quad (38)$$

It is also shown that since the 2nd order derivative of the integral in functional (36) has a positive sign, when the solution of (38) is satisfied, the objective functional (36) reaches a minimum. Thus, a simplified model is proposed that takes into account the influence of factors such as oil solubility in water, fraction evaporation and wind speed on the degradation process of oil spilled on the sea surface, according to which the minimum of the fractional amount of oil means a decrease in water toxicity. At the same time, the optimal interaction between the fractional amount of evaporation and the time dependence of the wind speed, which ensures the minimum of the fractional indicator of oil, has been determined.

CONCLUSIONS

1. A conditional interpolation method was developed to minimize aerosol pollution from a single strong source using the inverse-distance weighting (IDW) method, and the optimization problem was solved by determining the interaction between the size of a drop of artificial rain and the size of the aerosol pollution layer, which ensures the minimum of pollution in the surface atmosphere of industrial enterprises of the same cluster.

2. A method was proposed to compensate for the effect by representing the optical thickness of atmospheric aerosol at any wavelength as a linear sum of $PM_{2.5}$ and PM_{10}. It was demonstrated that the correction coefficients for a three-wave sun photometer can be calculated based on the regression relationship between the output signals of the spectroradiometer and $PM_{2.5}$ and PM_{10}.

3. The problem of minimizing the risk of exposure to PCBs emitted into the atmosphere, taking into account the dependence between the population and the attenuation coefficient of emissions,

was solved. By evaluating the integral quantity of the additional Weibull function, it was shown that the quantity indicator of that product reaches a minimum when there is a linear proportional relationship between the time of start of use of a product containing PCB and the lifetime of a sample of the set of PCB isomers.

4. The issue of selecting land areas for collecting used PCB-containing waste and constructing appropriate treatment facilities was resolved, a method for the decomposition of PCBs in atmospheric air and groundwater was developed. Methods for optimizing the purification of groundwater and atmospheric air, as well as the remediation of soil contaminated with PCBs were proposed.

5. The issue of forming a two-component model that provides the highest desorption index of the soil was resolved, the possibility of changing the rate of the photocatalysis process by varying the moisture content of soil contaminated with a small amount of aromatic hydrocarbons was shown. Based on the known kinetic equation, the optimal form of the time dependence of the rate of the photocatalysis process, which determines the extreme amount of purified soil, was calculated.

6. The operating algorithm of the proposed method for automatic determination of the degree of degradation of engine oil has been developed, the issue of optimizing the degraded oil components has been solved, and a mathematical model of the kinetics of the process has been built.

7. A model for determining the optimal rate of the photocatalysis process in water bodies exposed to various concentrations of pollution and a corresponding implementation algorithm have been developed. A parametric method for optimizing the photocatalytic process in a group in samples of heterogeneously polluted water environments and a model solution for minimizing pollution have been given.

8. A relative logarithmic indicator has been proposed as a new informative sign for assessing the viscosity of degraded oil, and a model of the oil degradation process on the sea surface has been developed. The relationship between wind speed and fractional

evaporation has been determined to achieve a minimum fractional amount of oil.

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Personal contribution of the applicant in joint works with co-performers

[3, 6, 7, 10, 12, 13, 15, 17] – independent work of the author

[1, 2, 4, 5, 8, 9, 11, 14, 16] – formulating the problems, conducting model calculations, calculating experimental data, developing the algorithm for realizing the photocatalysis process, solving variation optimization problems, and interpreting the results obtained belong to the author.

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