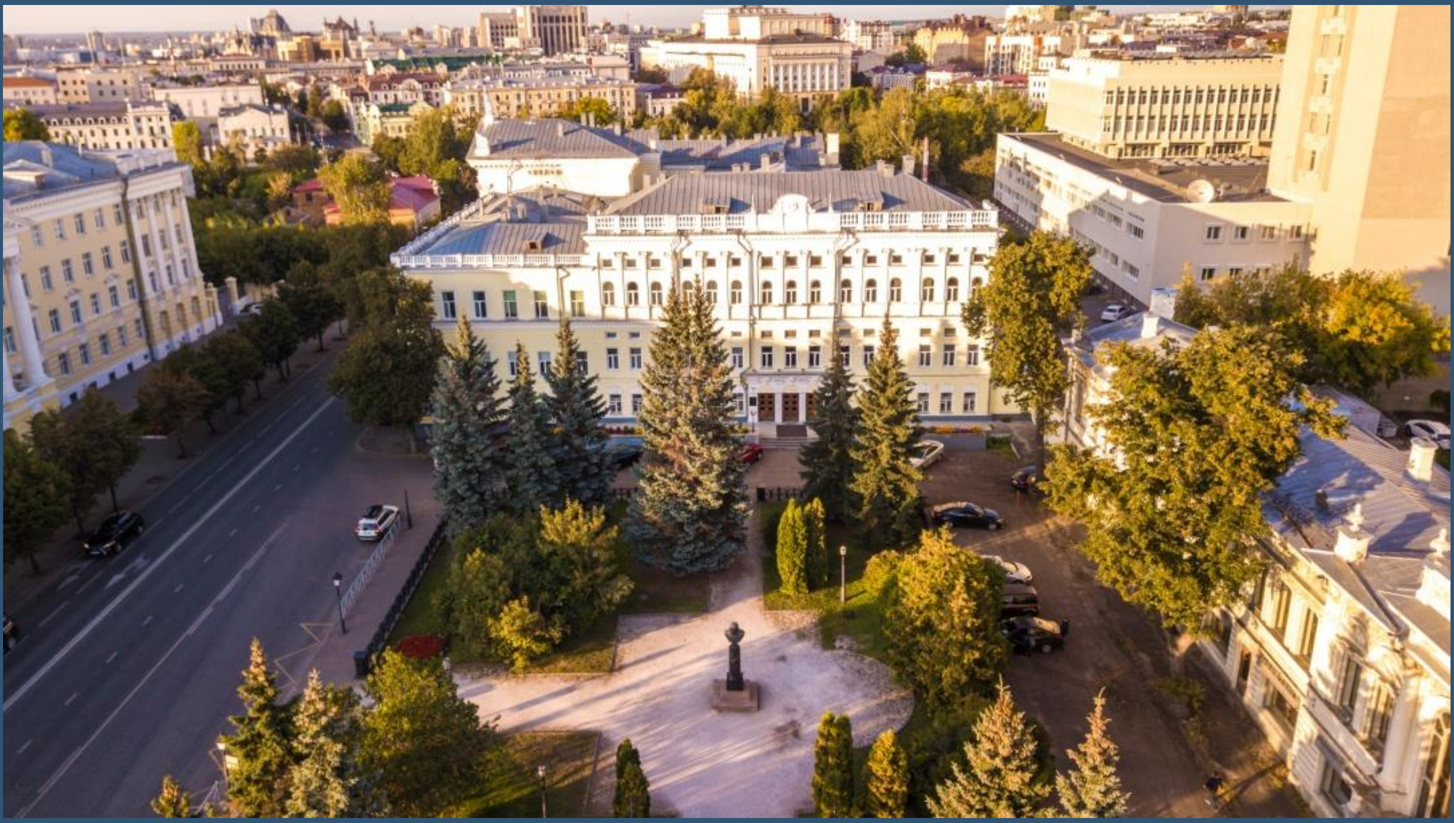
Vth INTERNATIONAL CONFERENCE
“ACTUAL SCIENTIFIC & TECHNICAL ISSUES OF CHEMICAL SAFETY”
ASTICS-2020



BOOK of ABSTRACTS

October 6 - 8 , 2020
Kazan, Russia

Ministry of Science and Higher Education of the Russian Federation;
Ministry of Industry and Trade of the Russian Federation;
N.N. Semenov Federal Research Center for Chemical Physics,
Russian Academy of Sciences;
Federal State Unitary Enterprise “State Research Institute of Organic Chemistry and Technology”;
Federal Research Center “Kazan Scientific Center of the Russian Academy of Sciences”;
A.E. Arbuzov Institute of Organic and Physical Chemistry — Subdivision of FRC Kazan SC of RAS
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Semenov International Center of Chemical Physics

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Book of Conference Abstracts includes Conference Program and summaries of scientific research results and activities in the field of fundamental and interdisciplinary research of chemical safety issues and protection of human health and environment from exposure to hazardous chemical factors.
The topical issues are:

- Chemical hazard sources. Toxic chemicals, including persistent organic pollutants, pesticides, emergency and hazardous chemical substances.
- Methods and tools for indication and identification of hazardous chemicals and mixtures thereof in environmental objects. Monitoring soil, air, and water status.
- Green technologies.
- Hazardous chemical facilities. Technologies for elimination of chemical hazards. Chemical hazard assessment and risk modeling. Chemical accident/incident prevention.
- Technologies, procedures and means for creating materials aimed at technical protection, prevention and remediation of chemical contamination consequences. Impact of hazardous chemicals on human health.
- Waste management. Utilization and biodegradation of hazardous wastes.
- General information on chemical safety.

The book contains abstracts of authors from Azerbaijan, Belarus, Kyrgyzstan, Latvia, Republic of Moldova, Russia, Tajikistan, Uzbekistan, and Ukraine.

For researchers and experts dealing with chemical safety, ecology, and environmental protection.

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Vth International Conference
Actual Scientific & Technical Issues of Chemical Safety (ASTICS-2020)

Notably, 2020 is the year of completion of the activities performed during the course of the federal target program “National System of Chemical and Biological Safety of the Russian Federation” (hereinafter – Program). The Program was carried out in 2 steps with the main activities conducted in the period 2009–2014, followed by the second step during 2015–2020. Ministry of Industry and Trade of the Russian Federation was the customer and coordinator of almost all the activities aimed on ensuring chemical safety. Russian Academy of Sciences and Semenov Federal Research Center for Chemical Physics stood at the origins of the development of the Concept of the Program and took an active part in its formation and implementation.

A good tradition has arisen to discuss the results of the implementation of the Program activities at conferences under the general title “Actual Scientific and Technical Issues of Chemical Safety”. In our opinion, and according to the participants and guests of the previous conferences, the topics of the discussed reports were extremely relevant. Practically all research and engineering problems in the field of creating a national system of chemical safety were considered, and the solutions of certain conceptual issues were proposed including the applied matters. Based on the materials of the conferences, in total 10 special issues were published of the journals: Russian Chemical Journal, Chemical and Biological Safety, Russian Journal of Physical Chemistry B and Chemical Safety Science.

In August 2019, the Government of the Russian Federation approved the Action Plan for the implementation of the Fundamentals of State Policy of the Russian Federation in the field of chemical and biological safety for the period up to 2025 and beyond. The plan entails the development and approval of the State Program “Ensuring Chemical and Biological Safety of the Russian Federation” in 2020.

The main task of the State Program is to stabilize the state of chemical and biological safety, to ensure an acceptable level of chemical and biological risk. The main elements of the state program will be grouped in priority areas of state policy in the related area and divided into the appropriate subprograms:

- monitoring of chemical and biological risks;
- development of public administration and resource provision of the national system of chemical and biological safety;
- neutralization of chemical and biological threats, prevention and minimization of risks.

These areas should become the basis for the related activities of all research and field-specific organizations in the near future.

As always, following the results of our conference, at the end of the year we will prepare a special issue of Chemical Safety Journal.

Dear colleagues, we wish you every success at the conference and in your daily scientific research!

Organizing Committee

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ABSTRACTS

Advanced technologies for ensuring chemical safety (following the results of federal target program “National System of Chemical and Biological Safety of the Russian Federation”)

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Nowadays, ensuring chemical safety has gained much attention all over the world. One of the priority areas of the state activity of the Russian Federation is to reduce the risk of negative impact of hazardous chemical factors on the population health and the environment to an acceptable level.

It was a decade ago, when a special program was launched to fulfill this goal – the federal target program “National System of Chemical and Biological Safety of the Russian Federation” (hereinafter – Program). At the first stage of the Program action (2009 – 2014), the foundations of the national system of chemical and biological safety were laid. Significant measures were taken to consistently reduce the risk of exposure to hazardous chemical and biological factors to an acceptable level. This work was continued from 2015 to 2020 and is being continued presently. Ministry of Industry and Trade of the Russian Federation was one of the main customers and coordinators of the Program activities. This report summarizes the principal results of the Program with the focus at the advanced technologies developed to provide solutions of the major chemical safety issues.

One of the most important outcomes of the implementation of more than 50 Program activities is the development of new technical and technological solutions in various areas of human and environmental interaction with hazardous chemical factors. Many of these solutions have been brought up to pilot plant level and are ready for implementation.

The most significant technological solutions are considered here. These technologies can be divided in three groups according to their targeting on solving the problems of the Program:

- technologies in the field of creating systems for analyzing the state of the environment;
- technologies in the field of creating new means for protecting humans and environment from hazardous chemicals;
- technologies for disposal and treatment of waste and recovery of the released territories.

The most effective technology of the first group is R&D project “Chemical Surveillance” which resulted in the creation of a single complex of chemical indication and monitoring of parameters of atmospheric air, water and soil. The developed complex can be used for creating a single branched unified network for persistent monitoring chemically hazardous objects.

The most promising results of the second group of the protective equipment technologies are focused on the development of personal protective equipment for the respiratory organs and skin, and efficient means for purifying drinking water from various toxicants and microorganisms.

The basis of technologies for the creation of protective equipment is research and development in the field of obtaining new materials and substances, the use of which can substantially improve the protective, ergonomic and operational characteristics that would provide adequate counteraction to modern and predictable chemical threats and meet the operational requirements of domestic and foreign standards. The laboratory protocols for obtaining highly efficient substances used for purification and disinfection of drinking water are described.

The relevant projects involved in the third group of technologies for waste treatment and land remediation are aimed at:

- ensuring the elimination of various chemically hazardous wastes, including those located on the territory of waste storage areas, dumps and burials;
- sanitation and rehabilitation of chemically and biologically contaminated objects and territories;
- destruction (utilization) of stocks of polychlorinated biphenyls and obsolete pesticides abandoned in industry or agricultural sector.

The effective destruction of hazardous waste of various classes can be carried out by using plasma-assisted technology, supercritical water oxidation technology or high-temperature pyrolysis in reductive conditions without combustion processes. The remediation (sanitation) of lands contaminated with various ecotoxicants can be successfully performed applying sorption/biological treatment procedure. The technology based on the enzyme-cavitation method has shown high efficiency in the disinfection of toxic wastewater sludge in the territory of large industrial facilities.

The technologies have been implemented in the form of experimental or pilot industrial installations, and their performance has been tested on real objects or prototypes. The scientific novelty, practical significance and level of implementation of the most promising technologies are highlighted.

Genotoxic and genoprotective effects of natural and synthetic compounds

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The presentation will summarize literature data on DNA binding, DNA protecting and DNA damaging activities for a range of natural compounds and some synthetic compounds being both exogenous and endogenous for humans. Small organic natural molecules bind DNA in a site-specific mode, by arranging tight touch with the structure of the major and minor grooves, as well as with individual bases in the local duplex DNA. Among exogenous compounds polyphenols are the best studied from this point of view, many of them demonstrate hormetic effects, meaning that these can produce both beneficial and damaging effects. An attempt to establish dependence of DNA-damaging or DNA-protecting on the concentration of the investigated compounds turned out to be successful for some polyphenols: daidzein, genistein and resveratrol which were DNA-protecting in low concentrations and DNA-damaging in higher concentrations, however there was no evident dependence on concentration for quercetin and kaempferol. Probably, DNA-protecting effect is associated with the affinity to DNA. Caffeine and theophylline are DNA-binders; in the same time, they favour DNA repair. Although most alkaloids damage DNA, berberine can protect DNA against damage. Among endogenous compounds, hormones belonging to amine class, thyroid and steroid hormones appear to bind DNA and produce some DNA damage. Thus, natural compounds continue to reveal beneficial or adverse effects on genome integrity and to ensure a promising source of therapeutic activities [1].

We have performed a series of studies on DNA binding capabilities of novel 1,4-dihydropyridine (1,4-DHP) derivatives. The investigation series was triggered by finding of a DNA-binding capacity for a water-soluble 1,4-DHP derivative AV-153 sodium salt (AV-153-Na), which was known as a compound with antimutagenic activity [2]. The docking analysis predicted its intercalation in the DNA molecule in a place of a single-strand break, the model was proven experimentally: the compound triggered extrusion of the ethidium bromide out of the complex with DNA, induction of the DNA breaks increased affinity to DNA [2]. Later it was shown that the compound protects DNA against damage by peroxinitrite and increases activity of the DNA excision repair enzymes [3]. Strikingly, both DNA-binding capacity and ability to protect DNA was dependent on metal ions forming salts with the AV-153 residue [4]. Further it was shown that a series of water-soluble monocyclic derivatives of 1,4-dihydropyridine with carboxylate groups in position 4 manifested different affinity to DNA determined mainly by substituents in positions 3 and 5 [5]. An ability to interact with DNA does not correlate with other effects produced by the compounds: radical scavenging or peroxynitrite binding [5].

Lipid soluble 1,4-DHP derivative with promising antidiabetic and neuroprotective activities, but with very weak Ca-channel blocker activities – cerebrocrast and its analogue etaftorone are considered to act mainly on mitochondria. We have observed the ability of these compounds to protect the cells against DNA damage produced by peroxynitrite and to bind DNA. Interestingly a “classical” DHP Ca channel blocker nitrendipine also could reduce the level of DNA damage induced by peroxynitrite, but to lower extent compared to cerebrocrast and etaftorone [6]. It seems that DNA binding capacity is an important feature of the 1,4-DHP derivatives, depending on their structure. Interestingly, representatives of this group can also bind unusual DNA structure – the G-quadruplexes, this was shown by us for the AV-153 salts and others for a series of novel derivatives.

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Dioxins and human health: competences for ecological safety management

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Sources of emissions and discharges of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are encountered in numerous places on the territory of Russian large and small cities where the majority of the population lives. The necessity to monitor and minimize the impact of these emissions on human health is evidenced by the toxic levels of these substances in human breast milk [1]. Experts consider landfills with municipal/industrial wastes as the most threatening sources of PCDD/Fs [2]. The problem of toxicometry* of PCDD/Fs low doses contaminating the environment in the vicinity of landfills and other sources has not yet been resolved and is under development for minimization (reduction) of the health hazard of PCDD/Fs.

Scientific and methodological foundations of activities on the risk minimization. The following requirements were accepted for a new approach to evaluate the environment contamination by PCDD/Fs discharged by the landfills and waste incineration plants: a) the harmful effects of environmental PCDD/Fs mixtures are determined by the toxicity of congeners absorbed by the organism, their doses (concentration) and exposure conditions; b) the key points in the chain of chemicals' transfer from the environmental matrices to the organism are the content of contaminated biotic products included in the diet; c) environment is obviously an active element responsible for the behavior of toxicants in natural systems, as well as their interactions within biotic components, and the extent of damage to living organisms and the population overall; d) The use of PCDD/Fs maximum permissible concentrations is limited by their extreme conditionality and sanitary safety regulations [3, 4].

The appropriate experimental design involves all these requirements and reflects an organism's interactions with PCDD/Fs by studying toxic effects in association with the characteristics of the environmental fate of these substances and the exposure conditions. The most objective assessment of such interactions is provided by the epidemiological methods. Their use in the risk management is limited by the high probability of individual toxic effects. Screening of PCDD/Fs' concentrations in wild animal tissues allows to control general (for humans and animals) patterns of these substances' accumulation in the real exposure conditions [5–7]. Small mammals follow this pattern and can be used as an available model for biomonitoring the ecotoxicological situation and consequences of exposure.

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*Toxicometry – system (summary) of principles, methods and techniques for chemical substances' toxicity and hazard evaluation [*Kasparov A.A., Sanotsky I.V.* (Eds.). Moscow, 1986. 428 p.]

Key results of current research. The adequacy of the considered foundations to solve the problem of environment contamination with PCDD/Fs discharged from the landfills was verified empirically on animals from local natural populations. Samples were collected in different residential areas: in two Moscow City districts in the vicinity of the landfill with municipal and industrial wastes Salaryevo (settlements Kartmazovo and Moskovsky), and compared with those previously obtained in Vietnam (from the ecocide region damaged during the US Army chemical aggression (operation Ranch Hand, 1962–1971).

Chemical analysis of soil and bottom sediments samples taken at a distance of ≈1 km (Kartmazovo) and ≈5 km (Moskovsky) from the landfill body showed good comparability of the WHO-TEQ$_{05}$ levels with octa-substituted and low toxic PCDD/Fs congeners domination in the examined samples. PCDD/Fs congeners' profiles and concentrations in bottom sediments and soil samples collected in 2016 and 2017 were comparable, thus, confirming persistence of contamination.

PCDD/Fs levels and profiles in the tissues were measured for several groups of animals living in the contaminated areas around the landfill: small mammals (Ural field mice *Sylvaemus uralensis*, bank voles *Clethrionomys glareolus*, common shrews *Sorex araneus*), fish (silver carps *Carassius auratus gibelio*) and bush snails (*Fruticicola fruticum*). The general pattern of PCDD/Fs congeners' bioaccumulation was revealed - the highly toxic congeners and primarily TCDD dominated in the animal tissues. The patterns of PCDD/Fs accumulation in mammals naturally exposed to landfill emissions were studied on the bank voles. Evidences has been found that PCDD/Fs accumulated in the tissues of female mammals are transferred to offspring by transplacental and lactation pathways - with the effect of TCDD and other highly toxic congeners accumulation in the tissues of litters. The same effects had been registered in Vietnam among population of the ecocide region in Vietnam. The biological effect of accumulated PCDD/Fs was revealed by the modifications registered on genomic and epigenomic levels. Assessment of hazard of PCDD/Fs currently accumulated in tissues suggests the probable toxicity for humans. The outcomes of toxic effects were manifested by the long-term medical consequences and dioxin pathology. The characteristics of toxic effects' manifestations are specified and discussed. Special attention is paid to the problems of risk to children's health. The prospects are considered of using methods of exposure biomonitoring, i.e. minimize probable health hazard in the presence of small doses of PCDD/Fs contaminating the environment.

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Possibility of microbial degradation of obsolete pesticides in soils around burial sites in Southern Kyrgyzstan

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Pesticides are widely used in agricultural production to prevent or reduce the losses caused by pests. At present, ~2.5 million tons of pesticides are used annually and the total number of registered active substances is higher than 500 [1, 2]. Currently, in the territory of Kyrgyzstan, 50 storage facilities of obsolete pesticides still exist which store about 5000 tons of these hazardous chemical, including persistent organic pollutants (POPs) [3].

Almost 50 years have passed, and the storage conditions in many dumping zones have become unsuitable for long-term storage, so, the integrity of the dam was destroyed, and the population began to dig up the dams for reuse. Consequently, these territories pose a serious threat to the people living there, to livestock, and to the environment [4]. Microorganisms are a vital tool for bioremediation of pesticides. The microbial degradation of xenobiotics, a process known as bioremediation, is a cost-effective method of removing pollutants from the environment [5].

The main purpose of this research was to study the microbial structural complexes of pesticide-contaminated soils in dumping zones, and to search for and select microorganism-destructors with cytochrome P450 genes for pesticide degradation. The selected bacteria for the bioremediation of heavily polluted soils around the burials sites were used in model soil experiments.

Environmental soil samples were collected from sites located around three dumping plots (Suzak A, Suzak B, and Balykchy) that had been long exposed to pesticide contamination. Soil samples taken from the contaminated sites were analyzed for pesticide concentration by capillary gas chromatography (GC) coupled to a mass spectrometer (MS; either single-quad MS or triple-quad MS-MS). Bacteria isolated from contaminated soils were grouped on the basis of their morphological, biochemical, and physiological characteristics. DNA was extracted from the enrichment cultures during the active phase of microbial growth, using the UltraClean™ Soil DNA Isolation Kit (Mo Bio Laboratories, Carlsbad, CA) and an alternative protocol developed by the Mo Bio Laboratories. ***In vitro* biodegradation experiments** were conducted to select active bacteria. In mineral medium, microbial cultures were incubated with various concentrations (0.2, 0.5, and 1.0 mg) of the pesticide Aldrin. The bacterium *Bacillus polymyxa* was found to exhibit the highest ability to degrade Aldrin in single cultures. This bacterium used 0.2 mg of Aldrin in its metabolism and reduced its content to 48.2% after 12 days of incubation. *Pseudomonas fluorescens* has also shown a good degradation capability. This bacterium degraded 43.2% of 0.2 mg Aldrin.

In situ biodegradation experiments Four variants of experiments were conducted according to the soil properties of the contaminated sites. In the first, uncontaminated soil was used without any changes in chemical contents and characteristics with the following local parameters: pH of 8.2–8.5, temperature of 22–25°C, moisture of 40–45%, the soil type was light sierozem with low organic matter content. In the second variant, to activate the soil microflora, 300 g of black soil and rotted manure in the ratio of 1 : 5 were added to 1000 g of the polluted soil. Bioremediation conditions, such as moisture (60–75%), temperature (26–27°C), dissolved oxygen, and pH (7.4–7.62) were monitored and maintained in the surface soil treatment unit. The soils in both variants were treated three times (i.e., once a month) with suspensions of a single culture or a blend of active bacteria ($1 \cdot 10^8$ cells/ml) selected in *in vitro* biodegradation experiments. Two control units without the addition of the bacteria culture were also run: soil alone with no treatment; soil alone + improved conditions for optimization. The quantification of the targeted POPs before and after biodegradation was performed by capillary gas chromatography coupled to a mass spectrometer. The obsolete pesticides such as Dieldrin, Alpha-endosulfan, Beta-endosulfan, 4-Heptachlor-epox pure were able to degrade in 6 months almost completely, up to 98–99.0 by bacterial association and single bacteria. Endrin aldehyde showed more resistance, since the associations of bacteria were able to degrade it to 59.77% in improved soil conditions.

In conclusion, in this study, the bioremediation of high concentrations of obsolete pesticides in the soils around the Suzak A and Suzak B burial zones was achieved by a microbial consortium (*Micrococcus flavus, Bacillus polymyxa, Pseudomonas fluorescens* and *Flavobacterium* sp.) and a single culture of *Pseudomonas fluorescens*. Recommenations for elimination the obsolete pesticides from the soil will include the implementation of agrotechnical and agrochemical adjustments to improve aeration, the balance of chemical elements, and pH of the ground before the addition of ready-made suspensions of active degrading bacteria. The addition of the ready-made suspension of active bacteria once a month with regular aeration would be desirable during 5–6 month-period at the optimum ambient temperature (27–28°C) and pH (7.2–7.6) to ensure the complete elimination of pesticides from the soil.

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Destruction of toxic organic and chloroorganic compounds on TiO_2-based photocatalysts

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Photodestruction of toxic chloroorganic compounds and other toxic chemicals on TiO_2 photocatalysts including those doped with metal ions or non-metal atoms is of great fundamental interest and has high potential for practical applications in the field of ensuring chemical safety, water purification, environmental protection, etc. [1, 2]. The scheme below represents an example of such process for photocatalytic mineralization of *ortho*-chlorophenol on the TiO_2 surface under UV-light irradiation:

$$o\text{-}ClC_6H_4OH + OH^{\bullet} \rightarrow \ldots \rightarrow \rightarrow HCl + CO_2 + H_2O$$

The main goal of this research is studying the structure, properties and applications of TiO_2-based nanosized and thin-film photocatalysts.

The photocatalytic activity of TiO_2 nanoparticles of different size has been studied in parallel with photodegradation of dichloroacetic acid (DCA), coupled with measuring the initial rate of the H^+ and Cl^- ions formation [2]. The catalyst efficiency was found to correlate with the specific surface area of the particles. The efficiency of the TiO_2 photocatalyst can be increased by doping the particles with copper ions. The influence of the pH value of the solutions and the content of adsorbed copper ion on the efficiency of the DCA photodestruction is discussed.

The processes of photocatalytic and photoelectrochemical conversion of aromatic and aliphatic chloroorganic compounds are accompanied by alterations in the mechanism of photosensitized transformations. It was shown that the process of photo- and electropolymerization occurring during photodestruction resulted in modifications of the semiconductor surface. Structural characteristics measured from EPR spectra for all paramagnetic centers were calculated according to the recommended procedures [3].

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Determination of toxic compounds and elements in human biological media for building evidential base of chemical hazards sources

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National Security Strategy of the Russian Federation considers chemical safety to be one of the priorities of the country's sustainable development. The relevance of this strategic area responds to the increasing negative impact of chemicals on public health and the environment.

The issues of management and control of potentially hazardous chemicals in environmental objects and human biological media can be attributed to major challenges in chemical safety ensuring field. There are hundreds of different chemical compounds in the environment which are characterized by high toxicity, the ability of accumulation in food chains and stability in the environment.

In this regard, health risk assessment is of priority concern of modern environmental investigations which puts forward a new task for the development of high performance analytical procedures. Medical and biological investigations belong to one of the promising areas of chemical and analytical research, including both qualitative and quantitative determination of chemicals in the human body which characterize its exposure to environmental factors.

The determination of chemical compounds and elements in human biological media using identification with structure assignment and confirmation of the mass spectra of the analytes along with their quantitative determination in biological media, is one of the most reliable methods that could be used for creating an evidential database of negative impact of anthropogenic environmental factors on human health and would provide assessment of the sufficiency of environmental measures for elimination of sources of chemical hazard.

For years, the research activities focused at chemical and analytical support of medical and biological investigations have been performed by laboratories of the Chemical and Analytical Department of the FBIS ‘Federal Scientific Center for Medical and Preventive Health Risk Management Technologies’.

The studies are carried out with the use of high performance equipment of gas and/or liquid chromatography and chromatography-mass spectrometry with selective and highly sensitive detectors; capillary columns; new methods of sample preparation and quantitative extraction of analyte from a multicomponent biological matrices using solid-phase extraction, derivatization of target components, equilibrium analysis of the vapour phase, etc.

Inductively coupled plasma mass spectrometry (ISP/MS) method was used to determine a wide range of elements and to provide high accuracy, selectivity and the required sensitivity, reliability and validity of the measurements.

Currently, the researchers of the Center have developed 40 methodological instructive regulations for determining 62 chemical compounds and elements in biological media (blood, urine). The regulations have been approved by the Head of Federal Service for Surveillance on Customer Rights Protection and Human Wellbeing and the Chief State Physician of the Russian Federation. Of these, 17 methods are listed in Federal Information Fund for Ensuring the Uniformity of Measurements (Rosstandart).

The developed methods for analysis of toxic elements and persistent organic compounds are used for assessing health risks when exposed to hazardous environmental chemical factors and evaluating the impact of chemical hazard sources in the territories of the West Urals, Eastern Siberia, Krasnoyarsk, etc.

Neutron activation analysis as a tool for tracing heavy metal content in samples of different types

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Neutron activation analysis due to its high accuracy, nondestructive nature and possibility to determine concentrations of more than 40 elements is widely used in the environmental studies, archeology and medicine. The principle of the method will be discussed. Types of neutron activation analysis will be briefly characterized in order to depict the most important information. Examples of application of neutron activation analysis at the IBR-2 reactor (Dubna, Russia) will be presented.

The main direction of neutron activation analysis application in Dubna is the assessment of heavy metal atmospheric deposition using moss biomonitoring technique. The first moss survey at the European scale was conducted in 1990 and has been repeated every five years since then. The coordination of the moss survey was passed on in 2014 to the Joint Institute for Nuclear Research in Dubna, with reporting continuing as part of the ICP Vegetation Programme. The examples application of moss biomonitoring technique in Russia and other JINR member states will be presented [1].

Neutron activation analysis at the IBR-2 reactor is widely applied for the assessment of efficiency of metal removal from industrial wastewater using different type of biological sorbents. Examples of application of biological as well as combined sorbent for metal removal from single and multi-component solutions will be given [2, 3].

The use of herbal medicinal products and supplements has increased tremendously over the past decades with about 80% of the world population relying on them for some part of primary healthcare. Safety continues to be a major issue with the use of medicinal plants. The elemental composition of 45 species of medicinal plants of *Lamiaceae* family was determined by neutron activation analysis and will be discussed in details [4].

Nanotoxicology is a new direction of neutron activation analysis application. The silver and titanium accumulation in different tissues of female mice and their offspring after prolonged oral administration of silver nanoparticles and titanium dioxide nanoparticles to the females during pregnancy and lactation was investigated. Obtained results showed accumulation of nanoparticles in all analyzed tissues of females and offspring as well. The obtained results are important for studies on developmental and reproductive toxicity of nanomaterials [5].

The information is addressed to researchers interested in the applications of neutron activation analysis or to those who are searching for an analytical technique suitable for environmental, biomedical and archeological studies.

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Nanopesticides - a new generation of plant protection products with increased safety and effectiveness

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Nowadays, a significant progress was achieved in medicine due to applying the supramolecular chemistry methods to design nanosized drug delivery systems. It allowed enhance the bioavailability and safety of various drugs [1]. This approach is based on using water soluble carriers (nanoparticles, liposomes, polymers, micelles, etc.) to increase the solubility of poorly soluble drug molecules and their permeation ability. The application of nanotechnology in agricultural sector is relatively new approach being at an early stage of development in Russia. Several critical reviews described the potential of nanotechnology in agriculture, in particular, for pesticide delivery [2].

During the last decade, nanotechnologies opened a new era in delivery of plant protection products through developing the nanosized controlled release systems, such as polymer nanoparticles, micelles, etc., using a wide variety of materials. For example, the use of amphiphilic water soluble polymers and micelles as nano-containers for pesticides delivery allowed encapsulation of hydrophobic molecules inside the hydrophobic matrix surrounded by a hydrophilic shell. This pathway has improved pesticide solubility in water which is an important requirement for pesticide dispersion. In addition, inclusion complexes of the ‘host-guest’ type provide protection of unstable organic molecules against harsh environment (UV irradiation, reactive oxygen species, and high temperature), improving chemical stability of ‘guest’ molecules which leads to prolongation of their activity [1]. ‘Nanoencapsulation’ approach also provides achieving a high surface to volume ratio in dispersions, thereby decreasing significantly the total amount of requested pesticide.

Due to the nanocarrier envelope, various delivery systems for active ingredients of pesticides can improve the utilization rates of pesticides and prolong their effects. Recent results demonstrated that nanosized delivery systems can significantly improve the controllable release, photostability, and biological activity which improves efficiency and reduces pesticide residues [3]. All these factors result in less negative environmental impact.

To develop innovative plant protection products, the ‘green’ mechanochemical technology for their synthesis has been applied [4]. The plant protection products with improved environmental properties were obtained using the polysaccharide arabinogalactan, glycyrrhizic acid and its disodium salt, as compounds that formed nanosized supramolecular systems composed of pesticide molecules. The high efficiency of the resulting compounds in regard to pathogenic microflora in treatment of spring wheat and barley seeds and in suppression of root rot development were demonstrated under laboratory and field conditions, along with the lack of the retardant effect and a positive impact on the productivity of these crops [4].

The formation of stable associates of pesticides with delivery systems in aqueous solution has been proved by various physical methods. We have found a noticeable increase in the penetration of pesticides into grains in the presence of all delivery vehicles with the greatest effect observed in the presence of arabinogalactan. Our data indicate that the effect of polysaccharides and oligosaccharides on the penetration efficacy of nanopesticides under the presowing seed treatment can be associated with the detected solubility enhancement, affinity of delivery systems for grains’ surface, as well as due to modification of cell membranes with poly- and oligosaccharides [5, 6].

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Monitoring of thiolic substances in the Dniester river water during the period of 2015-2019

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The river basin of the Dniester river occupies 57% of the territory of the Republic of Moldova. The Dniester river is the main source of surface water for the country. The largest consumers of water are the cities of Balti, Orhei, Dubasari, Chisinau, Tiraspol, among others [1–3]. The Dniester river provides 54% of the water needed for the country's economy, at the same time it represents a complex aquatic biotope [2, 3]. Therefore, monitoring of the chemical composition of this water is strictly necessary.

The normal state of natural waters is the oxidizing one, characterized by the dominance of typical natural oxidants: dissolved oxygen and hydrogen peroxide. The presence of increased amounts of reducing substances, such as thiols (R-SH), can disrupt the redox state of these waters. The main sources of thiols in natural waters can be divided into two groups: natives - thiols eliminated into water as a result of the metabolic processes of the hydrobionts and allochthonyls resulting from the industrial activity [2].

The content of thiol compounds in the water of the Dniester river was monitored near Vadul lui Voda city during the period of 2015–2019. The water samples were collected seasonally, with the frequency of 5–7 times per year, according to the known methodology.

Thiol concentration was quantified using the Ellman method. Taking into account that natural waters usually contain a lot of compounds that can interfere with the optical determination of thiol concentration, the water samples were preliminarily passed through the 0.45 μm pore size filter to remove humic acids [4].

The multiannual average content of thiols was found to be $6.15 \cdot 10^{-6}$ M. The maximum concentration of thiol-based compounds was revealed in the samples collected in summer ($7.41 \cdot 10^{-6}$ M), compared with the autumn ($3.92 \cdot 10^{-6}$ M) and the spring samples ($3.87 \cdot 10^{-6}$ M). The results obtained indicate the natural origin of thiols in the Dniester water (Table).

Table. Multiannual average levels of the ecochemical parameters monitored during 2015-2019

Monitored parameter	Multiannual average level		
	Spring	Summer	Autumn
$[R\text{-}SH] \cdot 10^6$, M	3.87	7.41	3.92
Eh, V	0.2908	0.2917	0.3185
rH	26.99	26.44	27.86

To determine the impact of thiols in the redox state of the Dniester water, Pearson linear correlations between thiol content and ecochemical parameters (oxidation-reduction potential (Eh) and the related rH parameter) were calculated. The values obtained indicate a weak-moderate inverse correlation ($r = -0.46$) in the case of Eh and a strong inverse correlation ($r = -0.79$) in the case of rH.

Therefore, the content of thiol compounds determined in the water of the Lower Dniester, near Vadul lui Voda city, varies within the range of concentrations of the order of 10^{-6} M. The detected fluctuations of concentrations are due to seasonal variations, indicating the predominantly natural origin of thiols. The inverse correlations between the thiol content and the parameters characterizing the redox state indicate that thiol compounds can participate in redox processes as carriers of the reducing equivalents, consuming natural oxidants, especially hydrogen peroxide.

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State of chemical pollution of main tributaries and snow-ice resources of the transboundary Amu Darya river

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One of the vital goals of the Millennium is to provide the population with clean and safe drinking water. Most rivers of the Central Asian region are transboundary and, along with their use for irrigation of agricultural lands in the lower reaches, are also a source of drinking water for the local population.

Consequently, systematic monitoring of the state of water, changes in the chemical composition and timely detection of toxic chemical elements of the water arteries in the region is an urgent task. The results are presented of long-term research on the chemical and isotopic composition of water objects in the formation zone of the Vakhsh and Pyanj rivers and snow and ice resources of river basins.

The objects of research were the Vakhsh River and its main tributaries Surkhob and Obikhingou, the Pyanj River and its tributaries Gunt and Vanch.

Methodology. For chemical and isotope analyzes, water samples were collected from the upstream to downstream of river at the distance of every 800–1000 m. Chemical analysis of the samples after conservation was carried out on a Ta-Lab spectrophotometer with a sensitivity level of 10^{-5}. Wavelength Scanned Ringdown Spectroscopy was used for isotopic analysis of water, snow and ice.

Results and discussion. Summarizing the results of the analysis, it was found that in the zone of formation of the Vakhsh and Pyanj rivers and their tributaries, no anthropogenic influences was revealed, and only in the downstream due to the flow of waste water a change in the chemical and isotopic composition of the rivers was observed.

The determined chemical composition of the snow cover on glaciers which is characterized by the presence of Ca^{+2}, Mg^{+2}, Na^{+}, and K^{+} cations and SO_4^{2-} Cl^{-}, PO_4^{3-}, NO_3^{-} anions along with a number of other cations and anions is apparently caused by the deposition of pollutants carried by air masses from the atmosphere.

Downstream, the isotopic composition of river water changes, i.e. the isotopic composition becomes heavier due to the volatilization of the light fraction and due to an increase in temperature in the lower reaches of the river.

Current state of the problem of ensuring chemical safety of low-tonnage chemistry industrial facilities

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The chemical complex is an important branch of Russian industry since its successful functioning lays the foundations for the long-term and stable development of the country, as well as it has a significant impact on structural changes in the economy. In accordance with the order of the Government of the Russian Federation dated December 15, 2017 No. 2834-r, an action plan (“road map”) for the development of the production of low-tonnage chemistry in the Russian Federation for the period until 2030 was approved. The Road Map is a set of measures to improve the mechanism of state regulation of low-tonnage chemistry production development in Russia. The list of product segments consisting of 27 main product segments has been determined, which is taken as the basis for priorities in the development of the roadmap and which includes, among others, the following products: high-tech polymers, plastics and rubbers for special purposes, inhibitors, initiators, adhesives, sealants, chemical reagents and solvents.

In this regard, the development and creation of modern chemical technological processes for the production of low-tonnage chemistry products is an urgent practical task.

The range of low-tonnage chemistry is constantly being updated, and competition in the market of low-tonnage chemistry products is growing up. Low-tonnage chemical industries include those producing from 0.1 to 10 tons of products per year [1].

Ensuring industrial safety of such industries has a number of specific features. At the design stage of the low-tonnage chemistry production, the following principles of inherent safety are used [2]: minimization - reduction of the amount of substances used and energy used; substitution - replacement of used substances with less hazardous ones; mitigation - using hazardous substances and materials in a less dangerous condition or production with a reduced impact of harmful substances emissions or energy (the principle of attenuation or limitation of effects); simplification - design of industrial facilities with the lowest level of complexity, which are less sensitive to failures of equipment, control or personnel (the principle of error tolerance). Stringent requirements are applied to autonomy, versatility, interchangeability, and the regulation of the range of chemical processes parameters and other characteristics of the equipment. The materials for the manufacturing equipment should be chemically and thermally stable. The control of the block-modular scheme of low-tonnage production plays a valuable role. Operational switching of production flows, rational loading of modules and other technological problems can be resolved only by qualified personnel operating at all hierarchical levels.

Low-tonnage chemical products are an indispensable condition for the sustainable development of civilization. Flexible manufacturing of such products is constantly evolving, combining the latest achievements of fundamental science, advanced technologies and contemporary management theory.

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Features for determination biomarkers expositions of industrial ecotoxicants in conditions of chemical safety ensuring

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A significant part of the able-bodied population in Eastern Siberia (more than 30%) works in harmful conditions and is exposed to adverse environmental factors. At present, chemical safety is one of the urgent problems of preventive medicine.

The modern production of vinyl chloride and polyvinyl chloride is most commonly characterized by an unfavourable sanitary and hygienic situation, in which the working personnel is exposed to a prolonged action of relatively low concentrations of hazardous toxicants – vinyl chloride (VC) and 1,2-dichloroethane (DCE) at the level ranging from 1.2 to 5.5-fold of concentration limit (Maximum Permissible Concentration, MPC) [1]. Taking into account the conditions of exposure to organochlorine hydrocarbons, the development of effective methods for determination of the metabolites of these toxicants in human biological environment is an urgent task aiming at determining the exposure value and assessing health risks. It should be noted that this production belongs to the category of carcinogenic hazardous production facilities which causes not only an occupational risk of exposure, but also a carcinogenic risk with the increasing annual amount of the cases of exposure.

To assess the harmful effects on the staff, there is an urgent need to search for a biomarker of this kind of exposure. A number of chemical substances and/or their metabolites can be used as biomarkers in biological matrices (blood, urine), such as 2-chloroethanol, monochloracetic acid (MCAA), thiodiacetic acid (TDAA).

The aim of the study was to develop procedures for the determination of VC, DCE and their metabolites in human biological matrixes and to evaluate their content in samples of the personnel of facilities producing vinyl chloride and polyvinyl chloride [2]. Modern methods for quantitative determination of organic compounds and their metabolites in biological matrices include gas chromatography (GC) and chromatography-mass spectrometry (GC-MS). To achieve this goal, we have carried out the development of an appropriate methodological support, namely, methods for the determination of VC and DCE in the blood by gas chromatographic head-space analysis; 2-chloroethanol in the blood and MCAA in the urine by gas-liquid chromatography; TDAA in urine by GC-MS. Mathematical planning was applied when choosing optimal conditions for derivatization of TDAA isolated from urine samples. The report will present the experience of the laboratory of analytical ecotoxicology and biomonitoring in the development of methods for determination of pollutants and their metabolites, including the aim of their subsequent introducing into the clinic.

This work was carried out within the framework of the funds allocated for the fulfillment of the state task of the East-Siberian Institution of Medical and Ecological Research.

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New physicochemical approach for assessing environmental risk of chemical exposure in low concentrations and developing physicochemical screening at the stage of pre-biological drug research

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Nowadays, there are more and more challenges related to the phenomenon of nonmonotonic concentration dependencies of bioeffects of highly diluted aqueous solutions of biologically active substances. First of all, we are talking about interrelated global issues of protection of the environment and preservation of public health. For example, it is now known that the presence of some toxic pesticides in water and soil in amounts below the maximum permissible concentrations does not guarantee safety for humans and wildlife [1–4]. Surprisingly, the issue of protection of aquatic ecosystems from pharmaceutically active substances has become especially acute [5]. Drugs consumed on a massive scale are poorly removed in the course of wastewater treatment and are detected in the water of rivers, coastal sea strip at concentrations of about 10^{-12}–10^{-9} M. It has been found that even in such low concentrations pharmaceutically active substances cause significant damage to hydrobionts [5, 6], which entails potential risks to humans.

This situation resulted in understanding the need for new fundamental knowledge to justify the bioeffects caused by chemicals at low concentrations and to assess their risk. Recently, a new physicochemical approach explaining the properties of highly diluted aqueous solutions of biologically active substances has been proposed at the Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences. This approach is focused on establishing the ability of such solutions to self-organize, i.e. to form a dispersed phase (nanoassociates) with nonmonotonically changing parameters when diluted, which naturally leads to a coherent change in the physical-chemical and biological properties of the systems [4, 6, 7].

The proposed approach provides a previously missing scientific rationale for significant non-monotonic changes in bioeffects arising under the action of water systems with low calculated concentrations of substances, and also shows the possibility of predicting bioeffects in this concentration range [8], which is necessary for assessing the environmental risk of both new and well-known chemicals present in water reservoirs, as well as for the development of technologies for monitoring and predicting the state of the environment, preventing and eliminating pollution.

The proposed methods of studying highly diluted systems of biologically active substances of different structure and spectrum of action can be the basis for development of physicochemical screening of newly synthesized substances at the stage of pre-biological research which can be successfully used in pharmaceutical centers for testing medicines in a wide range of concentrations. Detection of optimal doses and reduction of toxicity of drugs are essential requirements for transition to personalized medicine, health saving technologies coupled with rational use of medicines.

At present, innovative possibilities of the developed approach for predicting bioeffects caused by chemicals in low concentrations have been demonstrated in a number of publications by using the examples of pesticides and drugs [4, 6, 7], etc.

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Pesticides as highly toxic chemical pollutants of the environment

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Currently, the problem of pesticide toxicity is widely discussed all over the world and is hotly debated. We have been conducting an extensive research of pesticide behavior for more than 30 years and revealed the mechanisms of their effects on human health and the environment. We have shown for the first time [1] that bidentate complexes of eight pesticides are formed in cells of living organisms. Pesticides and their metal complexes exhibit acute and chronic toxicity (*Tetrahymena pyriformis*). The pesticide metal complexes are not almost decomposed by microorganisms and the UV component of sunlight [2].

We have proved for the first time that pesticides and their metal complexes interact with mono-, di-, and polynucleotides [3, 4]. The formation of the pesticide complexes with adenosine triphosphoric acid (ATP) results in an energy deficiency in the cells of organisms. We observed the direct correlation of the complex formation constants with the ability of pesticides and their metal complexes to inhibit grain growth, retard the growth and induce necrosis of vegetating plants, and decrease the level of chlorophyll formation in leaves both in dicotyledonous and cereal plants. Thus, the preparations studied were not selective in action [5]. The complex formation constants with ATP correlate with the decrease in the microarthropod population (collembolans of the *Folsomia candida* and *Xenylla grisea* sp.) and a decrease in the hydrobiont population (*Tetrahymena pyriformis*) [6, 7]. Thus, the inhibition of the energy metabolism and the appearance of the energy deficiency of the cell result in the toxicity of pesticides and metal complexes toward multicellular organisms.

We pioneered to show that pesticides/their metal complexes simultaneously inhibit the activity of several enzymatic systems in organisms such as transport enzymes Ca/Mg and K/Na-ATP-ases [8, 9]. The enzymatic activity of oxidizing enzymatic systems (NADH-oxidoreductase) is inhibited, first, due to the complex formation with dinucleotide (coenzyme) NADH. Second, due to the formation of the non-productive complex [enzyme-pesticide] in the active center of the enzyme. Different types of inhibition take place. The antireductase activity increases in the order: metal ion < pesticide < metal complex. The inhibition of the redox enzymatic system activity by pesticides/their metal complexes violate vital activity processes performed by the enzymes; the system of xenobiotic oxidation is blocked, and the body cannot excrete toxins. As a result, the elimination of species in the ecological system takes place, for example, species of activated sludge at sewage disposal plants [2]. Pesticides and their partial metabolism products are accumulated in cells, which results in the secondary intoxication of the organism.

The main reason for the toxic properties manifested by pesticides and their metal complexes toward plants and mono- and multicellular organisms is apparently the inhibition of energy metabolism and the appearance of an energy deficiency of the cell due to the complex formation of ATP. The energy processes and electron transport chains are broken, and the cycle of tricarboxylic acids and photosynthetic processes are blocked. The nucleotide 'branching' of the pesticide/pesticide metal complex mode of action occurs accompanied by complex formation with (a) mononucleotide (ATP), (b) dinucleotide (NADH), and (c) polynucleotides (DNA, RNA) [10]. Pesticides and metal complexes inhibit the redox enzymatic systems. In this metabolism cycle, the 'enzymatic branching' takes place, which is expressed as (a) binding of pesticide with metals that compose the free pool inside the cell and are necessary for the synthesis of metal-containing enzymes, (b) complex formation of pesticide with coenzymes (NADH, ATP), and (c) direct inhibition of the activity of enzyme(s). Thus, the parallel mechanism of formation of toxicity of pesticides and their metal complexes is the **inhibition of redox processes**, that is, blocking of the electron transfer chain in organisms of various trophic levels.

Pesticides and their metal complexes are able for complex formation with DNA and RNA. Here, we distinguish the conventional third 'genetic branching' of the toxic effect of pesticides and metal complexes: (a) nature of the DNA double helix is violated because of complex formation, (b) the direct mutagenic effect is manifested (as we have shown for the TA98 *Salmonella typhimurium* strain, mutations of the reading frame shift type are induced), and (c) promutagenity is revealed.

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Assessment of deicing materials impact on human health when used in urban areas

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Using deicing materials and reagents (DIMR) in big cities is an essential prerequisite for ensuring safety of city traffic and minimizing road vehicle accidents in winter.

At the same time, safe quality of the urban environment is determined by such indicators as the level and nature of population's chronic pathology of respiratory organs, since their occurrence is associated with unfavorable environmental factors in 40–60% of cases studied [1, 2]. Solid salt particles of DIMR can contribute to air pollution by adsorption of suspended particles on the surface which exhibit pronounced negative effects on human health [3].

A number of research reports are devoted to studying DIMR effects on the human and animal bodies. However, there is limited amount of studies devoted to the cause-and-effect relationship between DIMR appliance and bronchopulmonary diseases growth or their course burdening.

According to priority directions of the World Health Organization (WHO) activities, comprehensive assessment of polluted territories in practice can involve various methods for evaluating the relationship between public health and impact of pollutants and environmental objects, including epidemiological analysis and risk assessment methods [4–6]. However, little information is available on the level and dynamics of seasonal morbidity for conducting epidemiological analysis of interactions between population morbidity and environmental pollution with the substances that are part of DIMR, and for risk evaluation of potential DIMR impact on human health.

In this regard, the priority direction of our research was to study the effect of DIMR toxicity on the body of warm-blooded animals with chronic respiratory pathologies and/or allergic diseases during inhalation intake of the DIMR ingredients. The previously obtained data on the results of toxicological studies of DIMR percutaneous and peroral exposure do not allow us to accurately characterize DIMR effects on animal organisms. The results of the upcoming studies are aimed at the assessment of the potential harmful impacts of DIMR on health of population at risk including individual vulnerability to DIMR components.

The work was performed within the frame of the State assignment at Centre for Strategic Planning of FMBA of Russia.

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Analytical capabilities and experience of Multi-Access Analytical Center of the NIOCH SB RAS in the field of identification of compounds and organic pollutants in environmental objects

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The Novosibirsk Institute of Organic Chemistry of Siberian Branch of Russian Academy of Sciences (NIOCH SB RAS) is the head organization for the Multi-access Chemical Research Center (Analytical Center) integrating the unique and expensive equipment and setups available at chemical institutes of the Novosibirsk Research Center. The Analytical Center is equipped with modern high-precision analytical devices that allow performing analysis of food and industrial products, biological media, pharmaceuticals, and environmental objects. A set of analytical methods for high-level research and analysis is available in the Analytical Center and includes: radiospectroscopy (nuclear magnetic resonance and electron paramagnetic resonance), optical spectroscopy, gas and liquid chromatography, low and high resolution time-of-flight-mass-spectrometry, X-ray diffraction spectroscopy, microanalysis, toxicological and pharmacological analysis methods.

The Analytical Center provides also services of the Testing Center certified by the Federal accreditation service in the area of analysis of such objects as water, soil, number of compounds identification, toxicological and pharmacological analysis according to the verified accreditation area.

Concerning ecological activities, the Analytical Center performs ecological investigations from 1994. NIOCH SB RAS is supporting implementation of and capacity building under the Stockholm Convention on persistent organic pollutants as a national center of Russia and is hosting the International Regional Center of the Stockholm Convention. The Analytical Center supports all analytical activities and carries out analysis and identification of organic compounds and materials including the ‘trace’ and ‘ultra-trace’ analysis of persistent organic pollutants. The accreditation scopes cover today ~350 environmental assays.

In this report, the authors will present some recent results concerning analysis of impurities in chemical raw materials and final products for pharmaceutical companies, identification of medicinal compounds, waste chemical materials for chemical production companies, persistent organic pollutants including polychlorinated phenyl-containing compounds in soils, etc. In addition, results of analysis and identification of sulfur-containing pollutants in the air resulting from industrial waste will be presented. Numerous examples of the obtained results will illustrate that frequently only a set of physical-chemical analytical methods allows to identify compounds and organic pollutants in the environmental objects.

Ozonation of uracils in aqueous solutions

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It is known that ozone is able to absorb the UV radiation. Therefore, ozone layer is an effective protective barrier for our planet which can protect from the sun's hard chemical processes. Ozone is widely applied in different sectors of nation's economy. It is used for treatment of drinking water, industrial waste-waters and contaminated air. Ozone is also used for paper bleaching, antibacterial treatment of medical device and as a rocket-engine propellant. Ozone has become a popular therapy for common diseases in recent decades. However, little attention is paid to studying harmful effects of ozone on RNA and DNA in due course. In this regard, there is an urgent necessity to study the reactivity of ozone with respect to pyrimidine bases since some of them are the components of nucleic acids.

Ozonation kinetics has been studied by UV-spectroscopy method on UV-2600 «Shimadzu» spectrophotometer. Uracil (**I**) and its eight derivatives (UD) [thymine (**II**), 5-fluorouracil (**III**), 6-methyluracil (**IV**), 5-bromo-6-methyluracil (**V**), 5-hydroxy-6-methyluracil (*VI*), 5-nitro-6-methyluracil (**VII**), 1,3-dimethylthymine (**VIII**) и 5-hydroxy-1,3,6-trimethyluracil (**IX**)] have been chosen as objects of oxidation. It has been found that kinetic curves at equilibrium initial concentrations of reagents ($[UD]_0 = [O_3]_0 = C_0$) are good linearized in coordinates of second-order equation:

$$1/C = 1/C_0 + k\,t \quad (r \geq 0.995),$$

where k – rate constant of reaction of ozone with UD. By using bubbling installation, it is shown that 1 mole of absorbed ozone is accounted for 1 mole of consumed UD. Thereby, the UD ozonation reaction obeys the second order kinetic law (the first order – with respect to ozone, and the first – with respect to UD):

$$V = -\,dC/dt = k\,[UD][O_3].$$

In this work, the temperature dependence of second order rate constant is observed in the range of 285–309 K. Analysis of rate constant data suggests a sufficient high reactivity of ozone in relation to the uracils studied. The activation parameters of ozone reaction with uracils are calculated from the data of Arrhenius equation coordinates:

Uracils*	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**	**VIII**	**IX**
lg A, l/(mol·s)	7.4	5.1	10.5	9.4	6.6	8.3	10.2	9.0	12.9
E, kJ/mol	30.3	23.2	53.6	42.4	26.3	37.4	47.4	39.5	66.4

* Inaccuracy of the defined parameters is less than 12%.

It has been established that the reactivity of uracils (at 305 K) changes in the following row: 1,3-dimethylthymine (VIII) > 6-methyluracil (**IV**) > 5-bromo-6-methyluracil (**V**) > 5-nitro-6-methyluracil (**VII**) > uracil (**I**) > 5-hydroxy-6-methyluracil (**VI**) > 5-hydroxy-1,3,6-trimethyluracil (**IX**) > 5-fluorouracil (**III**) > thymine (**II**). It is follows from this row that thymine has the lowest reactivity towards ozone.

In addition, the correlation dependence (or compensation effect) has been found between the logarithms of pre-exponential factors and the activation energy of ozonation reaction of uracils. Perhaps, this dependence points to a single mechanism of the limiting step of the reaction.

Finally, we have observed that the oxidation reaction of uracils with ozone in aqueous solutions is accompanied by chemiluminescence in visible light spectrum, in our study.

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Rapid colorimetric nanoparticles aggreration test for monitoring mercury and cadmium ions in water sources

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The presence of highly toxic heavy metals in water continues to be a major concern in the world. The existing methods for their detection include atomic absorption- and fluorescence spectrometry, high-performance liquid chromatography, etc. Despite the advantages of these methods such as high sensitivity and accuracy, there is a need in rapid user-friendly techniques without sample pretreatment. Colorimetric techniques are in good accordance to mentioned requirements. They provide quantitative out-of-laboratory monitoring of heavy metal ions, and the obtained results can be estimated by the naked eye [1, 2].

Herein, new assay format has been developed. Freshly prepared gold nanoparticles were conjugated with mercaptosuccinic acid (MSA) through thiol group. The addition of mercury and cadmium ions to MSA-capped gold nanoparticles caused their aggregation accompanied by colour change from red to blue.

The quantitative determination of heavy metal ions was realized by plotting the absorbance ratio A_{530}/A_{600} as a function of target ion concentration. Under optimum conditions, the proposed colorimetric assay revealed detection limits of 10 ng/mL and 20 ng/mL for cadmium and mercury ions, correspondingly. Time of the assay is 1 min. The study on selectivity showed no cross-reactions with alkali, alkali-earth and transitional metal ions.

Thus, the developed technique is promising for mercury and cadmium ion detection in different water sources to confirm their safety.

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Metal removal from zinc-containing effluents using yeast *Saccharomyces cerevisiae*

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The efficiency of yeast *Saccharomyces cerevisiae* biomass in the removal of heavy metals from four synthetics and one real zinc-containing electroplating effluents was evaluated.

The removal of metal ions from synthetic effluents was studied as a function of pH (2.0–6.0), interaction time (5–120 min), nickel concentration (10–100 mg/L) and temperature (20–50°C). Characterization of biosorption equilibrium was evaluated employing the Langmuir, Freundlich and Temkin models.

The maximum sorption capacity of biomass for Zn(II) ions was 9.0 mg/g in Zn(II) system, 10.4 mg/g in Zn(II)-Sr(II)-Cu(II), 17 mg/g in Zn(II)-Ni(II)-Cu(II), and 9.3 in Ni(II)-Sr(II)-Cu(II)-Ba(II) systems. The kinetics of the biosorption was described using pseudo-first order, pseudo-second order, Elovich model and the intra-particle Weber and Morris diffusion models. According to the thermodynamic parameters, the biosorption can be described as a spontaneous process.

Fourier transform infrared analysis was carried out to identify the role of functional groups in metal ions binding, while thermodynamic calculations allowed to determine main metal species present in the solution at different pH values. Effect of pH (2.0–7.0) and sorbent dosage on metal removal from real industrial effluent was investigated. The two-stage sequential scheme of Zn(II) ions removal from effluent by addition of different dosage of new biomass sorbent was proposed. The obtained results have revealed that metal removal from effluents is a pH dependent process and it is possible to remove efficiently Zn(II) ions from electroplating effluents by varying this experimental parameter.

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Chromatographic profiling as a method for studying persistent organic pollutants in the environment

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Persistent organic pollutants (POPs) (organochlorine pesticides, polychlorinated biphenyls, polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, polycyclic aromatic hydrocarbons) are toxic organic compounds which persist in the environment for a long time, accumulating in biota, exhibiting an ability to cross-border transport and causing serious risks to human health and ecosystems even in low concentrations. Therefore, detection and monitoring of POPs in the environment is a relevant task.

The chromatographic profiling method is one of the most effective and informative approaches for such studies, since a ‘fingerprint’ of the toxic compound can be obtained using chromatography-mass spectrometry (GC/MS) and gas chromatography with electron-capture detection (GC/ECD). The data on the composition and content of POPs can be used to identify the main sources of pollution and assess transboundary transfers, to model and predict pollution levels and behavior of POPs, risk assessments for ecosystems and populations, and to develop effective environmental technologies. The main identification parameters in the analysis of POPs are: chromatographic profiles, retention times, mass spectra, and ratios of characteristic ions.

Highly informative chromatographic profiles of POPs in various objects can be obtained by gas chromatography-mass spectrometry in the following modes: a) SCAN, which is chromatography in full ion current mode for a review analysis with the possibility of subsequent processing the obtained chromatograms using the program technique of ‘ion extraction’ for characteristic ions of targeted POPs; b) SIM, which is chromatography in mass fragmentography mode, *i.e.* selective detection of individual diagnostic ions. The SIM mode is used for targeted analysis of micro-impurities in complex matrixes using data of the retention times and ratios of characteristic ions with the established criteria for changing the determined parameters. For organochlorine compounds, in some cases, an electron capture detector can be used.

The capability and algorithms of the GC/MS method have been demonstrated using the results of the long-term studies of the biogeochemical regularities of the contamination, distribution and accumulation of POPs in the largest lake-river ecosystem of Inner Asia in Russia and Mongolia, including lake Baikal, lake Khubsugul and the river basin Selenga [1]. Another example is discussed based on the results obtained for one of the large industrial centers of Western Siberia. Chromatographic profiles have been obtained, and compositions, quantitative levels and coefficients of bioconcentration of POPs in a variety of environmental objects have been established. The analysis of POPs sources in ecosystems are carried out by using the characteristic ratios of diagnostic compounds.

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Identification of atmospheric nitrogen pollution impact on forest ecosystems: case study of the Udmurt Republic

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Over the past 250 years, the global production of reactive nitrogen (N) has increased by 200%, with industry and motor vehicles as the main sources [1]. Anthropogenic nitrogen is actively involved in natural biogeochemical cycles, which leads to increased depositing of N in natural ecosystems. However, due to the multiple role of nitrogen (nutrient and acid element), it is often methodologically difficult to evaluate the environmental impact of its atmospheric deposition.

According to the State Report "On the State and Environmental Protection of the Udmurt Republic (UR)", emissions of nitrogen oxides (NO_x) from total sources increase annually and in 2016 amounted to 17.2 thousand tons [2]. Woody vegetation 'absorbs' 2–3 times more pollutants from the atmosphere than herbaceous and bushy vegetation. With a 37% forest cover in Izhevsk, this region is a good target for studying the impact of anthropogenic nitrogen deposition on terrestrial ecosystems.

Coniferous and deciduous forests were studied in the Umbric Albeluvisol in Izhevsk and Zavialovsky district. In key areas ($n = 21$), sites ($10\ m^2$) were selected where snow cores in March reached snow cover thickness ('envelope method'). The soil samples were taken in August (mixed sample in 5 replicates, humus horizon 0–20 cm, without plant litter). A geobotanical description of the vegetation was also carried out. To characterize the presence/absence of species – indicators of soil availability N_{min}, the G. Ellenberg ecological scale was used. The content of mineral nitrogen (N_{min}) was determined in soil and snow, including its ammonium (NH_4) and nitrate (NO_3) forms. In the soil, total carbon (C) and nitrogen (N) were additionally measured (dry combustion method with Elementar Vario EL III analyzer) and P_2O_5 (X-ray fluorescence method). The C/N ratios in the soil were calculated, which reflected the rate of mineralization of organic matter. The relationship between N_{min} atmospheric deposition, soil properties and ground cover structure was evaluated by Spearman's correlation analysis.

It was found that the total N_{min} deposition in the region under study ranged from 0.15 to 20.6 kg N ha^{-1} $year^{-1}$ (Fig. 1) with the highest values noted in the center (Izhevsk industrial region), with the ammonium form prevailed in the chemical composition. The increase in ammonia content in atmospheric deposition in forest areas may be the result of increased emissions from fires or the decomposition of large amounts of biomass. In the central and eastern parts of the city, the soil content of C, N was higher and their ratio was lower, but no correlation relationship with the N_{min} deposition was found for these indicators.

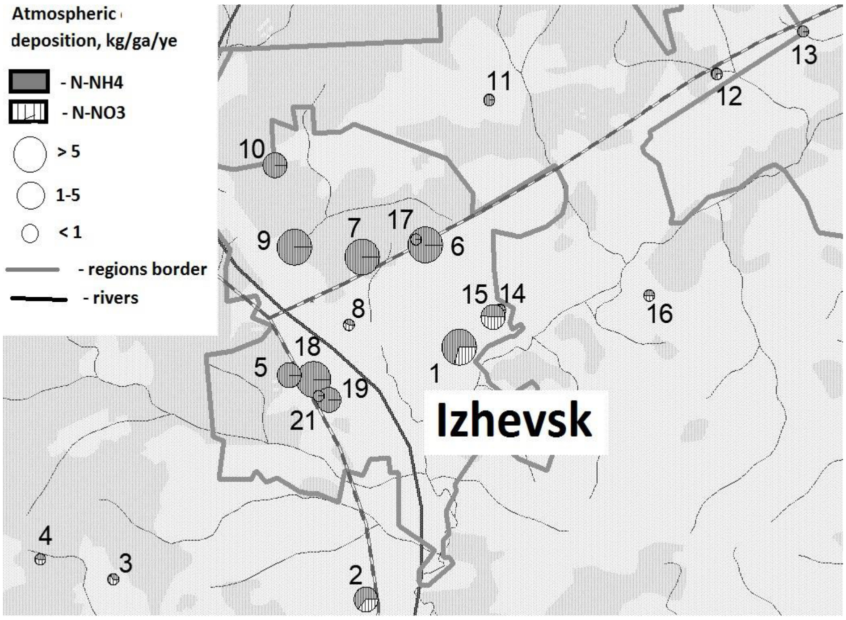

Fig. 1. Atmospheric N_{min} deposition (the sum of $N–NH_4$ and $N–NO_3$) in the forests of the key studied areas

Areas with a higher level of N_{min} deposition were found to have a higher $N–NO_3$ and $P–P_2O_5$ levels in soil ($p^2 = 0.5–0.7$), which indicates a change in the nutritional status towards eutrophication. The change in substrate nutritional status indicates a sharp growth of plant species that prefer nitrogen-rich soils (nitrophils). This fact was confirmed by our study, when we identified nitrogen-rich habitats in the studied areas, where plants are oligotrophs, occurring as an exception (score on the G. Ellenberg scale of 7), and are characterized by the highest N_{min} deposition levels. In addition, in the study area, N_{min} concentrations in precipitation were found to be higher than the critical values for oligotrophic and mesotrophic soil cover types in three ranges, and in 11 ranges these values were close to those critical for coniferous species indicating a risk of extinction of these species while maintaining or increasing the current levels of N_{min} deposition.

The work was performed as part of the state task No. 0191-2019-0048.

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Heavy metals accumulation by moss samples in the Donetsk-Makeevka agglomeration

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Donetsk-Makeevka agglomeration is one of the most economically developed regions in the Eastern Europe. The main cross-industry complexes are fuel and power, ferrous and non-ferrous metallurgy, machine-building, chemical industry, transport. The method of passive moss biomonitoring [1–3] was applied in the Donetsk-Makeevka agglomeration to assess the atmospheric deposition of heavy metals and trace elements in the region.

The main objectives of this work were: to determine the level of heavy metal pollution in the Donetsk-Makeevka agglomeration and to identify local sources of pollution (mines, power, ferrous and non-ferrous metallurgy, mechanical engineering).

The 113 moss samples were collected in May 2019 in accordance with the CLRTAP (2015) manual for moss sampling [4]. The *Ceratodon purpureus* (Hedw.) Brid was chosen for this study, since *Hylocomium splendens, Pleurozium schreberi, Hypnum cupressiforme, Pseudoscleropodium purum* [4] are poorly distributed on the territory of the Donetsk-Makeevka agglomeration.

The concentrations of Cd, Cu and Pb in the moss samples were determined by atomic absorption spectrometry (AAS) using iCE 3300 AAS Atomic Absorption Spectrometer with electrothermal (graphite furnace) atomization (Thermo Fisher Scientiic, Waltham, MA, USA).

Distribution maps (ArcGis software) of these elements was built for assessing pollution sources of the Donetsk-Makeevka agglomeration (Fig.1).

The average concentrations of the heavy metals studied at the same sampling location followed the order of Cu > Cd > Pb.

High concentrations of Pb and Cd were observed in coal mining area. Non-ferrous metal mining and smelting activities are the biggest contributors of heavy metal pollution as they discharge large volumes of wastewater, waste gases and solid waste into the environment. Main sources of copper emission are combustion of fossil fuels and wastes and windblown dust. In the same way, industrial activities including cement factories, non-metallic mining and smelting activities that include coal and regular ore mining release high amounts of heavy metal into the environment. One of the most important sources of Cd and Pb in the urban area is road traffic.

As for spatial distribution of Pb and Cu (Fig. 1 (b, c)), it was observed that the highest levels of contamination by heavy metals were localized in the central area (Donetsk) and South East (Ilovaisk). The elevated concentrations of Cd

(Fig. 1 (a)) in moss were recorded in the North East of the Donetsk-Makeevka agglomeration (Yenakiive).

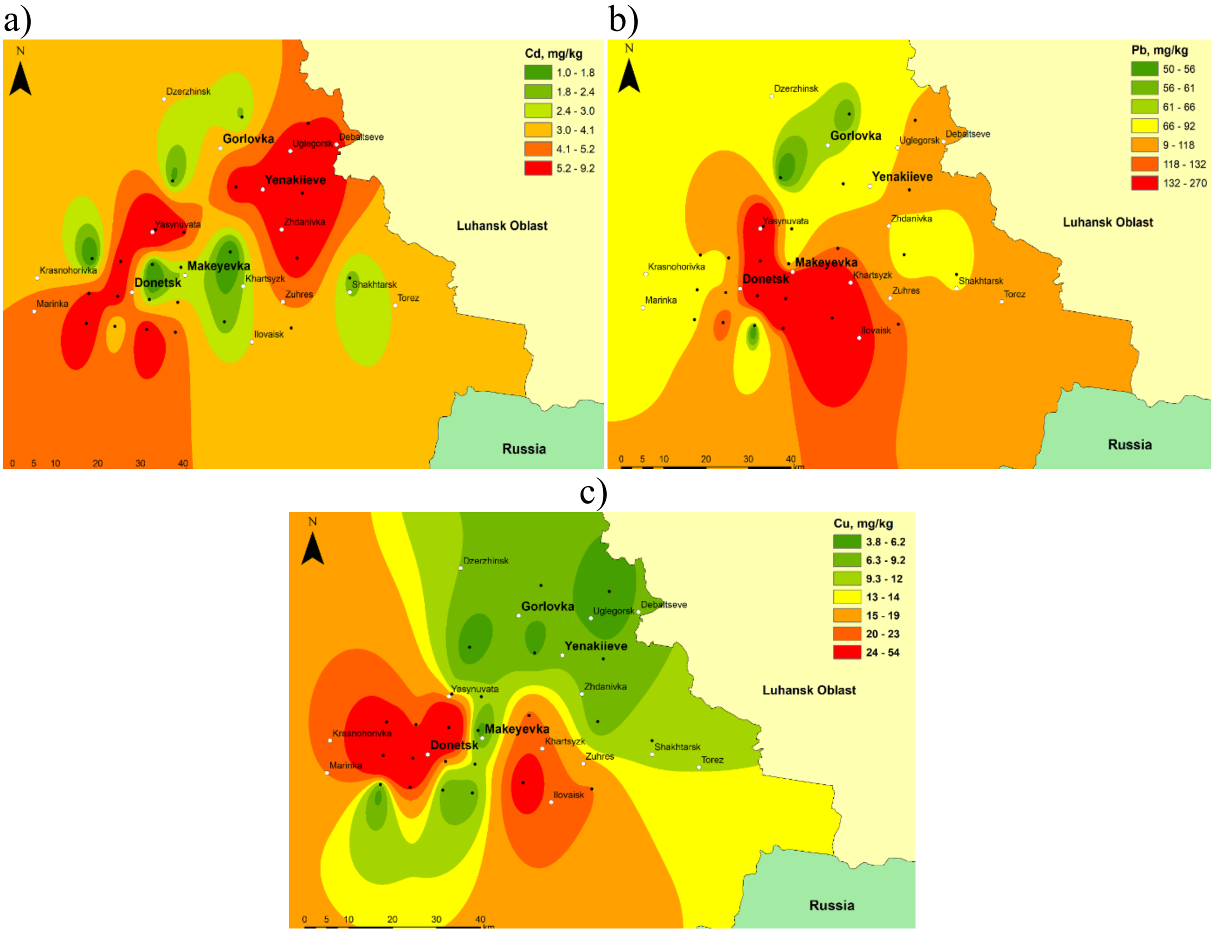

Fig. 1. The spatial distribution of Cd (a), Pb (b), Cu (c) in the Donetsk-Makeevka agglomeration

This study was carried out in the framework of the UNECE ICP Vegetation Programme (https://icpvegetation.ceh.ac.uk/).

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Hybrid nano-TiO_2/diatomite photocatalyst for AOPs mediated removal of toxic organic pollutants

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Advanced oxidative processes (AOPs) successfully remove complex organic pollutants because they can achieve complete oxidation. AOPs have a distinct advantage over many traditional treatment methods, such as biological processes, because higher decomposition rates are achieved and pollutants decompose instead of moving from one phase to another. In addition, there are no requirements for by-product removal. AOP processes can be tuned using a combination of chemical and physical agents such as a combination of oxidizing agents, an oxidizing agent plus ultraviolet, a catalyst or ultrasound, and a catalyst plus ultraviolet.

The recent huge research interest in using TiO_2 as a photocatalyst is attributed to its excellent ability to completely degrade a wide range of organic compounds to CO_2 plus H_2O as far as due to its low cost, chemical stability and high efficiency properties. Laboratory studies on photocatalysis are typically performed using nano-sized catalyst suspended in the reactor. In these designs the catalyst is evenly dispersed in the solution as it passes through the reactor. The uniform catalyst distribution provides very high surface area to volume ratios with low mass transfer limitations.

However, titania nanoparticles (TNPs) show disadvantages in terms of large-scale practical application and commercial benefits, which may result in a low photocatalytic efficiency and high cost: strong tendency to aggregate, difficulties with TNPs recovery from the solution after treatment and low adsorption capacity. To overcome these shortcomings, many researchers have been focused recently on immobilizing TNPs on supports having high surface area and excellent adsorption capacity. This approach may enhance the TNPs distribution in suspension which enables to adsorb and concentrate the target substances.

Recently, porous non-metal minerals have been considered as supports of TiO_2-based photocatalysts, such as perlite, zeolite and others due to their low costs.

The support must meet the following requirements: high surface area, good thermal resistance and mechanical stability, inexpensiveness, conformability to reactor configuration, and usability for coating process.

To this end, diatomite is one of the most suitable supports for titania nanoparticles covering due to its unique physico-chemical properties.

Diatomite (or diatomaceous earth) is mineral deposit of diatomaceous algae, which is accumulated starting from the Miocene period. Amorphous silica, a constituent of the diatom frustulae, is the main component of diatomite, although variable quantities of other materials (metal oxides, clays, salts (mainly carbonates), and organic matter) may also be present. Diatomite is abundant in many areas of the world and has unique physical characteristics, such as high permeability and porosity (35–65%), small particle size, low thermal conductivity and density, and high surface area. A combination of diatomite and nano-sized titanium dioxide can yield a photocatalyst with a high specific surface and photocatalytic activity.

This study is focused on photodegradation of such a toxic substance as phenol from aqueous solution using hybrid photocatalyst (DTD - diatomite/titan dioxide) under UV illumination. DTD was prepared via heterogeneous hydrolysis of $TiCl_4$ as a precursor of TiO_2 in the diatomite suspension at ambient temperature and normal pressure. The obtained product was further washed, dried and calcined at 450°C for anatase phase development. The amount of titania in the product is about 20%.

Phenols are important chemical compounds because of their widespread use in many production processes. Phenol is commonly used in the manufacture of phenolic resins, bisphenol A, caprolactam, and chlorophenols, such as pentachlorophenol. However, these chemicals pose a serious threat to many ecosystems, water supply and human health due to their inertness, toxicity, ability to destroy the endocrine system and carcinogenic behavior. The United States, Canada and the European Union include several types of phenols on the list of priority pollutants.

The limit concentration of phenol in wastewater as prescribed by the World Health Organization (WHO) is 5 mg/L. Therefore, wastewater containing phenols and other toxic compounds requires special treatment prior to their discharge into aqueous objects.

The removal efficiency of phenol from aqueous solution was studied as a function of catalyst dosage, solution pH, phenol initial concentration. Under dark conditions, only poor pollutant elimination by adsorption on the catalyst surface was observed. Similar results were found for the photolysis reaction. The experimental results have confirmed the elimination efficiency of photocatalysis with the DTD under UV irradiation.

The basic parameters of the process of photodegradation of phenol in the presence of DTD until intoxicating mineral products are as follows: the pH of the solution 4.5, the process duration 180 min, the dose of the photocatalyst 2 g/L at initial phenol content of 10 mg/L. The experimental results obtained for the photodegradation kinetics of phenol showed a good agreement with the Langmuir-Hinshelwood model with the external diffusion as the determining stage of the process.

In conclusion, the data presented indicate that photocatalytic oxidation is an effective and green technique for removing toxic organic pollutants, such as phenol.

Impact of hydrogen concentration on safety of methane-hydrogen mixtures

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The possibility of using hydrogen and its mixtures as a motor fuel aimed at improving the economic and environmental characteristics of internal combustion engines (ICE) is a subject of intense discussion. Accordingly, it becomes necessary to study the detonation characteristics of methane-hydrogen mixtures in conditions that correspond to the possibility of self-ignition in the ICE cylinder to analyze the effectiveness and safety of their use. Previously, the authors conducted similar studies for methane-alkane mixtures in the air [1].

Here we present the results of studying impact of hydrogen concentration on the delay of self-ignition τ for stoichiometric methane-hydrogen-air mixtures. Both experimental studies and kinetic modeling of self-ignition of such mixtures were carried out in the initial temperature range T_0 = 700–1000 K and initial pressure P_0 = 1–15 atm. The self-ignition delay was experimentally determined in a closed volume of static installation (high-pressure bomb method), which allowed covering the specified range [2]. It has been established that the addition of less than 50% hydrogen to methane has a weak effect on the burning rate and flame propagation limits, which raises the issue of feasibility of using mixed methane-hydrogen fuels.

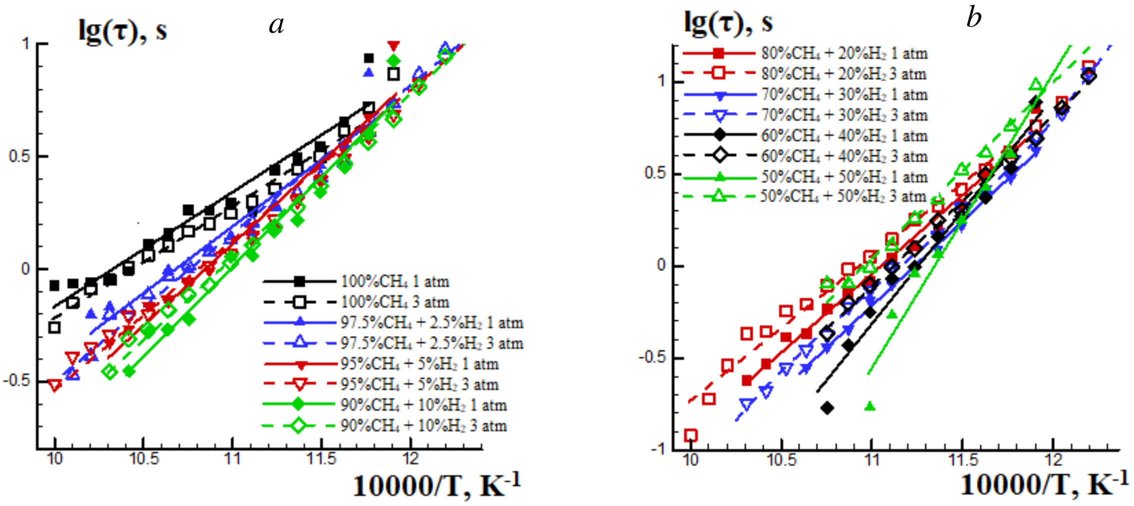

Fig. 1. Experimental comparison of self-ignition delays of stoichiometric methane-hydrogen-air mixtures at P_0 = 1 atm (solid lines) and P_0 = 3 atm (dashed lines): *a* – hydrogen concentration 0–10%; *b* – hydrogen concentration 20–50%

Kinetic modeling of self-ignition of stoichiometric CH_4-H_2-air mixtures with different hydrogen content in the mixture α_{H2} (% vol.) was carried out using the NUI Galway kinetic mechanism [3], which proved to be the most appropriate for these processes [4].

A significant difference in the temperature dependence of the delay of self-ignition of methane and hydrogen is shown, which is probably associated with fundamental differences in the mechanism of their oxidation, as well as the nature of changes in the mechanisms of oxidation of methane and hydrogen occurring near the temperature of 900 K, which has a significant impact on the processes of their self-ignition. The possibility of both promotion and inhibition of self-ignition of methane by hydrogen additives has been shown. An interpretation of these phenomena is proposed.

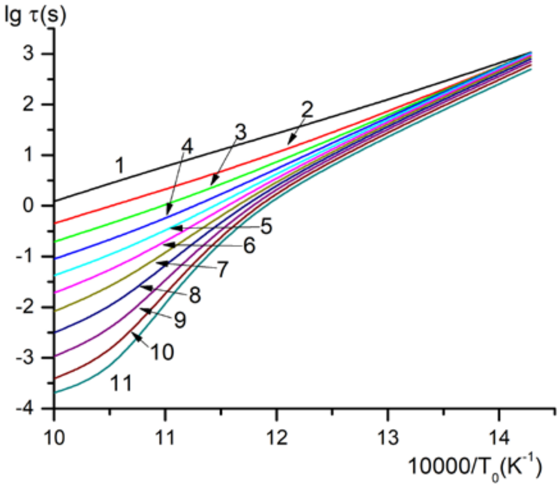

Fig. 2. Calculated temperature dependence of the self-ignition delay of stoichiometric CH_4-H_2-air mixtures on T_0 for various values of α_{H2} (%): *1* – 0, *2* – 10, *3* – 20, *4* – 30, *5* – 40, *6* – 50, *7* – 60, *8* – 70, *9* – 80, *10* – 90, *11* – 100; P_0 = 1 atm [3].

The reported study was funded by Russian Foundation of Basic Research (RFBR), project No. 19-31-90022.

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A dynamic model of phytocenosis taking into account interaction of biomass and resources

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Public attention is now increasingly focused on the environment and climate change. Given the emerging trend towards digitalization, information systems are expected in the foreseeable future that will combine a wide range of data relating to environmental conditions and climatic parameters. The effectiveness of such systems in assessing the current state and predicting trends in the development of environmental systems, will depend on how well the models, underlying such estimates and forecasts, will consider the relationships between parameters describing the behavior of environmental systems.

We have previously proposed an ecosystem model that takes into account the interaction of biomass and resources. The basic idea behind this model is that biomass growth is limited, and these limitations are determined by the availability of resources used for biomass growth and external impact. In addition, the presence of biomass in the system contributes to the accumulation of resources, whereas abiotic processes lead to the loss of resources.

Depending on the parameters of this model and the initial conditions, the system's solution either comes to a certain stationary state with non-zero biomass and resource density, or describes degradation with total loss of biomass and resources.

This paper considers the modification of this model and its potential application to the description of the functioning of phytocenosis, in particular, the description of the seasonal change of phytomass. It follows from the setting of the problem that changing external conditions should be considered as a periodic process.

A system of equations is proposed for description of the behavior of phytocenosis (1):

—

(1)

—

where

– density of phytomass,
– density of resources,
– intensity of external impact used for phytomass growth,
– limiting the growth of phytomass,

– speed factor for phytomass changes,
– speed factor for resource accumulation,
– speed factor for loss of resources,
– speed factor for conversion phytomass – resources.

Private dependency restrictions related to the availability of resources and external impacts used for the growth of phytomass, for example, photoactive radiation, are presented in the form of integral lognormal distributions.

This approach allows to take into account the non-linearity of the influence of factors stimulating the growth of phytomass. Two significant points are demonstrated namely: limited stimulant impact and the presence of a relatively narrow area of factor values with the major increase in the stimulant impact.

In addition, this approach makes it possible to describe the impact of negative influences as certain ‘depreciation’ of stimulant factors.

The general limitation of the growth of phytomass has been determined using the well-known Libich principle, i.e. as the minimum value of all private restrictions. The value of activation energy has been used for each of them to account for the temperature dependence of process rate ratios.

Model calculations have shown that the proposed model can, in principle, be used to describe some typical situations of phytocenosis existence.

In addition, the presentation is expected to discuss the possibility of using the proposed model to interpret Earth remote sensing data.

Soft nanocontainers for decomposition of organophosphorous toxins and treatment for pesticides poisoning

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Supramolecular systems based on amphiphilic compounds are of high practical importance in terms of their involvement in a variety of modern technological applications, including gene and drug delivery systems, food and cosmetics production, catalysis, etc.

Our recent work has focused on the development of nanocontainers based on amphiphilic compounds, in particular surfactants and their macrocyclic and polymeric analogues. These nanocontainers are highly efficient as confined compartment for the chemical reaction providing their acceleration up to several orders of magnitude. This strategy allows to design biomimetic nanoreactors based on cationic surfactants for fast decomposition of toxic phosphorus acid esters in mild conditions using factors of concentration of reagents and change in their microenvironment. Rate enhancement was shown to be strongly controlled by the surfactant structure and increase in the hydrophobicity of surfactant and substrate.

Supramolecular nanocontainers are of practical importance as nanocarriers for drugs with better bioavailability, lower adverse effects, improved biodegradability and circulation time. Beneficial property of incapsulated drugs is their penetration through biological barriers including blood-brain barrier. In our work, lipid formulations have been designed through noncovalent modification of liposomes with cationic surfactants for intravenous administration of reactivators (quaternized oximes) of acetylcholinesterase (AChE) inhibited by organophosphorous pesticides. The oximes loaded in nanocontainers succeed in reactivation of AChE of brain, in contrast to the reactivation failure of free drug delivery system.

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Studying level of salts in snow cover of Moscow in the context of application of deicing materials

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Anthropogenic environmental pollution has a pronounced effect on public health and with every passing year is gaining an increased attention in the modern society.

Currently, the degree of air pollution in the city of Moscow is associated with its role as the largest economic and transport center of the country, a place of attraction of labor resources and, at the same time, a major industrial city.

In winter, traditional air pollutants group is expanded by adding another type of pollutants – deicing materials (DMs), which are applied for treatment roads and sidewalks for ensuring city traffic safety. Taking into account that the main ingredient of many DMs is technical-grade sodium chloride, which belongs to the 3rd class of hazard in terms of its impact on the human body, safety measures must be introduced. Though protective measures are envisaged at the enterprises for the production of DMs and when using them for special purposes, residents of megalopolises remain unprotected from the potential harmful effects of these substances.

Typically, several kinds of DMs are used in Russian cities: mineral concentrate - halite, sand-salt mixture, marble chips (calcite) mixed with sodium chloride and an anti-corrosion inhibitor, crushed granite, composed of calcium chloride, sodium chloride and other salts.

One of the methods used for assessing the quality of snow cover on the territory of Moscow is the measurement of its electrical conductivity and calculation of the total salinity of snow samples. Electrical conductivity is a convenient total indicator of anthropogenic impact.

In total, 20 sampling points were selected for our study, located in various administrative districts of Moscow and the cities of the Moscow region. Snow samples were collected from the territories of bus stops and pedestrian roads adjacent to motorways. The selection of sampling sites is determined by the largest crowded public areas and the potential aerosol effect of DMs on public health. Three sampling points were located in the Moscow region, one was a control point (sample No. 13) (sampling was carried out in the place where DMs were not applied), samples Nos. 16–19 were an integrated sample with different anthropogenic loads.

Sampling was done twice a season. The electrical conductivity was measured by the conductometric method on an inoLab Cond-740 fluid analyzer. The measurement results are presented in Table 1.

Table 1. Assessment of total snow cover mineralization

Sample No.	**Electrical conductivity, µS/cm**		**Estimated mineralization, mg/dm^3**	
	First sampling	Second sampling	First sampling	Second sampling
1	8700.0	401.0	5655.0	260.7
2	1902.0	151.1	1236.3	98.2
3	4840.0	1280.0	3146.0	832.0
4	111.3	172.6	72.3	112.2
5	553.0	50.3	359.5	32.7
6	490.0	158.7	318.5	103.2
7	176.6	64.3	114.8	41.8
8	1921.0	76.1	1248.7	49.5
9	641.0	186.3	416.7	121.1
10	260.0	208.0	169.0	135.2
11	604.0	225.0	392.6	146.3
12	186.2	827.0	121.0	537.6
Control	8.2	7.9	5.3	5.1
14	4980.0	219.0	3237.0	142.4
15	1070.0	434.0	695.5	282.1
16	5350.0	152.1	3477.5	98.9
17	960.0	37.8	624.0	24.6
18	409.0	46.4	265.9	30.2
19	307.0	98.8	199.6	64.2
20	61.2	46.3	39.8	30.1

As can be seen from the table, samples nos. 1, 3, 14, and 16 of the first collection series showed the total mineralization values which significantly exceeded the permissible level (according to regulations established for composition and properties of surface waters, the total mineralization of water should not exceed 1000 mg/l). Mineralization in samples 2 and 8 of the first sampling series is slightly higher than normal with values of 1236.3 and 1248.7 mg/dm^3, respectively. When assessing the mineralization of the samples of the second sampling series, no excesses were revealed.

An analysis of literature sources on the experience of using deicing materials in Russian cities and abroad showed that DMs also affect various aspects of the functioning of urban infrastructure. Finding the best solution for maintaining safe roads in winter along with good population health is an important and time-consuming task for all major cities.

Influence of nature and content of nanofillers on performance characteristics of polyurethanes

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Polyurethane-based materials are extensively used in a wide variety of industries. The possibility of varying chemical structure and properties of polyurethane elastomers provides their use as a matrix in the preparation of filled composite materials, in particular, for polyurethane-coated constructions. However, the main limitations of the materials which are used to prepare polyurethane protective coatings are insufficient strength and heat resistance of the resulting coatings.

The introduction of a finely divided filler in polyurethane composition leads to the formation of spatial structures formed by an interfacial layer with the properties differing from the properties of the matrix; the proportion of the layer depends on the concentration of the filler. The general effect of such filler injection can induce a considerable change in the properties of the polymer [1–3].

The aim of this study was to evaluate the effect of the nature and concentration of nanosized additives on the physic-mechanical characteristics of polyurethane-based composite materials. To obtain the polyurethane compositions, we used the SKU PFL-100 prepolymer (Kazan Synthetic Rubber Plant OJSC, Russia) and the hardener 4,4′-methylene-bis-(*ortho*-chloraniline). The nanofillers used in this study are presented in Table 1.

The most of dependences of physical and mechanical characteristics of filled polyurethane-based polymer systems on the content of fillers were found to have extremal forms. The maximum values of physical and mechanical parameters were recorded with the introduction of 1% (mass.) of the studied additives, which allowed to increase the appropriate characteristic of the filled composition by 1.5–2 times. The highest values were recorded in the case of detonation nanodiamonds, which is apparently due to the presence of active functional groups on the surface of the particles, resulting in a complex interaction at the polymer-particle interface with the formation of ionic and covalent bonds.

In addition, the introduction of dispersed fillers was found to affect the thermal stability of the filled polyurethane compositions. The results of thermogravimetric analysis showed that the introduction of 1% (mass.) of detonation diamond powder provided an increase in the temperature of the destructive processes by ~20°C. The introduction of powders of copper oxide and iron oxide leads to an increase in the dissociation temperature of filled polyurethane by 5 and 10°C, respectively.

Table 1. Physical and mechanical properties of composite materials based on polyurethanes

Filler type	Content, %	σ_{Max}, MPa	E, MPa	ε, %
Without filler	0	3.50	10.00	649.5
SiO_2	1.00	3.70	16.90	746.2
	2.50	3.10	8.10	651.0
	5.00	5.10	12.40	565.7
Fe_2O_3	0.50	2.10	9.50	290.8
	1.00	4.50	10.90	883.1
	2.50	2.40	8.10	762.7
Al_2O_3	0.50	2.70	8.90	331.7
	1.00	3.20	11.90	142.3
	2.50	2.70	10.90	898.8
CuO	0.50	2.50	7.90	570.2
	1.00	5.00	11.30	767.3
Detonation diamond	0.25	2.89	9.53	482.9
	0.50	6.16	23.02	832.2
	1.00	7.40	18.94	728.2

It was found that the introduction of detonation diamond unambiguously affects the heat-resistant properties of the filled polyurethane composition as a result of the initiation of secondary synthesis reactions. The introduction of 1% additive was shown to increase the temperature of the dissociation onset by 20°C.

In summary, the results indicate that the introduction of highly dispersed metal oxides and nanodiamonds into polyurethanes leads to improved performance characteristics of the composite materials

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Green technologies for obtaining prolonged dosage forms in supercritical CO_2

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The creation of effective drugs with minimal side effects is an urgent problem of modern pharmaceutical technologies. One of the ways to address this problem is to develop drugs with a ‘controlled-release’ mode of active substance release. Currently, the most common medicines are the dosage forms of the matrix type which present a polymer matrix with the distributed drug substance. Polymer matrix systems (PMS) are able to provide a fixed rate of drug release in a fairly strict range of concentrations in blood. Despite the fact that there are many ways now to obtain prolonged dosage forms, a growing variety of pharmaceutical preparations requires the search for new optimal carriers and ways to create dosage forms of this type. Recently, a possibility of using supercritical carbon dioxide (sc CO_2) as a medium for introducing biologically active substances into polymer matrices for creating prolonged dosage forms, has been studied [1]. There are several benefits of using sc CO_2 as a medium compared to commonly used solvents when drugs are introduced into polymer matrices. First of all, these benefits are: non-toxicity and ecological purity, the possibility of complete removal of CO_2 from the matrix at the end of the process, the absence of the introduced compound solvation by CO_2 molecules. All this taken together facilitates interaction of biological active substances (BAS) with the matrix and provides the subsequent controlled release of the active substance into the medium. It is important that, even the weak equilibrium solubility of the BAS in the medium is sufficient upon impregnation in sc CO_2, which is apparently due to the practical lack of introduced compound aggregation in a weak solvating solvent and the presence of convective fluid flows that ensure effective transfer of the target components to the polymer matrix [2]. The processes using biodegradable and biocompatible polymer matrices for the production of prolonged dosage forms in the sc CO_2 medium, are obviously part of Green chemistry.

In this work, we studied the sc CO_2 impregnation process of biodegradable chitosan-based polysaccharides loaded with substituted arylimidazoles (AI) having antitumor and neuroprotective properties, and established the kinetic laws of the AI diffusion process from the obtained compositions into a model aqueous medium with a pH ~ 1.6, imitating the acidity of gastric juice.

When creating sc CO_2-impregnated prolonged dosage forms based on organo-soluble arylimidazoles, chitosan can be used as a biodegradable polymer matrix provided that the scf impregnation process is carried out in the presence of small amounts of water as a co-solvent, since chitosan has the properties of polycationite and practically does not swell in the medium of sc CO_2. In addition, chitosan can be impregnated with arylimidazole molecules even in the absence of water in the sc CO_2 medium, if the polymer is preliminarily modified with hydrophobic compounds, for example, hydroxycarboxylic acid monomers and polymers. However, the issue of optimization the release rate of arylimidazole molecules into the aqueous medium remains open.

An important result of this study is the establishment of the fact that hydrophobic arylimidazoles are released from chitosan matrices in the form associated with the fragments of the hydrophilic matrix, as evidenced by the intense luminescence of aqueous solutions of arylimidazoles transferred from chitosan matrices to an aqueous medium. This is another fact in favor of using the matrix systems based on chitosan impregnated in sc CO_2 with arylimidazoles for creating prolonged gastro-soluble dosage forms.

Additionally, the effect of water on the release rate of scf introduced arylimidazoles from the matrix into the model medium with $pH = 1.6$ was determined by evaluating the structure of the AIs. It was found that the kinetics of release of AI with a small number of substituents, did not depend on the presence of water in impregnation procedure; however, the presence of water in the sc reactor significantly slowed down the release rate of AIs with a sufficiently bulk structure from the matrix into the buffer solution after the end of the process.

Overall, it was shown for the first time that preliminary solubilization of biologically active molecules (before their scf incorporation into the polymer matrix) can be used as an additional effective way to prolong the action of matrix dosage forms and, contributing to their disaggregation, can apparently increase their biological activity.

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Lignocellulose biomass conversion into fuels and chemicals

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Plant biomass is a prospective resource for fuel and chemical industry which can successfully concur with oil and natural gas [1]. Annually, over 170 bln tons of biomass is formed during the photosynthesis. Lignin, cellulose and hemicelluloses are the main biomass components which compose over 80% of total biomass. Only 3–4% of the plant biopolymers are used for food and non-food industries [2]. Thus, these compounds can be considered as the prospective renewable resource for the production of fuels and chemicals. The processing of biomass polymers using supercritical fluids, green-solvents and highly selective catalysts is strictly in accordance with the principles of ‘green chemistry’ [3].

The primary step in the conversion of cellulose and hemicelluloses is their hydrolysis aimed at the formation of monomers (glucose, fructose) which are the platform to produce different chemicals (i.e. levulinic acid, gamma valerolactone, furfural, etc.). Hydrolysis is typically carried out in the presence of mineral acid or enzymes, however, the recent tendencies in polysaccharides conversion focus on the use of sub- or supercritical water for effective hydrolysis [4, 5]. Sub- and supercritical water is widely used for the conversion of cellulose into glucose and gluconic acid, and for the conversion of hemicelluloses into fructose and furan derivatives [6, 7]. Moreover, sub- and supercritical water allows the lignin to be successfully converted into phenolic compounds [8].

In this work, we describe the conversion of cellulose and hemicelluloses in the medium of supercritical water. The first approach is related to the one-step conversion technique (hydrolytic hydrogenation or hydrogenolysis of polysaccharides into polyols (sorbitol, ethylene glycol, and propylene glycol) using heterogeneous catalysts. By this way, gluconic acid can be also obtained using different oxidizers. The second method used consists of primarily hydrolysis of polysaccharides and their further hydrogenation into platform chemicals (γ-valerolactone, furfuryl alcohol).

The study of the temperature influence on the cellulose hydrolysis showed that the hydrolysis of amorphous part of cellulose starts at 150–170°C, while the crystalline cellulose is hydrolyzed at 220–250°C. The maximum of glucose yield was observed at 230°C for 60 min. Besides, some glucose destruction (caramelization) was also observed. The same studies for hemicelluloses (xylan) and inulin showed the maximum depolymerisation of xylan at 160°C for 50 min, and for inulin at 150°C for 45 min.

For further experiments, Ru-containing catalysts based on different supports were developed. Hypercrosslinked polystyrene, magnetite, zeolites were used as catalyst supports. Ru loading was varied from 0.5 to 5 wt. %. The synthesized catalysts were tested in the hydrogenolysis of cellulose and inulin, liquid-phase hydrogenation of glucose, furfural, levulinic acid. The studies showed that the polymeric matrix of hypercrosslinked polystyrene was found to be permissive support for Ru nanoparticles in all experiments.

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Supercritical approach to produce liquid fuels from biomass

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Fast depletion of fossil fuel sources as well as the high value of green-hose-gas emissions lead to the development of novel ways for the production of energy and chemicals [1]. Biomass is considered to be one of the most permissive resources for transportation fuels and chemicals as it contains a variety of compounds and is characterized by the high energy content [2]. Catalytic hydroconversion of biomass oxygen-containing components (i.e. hydrodeoxygenation) is considered to be the most optimal way for biofuel production [3]. Typically, hydrodeoxygenation is carried out in the medium of high-boiling hydrocarbons used as a solvent. Due to the high solvent viscosity and low hydrogen solubility, the process requires harsh conditions (temperature of 300–400°C, pressure of 1.0–2.0 MPa) to be used.

Recent trends in deoxygenation focus on the use of hydrogen-free approaches. For these techniques, the supercritical fluids can be applied [4]. In the current work, we describe the conversion of biomass compounds (stearic acid (99%, Chimmedservise, Russia), guaiacol (99%, Acros Organics, Belgium) and anisole (99%, Acros Organics, Belgium)) in hydrogen-free atmosphere. Hexane and the mixture of hexane–propanol-2 were used as supercritical solvents. The process was carried out in the presence of polymer-supported catalysts synthesized by the hydrothermal deposition of transition metals in the polymeric matrix of hypercrosslinked polystyrene (HPS, MN270, Purolight Ltd., UK) [5].

Deoxygenation experiments were performed in a six-cell reactor Parr Series 5000 Multiple Reactor System (Parr Instrument, USA). In a typical experiment, 1 g of the model compound was dissolved in 30 mL of solvent. The mixture was put into the reactor cell and 0.05 g of the catalyst was added. The reactor was sealed and purged with nitrogen three times in order to remove air. Then, the nitrogen pressure was set as 3.0 MPa, and the reactor was heated up to 270°C. After the reaching of the reaction temperature the pressure increased up to 6.8–8.5 MPa depending on the solvent composition. The solvent composition was varied from 0 to 50 vol. % of propanol-2 in n-hexane. The liquid phase was analyzed by GCMS using gaseous chromatograph GC-2010 and mass-spectrometer GCMS-QP2010S (SHIMADZU, Japan).

The influence of the solvent composition on the deoxygenation of the model compound was studied without the catalyst. The results of the experiments showed that the presence of 20 vol. % of propanol-2 in the solvent resulted in the highest conversion rate for all studied compounds. When the propanol-2 content was less than 20 vol. %, the model compound conversion decreased due to the low H-donor content. The increase in the propanol-2 concentration over 20 vol. % did not show any significant increase neither in the conversion degree, nor in the product yield. The analysis of the reaction products showed the preferred formation of the phenolic compounds (phenol and pyrocatechol) for anisole and guaiacol deoxygenation, while in the case of stearic acid, the formation of C_{10}-C_{12} hydrocarbons was observed.

The use of the catalysts synthesized by hydrothermal deposition provided a significant increase in the rate of model compounds conversion. The highest conversion rate for all components was observed while using Ni-containing catalysts. 5%-Ni-HPS was found to allow the highest yield of saturated and cyclic hydrocarbons (mainly, heptadecane, cyclohexane and methylcyclohexane) to be formed during deoxygenation of stearic acid, anisole and guaiacol, respectively. Moreover, trace amount of alcohols (stearyl alcohol and cyclohexanol) (up to 0.5%) was formed in the presence of this catalyst.

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Disposal of industrial waste and wastewater using supercritical fluid media

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Waste disposal is known to be one of the serious problems of chemical production facilities. Currently, modern methods of waste disposal (thermal disposal, burial, etc.) are not always effective. Further research of new ways of treating organic waste is an important scientific and technical task. In this context, an oxidation technology carried out in an aqueous medium under supercritical fluid conditions, is one of the promising and environmentally friendly methods for treating industrial and household waste. Basically, oxidation processes in a supercritical aqueous medium occur with the formation of either carbon dioxide and water for hydrocarbon compounds, or with the formation of nitrogen and nitrogen peroxide for nitrogen-containing compounds [1].

It is also worth noting that a large portion of chemical waste products are aqueous solutions of organic and inorganic compounds which contain valuable components that are irretrievably lost in the process of cleaning and disposal. The economic costs of the enterprise, along with environmental problems, determine the impossibility of an effective and cost-effective approach to the allocation of valuable components from wastewater and, therefore, this step is not included in technological scheme of industrial production [2].

In the course of experimental work, the authors studied the process of supercritical aqueous oxidation of an aqueous solution of a molybdenum-containing water runoff, with Mo concentration of 5%, in the temperature range $T = 673–873$ K, $P = 25$ MPa, with an excess of oxygen of 1.0–5.5, which served as an oxidizing agent. A significant decrease was found in the value of the qualitative indicator of water purity – chemical oxygen demand (COD) for the obtained reaction product in comparison with the COD of the initial water runoff sample [3].

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Catalytic pyrolysis of crosslinked polymers as a method for solid domestic waste disposal

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Nowadays, polyethylene composes over 70% of global market of plastics. It is a widely spread polymer because it has low cost and can be easily used in industry. To improve the technological properties and obtain thermoreactivity, polyethylene can be crosslinked. Crosslinked polyethylene is used for the production of cables, plumbing tubes and fittings [1, 2]. Currently, the wastes formed from crosslinked polyethylene reach over 100 000 ton per year [3]. At the same time, thermal and chemical stability of the crosslinked polyethylene leads to the difficulties in the waste utilization. At present, such polymeric wastes are burned or dumped [4]. The existing ways to utilize the crosslinked polyethylene are based on thermal or catalytic cracking resulting in the formation of liquid products [2]. Another method is the use of supercritical fluids for the destruction of the polymer [5]. However, these methods are ineffective due to the low productiveness.

In this work, we describe the conversion of crosslinked polyethylene using pyrolysis method to produce valuable gases and liquids. Crosslinked polyethylene thermal destruction was studied using a laboratory set-up for pyrolysis in the temperature range of 450–550°C. The kinetics of polymer decomposition was studied by thermogravimetry.

Crosslinked polyethylene showed high heat resistance up to the temperature of 400°C. To this end, the temperature range of 430–500°C was used to characterize the full loss of the sample weight. According to thermogravimetric data, the decomposition process proceeds in a single stage and includes a large number of reactions such as cyclization, dehydrogenation, and others. Thus, to produce the target product of polymer pyrolysis, the technological parameters (temperature, atmosphere) and catalysts are needed to be examined and evaluted.

The process of pyrolysis of the crosslinked polymer in a fixed-bed metal reactor was investigated. The influence of the process temperature on the yield of solid, liquid, and gaseous pyrolysis products was studied. The temperature of 450°C is a minimal temperature for decomposition of the crosslinked polyethylene. The solid residue yield for this temperature was found to be 43 wt. %. The solid residue was revealed to be composed of the nondestructured polymer. The yields of gaseous and liquid products were 11.5 and 45 wt. %, respectively.

The optimal process temperature was 500°C. At this temperature, the yields of liquid and gaseous products were 85.0 and 12.5 wt. %, respectively. Samples of the crosslinked polyethylene decomposed almost completely. The amount of carbon-containing residue was 3.5% by weight. The increase in temperature led to a slight decrease in the yield of liquid products and to an increase in the yield of gaseous products, but their total yield was unchanged.

For gaseous products, a qualitative and quantitative composition was determined. The main components of the pyrolysis gas were found to be hydrocarbons C_1–C_4. Moreover, the increase in temperature from 450 up to 500°C increases the yield of hydrocarbons by the factor of 4. The further increase in temperature led to the increase in methane, ethane and ethylene yield by 24, 14 and 36 vol. % respectively. The calorific value of pyrolysis gas obtained at the temperature of 500°C was 17 MJ/m^3. Thus, the pyrolysis process can be considered as a promising approach for disposal of crosslinked polyethylene wastes with the concurrent production of liquid hydrocarbons and combustible gases.

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Assessment of technologies for recycling energy-saturated materials

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The development of resource-efficient, environmentally sound technologies for the recycling of energy-saturated materials (EM) is receiving increasing attention, taking into account the ever-increasing importance of environmental safety at industrial facilities.

The progress of various approaches for disposal of EM enables selection of the most appropriate disposal method for each particular case. However, the technologies used must meet the best available criteria, which is a subject of ongoing discussions.

We have developed a versatile system of evaluation of EM disposal technologies, which allows to fully implement modern requirements in the field of environmental safety and resource saving technologies and takes into account the comprehensive assessment of the economic efficiency indicator of technologies (‘available’ technologies), as well as the ‘qualitative’ (environmental) indicator characterizing the impact on environmental objects (‘best’ technologies) [1, 2].

The value of the economic indicator is significantly influenced by the amount and cost of return resources generated by the disposal of EM.

After the environmental and economic indicators have been determined, the task of assigning the method of recycling EM to the best available is solved by using vector optimization elements.

Taking into account the amount of EM to be disposed off, three evaluation variants are provided, characterized by decomposition and, hence, complexity of using a mathematical apparatus, in particular, assignment of coefficients of relative importance to compared methods.

Risk impacts are also taken into account in the choice of EM disposal technologies and calculations are made in conditions of uncertainty. In addition, the change in costs depending on the number of products to be disposed off is taken into consideration.

The data obtained from the comparative analysis of various EM disposal procedures suggest that only technologies with a high level of resource saving potential can meet environmental, economic and technological requirements.

In conclusion, the evaluation of EM disposal technologies makes it possible to make the most appropriate decision on their use on an industrial scale, taking into account the tightening of the requirements of the legislation in the field of environmental protection.

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Thermocatalytic processing of wood waste

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The global annual growth of biomass is about 170 billion tons. This makes it possible to consider biomass as the source for the production of energy [1]. The use of plant biomass as a fuel and energy resource can help to decrease the emission of CO_2 to the atmosphere, as well as to reduce the negative impact on the environment by reducing the amount of unused waste.

According to the decree of the Government of the Russian Federation dated January 25 2018 No. 84-R, over 200 million cubic meters of waste of various types of wood is generated annually [2]. Thus, the development of processes for conversion of lignocellulose biomass into fuel and chemicals is an important task for research and practical application.

The complex chemical composition of lignocellulose biomass makes it difficult to obtain target fuels and chemicals with high yield and quality. The difference in chemical composition and structure in lignin, hemicellulose and cellulose is responsible for their significantly different reactivity [3, 4]. Currently, thermal processing technologies are effective methods for conversion of solid lignin-containing waste to obtain products valuable for industry [5]. The most effective and easily industrially feasible method for plant biomass conversion is pyrolysis [6], which allows to obtain gaseous, liquid and solid carbon-containing products.

A detailed study of the process of pyrolysis of wood waste using real samples of plant biomass is a relevant task. In this work, we studied the pyrolysis process of pine and birch sawdust with the moisture content of 3.1–3.2 wt. % and ash content of 0.1–0.4 wt. %. The sawdust particles with the mean diameter of 0.25–1 mm, 1–2 mm, and 2–3 mm were used. Thermogravimetric study of the wood samples was performed to estimate the optimal temperature range and possible destruction pathways.

The analysis of thermograms showed that the studied wood samples had the differences in the thermal destruction in the temperature range of 200–400°C. Such variations can be explained by the difference in the composition of hardwood and softwood plants, i.e. the content of polyoses, hemicelluloses, cellulose, and lignin [1]. According to the results obtained in the study, 250–450°C is the temperature range corresponding to the decomposion of main biomass components – extractives, polyoses, hemicelluloses and cellulose.

Consequently, the temperature range of 400–500°C was chosen for the pyrolysis experiments.

The increase in temperature led to an increase in the yield of gaseous products for all studied samples, meanwhile the yield of solid residue decreased. The maximum yield of liquid pyrolysis products was observed at 450°C for birch sawdust, and at 500°C for pine sawdust. The highest yield and maximum of calorific value of gaseous products was observed at 450°C for both samples. Noteworthy, the calorific value of gaseous products obtained from birch sawdust was higher than those obtained from pine sawdust. This may be connected with the higher content of ethane and lower content of hydrogen in the gaseous mixture for the studied samples.

The study of the composition of liquid products was performed using mass-spectrometry. It was found that the volatile products of the pyrolysis were the same for both studied samples and had the molecular weight of 80–90 r.a.w. The specific surface area of the initial samples of birch and pine wood waste was 9.3 and 8.5 m^2/g, respectively. The specific surface area of solid carbon pyrolysis residues for hardwoods increased by 2.4 times and for softwoods by 2.1 times, respectively, and reached values of 22.3 and 17.9 m^2/g.

The kinetic parameters of the pyrolysis process were obtained. The activation energies of the pyrolysis process for pine and birch sawdust samples were found to be 119.3 and 128.2 kJ/mol, respectively.

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Effect of copper salt on white phosphorus biodegradation

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We have been carefully studying microbial biodegradation of one of the most toxic substances – white phosphorus and present here another example that confirms our previous results [1].

White phosphorus is known to interact with ions of divalent copper even at room temperature, for this reason, we chose the Pridham-Gottlieb medium containing copper sulfate for our studies. The addition of an emulsion of white phosphorus to the medium led to the formation of a black color precipitate that indicated an occurrence of a chemical reaction. Thus, the growth of microorganisms could have taken place in the presence of fairly low levels of white phosphorus, which made our results less reliable. Therefore, in the present study, we carried out a further modification of the Pridham-Gottlieb nutrient growth medium, excluding from it not only phosphates as a source of phosphorus but also copper sulfate [2].

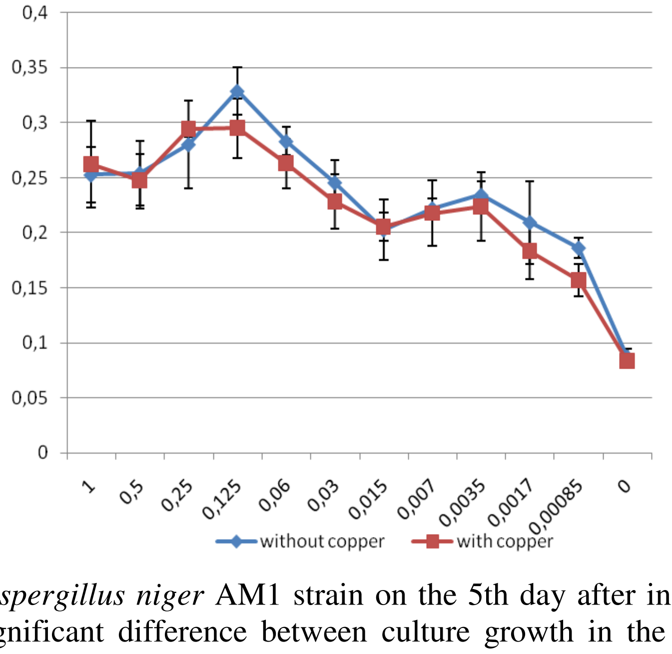

Fig. 1. Growth of *Aspergillus niger* AM1 strain on the 5th day after inoculation. As can be seen, there is no significant difference between culture growth in the medium comprising copper and medium without copper. X-axis - concentration (%) of white phosphorus; Y-axis - optical density (OD) at λ = 550 nm.

It was shown, that exclusion of copper sulfate from the composition of the nutrient growth medium with white phosphorus did not prevent the growth of fungi. In addition, the white phosphorus introduced into the medium did not form a precipitate but remained intact under these conditions for a longer period. This fact is a valuable argument in favor of biodegradation and can be used in practice for microbial detoxification of white phosphorus. However, a higher resistance of the *A.niger* AM1 strain in comparison to the other strains of the All-Russian Collection of Microorganisms (ARCM) was observed only when the medium contained copper. Hence, *A. niger* AM1 strain is the most resistant to the toxic products resulting from the reaction of white phosphorus with Cu^{2+}.

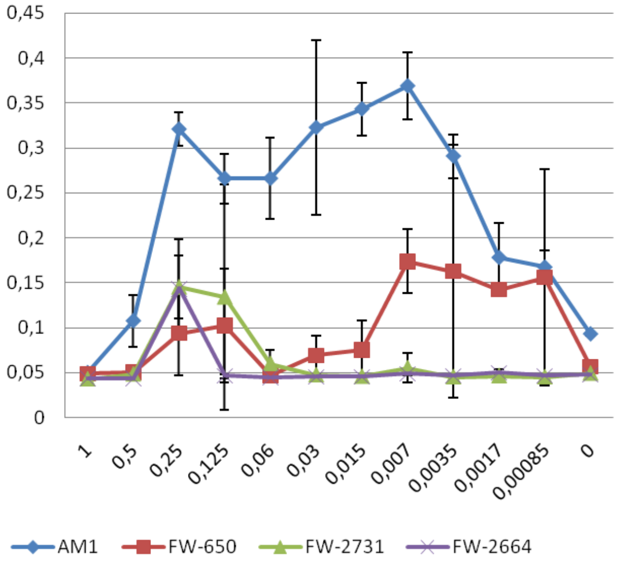

Fig. 2. Growth of different *A. niger* strains in a phosphate-deficient medium containing white phosphorus on the 3rd day of cultivation. X-axis - concentration (%) of white phosphorus; Y-axis - optical density (OD) at λ = 550 nm.

Additionally, we compared the white phosphorus resistance of both *A. niger* strains AM1 and AM2 with that of three strains obtained from the All-Russian Collection of Microorganisms (strains: FW-650, FW-2664, and FW-2731), as well as four different bacterial species [2]. Though the highest resistance was observed for the AM1 strain, the three other strains of *A. niger* obtained from the ARCM also showed higher resistance to white phosphorus than the bacteria.

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Mineralogical and geochemical analysis of soils at municipal solid waste recycling plant (Yanino)

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Population growth and urbanization has led to a sharp increase in the volume of generated municipal solid waste (MSW). Currently, the problem of disposal and storage of solid household wastes is the most urgent for any government in the modern world. The processed products are usually stored in the open air exposing weathering processes resulting in mechanical, chemical and biological decomposition with chemical elements and their compounds migrating to the surrounding territories. In many cases, the processes of solid waste removal and recycling have their own specifics in many large cities of Russia [1].

Waste-recycling plant MPBO-2 is located in the northeast part of St. Petersburg (Russia). The plant is a regional operator of the solid waste sector of St. Petersburg and the surrounding areas. Today, the main waste treatment method used at the plant is a technology of aerobic biothermal composting (biocomposting) [2]. Due to the unstructured scheme of waste collection in the city (unsorted waste collection), a certain amount of uncompostible fractions is present in the incoming wastes (plastics, glass, metals, construction and demolition waste, dirt, rocks, debris), therefore, the produced composts cannot be used for agricultural purposes.

The processed and crushed (to a fraction of 2 mm) material is disposed on the territory of the plant and polygons for solid wastes. The environmental factors trigger soil formation processes in the ballast. The components that make up the ballast interact with each other and the environment. The purpose of this study was to identify mineral and chemical composition of soils in the proximity of the waste recycling plant for the initial evaluation of ecological state of the territory.

The sampling area was located on territory of the plant. The study zone was divided into two areas: Old ballast – dense soils, New – loose soils. Samples were taken according to anthropogenic relief (lowland, slope, peak) of the territory. 14 soil samples were collected at the end of October 2019. The soils samples were taken at the depth of 10–15 cm from the surface. The weight of each sample was approximately 1000–1500 g. Relevant soil characteristics (color, structure, texture, amount of organic material, sampling location) were described in the field documentation and in the laboratory conditions before and after drying and sieving. Approximately 500 g of each soil sample in laboratory conditions was separated in a sealed bag for mercury analysis. The other part of soil samples was air-dried at room temperature after collection. The analysis of the mercury content in the samples was performed by using PA-915 + mercury analyzer, the PIRO-915 - pyrolysis unit and special software.

First, the analyses were arranged using classification based on color of soils (Gray, Brown and Black soils). According to particle size analysis in soils classified by color, different particle size distribution was observed. Small fractions (0.05–0.1 mm) predominated in Gray soils. Black soils mostly had almost uniform particle size distribution, while in Brown, 0.25–0.5 mm fractions prevailed. All types of soils also contained a large content of 2 mm fraction.

Mineralogical studies showed that Old soil samples were rich in mineral component. New soil samples were highly enriched with inclusions of technogenic material (plastics, glasses, metals, etc.). All soil samples (and all fractions) were analyzed using XRF (portable analyzer) and EDX spectroscopy. New soils were enriched with an organic component (CHN analysis), heavy metals (mercury, lead, zinc, copper, chromium). Gray (Old) soils were more clayey and were characterized by increased contents of heavy metals. Summing up the results, we can say that the components of the newly formed compost have been actively migrating to the environment, leaving their primary source. It is noteworthy that among the most migratory elements are the elements of the first hazard class (mercury, lead, zinc) and the second hazard class (copper, chromium).

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Socioeconomic aspect of risks of mycoses in grain production in Russia

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Mycoses are fungi that parasitize living organisms and cause diseases of humans, animals and plants. When plants are damaged, in addition to crop losses, mycoses release toxins into plant tissues and contaminate grain, which becomes dangerous to human and animal health. Toxins are accumulated in grain in the field, for example, most often cereal crops are attacked by facultative parasites from the genus *Fusarium.* Thus, during the years of epiphytotic spread of fusarium head blight in the Krasnodar Territory, the risks of grain contaminated with toxins in some years exceeded 4 million tons. Such grain becomes dangerous for use both for humans and animals [1].

Mycoses are the subject of research in medicine (in medical mycology) in zootechnics (veterinary mycology), in phytosanitary (phytopathology). In fact, the problem of mycoses is a general biological issue requiring not only detailed scientific research, but also demanding socioeconomic and practical solutions in the country.

The peculiarities of the development and spread of mycoses in the conditions of reforming the agrarian sector in Russia are associated with the following factors:

- the diversity of agricultural production with private ownership of land, with the basic economic law of a market economy - obtaining maximum profit;
- instability of weather factors associated with human production activities, manifested in chemical and biological pollution of the natural environment;
- insufficient development of innovative technologies for the production of crop products, with narrowly specialized crop rotations, depleting soil fertility technologies, insufficient provision of rural commodity producers with special varieties resistant to mycoses, low development of the latest achievements in information technologies, precision farming, biological and chemical plant protection.

We have conducted research on the danger of mycoses and possible ways to reduce this hazard taking into account the abovementioned factors and tasks of effective risk management of the danger of mycoses in grain production. We have also considered the progressive requirements for ensuring the parameters of the new Doctrine of Food Security of Russia, focused on achieving levels of self-provision of cereal products of at least 95%.

We have studied the lists and levels of distribution and harmfulness of mycoses species in connection with the risk of reducing the productivity of ecosystems of grain crops, in the administrative-territorial aspect, in terms of quantitative indicators of risks of danger of epiphytoties, differentiated from local (within an agricultural enterprise) to municipal (within a settlement), regional (federal level) and state (country as a whole).

Taking into account the areas of distribution of mycoses in the country and their harmfulness, the potential of danger in the territorial aspect at the federal level was determined for the three most common types of mycoses in the country. The estimated risk factors are as follows: septoria leaf spot – 5241 thousand hectares (by 30%); powdery mildew –3340 hectares (by 20%); leaf rust – 1926 thousand hectares (by 17%). The weighted average risk indicator of all three types of mycoses – 24.03%, i.e. 6.5 hundred kilograms per hectare (the average yield of grain crops in the country is 27 hundred kilograms per hectare), which corresponds to 6707 rubles/ha (when the prime cost is 878 rubles/center).

The spread of other mycoses at the municipal and regional territorial levels was observed in smaller areas and with less dangerous species. Taking into account the territorial distribution of mycoses, proposals were justified for cost-effective containment of the epiphytotic danger of affecting strategically important cereals crops based on improved methods of phytosanitary monitoring and progressive systems of protective measures with the use of chemical plant protection agents, effective and safe for useful fauna and flora [2, 3], along with using information technology based on the use of fungicides in the fight against mycoses. The effectiveness of all the proposed protective measures has been determined.

The total saved crop in the area treated with fungicides against mycosis in the country on the area of 15688 thousand hectares amounted to 86 billion rubles; with the cost of protective measures 30 billion rubles (net income – 56 billion rubles), the level of profitability 152.66%, which characterizes the validity of the system of protective measures applied in the country.

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Development of scientific and methodological approaches to analysis of performance of scientific and technical programs

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Currently, the complex of national strategic tasks of the Russian Federation is being implemented through scientific and technological programs [1]. There is a need to collect and systematize information on the implementation of program activities, organize an independent assessment of indicators of their relevance and practical feasibility, and contribute to the solution of the main tasks of the programs.

A series of fundamental and applied scientific results of interdisciplinary research were obtained within the framework of one of the programs [2]. The analysis of one of the program's (hereinafter referred to as Program) results has been carried out and the shortcomings of existing expert approaches to the analysis of scientific research are revealed. To begin with, a quantitative approach has been used, which is based on the numerical measurement of indicators. However, it is practically impossible to assign a priori quantitative assessment scales so that they would adequately express poorly formalized properties of scientific research and could be equally understood by different people. Moreover, the use of ordinal scales that have different numerical equivalents leads to completely different results. To process such numerical estimates, averaging convolutions have been used.

Scientometric approaches also have a number of disadvantages. The number of citations does not reflect the quality of the research, i.e. if the result is criticized, the indicators can also be artificially high. In addition, citation depends on the specific subject of the scientific field. If a result is important, but difficult enough to understand, then citations can be delayed for many years. Thus, the analysis of scientific research results belongs to the so-called poorly formalized and poorly structured decision-making problems where qualitative characteristics prevail. When using quantitative methods with many criteria convolved with weighting coefficients, it is impossible to restore the initial data according to the aggregated criteria which means that it is virtually impossible to explain the solutions obtained.

We have proposed to use the methods of verbal analysis of decisions that are free from the indicated drawbacks [3]. At the first stage, the most promising results have been identified from the set of generalized results of the Program analyzed. Three quality criteria have been used. The construction of criterion scales is considered as an ordinal classification problem where the classifications are combinations of grades of assessments of the initial criteria, and the classes of solutions are grades of assessments of the composite performance criterion. Thus, each grade of assessments on the scale of the composite criterion corresponds to a certain combination of grades of assessments of the initial criteria. The aggregation of the gradations of the initial criteria is estimated into a small number of verbal ordinal scales of the composite criterion characterizing the performance was carried out.

A multi-criteria express assessment of the Program results has been carried out. Using the developed decision rules for classification, an ordinal classification has been performed. The results obtained from the high performance class have been used for the subsequent more detailed examination. A roster of experts is recommended to be formed based on their competence. Further, expertise and multi-criteria analysis have been carried out. The task of ordering the results of the Program according to the criteria of relevance and feasibility is solved. The analysis of the ranking of results shows that the ranking of results in terms of relative proximity to the best reference situation and the final ranking which combines the three rankings, almost completely coincide. This fact testifies to good consistency of the rankings constructed.

In conclusion, the developed toolkit can be used to conduct a comprehensive examination of the results of scientific and technical activities, identifying promising areas and technologies [4]. According to the results of the examination, it can be noted that the demand for the results of the Program is rather high, and at the same time, the level of assessments characterizing the readiness for implementation of the results can’t be classified as high.

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Chemical safety issues solutions via integration of science and education

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The integration of education and science provides a mutually beneficial combination of the educational process in higher educational institutions and scientific research activities including those in academic institutions. Such an interaction is by no means compulsory, but is a natural interaction of both processes, dictated by the modern needs of the development of society. There are several reasons for this. The educational process must combine the best long-held traditions with the modern trends. It should adequately reflect the latest views, approaches, ideas highlighting natural science picture of the world. At the same time, present-day scientific research requires a steady inflow of young scientists and specialists, students and postgraduates, knowledgeable in modern research methods, familiar with the contemporary tools and technologies in various fields of science and technology.

Chemical safety research is one of the most successful examples of interaction between scientific organizations and higher educational institutes. Many specialized disciplines related to this field of science are currently taught at higher educational institutions and universities, such as: chemical safety, technogenic systems and environmental risk, assessment and forecasting of technological risks, environmental chemistry and ecological expertise. The development of these courses involves lectures and laboratory practicum.

Academic institutions are also involved in chemical safety research. For example, the Semenov Federal Research Center for Chemical Physics of the Russian Academy of Sciences performs the most important research in the field of chemical safety. To begin with, the Center carries out fundamental research to systematize and assess the risk level of toxic substances that may be hazardous to human health and the environment. The researchers use already known and develop new physical and chemical methods for neutralizing and removing toxic contaminants; they are also developing new methods for eliminating the consequences of anthropogenic and technogenic pollution in areas of environmental tenseness. In addition, new materials, substances and methods of analysis are being developed to address the urgent chemical safety issues.

Integrity of educational and scientific research processes includes: attracting students to participate in research and design work; carrying out diploma and course design, educational and industrial practices, targeted training of students and other forms of training.

Structures such as academic and scientific organizations, training and research centers, innovative enterprises should be mentioned as effective forms of integration between scientific research activity and educational process. The general principle of their work is, firstly, the involvement of specialists of scientific institutes, research organizations in the educational process at a higher educational institution or university. At the same time, students get the opportunity to learn about the state-of-the-art achievements in a particular field of knowledge, current research methods, discoveries, names of scientists working on the problems of the modern science. Secondly, practical and laboratory studies within such integration structures encourage students to take an interest in scientific work and provide them with the opportunity to get to know and gain experience with the novel equipment, installations and instruments. Such experience often leads to the organization of scientific cooperation, participation in the preparation of graduate qualification work and postgraduate dissertations and joint project activities.

The report presents specific aspects of the functioning of a number of integrated educational and research structures implementing innovative materials and technologies and combining educational activities and scientific research in a consistent and mutually enriching manner.

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Chemical export support through an environmental management tool: Environmental & Climate Declarations

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In the modern society, environmental and climate declarations are considered and used by producers of chemical products as a voluntary tool to improve their competitiveness in domestic and foreign markets. Currently, the global trend is the sustainable development, including the production of goods and services with a minimal impact on the environment and human health. This concept is documented in the objectives of the Strategic Approach to International Chemicals Management and the UN Sustainable Development Goals. Markets, particularly external ones, are currently in demand for products that have a lower environmental impact, can be recycled, and managed for the rest of their life cycle. Manufacturers can use environmental and climate declarations based on life cycle assessment studies as a tool to demonstrate that their products have lesser environmental impact and lesser negative influence on human health, or that the production processes have been improved.

The information on the environmental impact of goods and services is becoming an essential requirement of modern society and the market. This information is used in various areas of market activity including public and private procurements (e.g. in the EU countries). In order to meet the rising market demands in this area, companies are increasingly required to provide objective and reliable information on the environmental characteristics of their products, so that the consumer can make the correct and justified choice as well as to take full advantage this information on products in his activity.

The priority areas of export activities of the Russian Federation remain to enhance the competitiveness of Russian export products abroad by improving product quality and environmental characteristics, strengthening trade in the regions through the transition to new production and consumption patterns, improving the welfare of the population. The advantages achieved by producers who have registered environmental and climate declarations in terms of intensifying trade, increasing chemical products safety use and the efficiency of production processes, are, in one way or another, in line with the strategic goals of the country. In addition, the application of environmental and climate declarations can help to establish dialogue and increase the level of trust between the regulatory authorities and producers, producers and consumers, by strengthening voluntary initiatives, e.g. in product management and safe use.

As a general rule, the manufacturers or exporters must have at their disposal reliable documentation which would confirm that the exported products have ecological and quality characteristics that meet the requirements of the importing country and, possibly, in some respects leave behind similar products entering the importing country’s market. For example, it will not be possible to import construction materials to the Nordic countries from 2022 January 1, unless a climate declaration is drawn up for these materials, which, in turn, is based on the environmental declaration.

Thus, the environmental and climate declarations propose an additional voluntary mechanism for regulative authorities to encourage companies in sharing information about their products and improving production processes in order to reduce the negative impact of chemical products on human health and environment. This is a good opportunity for industry and business representatives to improve their competitiveness, corporate image, and expand their markets. At the same time, environmental and climate declarations can help consumers make informed choices about products that actually have lesser negative impact on human health and environment.

Prospects for studying tetracycline group antibiotics in the process of their accumulation in soils and translocation into plants

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Since the second half of the XXth century, antibiotics (ABs) have been widely used in various fields of human activities. Both in Russia and in other countries, ABs came into common use not only in medicine, but also in food industry. They are also used in animal and poultry breeding for animal treatment with the purpose of prevention of infectious diseases and as a feed additive. In crop production, ABs are applied as part of fungicidal and insecticidal agents [1].

It should be emphasized that antibiotics are excreted from human and animal organisms into environment up to 90% unchanged or in the form of their metabolites. ABs get into soil with manure used as organic fertilizer, as well as with the effluents of livestock complexes. In total, the AB content in soils of a number of countries reaches 900–1500 mg/kg.

In addition, antibiotics enter surface waters with runoffs from farmlands, waste water from livestock complexes and housing and communal services. Concentrations of various groups of ABs found in runoff and surface water in Asia, Europe and the United States vary in the range from 8 ng/l to 11 mg/l [1–3].

There is growing concern about the spread of ABs in the environment as well as their absorption and accumulation in crops.

At the moment, the content of residual amounts of antibiotic drugs both in the environment and in plant products is neither taken into account nor regulated which in turn can negatively affect human health, especially at raw food eating [4].

In this regard, the study of migration routes and mechanisms of antibiotics accumulation from soil through the root system to agricultural plants is a priority for hygienic research.

Analysis of the literature data allowed us to identify the most commonly used types of ABs in animal breeding and veterinary medicine: tetracycline group, macrolides, penicillin group, and levomycetin group of ABs (chloramphenicol).

Tetracycline compounds are one of the most widely used antibiotics in veterinary medicine. In Europe, they were the most consumed veterinary ABs in 2014 accounting for 33.4% of total sales [5].

From 65 to 90% of tetracycline group antibiotics are excreted from animal’s organism with urine and feces based on the physical and chemical properties, on characteristics of absorption and distribution thereof. The stability and accumulation of tetracyclines in the environment depends upon a number of factors and has been investigated in a number of studies [5, 6]. For example, the sorption capacity of tetracyclines in soils is affected by the pH of the medium, ion exchange capacity, organic matter content, soil type and the synergistic effect of other pollutants such as heavy metals. As a result of these factors, the decay time of the antibiotic can vary from 8 to 180 days [6]. Every year, AB groups of tetracyclines are locally detected in soils at concentrations up to 300–500 mg/kg.

So far, most studies aimed at studying the effects of antibiotics on agricultural plants have been focused on studying the phytotoxic effect, the effect of ABs on the growth and development of individual parts (roots, leaves, stems) and on the entire plant as a whole. There is a limited number of studies that assess the potential absorption and accumulation of antibiotics in agricultural plants [6]. It was found in these studies that the AB of tetracycline group accumulated in the following crops and concentrations (in different parts, roots, leaves, stems): spinach – from 4.8 to 6.3 ng/g; carrots – 23.0 ng/g; lettuce – 7.2 ng/g; celery – from 3.10 to 12.6 ng/g; coriander – up to 532 ng/g; celery cabbage – from 6 to 10 ng/g; corn – 6.6 ng/g; radish – up to 57 ng/g. It should be noted that most of these values exceed the permissible dose of the residual content of the AB tetracycline group in meat and dairy products (10 ng/g) [4].

Thus, one of the primary tasks for our research is to provide an experimental substantiation of cumulative effect of Abs of the tetracycline group on soils of agricultural lands distributed in Russia along with their translocational transition to plants.

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Synthesis and characterization of Bi_2O_3/Bi_2SiO_5 heterojunction photocatalysts

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The phenomenon of photocatalysis is currently actively used in chemical industry since it accelerates a broad variety of reactions of oxidation, reduction, polymerization, hydrogenation and dehydrogenation, deposition of metals, etc. Heterogeneous photocatalysis has become one of the most promising methods of water treatment over the past two decades due to effective non selective decomposition of organic pollutants to form nontoxic products.

Bismuth silicate (Bi_2SiO_5) has been applied in the field of photocatalysis and has lots of advantages, such as non-toxicity, chemical stability and excellent photocatalytic activity [1–3]. Recently, Bi_2O_3/Bi_2SiO_5 heterojunction photocatalysts were prepared by a facile one-step calcination method [4]. The Bi_2O_3/Bi_2SiO_5 heterojunction photocatalysts exhibited high photocatalytic activity in degradation of organic pollutants under simulated sunlight irradiation.

In this work, nine samples of Bi_2O_3/Bi_2SiO_5 heterojunction photocatalysts with SiO_2 mass fraction of 1%, 3%, 5%, 10%, 15% 20%, 25%, 30%, and 50% were obtained using the method proposed in [4]. Amorphous silicon dioxide used for synthesis of catalysts was obtained from rice husks according to [5].

Oxidative destruction of methyl orange was carried out in UV and visible (VIS) spectrum. The catalyst concentration was 1.0 $g{\cdot}L^{-1}$. Concentration of methyl orange was 10 $mg{\cdot}L^{-1}$.

Photocatalytic degradation in UV spectrum was performed in a quartz cell with a volume of 100 ml into which 50 ml of methyl orange and catalyst were placed. Irradiation source was a UV irradiator of 100P/F (maximum radiation with a wavelength of 365 nm). The solution was irradiated with a constant stirring on a magnetic stirrer (650 rpm) for 3 h. Sunlight photocatalytic degradation (VIS spectrum) of methyl orange was carried out in a simple photoreactor. The reactor was a laboratory glass bottle of 50 ml capacity. The photocatalytic degradation was carried out under the same conditions on sunny days between 9 a.m. and 4 p.m. in November for 3 h. Under the similar conditions, a control experiment without catalyst was conducted.

The catalysts showed low photocatalytic activity in the visible region of the spectrum in the methyl orange oxidation reaction. The degree of destruction of methyl orange in the solution after oxidation for 3 h did not exceed 26%. In general, it is noteworthy that destruction of methyl orange with the use of photocatalysts in the visible region was unstable.

Changing conditions of photocatalytic oxidation (adding H_2O_2, changing the pH of the medium to 3) did not affect the destruction of methyl orange.

In conclusion, UV irradiation significantly affected photocatalytic activity of Bi_2O_3/Bi_2SiO_5 heterojunction photocatalysts. Catalytic activity of the samples in methyl orange oxidation reaction depended on the proportion of amorphous silicon dioxide used in its preparation. The results of the study showed that the optimal SiO_2 content in the synthesis of catalysts is 15–20%. The degree of degradation of methyl orange in the presence of such photocatalysts was 83–84%. A decrease or increase of the SiO_2 amount in the samples led to a decrease in photocatalytic activity.

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Research and assessment of pollution of obsolete industrial areas

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At present, the chemical enterprises founded in the 1950s are characterized by excessive wear of facilities and buildings, obsolete equipment, highly contaminated solid waste sites and accumulation of liquid effluents. In Russia, more than 10,000 potentially hazardous chemical sites constitute a part of different branches of industry. In addition, 50% of them are located in the residential areas with a total population of over 100,000 people.

Environmental safety of vacated industrial territories re-use is guaranteed by both waste management, namely dismantling and liquidation methods of capital construction projects, and technologies for land remediation.

The selection of remediation technologies is based on the results of geo-ecological analysis (research).

Contamination of obsolete production facilities with hazardous pollutants remained from outdated technological processes takes place on the territory of the main production cycle, storage areas of raw materials and end-products. As a rule, it is due to excess and emergency discharges (spills) when loading raw materials.

A possibility of new building activity on the territory of former industrial areas is examined after evaluating soil chemical contamination based on quantitative chemical analysis. In some cases, additional studies of groundwater and soil air samples are required taken from the area where high contamination is suspected. The assessment should be based on a list of indicators that characterize the damage and contamination degrees.

The physical and chemical properties of chemical compounds are studied in contaminated soil samples. The depth of contamination of soil layer is determined taking into account the intensity and duration of the expected contamination, the permeability of the soil layer, and the conditions affecting the processes of pollution transformation.

In order to obtain reliable results, it is necessary to conduct sample preparation and select quantitative analysis procedures. The difficulty of ranking potentially contaminated sites by hazard level is associated with the lack of standards for the permissible level of contamination for many organic compounds. If there the established standard for the pollutant permissible concentration is absent, then, the contamination level is compared to the value of the pollutant concentration on the adjacent territory with the absence of negative impact on the environment. The experience of countries that have solved the problem of former industrial areas development suggests using soil pollution assessment standards that include information on how the territory has been reused after the removal of old industrial facilities.

Restoration of territories during the removal of chemical industrial facilities is a complex and multi-stage process that considers public opinions and requires interaction with regulatory and supervisory authorities, enterprises, investors and other interested parties.

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Potential application of bentonite clays of the Republic of Tatarstan and the Orenburg region for safety barrier materials

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The safety barrier system which is installed on the way of the ionizing radiation and radioactive substances migrating into the environment must ensure the long-term safety when applied for radioactive waste disposal. Most national concepts for the radioactive waste isolation and storage consider the application of the bentonite clay as a useful material for engineered barriers [1]. An essential property of bentonite is its high sorption capability towards a wide range of radionuclides [2, 3]. The largest in Russia bentonite clay deposits are located in the Republic of Tatarstan and the Orenburg region with their total deposit reserves up to 70 million tons.

In this work, sorption characteristics of the bentonite clay samples obtained from the Tatarstan and the Orenburg region deposits were evaluated with regard to ^{90}Sr, ^{137}Cs, ^{233}U, and ^{238}Pu. In the sorption experiments, the high recovery rate of strontium, cesium, and plutonium radionuclides from aqueous solutions was observed for all clay samples investigated. Cesium and plutonium were almost entirely adsorbed by the samples studied; the efficiency of sorption exceeded 99%. The bentonite clays adsorbed up to 82-93% of the strontium content in the feed solution. The bentonite samples from the Republic of Tatarstan deposits exhibited the high sorption capacity towards uranium (the efficiency of sorption reached 70-88%), whereas the bentonite clay from the Orenburg region deposits adsorbed merely 20-48% of uranium.

Overall, the experimental results indicate that the bentonite clays occurring in the Republic of Tatarstan and the Orenburg region deposits reveal rather high anti-migration characteristics towards the fission products and actinides and, thus, could be used as versatile components of the protective barrier materials.

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Potential sources of environmental tenseness in Arctic areas of Central Siberia

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The Arctic area of the Central Siberia is a territory of significant anthropogenic impact.

For several years, as a part of the implementation of Russian government projects, environmental monitoring studies were conducted in the lower reaches of the Yenisei River, belonging to the Arctic area of the Krasnoyarsk Region.

The purpose of our research was to identify potential sources of pollution and to assess environmental tenseness in the area under study.

The studies were conducted year-round during 2006–2018.

Analysis was carried out on the following samples: water taken from aqueous sources of different origin (groundwater, surface water bodies - rivers, streams, and swamps), atmospheric precipitation (snow, rain), soil, bottom sediments and the most common aquatic and terrestrial plants. The following methods were used to identify pollutants: inductively coupled plasma mass spectrometry for full-element analysis; gamma spectrometry and low-background alpha-beta spectrometry to identify radionuclides; ion liquid chromatography to determine the ionic composition of water bodies; chromatography-mass spectrometry to estimate levels of phenol and its derivatives; and gas chromatography to identify oil and related oil products.

It was found out that the main sources of pollution affecting the ecosystem of the Yenisei River are industrial wastes, as well as abandoned production facilities of enterprises of various types (those of Ministry of Defense of the Russian Federation, Mining and Smelting Company Norilsk Nickel, facilities of the Oil and Gas Industry, mining and processing enterprises, as well as transport facilities).

Accordingly, in the case of the wood processing industry, the primary source of pollution to be considered is wood waste. In addition, the decomposition of wood which has grown in obviously polluted areas causes metals to be released into soil substrates, which are found in all the components of the plant material. At the same time, the patterns of the intake and (or) formation of pollutants, as well as their distribution, largely depend on environmental conditions.

In bottom sediments, the distribution of radionuclides released into the ecosystem as a result of the activities of the nuclear fuel cycle facilities is affected by the geochemical composition of the bottom sediments. In addition, the ability of radionuclides to accumulate due to physical and chemical processes, as well as physicochemical properties of radionuclides and their ability to transform from one degree of oxidation to another with the changing environmental parameters have been determined.

Heavy metals belonging the first and second toxicity classes (Hg, Pb, Cd) were found to significantly exceed the maximum permissible concentration (1.5–5-fold increase with respect to the maximum permissible concentration) in the samples of snow cover, in some water sources, and plants. The potential source of pollution may be due to the activities of MSC Norilsknickel.

In addition, in the soil samples and water from water sources (groundwater and surface water bodies), the content of oil and oil products was found to exceed the maximum permissible concentration by up to 10 times.

Thus, in the course of the performed studies, potential sources of the environmental pollution in the Arctic area of the lower reaches of the Yenisei River have been identified.

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Protection of crops from herbicide residues in soils using antidotes

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Currently, weeds head the list of the factors that negatively affect the crop yield in our country. Herbicides are the only real tool for agricultural plant protection from weeds at the industrial scale. However, it should be noted that herbicides do not display specificity towards different kinds of weeds. Therefore, improving the selectivity of their action is one of the relevant issues. One of the ways to reach this goal is to protect cultivated plants from toxic effect of herbicides. Herbicides residues in soil can cause irreparable damage to the plants which will be grown on the field next year and, in some cases, even later. This limitation can be overcome by reducing the concentration of phytotoxic herbicides in soil (intensification of decomposition, sorption) and by application of antidotes (safeners, resistance inducers) which can remove or reduce the toxic effect of herbicides on a cultivated plant [1].

In recent years, the problem of soil pollution with the residues of highly active herbicides has reached a menacing proportion. This problem is getting even worse since the yield depression occurs unnoticeably, without showing the real cause. We can cope with this situation by improving the culture of application of herbicides and by using special techniques to protect crop from herbicides residues in soil. One of the key elements in the related technologies is the application of antidotes that protect the crops from the effect of phytotoxicants. The functioning mechanisms of antidotes have been unknown until recently and their elucidation is connected with the recent advances in molecular biology. We believe that we have accumulated enough material to present a complex analysis of the problem of relationship between antidotes and popular herbicides such as sulfonylureas to a wide range of specialists in agrochemistry.

In addition, the results of our own investigations devoted to the creation of new efficient antidotes to sulfonylureas are discussed. The protection of seeds from the sulfonylurea residues in soil is undoubtedly an urgent task. This problem is of special significance in our country due to the relatively low farming standards, especially towards the use of plant protection agents. The promising results for addressing this problem can be achieved by presowing treatment of seeds with antidotes. The available information indicated that the highest effect of this approach was demonstrated by using 1,8-naphthalic anhydride (NA). Our studies aimed at the creation of composition for presowing treatment of seeds were conducted with NA as a reference, since up to date there is no data on the industrial preparations which excel NA as antidote to sulfonylureas for presowing processing. Basing on the original plant growth regulator floroxan, fluoro-containing urea derivatives with high antidote activity in low concentrations were synthesized. An industrial antidote furilazole with high antidotal activity was tested as substitute for NA in composition of the complex protectant. There were no literature data on presowing treatment of seed with this antidote. Furilazole was shown to exhibit antidotal action in the much lower concentration than NA, but without providing full protection of plants from sulfonylurea effect. We suppose that furilazole can be used in complex technology for the protection of plants from residues of phytotoxicants in soil, which will be the subject of our future research. We also attempted to modify the furilazole structure and study the biological activities of resulting fluoro-containing derivatives.

An industrial safener isoxadifen-ethyl (IDE) was selected as another test object. This modern safener was used in mixture with herbicides of sulfonylurea family for weeding of corn and rice crops. In our assessment, IDE was inferior in the activity as compared to furilazole. In order to increase the IDE activity, we accomplished the synthesis of its fluoro-containing derivatives [2].

In summary, the use of antidotes in complex preparation for presowing treatment allows to overcome significantly the inhibiting action of residues of sulfonylurea herbicides in soil on plants. The application of these technologies does not require additional agronomical procedures and utilizes low doses of the already used antidote. At the same time, the application of the antidotes alone does not provide complete solution for the problem of the herbicide residues in soil. Considerable advances were achieved upon introduction of sorbent into soil, which binds the herbicide residues [3]. The combined use of sorbents and antidotes can solve the problem in complex cases of soil contamination with high doses of phytotoxicants.

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Assessment of feasibility of using desiccators to study aerosol effect of liquid deicing materials

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Aerosol effect of chemical pollutants of the environment is considered as one of the main factors affecting human health adversely. Thus, assessing air distribution of liquid deicing materials (hereinafter DIM), which are applied for road treatment in urban areas in winter, seems to be a relevant task.

Currently, desiccators are widely used in laboratory studies devoted to the acute or chronic aerosol effects of various chemicals along with climate chambers.

The aim of this study was to evaluate the feasibility of using desiccators in a model experiment to identify the chemical composition of liquid DIM in the air along with DIM distribution routes, and to determine the type of DIM distribution which produces the most significant chemical load on human organism.

Liquid DIM – modified calcium chloride (MCC) distribution was studied in a model experiment, with MCC composing of sodium chloride and calcium chloride in mass fractions of 6 and 22%, respectively. The technique for disinfectant evaluation was described in [1]. The experiments were carried out in airtight desiccators with a volume of 0.01 m^3. Calculations of the DIM load were made in compliance with the technical regulation [2], according to which the maximum density of treatment with liquid DIMs should be in the rage of 70–80 ml/m^2. Given the area of the desiccator (0.071 m^2), 6 ml DIM application dose was used. The study was conducted with the addition of two application doses of DIM solutions: 6 ml and 60 ml, with the second dose corresponding to a 10-fold increase of usual application dose, in order to establish a threshold level for determining the DIM components in the desiccator air, taking into account the sensitivity of the method of mass spectrometry with inductively coupled plasma (ICP-MS), which was used for further calculating elemental analysis of the spent aqueous solutions.

The introduction of the liquid DIM solution was carried out in three desiccators and in two concentrations (Table 1).

Volatile chemical compounds were captured during air pumping from desiccator atmosphere into bubbler tanks with bidistilled water during 4 min of air aspiration with an absorption rate of 2 dm^3/min on a PU-4E electric aspirator.

No exceeding of the concentrations of the DIM main components (Na^+, Ca^{2+}, Cl^- ions) was detected at DIM application dose of 6 ml.

At the application dose of 60 ml, the following levels of Cl^- ions were found: 0.25 mg/m^3 (D1), 1.00 mg/m^3 (D2), and 0.25 mg/m^3 (D3). When comparing the obtained results with the hygienic standards [3], Cl^- ions composition excess was revealed both for the maximum single concentration of 0.1 mg/m^3 and for the daily average concentration of 0.03 mg/m^3.

Table 1. Design of experiments for liquid DIM distribution assessment

Desiccator	Method of reagent application and air sampling	Amount of reagent, ml	
Desiccator 1 (D1)	Exposure of liquid reagent – 24 h, sampling – 24 h after reagent application	6	60
Desiccator 2 (D2)	Aerosol spraying, air sampling immediately after spraying the reagent		
Desiccator 3 (D3)	Application of liquid reagent, air sampling 5 min after the application		
Desiccator 4 (D4)	Control, distilled water		

In contrary, at higher DIM application dose corresponding to the 10-fold increase over the recommended levels for introducing liquid DIM according to the regulations [2], an excess of the maximum permissible concentration level of chlorine ions was observed. However, sodium and calcium ions levels were within the specification limits.

The highest indicators of the DIM main ingredients levels were observed in the air samples taken from desiccators with the aerosol spraying treatment mode.

In conclusion, a further study of the DIM effect on human organism is advisable with focus on inhalation application, including aerosol spray.

The work was performed within the framework of State assignment at Centre for Strategic Planning of FMBA of Russia

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Effect of temperature on adsorption of *o*-phenylenediamine and resorcinol by modified bentonite and activated carbon

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Wastewater coming from many industrial enterprises often contains hazardous chemical substances and requires high-quality treatment [1]. Adsorption methods have proven their effectiveness for wastewater treatment of industrial enterprises. Activated carbon is traditional sorbent used for the treatment of industrial wastewater from pollutants. However, activated carbon can be inferior in effectiveness as compared to cheaper mineral sorption materials. Among such materials, bentonites are considered to be the most promising sorbents. Bentonites are shown to be particularly effective for the extraction of amino and hydroxy derivatives of benzene from solutions [2].

The aim of this work was to study adsorption characterictics of amino derivatives of benzene (i.e., *o*-phenylenediamine) and hydroxy derivatives of benzene (i.e., example, resorcinol) by modified bentonite and activated carbon at different temperatures.

Studying temperature dependence of adsorption allows to classify the type of adsorption of the studied substance on a given sorbent (physical or chemical adsorption). This is very important for understanding the mechanism of adsorption and impact of the medium. We have studied the following sorption materials: 1 – fine bentonite fraction, calcined at a temperature of 570°C; 2 – medium-size bentonite fraction, calcined at 570°C; 3 – large-size bentonite fraction, calcined at 570°C; 4 – activated carbon of the trade mark BAU-A (GOST 6217-74, Russia). Laboratory studies were carried out according to the method described earlier [2]. The research results are presented in figures 1 and 2 for sorbent samples 1–4.

The most important features of the adsorption process are established as follows:

1) temperature has different effect on the intensity of adsorption of *o*-phenylenediamine by sorbents studied: the intensity of adsorption of *o*-phenylenediamine by bentonite increases with temperature increase, but it decreases for the adsorption by activated carbon (Fig. 1). By contrast, the intensity of adsorption of resorcinol decreases with temperature both for bentonite and activated carbon (Fig. 2);

2) bentonites have shown a higher adsorption capacity with respect to *o*-phenylenediamine, and a weaker adsorption capacity with respect to resorcinol as compared to activated carbon;

3) the most efficient sorbent for extracting *o*-phenylenediamine from water is large-size bentonite, calcined at a temperature of 570°C;

4) activated carbon is the most efficient sorbent for extracting resorcinol from water.

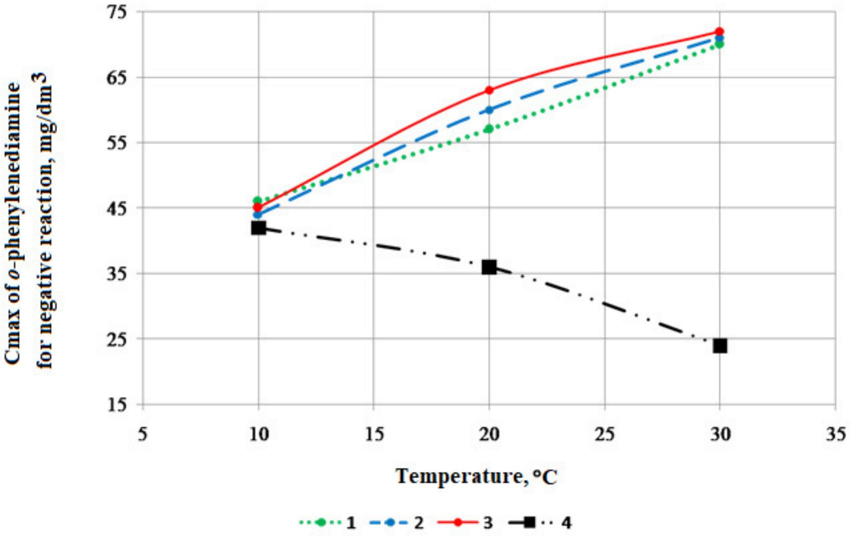

Fig. 1. Temperature dependence of adsorption of *o*-phenylenediamine

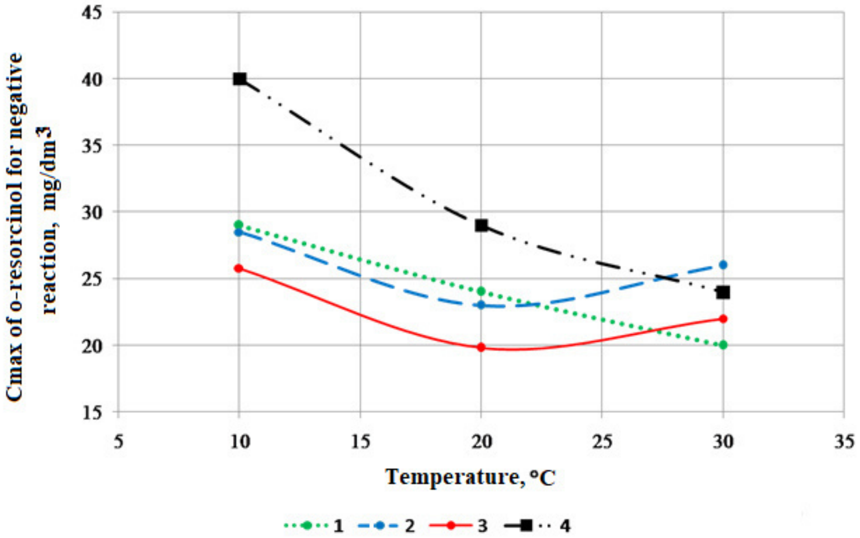

Fig. 2. Temperature dependence of adsorption of resorcinol

Thus, the research results have revealed different mechanisms of the adsorption which depend not only on the structure of the sorbent, but also on the nature of the adsorbed substance. An increase in adsorption intensity with increasing the temperature of the medium usually indicates to chemisorption. A decrease in adsorption intensity with increasing temperature points to physical adsorption.

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Treatment of water solutions containing heavy metal ions under the influence of constant atmospheric pressure discharge

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Heavy metal (HM) compounds are known as xenobiotics which are characterized by unpredictable impact on ecosystems. HM-containing wastes are often released in the form of emissions in natural water bodies, where they fall with insufficiently purified industrial sewage. Currently, a variety of methods of water treatment are used, with both advantages and disadvantages. Thus, one of the most commonly used methods – sorption has rather high efficiency. However, it requires high energy costs for regeneration of sorbents, and also leads to secondary environmental pollution [1]. The main limitation of chemical methods is due to the fact that the reduction-oxidation reactions are reversible, therefore, achievement of high degree of recovery requires applying a large amount chemical reagents, which also results in secondary pollution of water.

This problem can be addressed by means of methods based on the use of electrical atmospheric pressure discharges. The exposure of contaminated aqueous solutions to electrical atmospheric pressure discharges results in formation of active particles, which can be both oxidizing and reducing agents depending on the applied conditions. High oxidation ability of the particles is associated with the presence of $OH^{\bullet}$ and $HO_2^{\bullet}$ radicals, $O(^3P)$ atoms, hydrogen peroxide, ozone, atomic and molecular H, and solvated electrons [2, 3]. Little attention is paid to studying the processes of water purification from HM ions under the action of electrical discharge, therefore, new research in this area is a relevant issue.

Accordingly, the aim of the work was to study the kinetic laws of the processes occurring in model aqueous solutions containing chromium, manganese and copper ions when they are exposed to a direct current atmospheric discharge pressure, and to evaluate the effectiveness of purifying the solutions from HM-containing compounds. A description of the experimental setups and parameters of the cleaning procedure is given in [2, 4].

In summary, the results obtained in this work indicate that plasma treatment is an effective method of purifying water from HM ions which provides their transfer into less toxic forms. The water treatment efficiency of the developed procedure varies in the range of 60–99% and depends on the type of metal, its initial concentration in solution, and physical discharge parameters (discharge current, discharge gap value).

This work was carried out as part of the state assignment for research (topic No. FZZW-2020-0).

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Green technology for functional coatings

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Preservation of optimal environmental parameters for current and future generations might become possible due to the development of 'green' technologies. Generally, green or sustainable chemical technology is based on the development of products and processes that reduce the usage of hazardous substances and mitigate harmful effects on the environment. Activities in this area are performed in two main directions: reducing the amount of fossil raw materials and reducing the amount of waste by creating closed production cycles imitating natural cycles.

Accordingly, green technologies are a fundamentally new approach to solving environmental problems. The main efforts for the development of the chemical industry should be carried out in the field of the application of environmentally friendly, low-waste and nature-like technologies that ensure a reduction in specific energy consumption; reducing the amount of harmful and dangerous substances (poisons, acids, toxins) and replacing them with safer substances; introduction of 'three R' technologies: recycling, regeneration, recovery.

Such technologies not only provide reduction of harmful effects on the environment, but also help to make the work of people in the chemical industry much safer. This is facilitated by 'green' information and communication, and other technologies [1].

In the modern world of microminiaturized instruments and devices, functional thin films have been widely common, playing the role of semiconductor, conductor, dielectric, magnetic, sensor and other materials. They are manufactured using mainly microelectronics methods, equipped with cumbersome energy-intensive vacuum equipment, applying expensive targets and gas phases. Technologies for manufacturing microelectronics produce a large number of toxic substances, explosive and flammable gases and liquids, etc.

Thin functional films are now widely in demand not only in miniature devices, but also for using on large and complex surfaces. For example, the formation of self-cleaning, energy-saving, electrochromic glass and film solar panels requires the development of large-scale low-cost size products.

The extraction-pyrolytic technology [2] is an example of economically viable; safe low-waste procedure; with the possibility of automation, without intensive use of energy and resources. The essence of this technology is in the extraction of target components from aqueous solutions followed by pyrolysis of the films deposited on the substrate. The processes of applying thin wetting films in the paint and varnish industry are automatic and scientifically based. The working solutions used for film coating are salts of carboxylic acids and belong to hazard class IV, that is, they are harmless. The excess of solvent vapors is directed to an alkaline solution with the possibility of regeneration. Gases released during their thermal decomposition, consisting mainly of CO_2 and H_2O, are absorbed by adsorbent without emissions into the environment. Thus, the technology fully complies with the 'three R' principle: recirculation, regeneration, recovery.

Thin oxide films for various functional purposes were obtained by the extraction-pyrolytic method. Dye-sensitized solar cells (DSSC) on glass were manufactured using the extraction-pyrolytic method with a multilayer photoanode and ITO-electrodes with an interlayer electrolyte (polyethylene glycol with added solutions, KJ/J_2, and $LiClO_4$).

Transparent conductive films In_9SnO_{15-x} (ITO) were also obtained by the extraction-pyrolytic method. It should be noted that thin films obtained by extraction-pyrolytic method are characterized by a nanocrystalline structure (Fig.1).

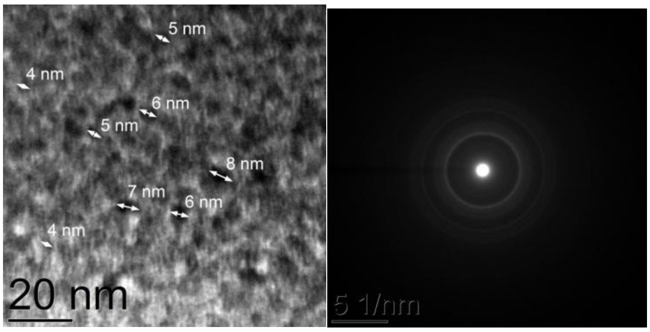

Fig. 1. Electron microscopic image of ITO coatings (a), electron diffraction (b).

The pyrolytic decomposition of the organic component is accompanied by the release of gaseous products, mainly carbon dioxide. Our future research will be aimed at developing a method for utilizing pyrolysis gases.

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Dephenolization of ammonia-tar liquor – by-product of phenol-formaldehyde resins production

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The existing technology for production of synthetic phenol-formaldehyde resins and the corresponding composite materials is accompanied by formation of a large amount of highly toxic phenol-containing wastewater, which requires neutralization [1]. This work is aimed on developing a resource-saving, low-waste technology for the disposal of highly toxic phenol-containing wastewater – ammonia-tar liquor using dephenolization procedure.

The known procedures for dephenolization of phenolic resin production by-product – ammonia-tar liquor, are usually based on the methods of thermal combustion and biochemical oxidation [2, 3]. The main drawback of these methods is the loss of valuable chemical raw materials and the formation of carbon monoxide (IV), the main greenhouse gas that contributes to the disruption of the carbon-oxygen balance of the Earth's atmosphere.

The developed technology is based on a combination of regenerative methods that allow the complete conversion of phenol from the ammonia-tar liquor into useful products and ensure high extent closed-loop technological cycle. The primary recovering process of phenol is carried out by immobilizing its molecules on the highly developed surface of softwood sawdust modified with NH_4OH solution and used as adsorbent filler.

The process of immobilization of phenol molecules occurs in the mixed-diffusion region (ΔE = 14.3 kJ/mol) with the limiting step – the external diffusion adsorption of phenol ($D = 0.94 \cdot 10^{-6}$ cm^2/c). The optimal parameters of the phenol adsorption process were established (t = 60°C; τ = 30 min; the fractional composition of the sorbent in the range of 0.5–5.0 mm), which provided the recovery of 96% by weight of phenol.

The subsequent conversion of phenol molecules both immobilized and remaining in the ammonia-tar liquor is carried out by the method of secondary polycondensation in the presence of an alkaline catalyst by introducing the calculated volume of the formalin solution into the repromotional mass. The optimal parameters of the conversion process were experimentally determined (mole ratio $CH_2O : C_6H_5ON = 1.9$, mass ratio W:T (hydromodule) = 3; t = 98–60°C; τ = 60 min; the mass of the modified waste of textolite (dispersion 0.2–3.0 mm) = 20% of the mass of the adsorbent filler), resulting in the total extraction of phenol of 99.3% by weight.

The product of the first step of the dephenolization is a wood-phenolic oligomer, which shows high reactivity and can be used as a technogenic raw material for further processing. The commercial technical product of the second step is a wood thermoplastic composite having physical, mechanical and operational properties suitable for manufacturing electrical products including items for machines and mechanisms.

While drying the composite, condensate waters are formed, which are subjected to further purification by ion exchange sorption leading to the residual phenol concentration of $2 \cdot 10^{-2}$ mg/l. Eluting phenol and ion exchange resin results in formation of sodium phenoxide as the crude product. All steps of technological process of the ammonia-tar liquor dephenolization are carried out in a single apparatus – a mixer, the design of which provides high intensification of mass transfer and reaction occurrence in heterogeneous media [4].

The operational flow chart of phenol recovering from both ammonia-tar liquor and wood-based and electrical industrial wastes is high extent closed-loop technological cycle and therefore can be integrated into the technological cycle of phenol-formaldehyde resins production contributing significantly to resource-saving economy (Fig. 1).

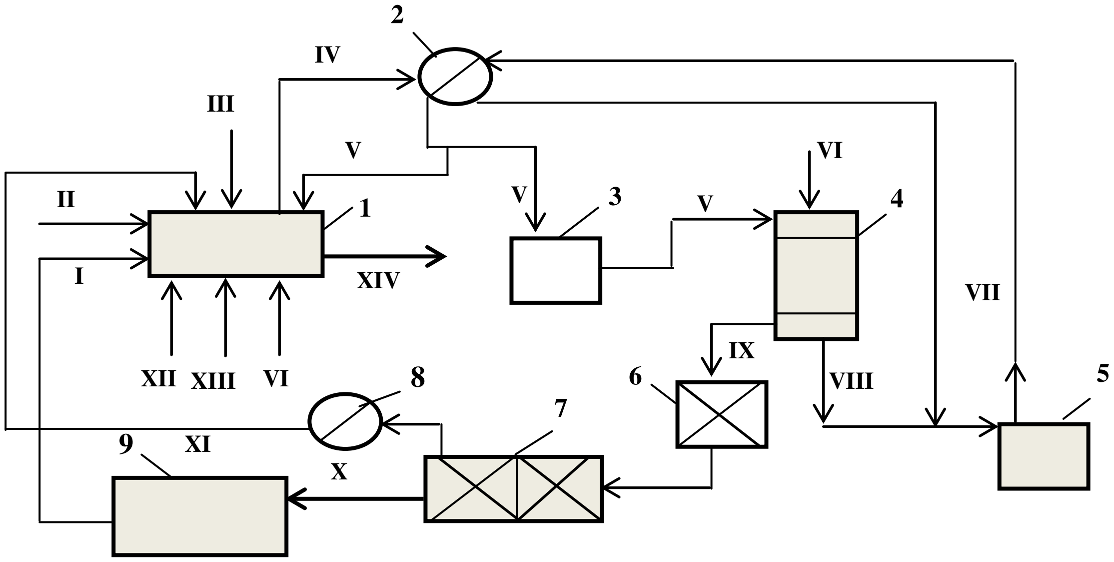

Fig. 1. Operational flow chart of ammonia-tar liquor treatment: 1 – mixer; 2 and 8 – condensers; 3 – condensate collector; 4 – sorption column; 5 – cooling tower; 6 – eluate collector; 7 – evaporation plant; 9 – preparing phenol-formaldehyde resins. Flows: I – ammonia-tar liquor; II – wood sorbent-filler; III – textolite crumbs; IV – phenol air-steam blast; V – condensate; VI – NaOH solution; VII – refrigerant; VIII – desphenolated ammonia-tar liquor; IX – eluate; X – sodium phenolate; XI – heat carrier; XII – NH_4OH solution; XIII – formalin solution; XIV – wood-polymer composite

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Two-phase anaerobic treatment of highly concentrated wastewater of confectionary industry to produce hydrogen and methane-containing biogas

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One of the promising approaches for solid organic waste disposal and treatment of highly concentrated wastewater containing a large amount of carbohydrates is realization of a two-phase process of anaerobic fermentation with the production of hydrogen and methane-containing biogas [1, 2]. The first step of the organic matter (OM) decay creates conditions for hydrolysis and acidogenesis processes. These processes result in formation of a large amount of hydrogen-containing biogas [3]. At the second step, the accumulated products of the OM decomposition are transformed into methane-containing biogas. The proposed two-step model of the anaerobic process provides a more complete decomposition of OM due to the creation of optimal conditions for both acidogenic and methanogenic microbial communities, and also improves the overall process stability [4].

Configuration of bioreactors and technological mode of their operation are significant factors which affect production of biogas during the process of anaerobic fermentation. The first stage of the study was dedicated to examining acidic fermentation of highly concentrated wastewater to produce biohydrogen. Highly concentrated wastewater (chemical oxygen demand, COD = 36.4 g/l) of the confectionary factory was used as a substrate.

Studies were conducted using a laboratory bench which included two identical devices with effective volume of $V_a = 0.8$ L. They were run continuously in the mesophilic mode (37 ± 1°C). Submission of the substrate and pumping out the fermented mass in time was carried out automatically. Small pieces of foam rubber were used as a feed matter for immobilization of biomass. The rate of upward fluid flow was kept by recirculation pumps and constituted 3 m/h for the first apparatus – anaerobic filter (AF), and 11.2 m/h – for the second apparatus with a fluidized bed loading (AFB). Preliminary acid treatment of inoculum was carried out in order to inactivate hydrogen-consuming microorganisms of active anaerobic sludge.

It was found that the highest yield of biohydrogen and its highest concentration in the gas phase (26-36 vol. %) during anaerobic fermentation of highly concentrated wastewater of the confectionary factory were observed during hydraulic retention time (HRT) 2–4 days at source wastewater pH = 7.0. The biogas yield for the AFB apparatus was 1.4-fold higher than that for AF. The COD reduction in wastewater was the highest for the AFB reactor with the value of 61–70%, while in the AF reactor it was 59–61%. The observed difference is probably due to the insufficiently efficient mass transfer process between bacteria and substrate for the AF compared to the AFB.

During the second stage of the two-step process with HRT equal to 9 days, the COD value of purified water was 2160 mg/l, pH = 7.43. The overall effect of the treatment of highly concentrated wastewater in case of the two-stage process in terms of COD was 95%. The biogas composition on the second stage involved 66% of methane and 20% of carbon dioxide.

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Assessment of impact of technogenic factors of uranium production on the environment

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Uranium production is one of the leading sectors in the industries of many countries of the world, including the Republic of Uzbekistan.

However, uranium mining and uranium metallurgy have a negative impact on the environment in the course of technological activities. The harmful impact of these industries on the environment can be estimated by analyzing samples of atmospheric air, soil, plants, drinking water, industrial wastewater and groundwater. Radioactive elements and their compounds occupy a special place among the toxic pollutants of atmospheric air, soil, plants, drinking, industrial wastewater and groundwater [1, 2].

This study is devoted to the assessment of the negative technological impact of the uranium production on the environment using the example of the Navoi Mining and Metallurgical Combine (Uzbekistan).

To assess the levels of soil contamination with radionuclides in the areas of underground leaching of uranium at depths of 0.25 m, 0.5 m, 0.75 m and 1.0 m from the earth surface, soil samples were collected and equivalent dose rates (EDR) of gamma-radiation of each sample were measured using DKS-96 radiometers. Afterwards, in laboratory conditions, the effective specific activity (A_{eff}) was measured followed by determination of specific activity of natural radionuclides ^{40}K,^{226}Ra,^{232}Th by the X-ray spectrometric method.

In atmospheric air samples, the HCN, NH_3, NO_2, SO_2, H_2S, H_2SO_4, Pb, and P_2O_5 concentrations were determined by the photocolorimetric method on a KFK-3 instrument, dust concentration – by the weighing method using a Metler Toledo laboratory balance, EDR power – in workrooms by DKS-radiometers 96. The volumetric activity of radon in the atmospheric air of settlements, and in the air of the premises of the working zone were measured using the ALPHA-GUARD device, and the equivalent equilibrium volumetric activity of the daughter products of the radon decay in the atmospheric air of settlements, in the air of the working zone, and in the rooms of uranium production was determined by the 'Search' and radon WL meter devices.

The activities of long-lived alpha-nuclides in the atmospheric air of settlements, in the air of the working zone and in the production rooms of uranium industries were obtained by sampling for suction filters AFA. The gamma radiation power was measured in continuous mode using the KRONA device for more than 10 years through monitoring the work of the uranium oxide-oxide calcination shop. This technique made it possible to determine changes in the values of the radiation background in the calcination shop of uranium oxide. The fractional composition of radioactive aerosols in the atmospheric air of the working zone of the uranium finished products calcining workshop was determined using nuclear filters with pore sizes of 0.7–4.0 μm manufactured at the Joint Institute for Nuclear Research (Russia, Dubna) in combination with the traditional AFA filters.

In drinking water, groundwater and industrial wastewater samples, the following components were evaluated: dry residue, suspended solids, pH, concentrations of oil products. Anions: Cl^-, NO_2^-, NO_3^-, CO_3^{2-}, HCO_3^- and SO_4^{2-}, cations: Ca^{2+}, Mg^{2+} were determined by the titrimetric method, concentrations of Si, F, As, Mo, Al, nitrite – by the photocolorimetric method, concentrations of K, Na, Fe total, Cu, Mn, Pb, Co, Ni, Zn, Cr – by the atomic absorption method, radon concentrations – by the emanation method, total specific alpha and beta activity – using a UMF-2000 instrument, and the isotopic composition of the uranium decay chain using an alpha spectrometer CANBERRA [3, 4]. Measurements were also made of the contamination with alpha-nuclides of the surfaces of industrial equipment, surfaces of rooms, special machines and special uniforms of working personnel using the DKS-96 devices.

The results indicate that transition from the traditional uranium mining method to the underground leaching mining has led to the significant decrease of the negative impact of radiation on the environment.

The annual technogenic effective dose of the sum of radiation factors received by the employees of uranium production facilities was found to decrease by 1.5–2 times relative to the permissible value (20 mSv/year). The changes in technology result in safety improvement: now the personnel receives an annual technogenic effective dose of as low as 2–5 mSv/year.

The results of the many years of the assessment of the radioecological state in the Navoi Mining and Metallurgical Combine allow us to conclude that the radiation situation in the region complies with the established standards, the effective annual dose for personnel working at uranium production facilities and for the population of settlements in adjacent areas does not exceed the values established in the regulations (SanPiN-0193-06). Systematic determination of the magnitude of the radioecological factors associated with the activities of uranium mining enterprises plays an important role in ensuring the radioecological stability and cleanliness of the environment.

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Assessment of influence of uranium underground leaching on state of soil and groundwater

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The mining of uranium deposits by underground leaching method results in contamination of soils and groundwater with radionuclides of the uranium decay chain – ^{234}U, ^{230}Th, ^{226}Ra, ^{222}Rn, ^{214}Bi, ^{214}Pb, and ^{210}Po. The reason of this contamination is violation of the technological regulations and rules for pumping, injection, leakage, poor condition of pipelines, improper transportation of productive solutions, etc. Soil contamination with radioactive elements in the areas of uranium underground leaching negatively affects its radiation, chemical, biological, erosion characteristics, and leads to the death or degradation of vegetation cover, loss of soil fertility, change and deterioration of groundwater quality.

For such facilities, the upper limits of the permissible concentration of radionuclides are established, and they are regulated by regulatory international (ICRP, GOST, ASTM, etc.) and republican (SanPiN, O'zDSt, etc.) documentation. Therefore, determination of radionuclides' content and their distribution in the soils of underground uranium leaching sites, and in the groundwater is an urgent task of analytical chemistry, applied nuclear physics and radioecology.

The aim of this study was to determine the content and distribution of radioactive contaminants both in soils of underground leaching of uranium, and in underground waters using acid and mini-reagent methods.

To achieve this goal, soils were collected from various sites of underground leaching of uranium, and the concentrations of rock-forming chemical elements were determined by X-ray fluorescence method on an EDX-7000 device (SHMADZU, Japan), along with the specific effective activity A_{eff} measured with the help of BDIA device. The specific activity of radionuclides as ^{226}Ra, ^{232}Th and ^{40}K was determined by gamma spectrometric method using a Gamma Progress instrument. Also, photocolorimetric method was applied for determining the amount of dry residue, pH values, anions: Cl^-, NO_2^-, NO_3^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}, NH_4^+ and their total concentration, cations: Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{3+} and their total concentration. The concentration of heavy metals in groundwater samples (Mn, Pb, Cu, Zn, Co, Cr, and Ni) were determined by the atomic absorption method on an AA-3300 spectrometer.

The underground leaching of uranium results in contamination of groundwater with various components of the working solution, as well as with the substances formed as a result of the interaction of the leaching solution with the ore-bearing rock. In addition, sulfuric acid leaching from the rock to groundwater leads to transfer of Fe, Al, Ca, Cu and Mo into groundwater in quantities exceeding the maximum permissible concentrations (MPCs).

Mineralization of groundwater reaches levels up to 30 g/l (with the established norm of total mineralization for industrial water – 1 g/l). The obtained uranium-containing solutions also contain radionuclides: ^{234}U, ^{230}Th, ^{226}Ra, ^{222}Rn, ^{214}Bi, ^{214}Pb and ^{210}Po.

The results of studying behaviour of radionuclides in groundwater show that the use of the sulfuric acid underground leaching of uranium leads to the following changes in the average groundwater parameters: pH shifts from 7.2–8.5 to 1.5–5.2, the dry residue – from 1840–28046 to 14964–70932 mg/l, the hardness of solutions – from 10.2–12.7 to 53.2–74.6 mg/l.

The following concentrations of the heavy metals were found in the groundwater by atomic absorption analysis (mg/l): Mn 0.003–0.004, Pb 0.06–0.10, Cu 0.006–0.009, Zn 0.006–0.01, Co 0.003–0.02, Cr 0.001–0.002, Ni 0.0009–0.0010. The values of the exposure dose rate (EDR) were found to range from 15.6 to 67.2 μR/h, while the specific activity of radionuclides varied in the range (Bq/kg): ^{40}K 105–599, ^{226}Ra 238–1534, ^{232}Th 11–41. The specific effective activity of alpha-radiation (A_{eff}) was evaluated as 18–1560 Bq/kg, and the pH values of the aqueous extract varied in the range of 7.54–3.60.

Two types of soil samples were compared: those collected from underground uranium leaching sites where mini reagent was used (concentration of H_2SO_4 in solution 10–15 g/l) and those where uranium leaching technology was applied (concentration of H_2SO_4 in solution 30–40 g/l).

As expected, the acidity of the soil correlated with the type of technology used for leaching of uranium: 7.54 for the mini-reagent, and 3.60 for the acid technology. On the contrary, the EDR values increased from 15.6 to 67.2 μR/h with a change from the mini reagent to the acid technology.

This fact shows that the use of the acid leaching of uranium results in the greater contamination of soil with radionuclides of the uranium decay chain than that for the mini reagent method. The groundwater analysis also revealed higher groundwater contamination with radionuclides for the acid leaching method vs. mini reagent procedure.

In summary, the results indicate that the applied geotechnological processes of underground leaching of uranium have a negative impact on the state of soil and groundwater with higher adverse effects for the acid method as compared to the mini reagent method.

Modern equipment of personnel protection from tritiated water vapor

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Operating nuclear reactors are known to generate the radioactive hydrogen isotope – tritium which is characterized by easy penetration into human body by breath and through skin, being incorporated into water molecules. This creates a potential threat to the health of the nuclear reactor operating staff.

This work presents the results of studying the rate of tritium penetration into human body speed in the water vapor, by breath and through skin, along with its distribution in the body and the rate of its natural elimination.

We supposed that the most rapid tritium accumulation in human body could be achieved for the personnel working with the heavy water moderator of the PIK nuclear research reactor built in the Petersburg Nuclear Physics Institute. A variety of cases of contacts with tritiated water vapors for personnel involved in this reactor operation activities have been reviewed, i.e. accidental leakage of heavy water, heavy water moderator equipment repairing, heavy water samples acquisition, etc. The recommendations for safe maintenance of the reactor are described in [1] where the safety is provided if the tritium concentration in heavy water does not exceed 2 Ci/l. To maintain such level of tritium concentration, a necessity arises of tritium removal from heavy water of the facilities. Otherwise, the tritium amount in heavy water will reach 5.3 Ci/l of heavy water per year.

Modern means of personnel's protection from radioactive aerosols are reviewed. For each mentioned case of personnel contact with tritiated heavy water, the estimation of received radiation dose is given taking into account tritiated water vapor penetration rate through protective gear. On the basis of the new information on tritiated water vapor rate of penetration through protective gear, a possibility of nuclear reactor PIK operation without tritium removal from the heavy water using facilities is discussed.

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Photodegradation of arsenic-containing food additives under UV-irradiation in the presence of natural photosensitizers

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p-Arsanilic acid (p-ASA) is a common representative of phenylarsonic feed additives which have been widely used in the livestock and poultry industries as veterinary drugs for promoting the growth and preventing animals' diseases. The large usage, good water solubility and slow biotransformation of these organic arsenic additives lead to their release into groundwater and surface waters. Even though commonly used phenylarsonic feed additives themselves exhibit low toxicity, their biological and (photo)chemical transformation can result in generation of toxic inorganic arsenic and other organic products. Taking into account this possibility, a necessity arises to study photochemical degradation pathways of this compound under solar irradiation in natural water systems [1, 2] or during UVC-disinfection treatment applied to farm wastewaters [3, 4].

In this work, we present a new insight in mechanism of p-ASA photochemistry which has been investigated for the first time by means of laser flash photolysis (λ = 266 nm) coupled with high resolution LC-MS [5]. The main primary photoprocess is found to be a monophotonic ionization (ϕ^{266nm} = 0.032) leading to formation of the hydrated electron and corresponding anilinyl radical. This primary species react with dissolved oxygen forming the reactive oxygen species (ROS) and peroxo-radical. These secondary species are responsible for generation of many organic photoproducts such as aminophenol and different dimeric products with unknown toxicity. The dependence of quantum yield of p-ASA photodegradation upon excitation wavelength has been obtained for the first time. This value is found to decrease slowly in the region 222–308 nm from 0.058 to 0.035. In general, direct UVC-photolysis of p-ASA is not very effective and does not completely remove both the target substance and its main photoproducts.

Our results also demonstrate that the efficiency of the UV decomposition of p-arsanilic acid induced by humic substances is comparable with the efficiency of direct UVC-photolysis of the acid due to the participation of active intermediates of humic substances photolysis in p-arsanilic acid photodegradation [6]. Presence of iron(III) oxalate complexes, another common photosensitizer in natural waters, allows to reach practically complete degradation of p-ASA and its aromatic by-products under UVA-irradiation at concentrations of p-ASA of less than 5 μM. The main oxidative agents in these conditions are ROS ($OH^·$ radicals) which are generated with rather high quantum yield equal to 0.06.

These results seem to be crucial for understanding a fate of p-ASA and other similar phenylarsonic feed additives during UVC-disinfection treatment and in the course of sunlight photolysis.

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Molybdenum-arsenic heteropoly acid – analytical form for preconcentration and subsequent determination of arsenic in water

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Arsenic is one of the most dangerous chemical elements known for its strong toxic effect on the human body. Typically, it enters water reservoirs as a result of leaching of various rocks, as well as with the runoff of industrial enterprises and agricultural lands.

A clear correlation between health incidence and arsenic content in drinking water has been observed in many countries. This is why the determination of arsenic in the human environment, and, in particular, in drinking water and food, is a critical and urgent task.

In Russia, the following arsenic MPC values are set for natural waters: 50 μg/l for water objects of drinking water supply, and 10 μg/l for waters of fisheries use. Domestic and international standards for methods for the determination of arsenic in waters are based mainly on the reduction of all forms of arsenic to highly toxic arsenic hydride. The highly sensitive ICP-MS method involves the use of expensive equipment and qualified personnel.

We have developed methods based on the preconcentration of arsenic(V) as hydrophobic ionic associates of molybdenum-arsenic heteropoly acid (MAA) with trioctylamine (TOA) from aqueous solutions for subsequent determination by X-ray fluorescence (XRF) spectroscopy, which do not have these disadvantages. The first option: MAA is extracted by melts of mixtures of fatty monocarboxylic acids (t = 80ºC) containing TOA as an alternative to toxic organic solvents. The choice of the extractant is due to the chemical and thermal stability of fusible organic acids during heating and melting, low solubility in water in a wide range of concentrations of hydrogen ions, the ability to quickly solidify. In addition, these extractants are easy to process by pressing to obtain a sample-emitter.

The second option: poorly soluble hydrophobic ionic associates of MAA with TOA obtained in an aqueous solution are extracted in a dynamic mode on paraffinized cellulose filters. The formation of MAA as well as the conditions for its extraction depend on the ratio of concentrations of mineral acid and molybdate ions. Based on constructed zones that simultaneously take into account influence of these two factors, the conditions for preconcentration of MAA have been optimized. For the extraction preconcentration of MAA with stearic acid melt: c_{HNO_3} 1–2 M, c_{Mo} 10^{-1}–10^{-2} M. The optimum conditions for the extraction of MAA as an ion associate with TOA on filters: c_{Mo} $1.3 \cdot 10^{-2}$–$1.8 \cdot 10^{-2}$ M, c_{HNO3} 0.2–0.4 M. The combination of XRF with the proposed methods of preconcentration allowed to solve the problem of matrix effects, which is intrinsic for this method, and create unified sample-emitters with a uniform distribution of the element being determined, and what is most important to increase the sensitivity of the XRF determination due to the preconcentration step.

Methods for the determination of arsenic in various types of water have been developed, including pre-oxidation of As(III) to As(V), formation of MAA, extraction and further determination by XRF spectroscopy. The accuracy of the methods has been verified by the standard addition method when analyzing samples of tap and river water. The limit of detection (LOD) of arsenic by the proposed methods is 2 orders of magnitude lower than the direct XRF determination and allows for determination of its content below the MPC level (Table 1).

The combination of the XRF detection with the developed preconcentration procedures improves analytical performance of the method itself whereas its selectivity makes it possible to determine arsenic in the presence of silicon and phosphorus which also form molybdenum heteropoly acids.

Table 1. Characteristics of the developed methods

Preconcentration method	Linearity range of the calibration graph (Content of As in the sample-emitter)	LOD	RSD, %
Extraction 1g of stearic acid, 1% TOA sample volume 50 ml, static mode	1–100 µg	5 µg/l	15
Paraffinized filter sample volume 100 ml, dynamic mode	5–100 µg	10 µg/l	20

The estimation of hazard index of endocrine disrupting pesticides

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The current situation in the Republic of Moldova deals with a serious public health problem that requires researchers to assess the health risks associated with priority chemicals which disrupt the human endocrine system, namely endocrine disrupting chemicals (EDCs). EDCs are chemical substances present in food and in many products used in daily life that interfere with the body's endocrine system and produce adverse health effects. Endocrine disrupting pesticides (EDPs) are the largest group of the EDCs. They actively affect the health at low concentrations through population daily consumption of contaminated food. Organisms under development are very sensitive to negative effects of the EDPs. The monitoring of EDPs levels could help guarantee food quality and estimate the health risks. In this context, the National Agency for Public Health is one of the key actors in the ensuring chemical safety within the health sector of Moldova.

The present research was conducted to assess the health risk associated with consumption of food products of vegetable origin contaminated with EDPs among the population of the Republic of Moldova.

The EDPs were detected using gas and liquid chromatography-mass spectrometry analysis following the acetonitrile extraction/partitioning and clean-up by dispersive SPE-QuEChERS-method. Referring to the List 2009 [1], eight of the pesticides detected in vegetables and fruits are listed as the EDPs. The estimated daily intake (EDI) was calculated according to equation: $EDI = C \times F/W$, where C is the concentration of pesticide residues in each commodity (mg/kg); F is the mean daily intake of food per person (kg/day); W is the mean body weight (60 kg). Dietary intake of fruits and vegetables per person was estimated considering the minimum norms of the food included in a living-wage food basket [2]. The calculated estimated daily intake (EDI) was compared with acceptable daily intake (ADI). Hazard indices (HI) were calculated by dividing EDI value by ADI value. Toxicological information (ADI) is available at EU pesticide database.

The EDIs have been estimated between 0.000001 and 0.0002 mg/kg of body weight/day (Table 1). The calculated values of EDIs are lower than the levels of ADI. The calculated hazard indices ranged from 0.0005 up to 0.15 for the analyzed pesticides. The highest value of hazard index was calculated for diazinon – 0.15. The total exposure to the detected pesticide residues, obtained by summing EDI values, is equal to 0.0008 mg/kg body weight/day.

Table 1. The estimated daily intake (EDI) and the hazard index (HI) of EDPs detected in vegetables and fruits

Food commodities	Detected pesticides	Mean, mg/kg	MRL*	EDI, mg/kg bw/day	ADI, mg/kg bw/day	HI (EDI/ADI)
Potato	dimethoate	0.0129	0.01	0.00007	0.001	0.07
Onion	dimethoate	0.0104	0.01	0.000007	0.001	0.007
Tomato	methomyl	0.0500	0.01	0.00004	0.0025	0.016
	dimethoate	0.0201	0.01	0.000017	0.001	0.017
Cucumber	carbendazim	0.07	0.1	0.000026	0.02	0.001
	dimethoate	0.0138	0.01	0.000005	0.001	0.005
Cabbage	dimethoate	0.0172	0.01	0.00002	0.001	0.02
	carbendazim	0.012	0.1	0.000013	0.02	0.0006
	malathion	0,0400	0.02	0.00004	0.03	0.001
Sweet pepper	dimethoate	0.0146	0.01	0.000004	0.001	0.004
	procymidone	0.0200	0.01	0.000005	0.0028	0.002
Pepper	dimethoate	0.0200	0.01	0.000002	0.001	0.002
Cauliflower	dimethoate	0.0250	0.02	0.000026	0.001	0.003
Garlic	dimethoate	0.0171	0.01	0.000001	0.001	0.001
Melon	dimethoate	0.0200	0.01	0.000006	0.001	0.006
Watermelon	dimethoat	0.0167	0.01	0.000005	0.001	0.005
Apple	diazinone	0.0167	0.01	0.00003	0.0002	0.15
	dimethoate	0.0207	0.01	0.00003	0.001	0.032
	fenitrothion	0.0145	0.01	0.00002	0.05	0.0005
	malathion	0.1186	0.02	0.0002	0.03	0.006
	mancozeb	0.13	5.0	0.0002	0.05	0.004
Pear	dimethoate	0.0126	0.01	0.000007	0.001	0.007
Table grapes	procymidone	0.0178	0.01	0.000008	0.0028	0.003
	dimethoate	0.0150	0.01	0.000007	0.001	0.007
Plum	dimethoate	0.0147	0.01	0.000008	0.001	0.008
Peach	dimethoate	0.0250	0.01	0.000014	0.001	0.014
Apricot	dimethoate	0.0200	0.01	0.00001	0.001	0.01
				∑ = 0.0008		∑ = 0.4

*MRL (maximum residue level) – the highest concentration of pesticide residue legally accepted in food products after the use of pesticides

Thus, the calculated hazard index values show that the long-term consumption of tested vegetables and fruits could pose a health risk for the population of the Republic of Moldova. It should be noted that EDPs can cause harmful effects over an extended period, usually following repeated or continuous exposure at low levels (even less than one part in one billion). Low-dose exposure doesn't always cause immediate effects, but over time, considering real-life cocktail exposure, they can cause very serious illnesses. The health sectors should play a leading role in minimization and prevention of exposure to EDPs and their risks to human health.

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Trends in using active carbon based sorption materials for development of modern personal protective equipment

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At present, most of the existing sorption materials for personal protective equipment are based on active carbon [1]. Active carbon is a universal adsorbent which can be regenerated by heating. Active carbon is produced in different forms such as grain, fiber and others. Active carbon based sorption materials are made by a number of technologies, for example, by inserting an active carbon grain in a polyurethane carrier during molding. A technology is also known which involves adding active carbon's spheres to a substrate named Saratoga®, Blücher Gmbh, Germany [2]. The described active carbon's spheres are made from polymer raw materials and exhibit unique sorption characteristics along with high BET surface area. The analogues of Blücher's spherical active carbon are active carbons made by Suracsh Filters Pvt. Ltd., India, and Kureha Corporation, Japan.

In the context of the increasing amount of new chemical and biological threats, materials for personal protective equipment based on active carbon need to be improved. This can be achieved by using additives based on nanocarbon sorbents, catalysts and biocides in combination with the known protective materials.

In this study, we present the comparative research results of the physicochemical and sorption properties of foreign and domestic active carbons made from polymer raw materials as a basis for sorption materials applied in new personal protective equipment. The results have shown that the BET surface area of the active carbon under a label PFT, produced by ENPO Neorganika JSC (Russian Federation), is characterized by more than 45% increase in BET surface area as compared with the active carbon sample produced by Blücher Gmbh, Germany. Sorption capacity for benzene in static conditions at $p/p_s = 0.1$ of the active carbons PFT and FAD of ENPO Neorganika JSC is found to have 2.3–2.7-fold increase in sorption capacity as compared with the abovementioned active carbon of the German company.

Consequently, the Russian active carbons of PFT and FAD series can be promising materials for development of sorption materials for novel personal protective equipment.

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Experience in biodegradation of certain types of waste from gunpowder production

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Over the past decade, we have gained a valuable experience in recultivation (rehabilitation) of former gunpowder production facilities and adjacent territories. This report provides information about the experience of neutralization of waste from the production of nitrocellulose powders at the former enterprise Rezhevskoi Chemical Plant (Sverdlovsk region).

The process of production and processing of powders leads to the accumulation of toxic, flammable and explosive wastes. The waste generated in gunpowder production primarily includes nitrate esters (nitrocellulose and nitroglycerin). They are traditionally considered as **non-toxic materials**, but at the same time, large volumes of this type of waste are equated with substances with a pronounced mutagenic effect. Nitrocellulose, in terms of environmental safety, belongs to the group of xenobiotics, i.e. chemicals that are foreign to living organisms and are usually not included in the natural biotic cycle. The presence of nitro groups contributes to the nitrocellulose increased toxicity. In addition, cellulose nitrates with a nitrogen content of more than 10% are fire-dangerous and explosive substances.

The universal character of natural enzymes' activity made it possible to transfer the achievements obtained in the area of removal of pollution by biological methods to the field of neutralization of waste derived from the production of gunpowder. Methods using biodestructors are expected to be the most promising ones **due to their versatility and relative simplicity**. In addition, they are attractive because of 'soft' reaction conditions: low temperature and pressure, the possibility of conducting the process directly in the environment, etc.

An ecobiopreparation 'Tsentrum-MMS' for industrial applications was used in this study as a biodestructor of nitrocellulose. This product was developed, tested and patented by LLC Research and Production Center Uralbiosintez (Yekaterinburg, Russia).

Nitrocellulose waste is accumulated mainly in the sewage systems of enterprises and their final link-slime accumulators (ponds-settling tanks) in the form of bottom silt with the following approximate composition: nitrocellulose – 20–50%; acid salts – 25–30%; water – 30–50%; sand – 5–10%. The dried sediment of the above composition is fire-dangerous and explosive.

The technology of bio-cleaning with the use of biological agents involves introducing relatively large amounts of active biomass of bacteria-destructors into the polluted environment in the presence of conventional mineral components (nitrogen, phosphorus, potassium, etc.).

The experiments at sludge collectors for bio-decontamination of nitrocellulose waste were carried out during summer season in the course of two calendar months. After applying the main amounts of biodestructor and mineral feed, the medium was mechanically mixed with periodic bubbling with compressed air. Consequently, a ~10-12-fold decrease in the concentration of nitrocellulose was observed in the end of the active phase of work. The complete decomposition of the original xenobiotic was observed after a year of exposure in natural conditions.

It should be noted the difficulties in determining the residual amounts of nitrocellulose in neutralized samples due to the lack of certified methods.

Finally, the explosive and technical tests of initial and neutralized samples of sludge sediments were carried out at the Explosives Testing Center of JSC Scientific Center VOSTNII (Kemerovo, Russia).

pH-Sensing properties of mixed oxide films on titanium deposited by plasma electrolytic oxidation

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Solid-state pH-sensors based on metal oxides have attracted considerable attention as an alternative to the glass electrodes due to their low cost, mechanical resistance and the possibility of miniaturization. In many cases, multicomponent oxide systems exhibit better sensory properties compared to individual oxides.

Plasma electrolytic oxidation (PEO) is one of the methods which provides technologically sound formation of metal-supported multicomponent oxide coatings by means of anodization of valve metals under spark and microarc electric discharges at the metal/electrolyte interface.

Here we present the results of the formation of PEO composites based on titanium oxides combined with oxides of molybdenum, tin or tungsten along with the results of studying their sensory properties.

TiO_2-MoO_x and TiO_2-SnO_x films on titanium have been formed using PEO technique under anodic-cathodic mode in electrolytes with molybdate anions or Sn-EDTA complex ions, respectively. TiO_2-WO_3 films were formed in galvanostatic conditions upon anodic polarization in an electrolyte containing 0.1 M $H_2C_2O_4$ with addition of 0.1 M Na_2WO_4.

The resulting electrodes were tested as pH-sensors in direct pH-metry and potentiometric acid-base titration. The potentiometric pH responses of some TiO_2-MoO_x, TiO_2-WO_x and TiO_2-SnO_2 electrodes reveal near-Nernst behavior, i.e. a linear working range from pH 2 to 12 with the slopes of about 64, 61 and 54 mV/pH, respectively. These sensitivity values are higher than most of the values reported previously for pH-sensors based on individual TiO_2 films. Additionally, the responses were not affected by the presence of K^+ and Na^+ ions.

All the PEO-formed electrodes exhibited high stability (over a 6 months), which is important for practical pH-measurements. The possibility of using electrodes based on mixed oxide films to accurately determine the alkalinity of technogenic waters has been shown. In addition, these sensors have a number of excellent analytical characteristics, such as sensitivity, good reproducibility and a simple preparation procedure.

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Evaluation of polycyclic aromatic hydrocarbons content in dust on the territory of Ivanovo, Russia

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The paper presents the results of monitoring the content of 16 priority polycyclic aromatic hydrocarbons (PAHs) in roadside dust in the city of Ivanovo (Russia). The need to control PAHs is an urgent task due to their widespread distribution in the environment, and also due to their high toxicity, since a number of compounds belonging to this group have carcinogenic, mutagenic, and teratogenic properties. PAHs are a large group of organic compounds (more than 100 compounds) containing two or more condensed aromatic rings in their structure [1]. Currently, the most comprehensive list of toxic PAHs is established by the US Environmental Protection Agency (US EPA - Environmental Protection Agency), which includes 16 compounds. In the Russian Federation, the content of PAHs in environmental objects is poorly controlled – the only regulated PAH is benz(a)pyrene (BaP), which is considered the most dangerous representative of this group [2].

It should be noted that heavy PAH molecules with more than four condensed benzene rings in their structure are the most stable in the environment and have higher toxicity [3]. Since all heavy PAHs have low volatility and practically do not dissolve in water, they are present in the atmosphere in aerosol form [4]. Coincidentally, a high content of suspended particles is observed in the surface air layer in urban conditions [5]. The authors of [2, 4] showed that heavy PAHs, such as benz(k)fluoranthene, BaP, benz(g,h,i)pyrene, indeno(1,2,3-cd)pyrene completely bind solid particles in the atmosphere. This leads to the fact that the main routes of migration of heavy PAHs, including BaP, in the air are physical and mechanical ones, which determines further distribution channels of toxicants in environmental objects, including living organisms. Therefore, control of PAHs in the dust fraction is strictly required.

The PAH content in dust samples was estimated by high performance liquid chromatography (HPLC) using a FLUORAT-02M fluid analyzer as a detector (the relative standard deviation did not exceed 9%).

It was found that the BaP content in the dust fraction varied in the range from 0.8 to 102.3 ng/kg. The maximum BaP content was observed in the industrial part of the city (102.3 ng/kg), the minimum – in the north (residential private sector) (0.8 ng/kg). A similar situation was revealed with the total content of PAHs, which varied from 33.3 to 1163.2 μg/kg with the maximum value observed in the western part of the city (1163.2 μg/kg), and the minimum

– in the northern part (33.3 μg/kg). It is noteworthy that the contribution of BaP to the amount of carcinogenic PAHs was insignificant and amounted to less than 1%. The proportion of carcinogenic PAHs was found to be ≥ 90% of the total PAH content in more than half of the sampling points (in 24 out of 46), with most of the control points located along the roads.

Thus, the analysis of the results shows that the most likely source of PAHs in the city is road transport, while the contribution of the fuel and energy complex is significantly less. These data are in good agreement with the previous results of BaP content measurements in the snow cover on the territory of Ivanovo [6].

Statistical processing of experimental data on the PAH content in roadside dust samples allowed us to obtain the following priority sequence from highest to lowest concentration: naphthalene > acenaphthylene > 2-methylnaphthalene > biphenyl > acenaphthene > chrysene > anthracene > benz(b)fluorantene > benz(ghi)perylene > fluorantene > phenanthrene > BaP > pyrene > benz(k)fluorantene > benz(a)anthracene > dibenzanthracene.

The results of measurements of the content of 16 compounds in the dust fraction belonging to the class of PAHs in this study allowed to:

1) determine the possible sources of origin of PAHs (vehicles, fuel and energy complex facilities);

2) identify criteria that need to be recommended for continuous monitoring PAHs in environmental objects in the studied territories.

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Engineered safety barriers used for isolation of low- and intermediate-level radioactive waste

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Nuclear fuel cycle facilities removal out of operation of is a challenging issue of the nuclear power industry since this kind of activities can lead to an increase in the radioactive waste volume. The final step of handling this waste involves either the long-term storage or disposal of the depleted solid or solidified waste. Accordingly, currently proposed concepts of safe radioactive waste isolation imply creating a multibarrier system in the repository consisting of the natural and engineered barrier materials. The type of barrier material and the technology of the barrier layer construction depend on multiple factors, namely, the type of radioactive waste, parameters of the repository, geological conditions, and others. They are selected at the step of design of the radioactive waste disposal facilities. As a rule, natural aluminosilicates, including clays, are considered to be suitable for use as relevant engineered barrier materials [1]. In Russia, a significant experience was accumulated on application of mixed barrier materials based on the industrial kaolin clay in combination with bentonite additives [2].

A mixture of the refractory clay of the Kampanovsky deposit (Krasnoyarsk region, Russia) and bentonite clay of the Dinozavrovoe deposit (Kazakhstan) was proposed for creating an inner barrier in the subsurface disposal site for low- and intermediate-level radioactive waste in Novouralsk. The barrier material contained about 65% of clay minerals, namely, montmorillonite, illite, kaolinite, and had a high sorption activity: the cation exchange capacity value was 53-57 meq/100g. The material provided the efficient removal of radionuclides from the aqueous solutions: the distribution coefficient (cm^3/g) reached 10^2 for ^{233}U, 10^3 for ^{90}Sr, and $5 \cdot 10^3$ for ^{137}Cs and ^{238}Pu. The material under investigation had low water permeability while its filtration rate did not exceed 10^{-5} m/day. Thus, the protective properties of the proposed barrier material were able to provide prevention of the radionuclide migration.

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Determination of bis(2-ethylhexyl)phthalate, a persistent organic environmental pollutant in food products

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Bis(2-ethylhexyl)phthalate (DEHP) is an *ortho*-phthalic acid diester, a persistent organic pollutant, the most common representative of the phthalate group in the environment. It is widely used as a plasticizer in the production of polyvinyl chloride, construction, and automobile manufacturing, it is present in medical products, toys, packaging material for food products, etc. [1]. DEHP, being an endocrine disruptor, disrupts the function of the thyroid, causes allergic reactions, diseases of the liver, kidneys and reproductive organs, and also belongs to the group of conditional carcinogens for humans [2–4]. The most probable way of DEHP entering retail food products is through its presence in various materials contacting with food products at any stage of the production process (during processing, storage, transportation, and preparation), as well as in food raw materials [5]. To assess the risk of phthalate adverse effects on health and to take regulatory measures, it is necessary to control the content of DEHP in food.

In this study, the results of the DEHP analysis in baby food products (canned food, dry milk and dairy-free porridges, dry milk formula and drinks) and general-purpose food products (juices, milk and kefir) are presented. The analyses were carried out on liquid chromatographs with diode array detector and mass spectrometry detector (Agilent Technologies, USA) in accordance with methodological instructive regulations MUK 4.1. 3160 – 14 «Measurement of mass concentrations of phthalates (dimethyl phthalate, diethyl phthalate, dibutyl phthalate, benzyl butyl phthalate, bis(2-ethylhexyl)phthalate) in milk by high performance liquid chromatography» and the appropriate standards for determination of the mass concentration of phthalates in baby food and juice products by liquid chromatography/mass spectrometry. As a result of the studies, the presence of DEHP was detected in 67% of samples in baby food products in the concentration range of 0.17–8.74 mg/kg and in 62% of samples in general-purpose food products in the range of 0.01–5.84 mg/dm^3 (Table 1).

The maximum concentrations of DEHP were found in a dry mixture of a milk drink (8.74 mg/kg) and apple-peach nectar with pulp (5.84 mg/dm^3). According to the total number of samples in which the DEHP was found, dry milk mixtures (88.9% of the samples) and canned meat for baby food (78.6% of the samples) are in the lead of the list. DEHP was not detected in dry milkless cereals.

Table 1. Results of analysis of DEHP in food products

Product name	Range of detected concentrations of DEHP	Average concentration of DEHP	Nnumber of samples with the presence of DEHP, %
Baby food:	*mg/kg (dry product)*		
Milk formula (n = 9)	0.23–2.49	1.12 ± 0.32	88.9
Milk drinks (n = 5)	0.57–8.74	1.86 ± 0.53	40.0
Milk porridge (n = 8)	0.75–2.12	0.90 ± 0.26	62.5
Dairy-free porridge (n = 3)	0	0	0
Canned meat (n = 14)	0.17–2.0	0.93 ± 0.27	78.6
General-purpose products:	*mg / dm*^{3}		
Juice production (n = 10)	0.14–5.84	1.07 ± 0.30	70.0
Milk (n = 10)	0.01–3.12	0.74 ± 0.21	70.0
Kefir (n = 9)	0.01–1.62	0.30 ± 0.08	44.4

Standards for the content of DEHP in food products have not been established in the Russian Federation, the DEHP content is only regulated in drinking water. Given the toxic properties of DEHP and its presence in food products, it is advisable to assess the risk of negative effects of this toxicant when it is ingested with food products, in order to establish standards for the content of DEHP in foods for baby food and general purposes food products.

It is noteworthy, that 13 different phthalates were found in some analyzed food samples, in addition to DEHP. Basically, 2–3 phthalates were present in the samples, less often – up to 5 phthalates. Thus, the results obtained confirm the urgent need to monitor the content of not only DEHP, but also other phthalates in food products of various categories.

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Kinetics of photochemical decomposition of N-(phosphonomethyl)glycine – Roundap herbicide

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The herbicide Roundup (or glyphosate, active substance: N-(phosphonomethyl)glycine (**I**), $C_3H_8NO_5P$, Fig. 1) is the most widely used weed control agent in the world [1]. A number of studies [2, 3] have shown its significant potential hazard for living organisms and humans. In 2015, the WHO International Agency for Research on Cancer included glyphosate in group 2A, corresponding to substances, probably carcinogenic to humans [4].

In this regard, an urgent task is arising – detoxification of Roundup-polluted soils and water, as well as the destruction of stocks of this herbicide, as a highly toxic persistent and environmentally hazardous chemical compound.

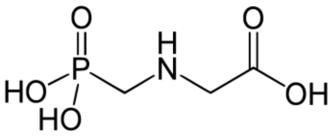

Fig. 1. The chemical formula of N-(phosphonomethyl)glycine, $C_3H_8NO_5P$, (**I**)

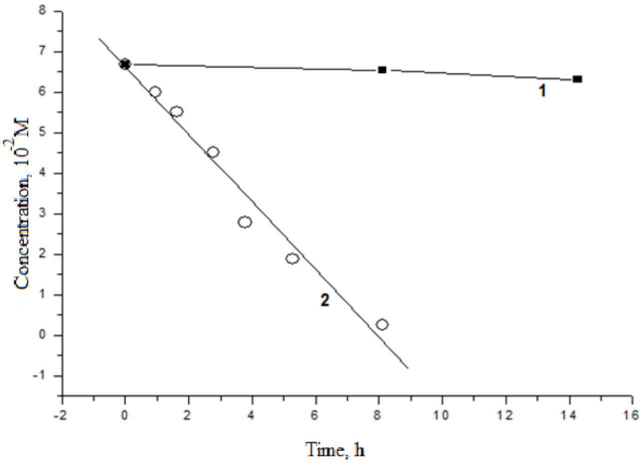

Fig. 2. Changes in concentration of the N-(phosphonomethyl)glycine, (**I**) depending on time of UV irradiation: 1 – blowing with ozone, lamp DRSh-1000; 2 – without blowing in air under the influence of sunlight

It has been previously shown [5, 6] that the most effective approach, which ensures the maximum decomposition rate of pesticides, is the photochemical method. The photochemical oxidation of aqueous solution of (**I**) under the influence of UV radiation was carried out in a round flat-bottomed quartz reactor with a volume of 500 ml. The reactor was installed at a distance of 2 cm from the radiation source, which was used as a lamp of the DRSh-1000 brand with radiation wavelengths in the range of 250–600 nm. The initial concentration of (**I**) was $6.68 \cdot 10^{-2}$ M, the sample volume was 100 ml. Ozone was released from an ozonizer as a mixture with oxygen, its content was 2.5%, or 3.35 mmol/h, or 160.8 mg O_3 per hour. The ozonation of solution of (**I**) with ozone was carried out through a 1 mm diameter teflon tube. The current concentration was measured on a PerkinElmer UV-VIS Spectrometer Lambda EZ 210 spectrophotometer, manufactured in the USA, at a band of $\lambda = 212$ nm.

According to electronic spectra recorded during decomposition of (**I**), the periods of formation of intermediate compounds are traced. After 3 h 47 min of irradiation, a peak $\lambda_4 = 258$ nm is identified, which is present in the samples up to 8 h and 7 min of observation. The peak $\lambda_5 = 238$ nm has been identified once after 5 h 28 min. The peak at $\lambda_3 = 286$ nm appears after 2 h 78 min, then, after 60 min it disappears and reappears in the sample from the time record of 11 h 28 min and is also no longer identified. These results indicate a complex multi-stage decomposition process of (**I**).

The kinetic curve of changes in the concentration of (**I**) as a function of exposure time is shown in Fig. 2. It can be seen that decomposition of (**I**) does not occur in the air under direct sunlight for as long as 14 h 28 min. However, the concentration of (**I**) decreases to $1.0 \cdot 10^{-3}$ M during the same period of time, under the influence of ozone and UV irradiation. The reaction proceeds at a rate of 0.406 M/h, demonstrating a zero order related to the main compound.

Thus, it was shown that the method of photochemical decomposition can be successfully used for practical purposes of the decomposition of the herbicide Roundup (glyphosate).

This work was carried out in the framework of the state task, theme 0089-2019-0014.

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Interconnection of fluorescent intensity and bioeffects of self-organized aqueous systems of herbicide based on N-(phosphonomethyl)glycine and succinic acid in low concentration range

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It has been found that pharmaceutically active substances and pesticides in low concentrations are able to cause a significant damage to hydrobionts, which poses potential risks to humans [1]. This fact led to an understanding the necessity for developing new original approaches to both revealing the substances capable of exerting bioeffects in low concentrations and evaluating their potential risk.

Recently, a new physicochemical approach has been proposed that explains the specific properties of highly diluted aqueous solutions of biologically active compounds. This approach explains the ability of such solutions to self-organize, i.e. to form a disperse phase (nanoassociates), the size and ζ-potential of which nonmonotonically change with dilution, which leads to a coherent change in the physicochemical and biological properties of the systems [2–5].

In this work, we have focused on a deeper studying the nature of the discovered phenomenon, and search for new physicochemical markers of bioeffects of diluted systems, including studying self-organization (dynamic and electrophoretic light scattering), physicochemical properties (specific electrical conductivity, pH, surface tension), UV and fluorescence spectra of multicomponent dispersed systems based on the N-(phosphonomethyl)glycine herbicide (**1**), succinic acid (**2**), with experimental checking their influence on some hydrobionts and wheat roots at low concentrations.

The results obtained in this work for the first time allowed to establish a relationship between non-monotonic concentration dependencies of the size of the dispersed phase (nanoassociates), physicochemical properties (specific electrical conductivity, pH) and fluorescence intensity (λ_{ex} at 225, λ_{em} at 340–350 nm) of a multicomponent dispersed system of **1** and **2,** and their bioeffects.

The results indicate that coherent changes in fluorescence intensity, physicochemical properties, and bioeffects are due to the rearrangement of nanoassociates during the systems' dilution. The observed coherence between the spectral properties of studied systems and the nanoassociates' parameters allows to conclude that the fluorescent characteristics can be used as potential markers of self-organization and bioeffects of highly diluted aqueous systems.

This study was supported by the Russian Foundation for Basic Research (project No. 20-03-00069).

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PAHs identification by solid-phase luminescence method in monitoring of environmental toxicants

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Ensuring the human life safety is closely associated with organization of control and consistent monitoring of various toxic substances' content in the environment. Polycyclic aromatic hydrocarbons (PAHs) are considered as one of the most hazardous pollutants [1]. PAHs are known to possess luminescent properties; consequently, highly sensitive luminescent methods have proved to be efficient for their detection [2], in particular, the solid-phase luminescence method [3, 4].

The aim of our study was to develop optimal conditions for PAHs sorption concentrating and solid-phase luminescent identification.

It is well known that the signal intensity of solid-phase luminescence in various substances depends on the matrix structure and properties, so, it can be changed by the appropriate modification of an analyte surface. Surfactants can serve as good modifying agents. Their use allows increasing reagent preliminary concentration efficiency on the matrix surface.

The fact of luminescence intensity increase of absorbed substances on solid matrices was experimentally confirmed. Thus, the fluorescence intensity of the common PAHs representative – pyrene, fixed on hydrophilic cellulose and hydrophobic polypropylene and viscose matrices was higher than that in the initial pyrene solutions. This was apparently due to the loss of mobility of the pyrene molecules during sorption and an increase in the probability of radiative luminescent transitions (fluorescence) from the first singlet excited state to the ground state.

The highest pyrene solid-phase luminescent signal was observed on hydrophobic polypropylene and viscose matrices, which could be explained by the greater efficiency of hydrophobic pyrene sorption from water onto hydrophobic matrices rather than on a hydrophilic cellulose matrix.

In addition, it has been experimentally determined that it is possible to increase the efficiency of pyrene sorption process on the studied matrices by increasing the sorption time and the volume of the solution.

Overall, the results of our study can be used to develop an analytical procedure for identification and quantification of PAHs as a substantial part of aquatic environmental monitoring.

The results of the study were obtained as a part of fulfilling the State Task No. 5.3922.2017/64 of the Ministry of Education and Science of the Russian Federation.

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Chemical reagents for test systems

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Express diagnostics is of great significance due to the increased unfavorable human impact on the environment.

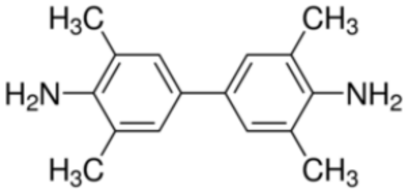
Chemical indicators are used for rapid qualitative and quantitative analysis in extreme conditions wherein indicators are usually based on visual observation of their color changes under the influence of certain substances [1].

The main chemical indicators for such analyses are chromogenic analytical chemical reagents that are also used as markers of biological substrates in a number of biological and immunological tests [2].

We have developed technologies for obtaining indicators for selective and unique coverage of the defined objects and analytes.

3,3′,5,5′-Tetramethylbenzidine (TMB) is a non-carcinogenic indicator applied in an oxidation reaction involving hydrogen peroxide, which is able to substitute the previously used carcinogenic benzidine and *o*-dianisidine.

TMB is used for determination of hydrogen peroxide and can also be applied for evaluation of the catalytic activity of alkaline phosphatase in the consequence of successive reactions for the selective determination of mercury(II), lead(II).

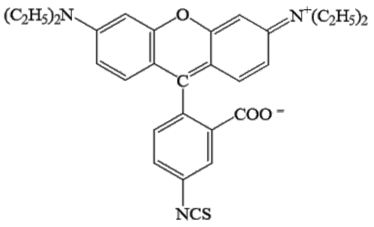
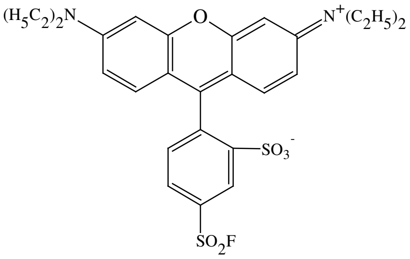
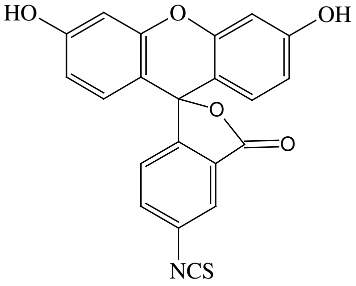


The antigen-antibody reaction is the basis of many highly sensitive immunological studies and test systems.

The use of fluorescent hydroxanthene dyes for antibody tags puts these dyes in the first place among the known protein tags due to the bright fluorescence of their conjugates in the area of maximum sensitivity for human eye and marked difference in the color of fluorescence due to autofluorescence of microorganisms and body tissues.

We have developed technologies for producing fluorescent indicators (Table 1): 4-RITC (4-rhodamine C isothiocyanate), Rhodamine C sulfofluoride, and 5-FITC (5-Fluorescein isothiocyanate) with a high purity of more than 99% [3].

Table 1. Fluorescent dyes

Dyes	Maximum fluorescence	Relative fluorescence intensity	Maximum absorption	Extinction coefficient
4-RITC  	582 ± 2 nm	80 Buffer in dimethylformamide	558 ± 2 nm	$9.2\cdot10^4$ > 95%
Rhodamine C sulfofluoride  	578 ± 3 nm	70	560 ± 2 nm	$8.1\ 10^4$ >90%
5-FITC  	542 ± 2 nm	85 In phosphate buffer	490 ± 2 nm	$8.5\cdot10^4$ > 99%

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New synthetic route to chlorinated cobalt dicarbollide, a component for cesium-137 extraction from radioactive waste

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First metallocarboranes were synthesized in 1965 [1]. Chlorinated derivatives of cobalt dicarbollides (CCD) were found to be sufficient extractants for radioactive cesium-137 by Czech researchers [2]. Then, different scientists have developed various processess using CCD [3–7] with the main goal of extraction of cesium-137 (and other radioactive isotopes like americium and europium isotopes) from radioactive waste. The standard approach to synthesize CCD is to use chlorine gas with different reagents or conditions. For example, gamma-irradiation in tetrachloromethane-nitrobenzene solutions gives mono-, di-, or hexachloro derivatives depending on the amount of radiation absorbed [8]. The presence of iron powder in tetrahydrofuran-isopropanol or HCl/NaOCl aqueous solutions gives dichloro derivatives [9]. However, it is obvious that using chlorine and nitrobenzene is highly dangerous for human as well as for the environment. For this reason, we started searching for some other reagents and solvents to make the process less hazardous and more eco-friendly.

In our study, we applied trichloroisocyanuric acid $C_3O_3N_3Cl_3$ (TCICA) as a chlorinating agent to $[commo\text{-}3,3'\text{-}Co(C_2B_9H_{11})_2]^-$ anions (in form of cesium and potassium salts) in boiling acidic media: from acetic acid to isobutyric acid with and without the addition of sulfuric acid. The reaction products include a mixture of penta and hexachloro derivatives $8,8',9,9',12\text{-}[Co(C_2B_9H_9Cl_2)(C_2B_9H_8Cl_3)]^-$ and $8,8',9,9',12,12'\text{-}[Co(C_2B_9H_8Cl_3)_2]^-$ with relative yield up to 80%. The by-product of the reaction is cyanuric acid which is ‘essentially nontoxic’ [10].

The reaction was carried out under the stirring in the air atmosphere, adding TCICA in portions at regular time intervals. After adding TCICA, we set the temperature at the boiling level and continued stirring for at least 6 h. The structure of the products was confirmed by the NMR spectroscopy method (^{11}B, ^{1}H, ^{13}C) and IR-spectroscopy (for cyanuric acid).

Thus, we developed a new synthetic route for CCD in mild conditions using less hazardous materials and producing less harmful co-products.

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Metallomicellar systems for solubilization of hydrophobic biologically active substances and ecotoxicants

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Novel metallomicellar systems have been developed which can be applied for solubilization of hydrophobic biologically active substances and ecotoxicants. The systems are based on 1-alkyl-4-aza-1-azoniabicyclo[2.2.2]octane bromide [Alk = C_nH_{2n+1}, n = 16 (D-16), 18 (D-18)] and copper(II) or lanthanum(III) salts. These metallosurfactants exhibit high aggregation ability and solubilization activity with respect to hydrophobic drugs furadonin (nitrofurantoin, NF) and griseofulvin (GF), as well as to organophosphorus ecotoxicants – 4-nitrophenyl-O-alkylchloromethylphosphonates (Alk = C_nH_{2n+1}, n = 4, 6) [1–3].

The solubilization capacities of [D-16×$CuBr_2$] associates with respect to NF, and [2D-16×$Cu(NO_3)_2$] and [2D-16×$La(NO_3)_3$] micelles with respect to GF were determined by spectrophotometry. The solubility of drugs in metallomicellar systems increases by one order which may contribute to an increase in the drug bioavailability. High binding constants (more than 3–4 orders of magnitude) of substrates (phosphonates) with [2D-16×$La(NO_3)_3$] and [2D-18×$La(NO_3)_3$] aggregates (K_s) were revealed. The transition of ecotoxicants to the micellar phase leads to up to 50-fold acceleration of their hydrolytic decomposition under mild conditions (Tris buffer, 25–30°C, pH = 8.0–8.3. The increase in the hydrophobicity of metallosurfactants and phosphonates contributes to an increase in the catalytic effect.

In accordance with pseudophase model of micellar catalysis, the catalyzed process parameters (the process rate constant in micellar phase, K_s, K_{Nu} and factors of the concentrating reagents [organophosphorus substrates and nucleophile (hydroxide ion)] in micellar phase (F_c), and the change in microenvironment of reagents during their transition from bulk phase into micelles (F_m) were determined. The main role of F_c was established.

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Mixed nonionic/cationic surfactant systems as adjuvants for pesticide compositions decreasing their consumption rate and toxic effects

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Surfactants find wide applications in biotechnologies, pharmacology and agriculture as solubilizers, vehicles for delivery of biologically active substances and adjuvants improving properties of drugs and pesticides. They provide superior solubility of compounds in aqueous systems, whereby increasing its bioavailability, enhance wetting of the surface and transport of target substrate into animal and plant cells. Significant portion of systems used for these purposes is micellar solutions based on low-toxic nonionic surfactants, however, they are often less effective than more toxic cationic amphiphiles. The latter ones exhibit high solubilization activity and capability to attain the better contact with biosurfaces due to both hydrophobic and electrostatic forces.

The presence of additional functional fragments in the structure of surfactants makes it possible to involve other types of interactions, in particular, hydrogen bonding. Compromise solution could be achieved through the application of binary systems that allows to combine advantages of two types of amphiphiles: reduced toxicity of nonionic amphiphiles and high effectiveness of cationic amphiphiles.

In the framework of this investigation, perspectivity of application of binary compositions based on Tween-80 and cationic amphiphiles bearing 3-hydroxypiperidinium fragments as fungicide carboxin boosters (used as seed dresser in agriculture) has been shown. Experiments have been aimed on (i) determination of wetting ability of these systems and quantitative characterization of its solubilization activity toward carboxin; (ii) design of approaches for analytical control of the amount of this fungicide in potato seed; (iii) establishment of factors affecting the penetration capability of tested composition (the nature and concentration of surfactant, pH of medium, exposure time, temperature).

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Wastewater treatment with ion exchange resin based on high-molecular weight heteroatomic oil components

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Wastewater generated as a result of the production cycle of chemical, petrochemical, metallurgical, pharmaceutical and other industrial sectors often contains hazardous ecotoxicants or xenobiotics. Consequently, treatment of industrial wastewater is one of the important environmental challenges of modern technological progress. The main ecotoxicants include heavy and rare-earth metals, non-metals, macroelements, radionuclides, various organic pollutants, such as phenol and its derivatives, benzopyrenes, polychlorinated biphenyls, etc. The harmful effects of ecotoxicants are manifested even at very low concentrations (for example, the maximum permissible concentration of phenol in water is 0.001–0.002 mg/l) [1]. The discharge of contaminated water into ponds and drains results in deteriorating general sanitary situation, affecting living organisms not only by applying the toxic action, but also producing a significant change in the composition of nutrients and dissolved gases (oxygen, carbon dioxide). Therefore, the proper treatment of industrial effluents from contamination with ecotoxicants is an important environmental task.

Numerous methods of wastewater treatment from ecotoxicants are known, where various sorbents are used, such as porous modified and unmodified coal, aluminosilicates, silica gel, zeolites, various organic materials, etc. Among commonly used organic materials, carbon ionites are of great importance for sorption processes. A promising carbon-containing raw material for the production of ion exchangers is derived from asphaltenes - high molecular weight heteroatomic components of oils and oil residues [2].

In this study, the preparation of ion exchange resins was carried out by the interaction of asphaltenes with sulfuric acid or a mixture of sulfuric acid and oleum at a temperature of 100°C at various periods of time [3–5]. Anion exchangers were prepared by reacting asphaltenes with nitric acid at a temperature of 60°C, followed by the reduction of nitro groups under various conditions. The sorption properties of sulfocationites and anion exchangers based on asphaltenes in the absorption of ions of various metals and phenol from aqueous solutions were evaluated. The developed sorbents exhibited effectiveness comparable with that of industrial samples, along with such advantages as low cost and availability of raw materials for its preparation.

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Development of pilot decaborane production technology based on sodium undecaborate oxidation by acetone

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Boron chemistry occupies one of the leading positions in modern science and industry. Surprisingly, diverse spatial and chemical structure of boron hydrides, carboranes, metallacarboranes and other derivatives predetermines not only the unique features of these compounds but also makes it possible to use them in a broad variety of applications, for example, in medical science as pharmacophores [1], in catalysis [2], in organometallic chemistry as ligands, in production of luminescent materials, polymers [3, 4], nanomaterials and liquid crystals, and also for cesium and strontium radionuclides extraction from nuclear waste [5, 6].

All this taken together gives a big impulse for developing technologies for production of compound which is essential for the whole boron-based chemical industry – decaborane, $B_{10}H_{14}$. An urgent need in decaborane is growing year by year, so the idea of developing a new efficient method for its synthesis has attracted much attention.

We have analyzed the available literature sources in this field [7, 8] and concluded that most optimal and safe method for obtaining decaborane is a two-step synthesis via intermediate undecaborate salts [9]. However, the methods described in the literature are neither effective nor eco-friendly [10]. For this reason, we began searching for new ways of undecaborate salts oxidation. In an attempt to address the above problem, carbonyl compounds such as aldehydes and ketones were chosen as oxidizing agents. It is worth noting that we applied a reaction which was unknown before and it produces decaborane from $NaB_{11}H_{14}$ with high yield comparing to the commonly used synthetic procedures [8, 10]:

$$2NaB_{11}H_{14} + 4R'C(O)R'' + H_2SO_4 + 6H_2O \rightarrow 2B_{10}H_{14} + 2H_3BO_3 + 4R'CH(OH)R'' + Na_2SO_4,$$

where $R' = H, CH_3, C_2H_5, C_6H_5$,
$R'' = H, CH_3, C_2H_5, C_6H_5, CH_2COCH_3$.

We have continued further development of this direction and invented a novel decaborane producing technology using sodium undecaborate oxidation with ketones. The invention has been successfully patented and is now being implemented into production in State Research Institute of Chemistry and Technology of Organoelement Compounds (GNIIChTEOS) [11].

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Changes in composition of menthol stereoisomeric mixture produced on modified nickel catalyst

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The main industrial method for producing synthetic *d,l*-menthol is catalytic hydrogenation of thymol [1]. Due to the presence of three asymmetric carbon atoms in the molecule, menthol can exist in the form of eight optical isomers (enantiomers), in four pairs of racemates: *d,l*-menthol, *d,l*-neomenthol, *d,l*-isomenthol, and *d,l*-neo-isomenthol. However, regardless of the catalyst used, the product of catalytic hydrogenation of thymol is obtained as the mixture of all menthol isomers in different ratios [2-4]. This significantly complicates the technology since the separation of *d,l*-menthol from other isomers and its purification require the use of high-efficiency deep vacuum rectification step which is accompanied by significant loss of the end product.

This work was focused on the modification of the existing technology of thymol catalytic hydrogenation in order to increase the concentration of *d,l*-menthol in the hydrogenation product.

The technology considered in this study involved the process of hydrogenation of thymol in the melt over an industrial nickel-based catalyst «NIAP 14-01» followed by catalytic isomerization of the hydrogenation product over the same catalyst.

We used in the experiments a sample of crystalline thymol (Symrise, Germany), and a nickel-based NIAP 14-01 catalyst (NIAP-KATALIZATOR, Russia). The reaction mass analysis was performed with the use of an Agilent 7820/5975 chromatography-mass spectrometric system (Agilent Technologies, USA).

The process of thymol hydrogenation was carried out in an RVD-3-700 autoclave reactor (UOSLab, Ukraine) with a volume of 700 ml, at a temperature of 165–175°C, at a hydrogen pressure of 1.5–5.0 MPa for 5–10 h.

As expected, the experimental results showed that under the selected conditions the reaction did not occur stereospecifically, and the hydrogenation product was a mixture of spatial menthol isomers with a maximum *d,l*-menthol level of not more than 35%. Moreover, the use of the vacuum rectification step did not significantly increase the concentration of the product due to the low efficiency of the columns used. To this end, an attempt was made to increase the concentration of *d,l*-menthol in the process of catalytic isomerization of the hydrogenation product at the temperature of 165–175°C under the pressure of 5–

6 MPa for 4–10 h using a fresh portion of the catalyst. As a result, the content of *d,l*-menthol in the reaction mass was raised to 55.4% due to isomerization reactions.

Thus, the approach proposed in this study provides the significant increase in the concentration of *d,l*-menthol in the end-product of thymol hydrogenation. It is noteworthy that the main advantages of the described technological procedure include the use of the same catalyst at both hydrogenation and isomerization steps, as well as the fact that an additional processing equipment is not required.

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Biotesting method for assessing changes in quality of milk during its industrial heat treatment

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It's a common knowledge that human health, performance, behavior, creative activity and ability to resist negative environmental impact strongly depend on good nutrition. Nowadays, the food products that can increase the antioxidant effects, has become extremely important. The antioxidant effect is necessary to decrease the toxic effects caused by the excess of free radicals which are harmful to humans and accumulate in large quantities in the current unfriendly environmental situation [1, 2].

Milk and dairy products are one of the main sources of vitally important substances with antioxidant activities. However, milk is a perishable product, therefore, it is subjected to mandatory heat treatment at dairy plants, which leads to a significant change in its quality, and therefore decreases its antioxidant effect [3].

Bioassay is one of the useful methods of comprehensive study of the milk quality changes under the various factor exposures.

Thereby, the purpose of this study was to evaluate the impact of the several industrial modes of pasteurization of cow's milk on the stress resistance of *Paramecium caudatum* ciliates.

Hydrogen peroxide (1.5% aqueous solution) was used as the stressor, indicating damages mainly the lipid part of the cells membrane [4].

The time of paramecia immobilization under the stressor effect was recorded as the main research parameter during the experiments.

The following industrial pasteurization modes were studied in the work: 65°C for 30 min; 76°C for 5 min; 90°C for 20 s; 95°C for 5 min.

According to the results obtained (Fig. 1), the most stress-resistant ciliates are the ones that have been cultivated with the addition to the Lozin-Lozinsky's medium of cow's or goat's milk treated at 76°C for 5 min and 90°C for 20 s. This is apparently due to the maximum preservation of casein in the milk in the current heat treatment modes of vitamins and the release of low molecular weight peptides and amino acids into the plasma of milk, which play the role of additional growth factors with the antioxidant properties [3].These substances can hinder the oxidating damaging processes in the cell, thereby increasing the survival time of ciliates in the acute experiment.

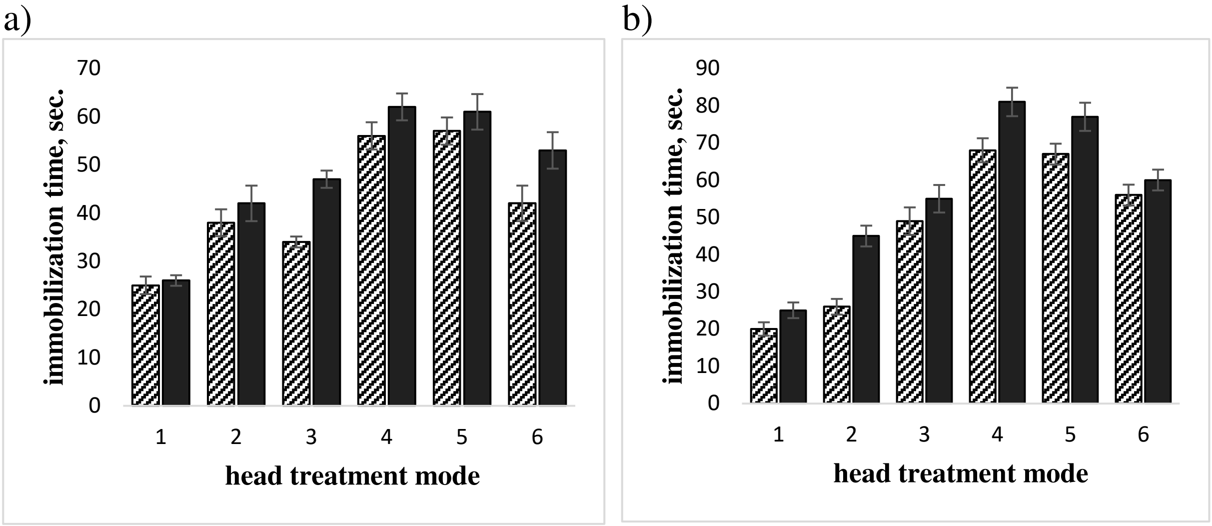

Fig. 1. Effect of adding cow’s milk to the culture for evaluating *Paramecium caudatum* stress resistance to hydrogen peroxide. 1 – control milk sample; 2 – raw milk; 3 – 65ºC 30 min; 4 – 76ºC 5 min; 5 – 90ºC 20s; 6 – 95ºC 5 min.
▨ – 3 days, ■ – 5 days

Thus, the stidy has revealed an increase in stress resistance of the ciliates *Paramecium caudatum* when native cow’s milk was added to the nutrient mixture as compared to the control experiment. The high sensitivity of the selected test-object to a change in the antioxidant properties of milk processed under various pasteurization modes has been established. Besides, optimal heat treatment modes have been identified that ensure the highest preservation of the antioxidant activity of cow’s milk and, accordingly, provide higher stress resistance of the *Paramecium caudatum* ciliates: 76°C for 5 min and 90°C for 20 s.

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Oxygen effect on degree of nitro groups abstraction in alkaline degradation of nitrocellulose-containing waste

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Manufacturing processes of gunpowders, filter materials, varnishes, paints, artificial leathers and others are accompanied by formation of hazardous waste, nitrocellulose (NC). The discharge of NC-containing wastewater without treatment into sludge collectors leads to the accumulation of NC in the form of explosive bottom sediments. The development of an effective and safe method for the disposal of this type of waste, which could reduce the negative burden on the environment and eliminate the sources of emergencies, is more than relevant.

Due to the fact that microorganisms are not able to efficiently decompose cellulose nitrates in the case of highly concentrated waste with an NC content of up to 70–80%, we have proposed a method of waste pretreatment using alkaline hydrolysis. Cellulose nitrate decomposition was carried out in the presence of slaked lime ($Ca(OH)_2$). The aerobic and microaerophilic hydrolysis conditions were studied in the pH range from 11.5 to 12.0.

In total, 30 sediment samples were taken up from different depths of the sludge collector of nitrocellulose-containing sewage sludge (NCCSS). The average content of NC in bottom sediments was 751.16 g/kg dry sediment (75.1%). At the same time, the studied NC sediment samples had neutral pH values and contained a large number of soil nutrients (carbon, nitrogen, phosphorus) and indigenous microorganisms (total germ count averaged at the level of $5.0 \cdot 10^9$ CFU/kg dry sludge).

It was found that alkaline hydrolysis of NCCSS under microaerophilic conditions provided reduction of NC degradation degree by 54.6% in 35 days. In this case, the rate of NC degradation and the half-life of the NC were found to be 0.023 days^{-1} and 31 days, respectively. Alkaline hydrolysis of NCCSS under aerobic conditions provided reduction of NC degradation degree by 47% in 16 days. At the same time, the rate of degradation of NC showed more than 2-fold increase (0.043 days^{-1}) while the half-life of NC decreased (16 days).

A high accumulation of nitro groups in the liquid phase was observed during hydrolysis. Under microaerophilic conditions, the accumulation of nitrites and nitrates was observed up to 6187 mg NO^{2-}/l and up to 4536 mg NO^{3-}/l, respectively. At the same time, it should be noted that aerobic conditions resulted in decrease of the concentrations of nitrites and nitrates by 3.3 and 3.4 times, respectively.

It was established that the community of indigenous microorganisms was exposed to the toxic effect of accumulated nitrite ions in solution. As a result, the total number of microorganisms during alkaline hydrolysis decreased by four orders of magnitude and amounted to $3.19 \cdot 10^5$ CFU/kg dry sediment, with most fungies survived.

It was shown that wastewater generated in the course of alkaline hydrolysis of NCCSS under aerobic conditions required additional purification, since it contained nitro groups in concentrations significantly higher than the MPC. A low efficiency of removing nitrites from solution was achieved, both by chemical and sorption methods. The use of the commercial drug Toxivec at a concentration of 10% provided the removal of nitrites at the level of 23.5%. The use of the commercial preparation Agroionit allowed to remove nitrites by 7.0%.

Thus, the biological conversion of nitrites into a safe nitrogen-containing form, nitrates (potential fertilizers) is recommended to carry out using the nitrifying ability of aerobic microorganisms. In contrast, to obtain safe molecular nitrogen, the denitrifying ability of some aerobic and anaerobic microorganisms can be used.

Kinetic parameters of degradation of nitrocellulose-containing sewage sludge under anaerobic conditions

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The production of nitrocellulose (NC) in Russia amounts to thousands of tons per year and finds a lot of applications, both military and civilian. The specificity of the technology for the NC production is characterized by formation of a significant amount of wastewater containing particles of cellulose nitrates. Precipitation of industrial effluents with up to 50–80% of irrevocable nitrocellulose is usually accumulated under a layer of water in special sludge collectors. Such storages, as a rule, are already crowded and require constant maintenance, since NC precipitation represents a high hazard due to the possibility of its explosion. Therefore, the search for methods of disposal of accumulated NC-containing waste is an urgent issue.

Biological methods, in our opinion, look more attractive in comparison with the physicochemical methods of utilization of NC, both in terms of environmental safety and cost effectiveness. Nevertheless, in the case of highly concentrated wastes with an NC content of up to 70–80%, aerobic and microaerophilic microorganisms are not able to quickly and efficiently decompose cellulose nitrates *in situ* without preliminary destructive treatment of the sediments.

To avoid the difficult step of waste treatment, we decided to check the possibility to decomposing highly concentrated NC sediment by cellulolytic active anaerobic microbial associations in bioreactors with optimal conditions for microorganisms, along with evaluation of kinetic parameters of degradation. We used bottom sediments with a humidity of ~80% and an NC content of about 75.1% of dry matter. The pH value of the sediments was ~7; in addition, they contained mobile nitrogen and phosphorus in biogenic concentrations. Anaerobic consortia from two water treatment plants – municipal and industrial effluents and food effluents at growth temperatures of 55 and 35°C, respectively, were used as biocatalysts. Decomposition of NC by methanogenic and acidogenic groups of consortia of microorganisms was studied in comparison with the action of native sediment microflora, which was $\sim 5 \cdot 10^5$ CFU/g of absolutely dry sediment.

The duration of the experiment was about 3 months with periodic determination of NC in the treated sediment. The study resulted in obtaining the kinetic curves for decomposition of NC sediments depending on the degree of loading of the reactor with a biocatalyst, along with the curves of biogas accumulation with multiple differences, which made it possible to determine the optimal conditions for biocatalysts' use.

The results will be useful for development of special mobile biogas plants for environmentally friendly waste-free processing of NC-containing waste products to produce biogas and safe solid sediment.

Use of chlorin e_6 for development of safe photosensitizers for photodynamic therapy

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Photodynamic therapy (PDT) is now one of the most promising conservative treatments for cancer. This method is based on photosensitizer's (PS[§]) ability to accumulate selectively in tumor or other target tissues and generate singlet oxygen or oxygen-containing free radicals under local exposure of radiation of a certain wavelength corresponding to maximum absorption of PS. These active oxygen forms are extremely cytotoxic and play a defining role in malignant cell death.

Nowadays, tetrapyrroles as photosensitizers are widely used in Russia and abroad. They can be classified in three categories: 1) porphyrin-based, 2) chlorophyll-based, and 3) dyes. The development of the PDT method is targeted at the creation of the so-called 'ideal PS' with high selectivity, low phototoxicity and rapid pharmacodynamics. Chlorin-based compounds are among the most promising ones are, including chlorin e_6 (Ce_6) [1, 2]. They are characterized by an intense absorption band in the long-wave region of the spectrum (600–800 nm), in which biological tissues are more optically transparent (so-called 'therapeutic window') and have a high capacity to accumulate in the target tissue. The availability of raw materials plays a main role in the development of chlorin-based compounds, while chlorins' precursor chlorophyll *a* is produced, for example, from *Spirulina platensis* microalgae or nettle leaves. Moreover, chlorophyll, as an element of the conventional nutrient media, is safe for humans. However, the main challenge in the pharmaceutical use of tetrapyrroles, including chlorins, is their low solubility in physiological solutions. This makes it difficult to obtain effective pharmaceutical solutions for their use in PDT.

In attempts to address this issue, we have synthesized new supramolecular compounds based on Ce_6 with different excipients, such as polyvinyl alcohol hydrolyzed (PVA), poly-N-vinylpyrrolidone (PVP), sodium salt of carboxymethylcellulose (Na-CMC), Cremophor® PEG-40 (polyethyleneglycol, PEG) and investigated their photophysical properties. Our choice of these water-soluble excipients is explained by the fact that they are safe and widespread

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[§]PS are natural or artificially synthesized substances capable of biological tissues photosensitizing.

biologically-compatible substances which are used as ingredients of pharmacological drugs and cosmetic products.

Absorption spectra (200-900 nm) of these supramolecular compounds were recorded with TU-1901 UV-Vis spectrophotometer (Beijing Purkinje General Instruments Co Ltd, China). The fluorescence spectra were recorded in the range of 550–800 nm using a Fluorat-02-Panorama spectrofluorimeter (Lumex, Russia) with the excitation wavelength of 410 nm. All measurements were conducted at 20°C.

The analysis of the spectral and fluorescent data indicate the consecutive degradation of chlorin e_6 aggregates and excipient-Ce_6 complex formation. In addition, the rate of Ce_6 aggregates degradation in the aqueous medium is found to vary in the presence of different excipients. Moreover, a shift to a long-wave region of the absorption spectrum is observed for all supramolecular systems presented here which can be a good prerequisite for increasing tissue permeability for visible light and reducing the absorption of light by blood haemoglobin in the 500–600 nm region, resulting in a significant increase in the PDT efficiency. Furthermore, the addition of all the excipients leads to the increase in intensity of Ce_6 luminescence.

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Designing concept of structure and content for data bank 'Persistent Organic Pollutants in Russia'

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The Stockholm Convention on Persistent Organic Pollutants (2001) is the main international legal act aimed at protecting the environment and public health from exposure to highly hazardous chemicals – persistent organic pollutants (POPs). The Convention was ratified by the Russian Federation in 2011 [1]. To fulfill international obligations provided for by the Stockholm Convention, the Government of the Russian Federation adopted the appropriate Resolution [2]. In September 2017, the Novosibirsk Institute of Organic Chemistry of the Siberian Branch of Russian Academy of Sciences was appointed the National Focal Point of the Russian Federation, created to exchange information on fulfilling the obligations of the Russian Federation provided for by the Stockholm Convention on Persistent Organic Pollutants (POPs) [3].

A necessity for information exchange with other participants requires creating a data array that ensures compliance with and fulfillment of the obligations of the Russian Federation on POPs. In addition, this is an urgent request of the Secretariat of the Stockholm Convention. Development of the information data bank has started. The data bank will contain information on the chemicals included in the list of POPs (Annexes A, B and C of the Convention) as well as on candidate substances that can be proposed for inclusion in the annexes in accordance with Article 8 of the Convention. Open source information on the chemicals is being collected according to the criteria set out in Annexes D, E and F of the Convention (identification data, persistence, bioaccumulation, long-distance transportability, toxicity/ecotoxicity, analysis, sources, waste, risks, and regulatory measures).

Accumulation, processing, analysis and integration of information regarding POPs and candidate substances is carried out to form the data bank as a component of an intellectual system (expert system) on POPs, including a set of electronic arrays managed by the MariaDB DBMS (electronic collections of documents in PDF format - scientific articles, reports, standards, methods and a database of their bibliographic descriptions in RIS/BibTeX formats). Access to the data bank is implemented via the Internet by the http protocol.

The creation of the data bank will assist in systematization of information on POPs in Russia and ensure its free dissemination.

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Digital technologies in the field of informing on hazardous chemicals

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Chemicals, through the different steps from their production to their handling, transport and use, can pose a real danger for human health and the environment. The Globally Harmonized System of Classification and Labelling of Chemicals (GHS) is a system for chemical classification and hazard communication developed by United Nations. GHS addresses classification of chemicals by types of hazard and proposes harmonized hazard communication elements, including labels and Safety Data Sheets (SDS) for chemical products. In the legislation of the Russian Federation, this document is implemented through a number of standards including State standard GOST 30333-2007 “Safety Data Sheet for chemical products. General requirements”. SDS has an informative character for those who come in contact with chemicals throughout their life cycle as well as contains information on the main manifestations of dangerous effects of products on population environment.

In accordance with the Technical Regulations of the Eurasian Economic Union (TR EAEU 041/2017), SDS is involved in the procedure of state registration of chemical products. The information provided in the set of applied documents (including SDS) is checked for compliance with the requirements of national standards with subsequent entry of reliable information into the national part of the registry.

Currently, voluntary registration of SDS is envisaged in Russia with their accumulation in the database – Register of SDS of Russia and the CIS-countries (Certificate of state registration No. 2018670022). Chemicals with SDS included in the Register would be able to undergo a further simplified procedure for the state registration. Previously, to be included in the Register of SDS, the applicant had to submit a complete set of documents in paper format and exchange documents in hard copies with contractors. From 2020, it was decided to convert the exchanging documents in electronic format for convenience and reducing time needed to registration of SDS where each SDS is assigned a unique registration number and QR-code. Using QR-code applied on the SDS cover page allows easy and quick information access from the SDS Register database. An applicant, supplier or consumer of hazardous chemicals can check SDS registration details, registration date, general information on applicants as well as hazardous properties of the chemicals. Introduction of the electronic verification of SDS provides an opportunity to streamline operating procedures, reduce the number of SDS containing unreliable content, and systematize the data on chemicals being traded in the territory of the Russian Federation.

Synthesis and study of spectral-luminescent properties of chelate complexes based on 8-hydroxyquinoline

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Organic metal complexes based on 8-hydroxyquinoline ligand have a broad spectrum of applications. For example, these complexes are used in analytical chemistry due to their ability to detect metal ions, as solidifiers of organosilicon and other resins, as antiseptic material (8-hydroxyquinoline of cooper), etc. [1]. Besides, they are known for their electroluminescent properties and used for fabrication of organic light-emitting diodes (OLED) for electroluminescent displays – a technology of optoelectronic devices, which has been developing in the last 30 years in informational display systems [2]. One of the most commonly used fluorescing agent is tris(8-hydroxyquinolinato)aluminum. It is a fluorophore with green light, used as electronic light of transport layer.

We have synthesized a series of coordination compounds based on organic ligand (8-hydroxyquinoline) and the coordinating metal atom (Me = Sb, Ti, Sn, Ge).

The chelate complex synthesis was conducted by the following scheme:

$$MeCl_n + nC_9H_7ON = Me(C_9H_7ON)_nCl_n$$

Oxyhydrate metals were synthesized according to the known procedures.

The structure of the synthesized compounds was proved by physical-chemical characterization and spectroscopic methods of analysis.

All the synthesized 8-hydroxyquinoline metal complexes were recrystallized before the measurements to exclude the decomposition of the compounds during their storage.

The electronic absorption spectra were registered by UV rays DRT-1000 lamp with different time exposure. First of all, the electronic absorption spectra 8-hydroxyquinoline and the chelate complexes were registered in the range of 190–500 nm. In this range the three clearly defined maximums were observed with the wavelengths of 195.4, 252.2, and 248.8nm.

According to the irradiation results, the following changes were revealed: leveling the signal through the visible part of the spectrum and, at the same time, a hypochromic shifting of the UV maximums of 252.2 nm and 248.8 nm. The last changes are characterized by hypochromic effect, since the new shorter wavelength absorption band has lower optical density than that of the starting compound without UV light radiation effect. The electronic absorption spectra siftings are typical for π→π* transitions with LQA on HOMO in heterocyclic compounds.

The blue band shift absorbing is apparently the result of hydroxyl 8-oxyquinolate complex oxidation reaction under the UV-radiation with the formation of the corresponding quinine, which occurs with extra hypochromic effect. Using of 8-hydroxyquinoline metal complexes in production of organic light-emitting diodes is based on higher stability of the coordination compound as compared to the starting ligand. The electronic spectra of the synthesized compounds show that $Ge(Oxin)Cl_3$ has the most pronounced spectral properties. The results of the study will be used in further synthesis of chelate complex of 8-oxyquinolate, as the potential material for forming the light-emitting layers of OLED devices.

In addition, the synthesized complexes were exposed to biological screening. The results indicate that some of the synthesized compounds have strong microbiological activity. Possible mechanisms of their biological effects and the relationships ‘structure-microbiological activity’ are discussed.

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Methanotrophic bacteria-mediated formation of silver nanoparticles

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Silver is considered as a heavy metal and can exhibit toxic effects at its excessive levels. At the same time, disinfecting properties of silver are also known. Meanwhile, silver nanoparticles are widely used to obtain a broad variety of materials with antiseptic properties. Therefore, it is of great interest to continue studying the effects of silver nanoparticles on living organisms with the purpose of creating novel, improved procedures for their preparation.

Currently, different microorganisms such as bacteria and microscopic fungi have been used to develop non-toxic methods to synthesize nanoparticles. Methods of microbial production of nanoparticles are found to be relatively cheap, environmentally-friendly and extremely diverse. We have studied in this work a posibility of synthesis of silver nanoparticles by methane-oxidizing bacteria *Methylococcus capsulatus* (M) capable of utilizing methane as their only carbon and energy source.

Methylococcus capsulatus (M) cells were cultivated under continuous perfusion conditions in the Ankum 2M fermenter in a standard mineral medium at 42°C, pH = 5.6. The biomass of microorganisms was separated from the nutrient medium by centrifugation for 10 min at 7000 rpm and transferred to solutions of silver nitrate of various concentrations containing Ag+ ions in the range of 5–1000 mg/L. Incubation took place at room temperature during five days.

The results revealed extracellular formation of silver nanoparticles by bacteria which was observed by spectrophotometrically. In addition to silver nanoparticles, microparticles with a diameter of several microns were also formed along with nano-silver.

Thus, it can be concluded that silver is not toxic for methane-oxidizing bacteria *Methylococcus capsulatus* (M) and bacteria are capable to form silver nanoparticles in addition to methane utilization.

Biopesticides based on extracts of some plants of the genus *Centaurea* L.

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Every year, bacterial and fungal microorganisms directly or indirectly cause significant crop losses worldwide [2]. Pesticides, produced from chemical substances, are used globally as the main plant protectors. However, their prolonged and inappropriate use leads to the accumulation of chemical compounds and their metabolites in components of ecosystems, food chains, and, finally, in food [6]. Recently, an alternative strategy for control of agricultural pests, bacterial and fungal diseases, based on the use of biopesticides, has been actively introduced. Biopesticides have a number of advantages, in particular, they are biodegradable and, in most cases, do not lead to the formation of resistant strains of bacteria and fungi [4]. Studies of bactericidal and fungicidal activity of plant components and metabolites are extremely important in terms of their potential use as biopesticidal resources. Plants of the *Asteraceae* family are of particular interest as a source of raw materials for biopesticides. It is a large family of flowering plants represented by more than 23000 species. Numerous members of this family have significant therapeutic potential and are actively used in traditional medicine [5].

The objects of our research were extracts from plants of the genus *Centaurea* L., i.e. *Centaurea cyanus* L., *Centaurea jacea* L., and *Centaurea scabiosa* L. The extracts were obtained by maceration of air-dried and crushed aboveground plant biomass in ethanol.

The antimicrobial activity of extracts was determined by the serial dilution method [1, 3] to establish minimum inhibitory concentrations that inhibit the growth of bacteria and fungi, as well as minimum bactericidal concentrations, and minimum fungicidal concentrations causing cell death of microorganisms. The phytopathogenic strains of bacteria (*Clavibacter michiganensis* and *Xanthomonas arboricola*), and fungi (*Alternaria solani*) were studied. Chloramphenicol (Kazan Pharmaceutical Factory, Russia) and diphenoconazole (Score250 EC, Syngenta, USA) were used as reference compounds in the experiments.

The results of the antimicrobial activity of the investigated plant extracts indicated the presence of bacteriostatic properties. The minimum inhibitory concentrations were observed in the range of 0.0625–1%. Bactericidal action of extracts concerning phytopathogenic bacteria was revealed in concentration range of 0.0625–2%. The minimum fungicidal concentrations varied in the range of 0.1–0.5%. In most cases, the highest activity was found in *Centaurea scabiosa* L., and the lowest – in *Centaurea jacea* L.

Clavibacter michiganensis was characterized by the highest sensitivity to components of plant extracts. *Clavibacter michiganensis* is known as an optional parasite of plants in the *Solanaceae* family. The disease is manifested by withering and necrosis on stems, leaves and fruits during flowering of plants.

In summary, *Centaurea scabiosa* L. extract exhibited a high antibacterial activity against *Clavibacter michiganensis* and, therefore, can be used to create environmentally friendly preparations for processing of agricultural plants of the *Solanaceae* family (tomato, eggplant, potatoes, etc.).

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Environmentally safe technology for production of pectin from beet pulp

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The aim of this work was studying the process of hydrolysis-extraction of pectin from beet pulp, optimization of technological parameters and the development of environmentally safe production technology.

Beet pulp – the large-tonnage waste of the sugar industry – was the object of our research. The involvement of beet pulp in the economic turnover would address the issues of resource conservation and environmental protection. The introduction of environmentally friendly technologies involving the disposal of waste will reduce the impact of anthropogenic factor on agrolandscapes [1].

To optimize the technological parameters of the process of hydrolysis-extraction of pectin from beet pulp, a series of extraction experiments was carried out, varying the concentration of the hydrolyzing agent – oxalic acid (0.5%, 0.75%, 1.0%) and temperature (65 and 75°C).

The hydrolysis-extraction process was implemented with constant stirring on a magnetic mixer with a ratio (raw material: extractant) of 1 : 7 for 7 h. The separation of the pectin-containing extract was conducted through lavsan fabric, the concentration process was implemented on a rotary evaporator IR-1LT at 40°C under vacuum. Beet pectin was precipitated with a double volume of ethanol. Pectin was separated by centrifugation (Sigma 4-15, Germany) within the space of 30 min at a rotor speed of 4000 rpm and then dried at a temperature of 55°C.

Dried pectin was characterized in accordance with the requirements of international standards (FCC, JECFA). Physico-chemical properties of beet pectin obtained under optimal conditions are presented in Table 1.

Table 1. Physico-chemical characteristics of beet pectin

Characteristics	Extractant – oxalic acid (0.75%)
Degree of esterification, %	51.3
Molecular weight, kDa	19.7
Complexing ability, mg Pb^{2+} / g	143.1
The protein content (N x 6.25), %	3.1
Solids content in pectin after processing KU – 2-8, %	1.0
pH of 1% solution	2.5
Humidity, %	9.9

The optimal parameters of the hydrolysis-extraction process were experimentally established: 0.75% solution of oxalic acid, 75°C, raw material : extractant ratio of 1 : 7, a process duration 7 h (Fig. 1), which provided the maximum pectin yield of 9.3% [2].

To implement the proposed environmentally sound technical solution, it is advisable to organize modular production on the basis of the existing canning industry enterprise producing fruit juices.

Fig. 1. Beet pectin after centrifugation

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Determination of *o*-xylene and polycyclic aromatic hydrocarbons in atmospheric precipitation by gas chromatography-mass spectrometry with sorption preconcentration

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A huge number of substances of various degrees of toxicity enter the environment as a result of human activity. The content of ecotoxicants is controlled by regulatory standards for most natural objects, but these standards are not available for atmospheric precipitation. According to the literature data, numerous organic substances of various classes are found in atmospheric precipitation. Special attention is paid to a group of the most hazardous substances – polycyclic aromatic hydrocarbons (PAHs), particularly, benzopyrene.

Since the content of many compounds in atmospheric precipitation is too low for their direct determination, it is necessary to use pre-concentration and highly sensitive methods of analysis. In most cases, liquid extraction is used to concentrate ecotoxicants. The main methods of their analysis are gas and liquid chromatography with mass spectrometric detection (GC-MS and HPLC-MS).

Liquid extraction concentration is characterized by a number of significant disadvantages. Typically, the distribution coefficients of micro-components are low, therefore, a large volume of toxic organic solvents is required, and the process is difficult to automate.

Sorption methods of concentration are free of many of these shortcomings. However, the literature data on the use of sorption in the analysis of precipitation are poor with the lack of information on the quantitative characteristics of the extraction of analytes.

We have systematically studied the dynamic sorption concentration of *o*-xylene, naphthalene, phenanthrene, anthracene and pyrene on various sorbents and their subsequent determination by GC-MS. The highest extraction efficiency has been observed in the case of the use of super-crosslinked polystyrene (SSPS). Quantitative desorption is possible with 2 ml of acetonitrile or dichloromethane. Using the standard method of hexane extraction concentration and subsequent determination by GC-MS in SIM mode, all the studied compounds have been found in melted snow extracts.

Graphs of the dependence of the chromatographic peak area on the concentration of all studied substances in dichloromethane are linear in the range of 0.05–0.5 mg/l.

The degree of extraction of ecotoxicants from 200 ml of melted snow was determined and their concentrations were calculated (Table 1).

Table 1. Results (μg/l) of *o*-xylene and PAH determination in 200 ml melted snow (01.02.18) with pre-sorption and extraction concentration (n = 3, P = 0.95)

Method*	*o*-Xylene	Naphthalene	Phenanthrene	Anthracene	Pyrene
LLE	18 ± 2	2.8 ± 0.4	0.98 ± 0.15	0.30 ± 0.07	0.43 ± 0.09
SPE	16 ± 2	3.1 ± 0.4	1.1 ± 0.2	0.23 ± 0.07	0.50 ± 0.08

* LLE – liquid-liquid extraction, SPE – solid-phase extraction

Sorption of the studied compounds at a low level of content (7.5 μg/l) was found to decrease with increasing sample volume and increase with increasing sorbent mass. Reducing the detection limit can be achieved by passing through the sorbent the maximum possible sample volume (the volume providing the largest absolute amount of the extracted substance), while the degree of extraction does not necessarily have to be the maximum. Based on the calculation method proposed in [1], the optimal volume for group extraction of the studied substances on the sorbent suspension of 0.2 g at a transmission rate of 4–5 ml/min, equal to 300 ml, was determined. The levels of environmental contaminants in melted snow from preliminary sorption concentration at SSPS were evaluated. The additive method was used to calculate the content of components. The data obtained are consistent with the results of analysis of the same samples using the standard method of liquid extraction. The detection limits for different concentration variants are comparable (Table 2) but the detection limits of the direct method are two orders of magnitude lower.

Table 2. Detection limits (μg/l) of investigated substances

Substance	GC−MS determination	GC−MS with Liquid extraction concentration	GC−MS with Sorption extraction concentration
o-Xylene	1.2	0.024	0.012
Naphthalene	2.5	0.050	0.030
Phenanthrene	3.6	0.061	0.035
Anthracene	5.0	0.077	0.043
Pyrene	4.5	0.089	0.050

Overall, the use of sorption methods makes the process of extracting ecotoxicants less labor-intensive, environmentally friendly, and also allows for sampling at the sampling site.

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Synthesis and study of sorption of Cu(II) and Cd(II) ions by SnO_2 microparticles

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Cu(II) and Cd(II) ions are known as one of the most hazardous pollutants of the environment. These substances have a negative impact on the environment when released into water bodies from mining, processing, ferrous and non-ferrous metallurgical and machine engineering industrial facilities. They can further on get into food products through the chain ‘water - flora - fauna - human’ and can cause poisoning and various diseases [1]. Therefore, water must be carefully cleaned from such substances before its use for domestic purposes.

Compounds of Cu(II) and Cd(II) bind to the sulphydryl groups of proteins and block oxidative processes, disrupting protein synthesis at various stages and deteriorating the exchange of sulfur, selenium and phosphorus. The target organs for their excess accumulation are bone marrow, gastrointestinal tract, skin, lungs and kidneys [1].

One of the most efficient procedures for treatment of industrial wastewater from the excess of such compounds is sorption with the commonly used sorbents such as coal, peat, metal oxides, silicon, etc. However, there are several limitations in this area: low sorption efficiency of used materials, high cost of materials applied for maintaining the sorption process, etc.

In recent years, due to the progress in nanotechnology, high expectations are connected with the development of new sorbents based on nano- and submicroparticles materials.

The aim of this work was to explore various methods of synthesis of tin(IV) oxide in the submicroscale state and to study the efficiency of sorption of the obtained material in relation to toxic ions Cd(II) and Cu(II).

One of the advanced approaches to obtain finely dispersed metal oxides formation is the method of chemical vapor deposition which includes the stage of reaction products deposition.

To obtain tin oxide, we have applied the known in inorganic synthesis reactions – interaction of aqueous solutions of tin salt $Sn(SO_4)_2$ with sodium hydroxide in different concentrations with heating [2]. A number of organic acid salts and other substances have been studied to stabilize the size of tin oxide particles, for example, glycerol and polyethylene glycol..

Studying Cu(II) and Cd(II) ions sorption by SnO_2 particles was carried out by static method. Quantitative analysis of ion content before and after sorption was determined by atomic absorption spectroscopy and photometric analysis.

Efficiency of sorption R and value of sorption G were calculated by the formulas:

$$R = [C_0 - C / C_0] \times 100\%,$$

$$G = (C_0 - C) \cdot V/m,$$

where R is the degree of ion extraction (%), G is the value of sorption (mole/g); C_0 and C are initial and equilibrium concentrations of ions, respectively, mole/l; V is volume of salt solution, l; m is mass of sorbent, g.

It has been experimentally established that tin(IV) oxide with the smallest particle size of 5–7 μm can be obtained by interaction of aqueous $Sn(SO_4)_2$ solution with sodium hydroxide of different concentrations. In addition, the highest stability of the SnO_2 particle size is observed when glycerol is introduced.

We have studied and established the following optimal conditions for sorption of the studied ions by SnO_2 particles: pH of sorption = 6; temperature 20°C, time of contact 20 min, ratio of sorbent mass to volume of aqueous salt solution = 1 gram per 25 ml of aqueous solution.

Experiments have shown that sorption isotherms of the studied ions by tin oxide particles have the form corresponding to the isotherms of Langmuir sorption, i.e. sorption proceeds according to the monomolecular mechanism.

Table 1 presents the values of sorption characteristics for sorption of Cu(II) and Cd(II) ions by SnO_2 particles under the optimal experimental conditions.

Table 1. Extraction degrees, sorption values, and sorption constants of SnO_2 sorption of Cu(II) and Cd(II) ions, C_{ions} = 1 g/l

Ion	R, %	G_∞, mole/g	$K_{sorption}$
Cu(II)	99.8	0.65	22.1
Cd (II)	99.4	0.67	22.5

The specific surface area of SnO_2 is 154 m^2/g.

In summary, the data presented in the table indicate that tin(IV) oxide SnO_2 effectively sorbs the studied ions, with a little better sorption degree for Cu(II) ions in comparison with Cd(II) ions.

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Oil recovery from liquor production wastes

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Bird cherry fruits are raw materials for the liquor industry (production of balms, filling, sweet and bitter infusions, wine drinks). As a production waste, bone cake remains, which contains biologically active substances (BASs), and is suitable for recycling. Lipids are the most abundant ingredients of the BASs contained in the cake. Oleic (18 : 1), linoleic (18 : 3) and linolenic (18 : 2) acids are dominated in fatty acid composition of the lipids. These acids account for 92–93% by weight of the total content of fatty acids contained in lipids. The amount of saturated fatty acids is insignidicant with the prevailing component – palmitic acid reaching 2%.

The aim of this work was to optimize the conditions of the supercritical CO_2 extraction (SCFE) of the cake. The method of full factor experiment was used. The main parameter to be optimized was the yield of oil (W) in the experiment under technologically acceptable conditions.

Bird berry fruit cake sample was provided by OOO “Arkhangelsk Liquor Plant” (Russia). It was dried to humidity of 5% and ground to fraction of 2.0–0.2 mm. Supercritical fluid extraction was performed at MV-10ASFE (Waters, USA) device [1]. Fatty acid composition of the obtained oils was determined according to GOST 30418-96.

Determination of the weight fraction of oil in the feed was carried out using a standard procedrure based on extraction of the feed with hexane in a Soxlet apparatus. The resulting sample was used as a control sample and its yield was 8.2%.

A planned experiment was implemented in order to obtain a mathematical description of the extraction process depending on the selected variables and to determine the optimal parameters of the process. The following parameters were chosen during creation of the plan: the main level of pressure (X) 250 atm, temperature of experience (Y) 60°C, and duration (Z) 55 min. Intervals of variation made 60 atm, 15°C and 15 min with a star shoulder of the plan (α) 1.682.

Mathematical processing of experimental data results in a regression equation adequately describing the extraction process:

$$W = 3.50 + 0.49\frac{(X-250)}{60} + 0.16\frac{(Y-60)}{15} + 0.62\frac{(Z-55)}{15} + 0.62\left(\frac{(X-250)}{60}\right)^2 + 0.58\left(\frac{Z-55}{15}\right)^2$$

Optimal values of process factors were calculated as 350 atm, 85°C and 80 min, which corresponded to the oil yield – 9.1 ± 0.4%. In a confirmation experiment, an oil sample was obtained in 9.4% yield. The relative model error was 1%.

Unlike the standard sample, SCFE bird cherry cake oil had a characteristic saturated smell inherent for bird cherry and an attractive yellow color, which is a positive quality of the product when used in cosmetic production.

The fatty acid composition of the oil obtained by the SCFE method was found to be close to that of the comparison sample, but was characterized by a significantly lower content of palmitic acid and a slightly higher content of palmitoleic, linoleic, and oleic acids. Elaidic acid, which is a component of trans-fats, has been halved in SKFE oil. It is likely that elaidic acid is formed from oleic acid in the extraction step. Thus, SCFE, being a softer extraction method, provides reduced activity of isomerization processes.

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Urinary metabolic profile of bemithyl protective effect against organophosphorus compounds poisoning on the example of O-isopropyl methylphosphonofluoridate

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Urinary metabolic profile investigation is one of the leading trends in metabolic profiling that has gained a widespread application in pharmacokinetics and toxicokinetics. It is known that oxidation stress that occurs with nerve agent poisoning leads to secondary neuronal damages. The neuroprotective effect of antioxidants has been proved; however, the molecular mechanisms underlying the protection action have not yet been studied. The most effective antioxidants are small molecules with high affinity for enzymes providing antioxidant balance, in particular, gluconeogenesis and oxidative phosphorylation. Bemithyl meets all the requirements mentioned above.

The aim of this study was investigation of excretion profiles of bemithyl and its hydrolytic metabolite – O-isopropyl methylphosphonofluoridate (GB) in the context of preventive pharmacological protection.

The protective effect of bemithyl was studied in the experiments with subcutaneous administration of O-isopropyl methylphosphonofluoridate (GB) to anesthetized rats at a dose of ¼ LD_{50} (45 μg/kg) (Table 1).

Table 1. Experimental design

Days	Group A	Group B	Group C
0	Control	Control	Control
1	Bemithyl 25 mg/kg IG	Bemithyl 25 mg/kg IG	Water IG
2	Bemithyl 25 mg/kg IG	Bemithyl 25 mg/kg IG	Water IG
3	Bemithyl 25 mg/kg IG	Bemithyl 25 mg/kg IG In 2 h GB ¼ LD50 (45 μg/kg) SC	Water IG In 2 h GB ¼ LD50 (45 μg/kg) SC

IG – intragastrically, SC – subcutaneous

Rat urine samples were collected on a schedule within 4 weeks after the end of the experiment. The excretion profile of hydrolytic metabolite of O-isopropyl methylphosphonofluoridate – isopropyl methylphosphonic acid (IMPA) was studied by high-performance liquid chromatography coupled with tandem high-resolution mass spectrometry (HPLC−HRMS/MS). Determination of IMPA concentration in urine was conducted in accordance with the known methodology [1]. IMPA level in rat urine in both groups B and C was higher than the limit of detection (LOD) of the methodology (1 ng/ml) within 7 days after the end of the experiment, while the difference in concentrations between two groups was observed only within the first 24 h of the experiment. The IMPA content in urine samples of rats treated with bemithyl (group B) was 1.3-fold lower than that in group C. However, bemithyl excretion profiles differed radically in groups A and B. Bemithyl concentration in rat urine measured by reverse phase HPLC-MS/MS with characteristic MS/MS transition 179.06375 → 151.03037, was higher than the LOD (1 ng/ml) in accordance with the methodology [2] over the whole observation period (4 weeks). Moreover, over the observation period, the total amount of bemithyl excreted with urine in rats of group A was 3 times greater than that of group B. The greatest differences (5 times) were noted on the 3rd day after the injection of GB.

In conclusion: Rat poisoning with a non-lethal dose of O-isopropyl methylphosphonofluoridate against preventive therapy with bemithyl at a dose of 3 x 25 mg/kg led to the 3-fold decrease of the unchanged bemithyl excreted with urine. In addition, the content of each identified bemithyl metabolites [2] in the urine of rats exposed to GB was also significantly lower. It could be explained by both the binding of bemithyl and its excretion in a form that has not yet been determined.

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Development of co-determination method of O-isobutyl-S-[(2-diethylamino)ethyl]methylthiophosphonate and it hydrolysis product on surfaces and internal samples of different materials

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Safe levels of highly toxic O-isobutyl-S-[(2-diethylamino)ethyl]methyl thiophosphate (VR agent) on different surfaces and waste of building materials were established during the execution of chemical weapon destruction (CWD) program and amounted to $2·10^{-6}$ mg/dm^2 for surfaces and $5·10^{-5}$ mg/kg for waste, respectively. The highly selective procedures based on gas chromatography (GC) have been developed and introduced in addition to the known biochemical methods used for the control of compliance of the established standards. Direct determination of VR in standard GC conditions can’t be performed with the detection limit which is required for controlling this compound at the level of the established hygienic standards. Therefore, a known approach is applied which involves the conversion of VR into isobutyl methyl fluorophosphonate on the tablet, impregnated with silver fluoride followed by isobutyl methyl fluorophosphonate thermodesorption into gas chromatograph from sorption tube. This approach was taken as a basis for the development of all known domestic protocols for VR determination in surface flushings and internal samples by GC method coupled with mass spectrometric, thermoionic, flame photometric and pulsing flame photometric detectors. At present, tablets for conversion VR into isobutyl methyl fluorophosphonate are not produced, so, the analysis specified in the previously certified methods is unfeasible. No established procedures are described for determination of VR hydrolysis toxic product formed upon the cleavage of O-isobutyl group.

Monitoring the chemical safety of these chemical compounds is extremely important when considering the possibility of involving part of the infrastructure elements remained after former chemical weapons destruction facilities in economic turnover. VR and its hydrolysis product are identified among the priority toxicants during the safety control of the studied objects. A new procedure has been developed for determining these compounds by high-performance liquid chromatography coupled with tandem mass-spectrometry selective detection (HPLC-MS/MS) in flushes and crushed solid samples, which provides an integrated approach to the analysis of matrices of various nature and sensitivity corresponding to the thresholds of the toxic action.

The stability of the determined substances was confirmed in flushes when stored in freezers for 2 weeks and in solid samples when stored at a temperature not exceeding 4°C no more than 3 months. Thus, a possibility is shown for samples collection at the monitored facilities with their subsequent delivery to the laboratory for storage and analysis.

To determine the contamination of controlled objects with VR and the most toxic product of its conversion – S-(2-diethylaminoethyl)methylphosphonothioate, the HPLC-MS/MS method was used with the help of the Shimadzu LC-20AD device equipped with an autoset and a Shimadzu LCMS-8050 mass-selective detector with electrospray ionization at atmospheric pressure. The method involves adding an internal standard of paraoxone to the sample (flushing from the surface or hovering a crushed solid sample), extracting the sample with an organic solvent, concentrating the extract in a nitrogen current, followed by analysis by HPLC-MS/MS in the mode of multiple reaction monitoring (MRM) with registration of positively charged ions.

The HPLC-MS/MS technique for trace detection of analytes in complex matrices at the level of detection limits yields confident negative results, but in the case of detection of the target analytes, a confirmatory identification is provided using high-resolution HPLC-MS/MS.

Thus, a method has been developed for measuring mass concentration of O-isobutyl-S-[(2-diethylamino)ethyl]methylthiophosphonate and its hydrolysis product S-(2-diethylaminoethyl)methylphosphonothioate in flushes and solid samples (waste, fragments of building structures, engineering infrastructure of industrial premises, etc.) by HPLC-MS/MS. The method is certified (Certificate №. 00000070.01.20-30058-13) dated January 31, 2020 and entered the Federal information Fund.

Steady-state kinetics analysis and molecular modeling of human cholinesterases competing substrates over wide concentration ranges: toxicological and pharmacological implications

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The main function of acetylcholinesterase (AChE) is to terminate the action of the neurotransmitter acetylcholine in nervous system. The physiological functions of butyrylcholinesterase (BChE) are still unclear. However, BChE has a toxicological and pharmacological importance in hydrolyzing or scavenging natural and artificial poisonous carboxyl-, carbamyl- and phosphyl-esters, including drugs, industrial toxicants, organophosphorus (OP) pesticides and banned nerve agents. Medical countermeasures against these chemicals are imperfect [1]. Although catalytic and inhibitory mechanisms of ChEs have been thoroughly investigated for more than 70 years, the interplay between 3D-structure, molecular dynamics, and ligand binding/catalysis has not been completely deciphered. Thus, improvement of treatments against anti-ChE poisoning is highly dependent on this knowledge. The present work is aimed at filling gaps between binding/catalytic steps and enzyme conformational response upon competing ligand binding.

Substrate competing kinetic analysis provides useful information on catalytic and inhibition mechanisms [2]. In the present work, substrate competition for human AChE and BChE was studied under steady-state conditions, using the same couples of substrates over a wide range of concentrations. To simplify analysis, both substrates were acetyl-esters in order to provide the same acyl-intermediate. Phenyl acetate was the reporter substrate and competitors were either acetylcholine or acetylthiocholine. At the same time, molecular dynamics simulations with dynamical network analysis and QM/MM calculations of binding/catalytic processes were performed.

Kinetic studies showed for both enzymes that the competitor binds only to the catalytic active center at low concentrations, acting first as a competitive inhibitor and then as a partial mixed-type inhibitor. Next, with increasing the concentration, a second competitor molecule binds to a peripheral anionic site (PAS), and determines a complex partial uncompetitive inhibition/activation. Molecular modeling depicts the allosteric effects on catalytic events upon binding of ligands on PAS. These effects occur through the Ω-loop that interconnects peripheral and cation-binding sites. Binding of competitor molecule on PAS affects motion of Trp82/86, and thus, leads to dissociation of tetrahedral intermediate of the catalytic acylation step.

The competitive binding of ligands on ChE catalytic center has been exploited for current prophylaxis (pyridostigmine) and antidotal treatment of OP poisoning (oxime reactivators). The allosteric effects caused by ligand binding on peripheral site open up new possibilities for safer and more effective therapeutic interventions.

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Impurities and cutting agents in smoking mixtures containing synthetic cannabinoids as objects of expert chemical analysis

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Synthetic cannabinoids (SCs) are widespread in drug trafficking. Due to the high physiological activity and variability of the component composition, they can pose a serious threat to the life and health of people [1, 2]. In this regard, monitoring and profiling of impurities and cutting agents in the SCs containing mixtures can be used by law enforcement agencies for the following purposes:

- confirming or refuting the relationship between two or more samples;
- providing general operational information regarding the distribution network (local, national or international).
- detection the relation between samples that do not have bonds established in other ways.
- monitoring the methods used in the production of drugs, and identifying possible new trends.

Illicitly manufactured SCs in clandestine laboratories have varying degrees of purity, however, depending on the synthesis conditions, they will always contain traces of starting reagents, solvents, catalysts, and reaction by-products [3]. The presence of impurities and their relative concentrations will depend on many factors, such as: the synthesis method, initial reagents and their possible impurities, proportions of the chemicals involved in the synthesis, general reaction conditions (temperature, pressure, time), extraction and purification processes (including crystallization and washing).

The purpose of chemical analysis is to identify these impurities and determine their relative concentrations. With this approach, a ‘profile’ is defined for a substance - a characteristic chemical signature that individualizes each batch of a substance. The information obtained can be used to establish communication between two or more samples. Analysis of data on the relationship of samples can provide important information on the supply and distribution routes of SCs both locally and internationally.

Also, the profile of impurities can help in determining the production method and the set of those reagents - precursors that are used for illegal synthesis.

In addition to impurities associated with the main narcotic active substance, samples removed from illegal trafficking may contain fillers - cutting agents. Cutting agents of narcotic drugs in illicit trafficking have three main roles [4]:

1) Weight gain. In this case, widely available, legal and relatively inexpensive substances are used.

2) To enhance or simulate the physiological effect or organoleptic characteristics of the main narcotic active substance.

3) To make the drug more convenient to use, including by smoking.

SCs are generally powdered substances with very high physiological activity, the exact dosage of which in artisanal conditions is difficult. Because of this, they are most often used after application to a plant substrate or in the form of plastic mixtures similar to hash. Unlike previously common cutting agents, as a rule, representing one substance or a mixture of a small number of components, plastic mixtures containing SCs are complex systems of substances of various nature [5]. Plastic smoking blends containing SC are not diluted after manufacture, so homogenization of a viscous plastic substance of small weight in domestic conditions is difficult.

Thus, the combination of factors: the invariability of the component composition in the distribution chain, a high degree of individuality due to artisanal manufacturing, as well as the possibility of studying the instrumental methods available in expert departments makes the composition of impurities and cutting agents in plastic smoking mixtures containing SC criminalistically significant signs characterizing the relationship between samples. In this regard, the development of sample preparation and analysis techniques is of high importance.

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Nanoscale oxime-delivery systems based on lipids and surfactants for central nervous system protection against neurotoxic inhibitor paraoxon

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The prevention of irreversible brain damage consecutive to acute organophosphorus (OP) poisoning is a public health concern in developing countries, where OPs cause the death of ~200 000 people per year. The nanotechnological approach to solve this problem, is an innovative strategy of high potential for achieving reactivation of OP-inhibited human acetylcholinesterase (AChE) in the central nervous system (CNS). Pralidoxime chloride (2-PAM) is a long established clinically used AChE reactivator for treatment of OP-poisoning. However, 2-PAM does not cross significantly the blood brain barrier.

Recently, our group showed that 2-PAM-loaded solid lipid nanoparticles were able to reactivate brain AChE and protect against paraoxon central toxicity [1]. In addition, our group implemented the use of lipid nanoparticles with a combination of oximes to expand the therapeutic window [2]. The nose-to-brain pathway using 2-PAM-loaded nanoparticles was tested [3]. In the present work, brain AChE reactivation efficacy was increased by PEGylation of 2-PAM-SLNs, using PEG-lipid N-(carbonyl-methoxypolyethylene glycol-2000)-1,2-distearoyl-*sn*-glycero-3-phosphoethanolamine, sodium salt) (DSPE-PEG$_{2000}$) as a SNL surface-modifier. 2-PAM-DSPE-PEG$_{2000}$-SLNs of mean size 80 nm (PDI = 0.26), zeta-potential of -55 mV and of high *in vitro* stability demonstrated 3-fold prolongation of 2-PAM elimination from the rat bloodstream compared to that of free 2-PAM. An increase in reactivation of POX-inhibited human brain AChE up to 21% after intravenous administration of 2-PAM-DSPE-PEG$_{2000}$-SLNs (dose of 2-PAM is 5 mg/kg) was also achieved.

Thus, the implementation of different approaches for targeting and modifying nanoparticle surface gives hope for improving the antidotal treatment of organophosphorus poisoning by marketed reactivators.

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Development of biodegradable film composition for food packaging

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The solid waste disposal is one of the major concerns of our days. Annually, ~200 million m^3 of solid household waste are produced in Russia. Most part of the waste is food packaging. Biopolymers have been developed as an alternative to conventional polymers used in food packaging. They are capable to decompose under the exposure of chemical, physical and biological factors. Biodegradation is the process of destruction of complex substances under the influence of various factors, i.e. air oxygen, heat, sunlight, and some biological microorganisms (yeas, fungi, etc.). These factors work apart and together, which results in the material fragmentation by breaking down molecules and generating low-molecular compounds which are involved in the circulation of substances in nature. The search for new food packing material with neutral physical and chemical properties without any toxic effects and, at the same time, easily degraded is a relevant and significant task.

The biodegradable polymers are usually obtained by polymerization of biologically-based raw materials. This property of the new food packaging material will help to solve the waste disposal problem [1].

The information about using gelatin for the preparation of films capable of biodegradation is mentioned in some studies. The albuminous product consists of polypeptides of different molecular weights capable to form aggregates with high molecular weight molecules. Besides, it has neither smell nor taste, and swells in water.

We have prepared a film, with gelatin, propylene glycol, transglutaminase and whey components in its structure. The reaction of transglutaminase and substrate protein in different ratios is determined by the availability of the necessary amino acids in gelatin, as well as factors that contribute to the activity of the enzyme (pH value, fermentation time, temperature). The reaction results in generating the covalent cross-linked bonds between proteins, providing a grid matrix. Introduction of plasticizer (propylene glycol) helps to keep the optimal level of humidity during storage. Dissolution and simultaneous activation of the enzyme is provided by using whey, a by-product of milk processing. The whey contains milk plasma proteins, vitamins, minerals, and traces of fat. Whey proteins have a high affinity for transglutaminase, thus, the whey's presence in the composition improves the physical and mechanical properties of the resulting films. In addition, the cost of the finished film is reduced by ~2 times due to the use of cheaper whey [2].

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Assessment of contamination of infrastructure elements of former chemical weapons destruction facilities with products of transformation of organophosphorus toxic substances

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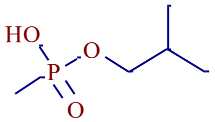
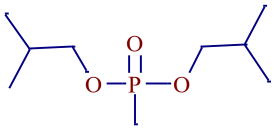
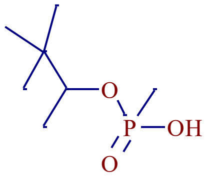
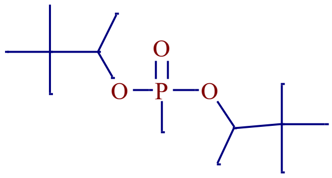
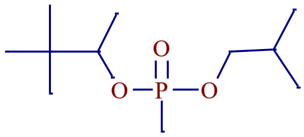
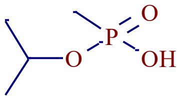
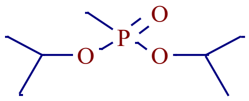
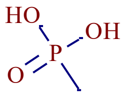
A decision on the involvement of individual elements of infrastructure in economic circulation upon liquidation of the objects of destruction of chemical weapons should be taken basing on the assessment of the degree of contamination of construction materials and equipment with residual organophosphorus substances (OPS), including their transformation products (isopropyl, isobutyl, pinacolyl mono - and diesters of methylphosphonous acid and methyl phosphonic acid (MPA)). Neutralization of sarin and soman is usually performed using formulations containing potassium isobutylate, which results in the additional formation of isopropyl-isobutyl and pinacolyl-isobutyl diesters of MPA. It is noteworthy that the analytical aspects of ‘asymmetric’ MPA diesters, i.e. containing different alkyl radicals, have been extensively studied by Russian analysts. No information on the properties of these compounds could be found in the available literature sources. According to our data, both symmetrical and non-symmetrical diesters of MPA are stable in aqueous solutions in a wide pH range. These are persistent substances, the detection of which indicates the contamination of the studied objects with reaction mixtures resulted from the neutralization of OPS, rather than with the initial substances.

Determination of MPA and its esters in methanol extracts from crushed materials was carried out by high-resolution HPLC-MS/MS using a Dionex UltiMate 3000 liquid chromatograph with a mass-selective detector Thermo Scientific Q-Exactive with electrospray ionization at atmospheric pressure. An integrated methodology was used to analyze materials of different matrix composition (bricks, polymers, concrete). Paraoxone was used as an internal standard. The detection limits for analytes in building materials were in the range of $4.0 \cdot 10^{-4}$ – $4.0 \cdot 10^{-3}$ mg/kg. The analytes had different degrees of extraction from different matrices established in model experiments, which were not taken into account when assessing concentrations. Thus, the content of free (recoverable) forms of analytes in the studied objects was estimated.

The components were separated on a Gemini-NX 3u C18 110A (Phenomenex) 150 mm×2 mm×3 µm column in a gradient mode: component A – 0.1% solution of ammonium formiate in deionized water; component B – 0.1% solution of ammonium formiate in methanol. Detection was carried out in the mode of multiple reaction monitoring – MRM (MS/MS): registration of product ions formed during the fragmentation of the precursor ion with positive ESI (+) or negative ESI (-) ionization was performed by characteristic transitions (Table 1).

Table 1. Analytical characteristics of MPA, its mono-and diesters

No.	Compound / ionization mode	Structure	Brutto formula, mol. mass	MRM mode
1	O-isobutyl MPA ESI (-)		$C_5H_{13}O_3P$ 152.06023	151.05→95.05 151.05→77.05 151.05→79.05
2	Diisobutyl ester MPA ESI (+)		$C_9H_{21}O_3P$ 208.12283	209.00→96.95 209.00→79.00 209.00→47.00
3	O-pinacolyl MPA ESI (-)		$C_7H_{17}O_3P$ 180.09153	179.10→95.05 179.10→79.00
4	Dipinacolyl ester MPA ESI (+)		$C_{13}H_{29}O_3P$ 264.18543	265.00→97.00 265.00→155.10 265.00→79.00
5	Isobutyl- pinacolyl ester MPA ESI (+)		$C_{11}H_{25}O_3P$ 236.15413	237.00→97.00 237.00→153.05 237.00→79.00
6	O-isopropyl MPA ESI (-)		$C_4H_{11}O_3P$ 138.04458	137.00→95.05 137.00→79.00
7	Diisopropyl ester MPA ESI (+)		$C_7H_{17}O_3P$ 180.09153	181.00→96.95 181.00→79.00 181.00→47.00
8	MPA ESI (-)		CH_5O_3P 95.99763	95,00→78.95 95.00→63.00

There are no hygienic standards for mono- and diesters of the MPA. The toxicity of these compounds is currently predicted in the *in silico* mode.

Further research will be aimed at evaluation of toxicometric parameters of the studied compounds.

Development of a unified method for determining sulfur mustard in objects of various matrix composition by gas chromatography-tandem mass spectrometry

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The conversion of former chemical weapons destruction facilities for civilian use is preceded by the expertise taking into account results of assessment of chemical safety of their infrastructure. The most important assessment issue is determination of residual amounts of toxic substances that were previously destructed on the facility. Sulfur mustard is capable of self-encapsulation and long-term conservation in micro cavities of brick, concrete, ceramics, polymers, etc. Existing methods for determining sulfur mustard are laborious and time-consuming.

The aim of this work was to develop a highly sensitive method for determining the content of sulfur mustard in different matrices. To achieve this goal, it was necessary to choose an analytical procedure that ensures the selectivity of the analysis in the presence of interfering compounds of various, including unknown, composition. The gas chromatography coupled with tandem mass-selective detection with electron ionization (GC-MS/MS-EI) was the method of choice.

The developed procedure involves extraction of the analyte with organic solvent, concentration of the extract under a stream of nitrogen followed by analysis using gas chromatography tandem mass-spectrometry with electron ionization. The investigated materials were homogenized and ultrasonic technology was applied for analyte extraction prior to the analysis.

An important step of the investigation was the choice of the extraction solvent. Since the polymers are known to dissolve in most chlorine-containing organic solvents, particularly in methylene chloride, chloroform or dichloroethane, it was necessary to find the one that would intensively penetrate into various materials, extract the sulfur mustard from them, but would not dissolve any of the materials. It was also necessary to take into account the acceptability of the solvent for the chromatographic analysis. As much as 2-chloropropane has all the above aforesaid properties, it was chosen for the purpose of analysis.

The parameters optimized for the detection of sulfur mustard using gas chromatography tandem mass-spectrometry with electron ionization (GC-MS/MS-EI) are given in Table 1.

Table 1. Parameters for detection of sulfur mustard by GC-MS/MS-EI

Analyte	RT, min	MRMs (collision energy, eV)
Sulfur mustard	8.9	109 → 63 (6) 158 → 109 (3)

The procedure developed for the analysis of solid samples has been applied to the analysis of wipe samples from various surfaces. The surfaces of infrastructure elements of former chemical weapons destruction facilities may be contaminated with detergents, components of degassing formulations, etc. This creates additional difficulties for analysis, which can be overcome due to the high selectivity of the GC-MS/MS method.

The limits of quantitation (LOQ) of sulfur mustard in wipe and solid samples were determined in preliminary experiments. It is noteworthy that all the LOQs did not exceed the requirements of hygiene standards (Table 2).

Table 2. The limits of quantitation of sulfur mustard in wipe samples from the surfaces of technological equipment and in solid samples

Parameter	Wipe samples, mg/dm^2	Solid samples, mg/kg
LOQ	$2 \cdot 10^{-7}$	$2 \cdot 10^{-4}$
Hygiene standard	$2 \cdot 10^{-4}$	$1 \cdot 10^{-2}$

The developed procedure has been applied to the analysis of samples from a former chemical weapons destruction facility. Total run time of the GC-MS/MS analysis was about 20 min, while simultaneous preparation of 10 samples took approximately 1 h. Thus, it was possible to analyze 50 samples taken from the facility in 3 days, including rechecking of the random samples using the standard addition methodology.

Toxicity of glyphosate photochemical decomposition products determined by changes in bioluminescence intensity of bacterial test system Ecolum

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Recently, a number of new technologies for detoxification of hazardous chemicals used in agriculture as plant protection products, has been introduced. Accordingly, the issue of controlling the degree of toxicity of products resulting from the use of these technologies, for environmental objects and human health is of great importance. At present, the most effective approach for assessing the toxicity of the products of transformation of the initial hazardous chemicals is biotesting method, which allows to quantify the total toxic effect of substances formed as a result of the transformation of the initial hazardous chemical substances.

In this work, N-(phosphonomethyl)glycine (Glyphosate) was chosen as the object of study, which is the active ingredient of the most commonly used herbicide in the world and is extremely dangerous to humans. We studied changes in the degree of toxicity of glyphosate as a result of its treatment with harsh UV-radiation in combination with ozone. UV-irradiation was generated using a DRSh-1000 mercury lamp (λ = 250–600 nm). Ozone came from an ozonizer, the content of ozone obtained in a mixture with oxygen was 2.5%.

The preparation of lyophilized luminescent (luminous) bacteria of the Ecolum series was used as the test system [1, 2]. This methodology for determining toxicity is approved for state environmental control and is based on the fact that luminous bacteria, when exposed to toxic pollutants contained in the test water, change their physiological and biochemical functions, including the activity of the bacterial luciferase enzyme responsible for the intensity of bioluminescence. The toxicity assessment is based on determining the magnitude of the change in the intensity of the bioluminescence of bacteria under the action of toxic substances contained in the test water samples compared to the control. A decrease in the intensity of bioluminescence is proportional to the toxic effect. Some samples cause activation of the light emission of the test system and a negative value of the toxicity index is recorded. In this case, the index T is taken equal to zero [1], and the sample is considered as non-toxic.

A quantitative assessment of the test reaction parameter is expressed as a toxicity index as follows: $\mathbf{T = 100(I_o - I)/I_o}$, **%**,
where I_o and I are bioluminescence intensities of bacteria of the control and test sample, respectively. The toxic effects of the test sample were determined over a 5- and 30-min exposure period.

The table below shows toxicity values (T, %) for the initial (the concentration of the initial sample was 6.7–2 10^{-2} M) and the irradiated sample of glyphosphate:

Table 1. Toxicity of glyphosate solutions before and after UV-irradiation

Initial sample			Irradiated sample		
dilution	T% (5 min)	T% (30 min)	dilution	T% (5 min)	T% (30 min)
0	**100***	**100**	0	**100**	**100**
1/10	**100**	**100**	1/10	**41.3**	**77.6**
1/100	**80.8**	**91.8**	1/100	-16.8	15
1/1000	-9	8.8	1/1000	-27.5	-23.8
			1/10000	-21.6	-27.9

*toxicity index T is given in bold values for explicitly toxic samples

The toxicity of the initial sample is preserved until its 1000-fold dilution with pure water, the initial sample belongs to the III (third) hazard class for objects of the environment (moderate hazard) [3]. The toxicity of the irradiated sample is maintained until its 100-fold dilution with pure water, the irradiated sample belongs to the IV (fourth) hazard class for objects of the environment (low hazard) [3].

Thus, using the combination of UV-irradiation and ozonation treatment procedure resulted in the reducing of glyphosate toxicity: the hazard class for environmental objects has been decreases from III (third, moderate hazard) to the IV (fourth, low hazard). Consequently, the proposed approach along with the biotesting procedure are sufficiently effective for the detoxification of organic chemicals used in agriculture and the appropriate hazard control.

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Reliability and safety analysis of test complex equipment

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Considering safety and reliability of industrial production facilities, one can keep in mind a complexity of these technological systems in which sequential and parallel processes occur, starting from the processes of preparing raw materials and ending with the processes of shipment of the finished product to consumer.

Reliability and safety of implementation of any technological process, first of all, depends on the reliability of the equipment applied for realization of the process. The problem of ensuring safety and reliability of the equipment of industrial production facilities is relevant and covers all steps of the equipment life cycle [1].

Here the results are presented of evaluation study of reliability and safety of chemical technological system equipment taking into account its potential emergency failures. The system represents a test complex consisting of a hollow cubic apparatus equipped with a heat exchanger supplied with a thermostat with heat-transfer liquid.

Basing on the technological scheme of the process, a block diagram of the reliability of the equipment has been developed, including four blocks, precisely, a block of control and measuring devices, a block of preparing the starting materials, a block of regulating parameters of the operation media, a block of check valves and electrical drive devices, while each block is characterized by indicators of failure rate and recovery rate.

The main single indicators for the systems being restored are the failure rate and the maintainability indicator, i.e. the average recovery time. Also, in addition to single reliability indicators, complex indicators have been determined, such as, the element availability function and the downtime function [2].

A model has been designed for assessing reliability of the system, which is characterized by the probability of failure-free operation, which includes the following indicators: system failure rate, average run-to-failure, average system recovery time, system availability function and stationary system availability coefficient.

The probability of bringing a system into a trouble-free state is required for assessing technology-related risk, i.e. risk arising from equipment failures [3], which is an inevitable attribute of equipment operation. Risk is one of the most important indicators of equipment operation. Technology-related risk is determined as the product of the average number of the technological system failures over a period of time and the damage caused by failures of system elements, expressed in conventional units (for example, monetary).

An analysis of reliability and safety of the test complex involves the following steps: development of a structural-functional system with the definition of relationships between elements (structural diagram of reliability); selection of parameters characterizing the reliability of elements, units and the system as a whole; formation of initial data on the reliability of structural elements; calculation of reliability indicators of elements, units and the whole system and assessment of technological risk.

The reliability of the technological system is calculated from the results of the assessment of the reliability parameters of the constituent subsystems (blocks), main and auxiliary systems [4].

Using the above calculation procedure, the predicted value of the readiness coefficient of the test complex has been obtained, which is found to be 0.97, suggesting high reliability and safety of the system.

The applied methodology can be recommended for assessing reliability and safety of chemical technological equipment at all steps of its life cycle.

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Development of procedure for chromate-free passivation of aluminum surface

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The surface of aluminum and its alloys is rather resistant against corrosion due to the presence of a thin natural oxide film, so in some cases, aluminum-based materials can be used without special corrosion protection. However, due to the poor thickness of the natural film formed on the surface of aluminum, the presence of such film is frequently insufficient as the sole corrosion protection method, for example, for applications in humid industrial atmosphere or in saltwater [1].

Conversion chromate coatings are widely used to create a thin adhesive layer as a base for paint coatings on the surface aluminum and its alloys. Chromate adhesive coatings are also preferable for painting products with a complex profile, because, in the case of such products, anodizing is known to cause difficulties and thus additional spending and technical tricks are required [2, 3]. It is also known that chromate solutions are highly toxic due to the hexavalent chromium ions.

In recent years nanoscale particles obtained from hexafluorozirconic and hexafluorotitanic acids are increasingly used as an alternative to chromate layers in the world practice [4–9]. Currently, world leading companies are actively developing the technologies for production of such surfaces.

The goal of this work is development of protective and adhesive titanium, zirconium-containing conversion coating application methods on 5556 alloy with the aim of replacing toxic chromating processes in automobile industry.

Acid concentration ranges, which allowed the formation of continuous coatings on the aluminum alloy surface with maximum protective capability have been determined.

Studies made it clear that allowable pH values of solution are found in the range from 4.0 to 5.0 units. The pH values beyond this range result either in failure in coating formation ($pH \leq 4.0$) or nonuniform easily broken coatings ($pH \geq 5$).

As can be expected, the protective ability of the coatings depends on the duration of their formation period: Akimov protective capability coefficient rises during the first 60 seconds and then stabilizes. This constant is consistent with the results of ellipsometric research. The coating thickness grows over the first 60 s followed by its stabilization at 100 nm.

Saline fog chamber corrosion tests (ASTM B117) of aluminum alloy AMг6 samples with adhesive Ti,Zr-containing coating have been conducted. The results indicate that the protective properties of Ti,Zr-containg coatings formed in the developed solution satisfy the appropriate requirements since the corrosion penetration breadth away from the cut does not exceed 2.0 mm after 750 h of testing. It should be noted the anticorrosion properties of these coatings are not only similar but even exceed that of the chromate coatings.

The strength of paint adhesion for coatings on aluminum alloy with and without adhesion sub-layers was determined by the detachment method. The measurements were carried out before and after corrosion tests. The results showed that the adhesion properties of the developed coatings formed in Ti,Zr -containing solution are comparable with that of the chromate analogue. In addition, Ti,Zr-containing coatings had a minimum adhesion loss value of 8.3% after corrosion tests.

Corrosion tests (ASTM B117) of independent anticorrosive titan, zirconium-containing coatings in the saline fog chamber have shown that the coatings formed on 5556 aluminum alloy in Ti,Zr-containing solution exhibited the highest anti-corrosion resistance. First corrosion pockets appeared after 170 h of testing, whereas they appeared after 160 h on chromate coated 5556 alloy, and after 24 h on 5556 alloy.

Overall, it was shown that the developed titanium,zirconium-containing coatings on aluminum alloy 5556 are comparable to chromate coatings in terms of their protective ability and adhesion properties and thus can be a promising alternative to toxic chromate coatings for applications in automotive and other industries.

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Software for assessing safety of low-tonnage chemical production technologies

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Modern low-tonnage chemical production involves a complex set of equipment that includes devices designed for chemical, mass transfer and heat transfer processes.

The potential hazard of such productions is due to a number of their specific characteristics. These include: operating in a periodic mode; a great number of manual operations; placing equipment in small rooms.

At the same time, accidents at such plants rarely lead to serious consequences, since the quantities of circulating substances are relatively small. However, the issues of ensuring the safety of personnel located in the immediate vicinity of the equipment seem to be relevant.

At the stage of design documentation development for such industries, it is necessary to identify the most dangerous steps of the technological process in order to provide preventive measures to reduce the risk of possible accidents that could lead to negative consequences. To assess the probability of such accidents and the extent of their detrimental consequences, a software has been developed [1, 2].The main software modules for assessing the safety of low-tonnage chemical production technologies are:

1. Database of physicochemical and toxicological characteristics of substances.
2. The module of selecting hazardous process units.
3. The module of standard accident scenarios.
4. Block modeling physical phenomena accompanying different stages of accidents evolution (evaporation, outflow, etc.).
5. The module of calculating the effect areas of factors affecting accidents.
6. The module of assessing quantitative risk indicators of accidents.

The developed software is proposed to be used at the designing step of low-tonnage production to select the safest technology for industrial implementation. Besides, this software product may be used for the development of industrial safety declarations and action plans for localization and liquidation of accidents consequences.

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Industrial wastewater monitoring on enterprises in case of emergency

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In order to determine the quality of wastewater treatment, a number of water indicators are monitored, both at the inlet and outlet points of the treatment system. The indicators for monitoring are selected taking into account the specificity of technology and technical means used in wastewater releasing facilities. The purpose of wastewater monitoring is to study both inlet and outlet contamination parameters of wastewater treatment system which can result in making decisions to improve the application of wastewater treatment techniques, for example, by choosing a specific type of filter for wastewater treatment line. As a rule, monitoring is carried out with a certain frequency of sampling, measurement of parameters and processing of the collected data.

However, traditional wastewater monitoring systems do not take into consideration a possibility of emergency situations which can occur at production facilities with incidental discharge of chemicals into the wastewater system disrupting the operation of filter elements and resulting in discharge of contaminated wastewater into water bodies. Apart for beyond design basis emergencies with pollutants appearing for a limited time in the form of clots in the wastewater of the enterprise, there may be accidental spills of stored substances, for example, oil and fuel lubricants, oils, chemical detergents, etc.

In order to organize monitoring of discharge of contaminants in case of beyond design basis accidents, it is proposed to extend the system of wastewater monitoring by adding an optical-electronic device for detection of emergency clot of contaminants in the waste pipe. The main element of the device is a laser radiator operating at a wavelength which can be tuned basing on analysis of the spectrum of substances stored at the enterprise. At the same time, the spectrum of wastewater of the enterprise is also taken into account proceeding from dynamic statistical estimates registered under the normal operation conditions of the enterprise.

Monitoring is performed in real time mode. When a contamination clot is detected, a decision is made to put into action a special gate located in the waste pipe so that the main wastewater stream could be shut off and redirected to the prepared settling tank.

The proposed monitoring scheme allows maintaining the operability of the main filters of the system and eliminating the consequences of emergency situations with preservation of the purity of the water basin. Patents for the invention and a useful model confirm the novelty of the proposed scientific and technical solution (patent RF 2710358, 2019; patent RF 153362, 2015).

Complex use of household waste for production of fertilizer containing both organic and mineral ingredients

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Nowadays, growing accumulation of large amounts of waste products of various origin has become a cause of great concern which requires searching for new ways of waste disposal. An unfavourable environmental situation obliges the society to focus its efforts on improving the state of environment. One of the possible solutions of this problem is creation of technologies using food waste (domestic garbage) as a secondary raw material for production of fertilizers.

The total volume of applied mineral fertilizers provides only 25-30% compensation of loss of nutrients removed by plants from the soil. In this regard, more attention has been recently paid to the production of organic and organomineral fertilizers from wastes of various origin as raw materials [1, 2].

The authors have developed a method for producing fertilizers containing both organic and mineral constituents which is based on the use of household, industrial and natural waste.

To prepare fertilizers, an organic part of everyday life household waste was used as raw material which consisted of 20–24% food waste of animal and plant origin, with the following chemical composition (wt%): organic compounds – 52–76; N_{com} – 0.6–1.5; phosporus – 0.55–0.72; potassium – 0.4–0.7; calcium – 4.1–6.5; sulphur – 0.2–0.25; carbon – 30–33. Humidity of total mass was 36–51%, pH = 6.5–7.5.

The other source of raw materials was an industrial wastewater salt solution with the density of 1.094 g/sm^2 and the following composition (wt%): Ca^{2+} – 8.54; Mg^{2+} – 3.05; Cl^- – 81.88; Sr^{2+} – 0.231; Na^+ – 38.35; SO_4^{2-} – 0.83; B_2O_3 – 0.06 (manufacturer – the plant of iodine production in Neftchala region, Azerbaijan). When realizing the proposed method, liquid effluents of mud volcano Girovdag of Apsheron Peninsula (Azerbaijan) with the following composition was used: Na_2O – 2.91; MgO – 3.35; Al_2O_3 – 13.14; SiO_2 – 44.85; P_2O_5 – 0.18; SO_3 – 0.52; K_2O – 0.52; CaO – 10.12; TiO_2 – 0.78; MnO – 0.11; Fe_2O_3 – 6.43; Cl_2O – 1.26; iodine containing inclusions – the rest. Additionally, effluents contained Ba, Zr, Cu, Cr, Zn, Ni and other microelements.

The proposed method includes: separation of mechanical impurities from the solid waste; mixing the separated organic components of household waste with the solution representing iodine production waste; stirring the mixture within 10–15 min. Liquid mud volcanic effluents are added to the resulting mass and stirred until a homogenous mass is obtained. The formed mixture is placed in a drying box and kept at 100–110°C for 1.5–2.0 h.

The ratio of organic components (solid household waste : iodine production waste : liquid effluents of mud volcanoes) corresponded to (1–5) : (0.75–2) : (1–6).

Some quantity of shell rock was added to the powdery mass for bringing pH of medium up to 6.5–7.5, and stirred till a homogeneous state. To neutralize the local shell rock of the coastal zone of Apsheron Peninsula with a porosity of 27–31% and a water absorption of 0.9–1.2%, a product of the following composition (wt%) was used: CaO – 51–57; MgO – 1.33; CO_2 – 38–48; Al_2O_3 – 2.0; Fe_2O_3 – 0.3; K_2O – 1.2; Na_2O – 0.5.

Content of nutritious elements in the obtained fertilizer depending on initial quantity of raw materials is shown in Table1.

Table 1. Chemical composition of the obtained fertilizer samples

Sample	Organic component of household waste, g	Iodine production waste, g	Liquid effluents of mud volcano, g	Main indices of granular fertilizer, wt%							
				Microelements	N_{total}	P_2O_5	K_2O	CaO	Organic component	H_2O	Solid fraction
1	50	40	20	0.10	0.46	0.60	0.50	2.1	30.0	1.90	1.94
2	40	20	20	0.30	0.10	0.40	2.0	6.6	30.5	2.40	2.5
3	20	25	25	0.26	0.26	0.51	2.0	7.3	35.0	2.75	2.44
4	20	15	15	0.31	0.31	0.60	2.4	8.3	35.5	2.3	2.39
5	40	20	20	0.50	0.50	0.45	2.45	9.0	34.3	2.36	2.64

In summary, the proposed method based on the complex use of waste of household, industrial and natural origin, makes it possible to obtain a fertilizer containing both organic and mineral constituents, i.e. representing an analogue of organomineral fertilizers. The fertilizer contains a sufficient amount of nutrients which could provide the growth and development of plants and, at the same time, the method contributes to solving the waste disposal problem.

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Behavior of natural radionuclides in soils and vegetation of tobacco in Sheki-Zaqatala region of the Azerbaijan Republic

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Soils and vegetation in the biosphere are one of the most important environments for the migration of radionuclides in terms of their potential exposure to plants, animals, and humans. Soils and vegetation are the most important channel for the involvement in the biological cycle of natural radionuclides entering the biosphere in the complete fuel cycle based on the chemical basis of radionuclides. Thus, when radionuclides enter the environment with the intensive development of energy and technology, the transfer of radioactive substances along the chain, soil-plant-tobacco is the main transport link for radionuclide migration in the biosphere.

In recent years, interest in problems of migration of heavy natural radionuclides U, Th, Ra and their decay products in the soil-plant-tobacco system, has grown markedly. Many phosphorus and nitrogen fertilizers are enriched in U, Th, Ra and their decomposition products. The concentration of these heavy natural radionuclides in fertilizers is higher than in soils. Consequently, prolonged application of these fertilizers in soils resulted in increase in the concentration of natural radionuclides in the root-inhabited layer. Thus, the transition of the said group of radionuclides from soil to plants and further to agricultural products is increasing.

The relevant issue in the radioecology of soils and plants is the analysis of soil contamination by tobacco sowing. The use of the approach of radioactive indicators makes it possible to analyze the rate of metal migration by tobacco sowing in soils, and further migration along biological chains. Examples of research in this direction are studies describing use of the compounds of ammonium nitrate, alkaline earth metals, and urea, as well as their introduction into the soil at various depths. The heavy natural radionuclides located in the soil pass into tobacco and are included in the biological cycle. Radioactive isotopes that accumulate in the cortex remain there until the end of plant life. Those radionuclides that are distributed in leaves and needles periodically return to the soil. Under certain soil conditions, the mobility of radionuclides can increase significantly. For example, if specific sorption sites in the crystalline structures of minerals turn out to be completely saturated (potassium or radium) or the soil exchange capacity is small, then ^{232}Th can be sorbed by certain type of exchange-ion absorption. In this case, conditions are created that provide increased availability of ^{232}Th for plant root systems. In particular, the increased mechanical mobility of ^{232}Th in the lungs is explained by the fact that ^{232}Th absorbs moisture from the soil more intensely than other radionuclides, while the availability of ^{232}Th for tobacco is higher than ^{226}U (Ra). For comparison, we can point out that under normal conditions, the accumulation of ^{226}U (Ra) in tobacco is about 3–4 times higher than that of ^{232}Th.

The content of radionuclides in plants depends on a number of factors. The main factors are the concentration and forms of radionuclides in the root layer of the soil, the geochemical characteristics of radionuclides and the presence of elements with similar chemical properties, as well as species characteristics of plants.

Migration and distribution of natural radionuclides in tobacco crops has not been sufficiently studied. Therefore, we have studied the distribution of soil-plant radionuclides in different parts of tobacco, depending on the climate. It has been revealed that the specific activity of ^{226}U (Ra), ^{232}Th, and ^{40}K radionuclides corresponds to sanitary standards, though in some cases the specific activity exceeds the permissible level. In our opinion, in recent years various fertilizers have been actively used in cultivation of tobacco crops and, as a rule, nitrogen and phosphorus based fertilizers can strongly affect the plant composition. These fertilizers are often enriched with natural radionuclides and, thus, the activity of these radionuclides in some locations can be higher than normal. Our study presents the results of natural radionuclides' behavior in soils and vegetation of tobacco in a separate zone of Azerbaijan, in Sheki-Zaqatala region.

Adsorption of amino benzene compounds by modified bentonite

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Currently, industrial enterprises have often become sources of chemical pollution of natural water bodies with their wastewater [1]. Wastewater coming from dye-producing enterprises and drug-producing enterprises is particularly harmful since it contains toxic aromatic amino compounds.

The adsorption method is a widely applied technique of water purification. The use of sorption materials based on natural mineral raw materials, such as clay rocks, has recently gained a particular interest [2].

The aim of this work was to study the characteristics of adsorption of aromatic amino compounds on modified bentonite in hydrodynamic conditions and under the influence of temperature changes, using *o*-phenylenediamine as an example of aromatic amine compound.

Experimental studies were carried out at the Scientific and Educational Center ‘Industrial Ecology’ of the Department of Ecology, Yuri Gagarin State Technical University of Saratov.

Studies of the sorption properties of various modifications of bentonite were carried out by the method of qualitative drop analysis (according to F. Feigl, described in [3]).

The following sorption materials based on modified bentonites were applied for the research:

- sorbent No. 1 - bentonite calcined at a temperature of 550°C, fine fraction;
- sorbent No. 2 - bentonite calcined at 550°C, medium-size fraction;
- sorbent No. 3 - bentonite calcined at 550°C, large-size fraction;
- sorbent No. 4 - bentonite calcined at 570°C, fine fraction;
- sorbent No. 5 - bentonite calcined at 570°C, medium-size fraction;
- sorbent No. 6 - bentonite calcined at 570°C, large-size fraction;
- sorbent No. 7 - bentonite, modified with magnesium hydroxide, calcined at 570°C, fine fraction;
- sorbent No. 8 - bentonite, modified with magnesium hydroxide, calcined at 570°C, medium-size fraction;
- sorbent No. 9 - bentonite modified with magnesium hydroxide, calcined at 570°C, large-size fraction.

A variance analysis of the influence of two factors (temperature and mixing speed) on the adsorption process of *o*-phenylenediamine by the bentonite samples was performed. The analysis of the obtained graphical dependencies allowed to evaluate the influence of the considered factors on the adsorption of *o*-phenylenediamine by the studied sorbents. Both factors were found to affect the adsorption process, though to varying degree. The experimental results are shown in Table 1. The results are interpreted in terms of F and F_{crit} values: if $F > F_{crit}$, then the impact of the studied factor on the adsorption is considered as significant, and if $F < F_{crit}$, the impact of the factor is of low significance.

Table 1. The values of F and F_{crit} for each sorbent sample according to the results of the variance analysis

Sorbent	**Temperature**		**Mixing speed**	
	F	F_{crit}	*F*	F_{crit}
Sorbent No. 1	28.92	6.94	5.08	6.94
Sorbent No. 2	21.57	6.94	2.34	6.94
Sorbent No. 3	22.11	6.94	3.16	6.94
Sorbent No. 4	16.42	6.94	6.57	6.94
Sorbent No. 5	14.18	6.94	5.14	6.94
Sorbent No. 6	6.68	6.94	3.15	6.94
Sorbent No. 7	35.04	6.94	14.28	6.94
Sorbent No. 8	64.68	6.94	15.27	6.94
Sorbent No. 9	72.29	6.94	17.73	6.94

Comparing the values of F and F_{crit}, it can be noted that temperature seems to be a significant factor for almost all the sorbents, except for the sorbent No. 6 (however, it's worth noting that the difference between F and F_{crit} is not large for this sorbent). The mixing speed is a significant factor for sorbents No. 7–9, but it has low impact in the case of using other sorbents. However, it can hardly be concluded that this factor is absolutely insignificant based only on the results of the analysis of variance, since with an increase in the stirring rate, the indicator of sorption ability becomes higher. Although, the mixing rate makes a smaller contribution to the adsorption process as compared with the temperature effect for studied sorbents.

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Removal of methylene blue and Ni(II) ions by adsorption onto activated carbon prepared from *Litsea glutinosa* seeds

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Water pollution has been a serious problem in recent years. Effluents containing organic dyes and heavy metal ions from textile, leather, galvanic and battery industries can have a significant negative impact on the environment. These pollutants are highly toxic and non-biodegradable substances that accumulate in human body and may cause many serious diseases such as dermatitis, headache, nausea, anemia, diarrhea, damage of lungs and kidney, dysfunction of cardiovascular and central nervous systems, etc. Consequently, wastewater contaminated with dyes and heavy metals must be treated prior its discharge into the environment. Among wastewater treatment approaches, adsorption is the most commonly used method for removal both dyes and heavy metals due to its high efficiency, easiness of operation, low cost, and availability of various raw resources. In general, there are many adsorbing materials, such as silica gel, alumina, activated carbon, zeolite, etc.

Activated carbon (AC) is characterized by large specific surface area, high-developed porosity, a possibility of modification with various surface functional groups, accordingly, it has been widely used in wastewater treatment [2]. Nowadays, the AC obtained from biomass, lignocellulosic precursors is being continuously developed to replace expensive commercial activated carbon. Although activated carbon powder has been shown to be effective in adsorption, it is difficult to separate and reuse powdered AC after adsorption treatment, which results in adsorbent loss and secondary pollution. Meanwhile, the use of activated carbon beads makes it possible to overcome these shortcomings.

Litsea glutinosa (LG) is an evergreen plant from the laurel family found in southern China, the Indian subcontinent, Myanmar, Thailand, Cambodia, Laos, Vietnam, Malaysia, Indonesia, the Philippines, and Australia. The parts of the tree such as trunks, roots and leaves are used for producing paper pulp, rope manufacture, and in traditional medicine. The LG seeds have been used to make candles and soaps [3]. In addition, LG seeds containing 17.4% cellulose, 25.5% hemicellulose, and 27.6% lignin were used as precursors for preparing activated carbon to remove dyes and heavy metals.

In this work, we used seeds from *Litsea glutinosa* to prepare activated carbon in bead form. Unlike AC powder, activated carbon beads (ACBs) have useful properties, such as ease of separation from aqueous solution, high mechanical strength, and excellent durability. ACBs were prepared in several steps. Firstly, *Litsea glutinosa* seeds (5–8 mm in diameter) were collected as raw material in the forests of Central Vietnam. Next, they were washed from dust and dirt, and dried at 50°C for 3 days. Then, the seeds were impregnated with 5% $NaHCO_3$ solution and subjected to carbonization at 450°C for 1 h. The obtained ACBs were washed with 1% HCl solution and distilled water until no change in pH.

The adsorption of methylene blue and nickel ions from aqueous solution onto ACB was performed using a batch technique. After the reaction period, the residue concentration in the solution was determined using a UV-visible spectrophotometer. The concentration of methylene blue was measured at 664 nm maximum absorption wavelength; the nickel ion concentration was determined by measuring at 470 nm wavelength by preconcentration of Ni(II) ions with dymethylglyoxime.

Figure 1 shows the effect of adsorbent dosage on removal degree of methylene blue and nickel ions. In the adsorbent weight range from 4 to 12 g/L, the ACB removal effeciency increased from 85.7 to 92.2% for methylene blue, and from 74.1 to 93.4% for Ni(II) ions. The results can be explained by the presence of activated sites on ACB surface with improved availability. However, the removal efficiency of methylene blue showed only a 1.1-fold increase (from 85.7 to 93.5%) while the adsorbent dosage was tripled (from 4 to 12 g/L). As can be seen in Fig. 1, the adsorption of Ni(II) ions rapidly increased up to dosage of 8 g/l, followed by a decrease in effective adsorption upon further increase of the adsorbent dosage. This may be due to the full use of adsorption sites, resulting in a reduction in the adsorption surface area available to nickel ions. Thus, the adsorbent dosage (8 g/L) was considered as the optimal for removing methylene blue and Ni(II) ions from aqueous solutions.

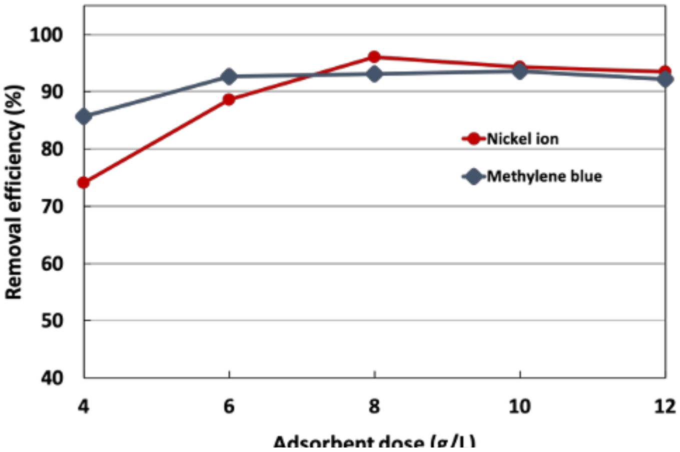

Fig. 1. Effect of adsorbent dosage on adsorption of Methylene blue and Ni(II) ions by ACBs (C^{o}= 20 mg/L; T = 25°C; t = 10h; pH 6 (Methylene blue), pH 4 (nickel ion))

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Reagent treatment options for biological wastewater treatment facilities

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Currently, the processing of wastewater sediments, including excess activated sludge, and developing its disposal procedures compose an extremely urgent problem, while universally applicable approaches for solving this problem have not been found yet despite of numerous efforts undertaken over the past decades.

It was established that the problem of treating sludge produced at existing and newly constructed wastewater treatment facilities has two main aspects:

– technological aspect;

– social and environmental aspect.

Taking into consideration the above, wastewater raw precipitation formed needs to be processed.

The workflow sequence of sludge treatment should be carried out according to the following scheme: initial sludge treatment – stabilization – disinfection – dehydration – disposal [1].

The most important step in the processing of wastewater sediments is their stabilization.

Among stabilizing reagents, calcium oxide is the most widely used due to its low cost. Its action is based on increasing the pH and temperature of the processed sediment mass.

In this work, experimental studies were conducted to stabilize the rainfall of urban wastewater treatment facilities using calcium oxide. The thermal (temperature changes) and moisture-releasing (volume of superficial water) properties were evaluated.

A moisture level was measured which showed that using calcium oxide provided decrease in humidity value by 3.6%.

It was further determined that the dose of calcium oxide for a particular type of precipitate should be optimized in the course of pilot trials [2].

Samples of activated sludge were also precipitated in the presence of a variety of chemicals to coagulate and flocculate solid particles which must be separated from the aqueous phase.

For reagent treatment of sediments, iron chloride was used together with lime.

The results of the study showed that the efficiency of separation of sediment samples using iron sulfate was higher. The optimal dose of reagent was also selected to obtain the maximum separation effect.

Thus, the results obtained in this study show that the use of the reagents applied is not only effective, but also can be developed in a universal procedure for treatment of sewage sludge produced at wastewater treatment facilities.

Basing on the data obtained, ways of further processing, placement and disposal of sewage sludge will be further considered [3].

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Bifunctional coumarin-based chemosensors for detection of cations and anions in the environment

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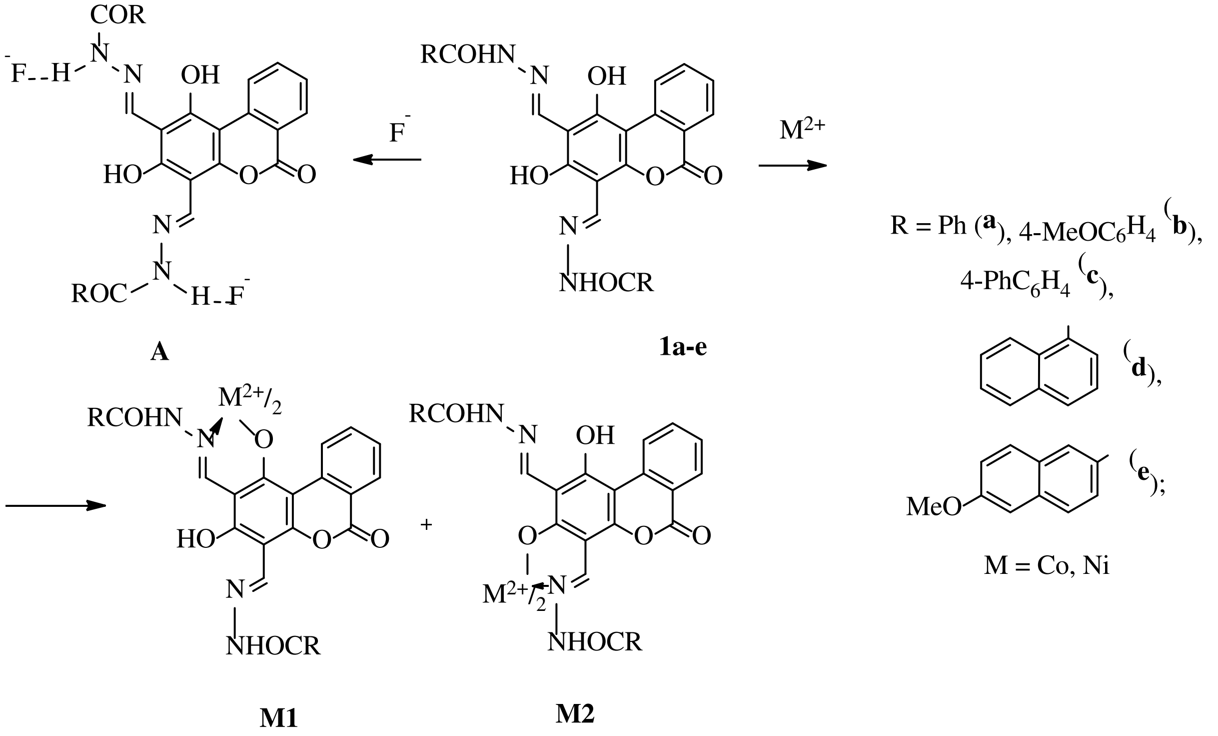
Chromogenic and fluorogenic chemosensor systems are widely used in organic, biological, medical chemistry and environmental sciences for express monitoring of heavy metal cations and toxic anions in real time and space [1, 2]. They represent a serious alternative to traditionally used for this purpose bulky, expensive, non-transportable technical devices such as atomic absorption, atomic emission and XRF spectrometers. The coumarin moiety is one of the most versatile frameworks for designing and modification of ion-active systems [3, 4].

We have implemented the design and developed synthetic methods for obtaining of aroylhydrazones of 1,3-dihydroxy-6-oxo-6*H*-benzo[*c*]chromene-2,4-dicarbaldehyde **1a-e** that represent bifunctional “naked-eye” chromogenic and fluorogenic chemosensors for detection of cations and anions in solutions (Scheme 1).



Scheme 1.

Compounds **1a-e** display fluorescence at 520–580 nm region with large Stokes shifts which is associated with the ESIPT-effect caused by the rapid intramolecular O→N proton transfer in the singlet excited state. Their interaction with F^-, CN^- and AcO^- anions leads to a change in the color of the solution from yellow to orange-red (Fig. 1) and quenching the initial fluorescence.

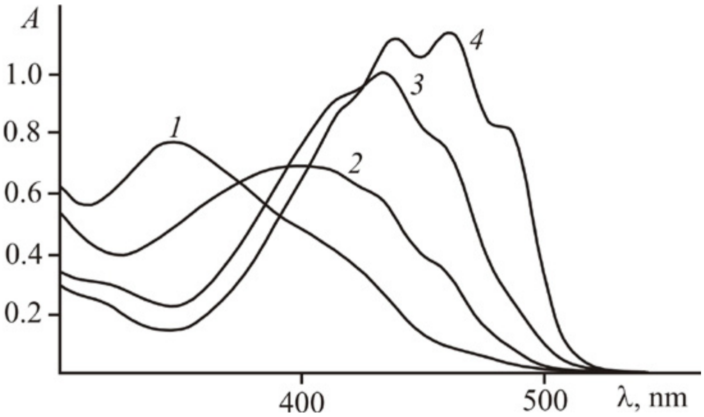


Fig. 1. Electronic absorption spectra of **1c** in acetonitrile before (*1*) and after addition of anions AcO^- (*2*), CN^- (*3*) and F^- (*4*) in DMSO (*c* $1.25 \cdot 10^{-5}$ M)

In the presence of Zn(II) cations, there a change in color from yellow to orange and a significant increase in the intensity of fluorescence are observed. Cations of Co(II) and Ni(II) cause a similar “naked-eye” effect which is accompanied by quenching of the emission properties.

The proposed mechanism of sensing properties of bifunctional aroylhydrazones **1a-e** is shown in the Scheme 1, taking into account spectral data and the isomolar series method results.

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Study of removal of pollutants from aqueous medium by dynamic adsorption

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Currently in Russia, the content of chemically hazardous substances in water is regulated by two kinds of hygienic standards that determine the maximum permissible concentrations (MPCs) of chemical substances in the water of reservoirs used for drinking and household water use, and in the water bodies used for recreational and cultural and domestic purposes.

The composition of industrial wastewater produced by various enterprises is specific, which requires a detailed justification and an effective choice of wastewater treatment technology, as well as processes and auxiliary materials (substances) for their implementation including treatment agents in each specific case. Until now, the semi-batch type water treatment facilities (continuous in terms of water and batch-type in terms of coal) based on dynamic adsorption processes have been the most widely applied in practice for wastewater treatment.

The dynamic adsorption method is currently broadly used for purification of industrial waste gases, drinking water and wastewater. Dynamic adsorption process is typically implemented in open systems when a stream of gas or liquid containing contaminants is passed through a column with an adsorbent that removes these contaminants from the stream. The most important characteristics of column dynamic adsorption can be obtained from the analysis of the output (breakthrough) curves describing the dependence of concentration of a substance in the mobile phase at the outlet from the column upon reaction time or eluent volume of the solvent.

The most commonly applied dependences are the breakthrough curves, i.e. time dependences of the ratio $C(t)/C_0$, where $C(t)$ is the concentration of the test substance at the outlet of the sorption column at time t, and C_0 is the initial concentration of this substance at the inlet to the column.

Studying dynamic adsorption in a fixed bed of an adsorbent of some pollutants dissolved in water is a relevant and challenging task.

The authors have developed a new approach to the mathematical description of the dependences of the breakthrough curve upon the spatio-temporal profile of the concentrations of pollutants along the fixed layer of the sorbent in the process of sorption water purification. An equation has been derived that determines the breakthrough concentration C on time t for a pollutant in water flowing out of the fixed bed, which makes it possible to determine the rate of sorption, knowing the dynamic adsorption capacity of the adsorbent.

Enzyme-polyelectrolyte complexes for detoxification of mycotoxins

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Mycotoxins are hazardous natural compounds possessing neuro-, nephro- and hepatotoxicity, consequently, the presence of various mycotoxins in raw materials and agricultural products is carefully controlled using specially developed highly sensitive methods of analysis [1]. However, if their quantity exceeds the values of tolerable daily intake, effective detoxification is necessary. Currently, enzymatic transformation of the toxic compounds seems to be the most promising method for detoxification of mycotoxins [2]. The preferable enzymatic agents are enzymes in stabilized form which extends their effective functioning period. Usually, a combination of several enzymes that modify different mycotoxins should present in the preparation, since the raw materials and products are often contaminated simultaneously with several compounds.

The aim of this work was to develop stabilized forms of combined enzyme preparations by forming similar non-covalent enzyme-polyelectrolyte complexes (EPCs) for their subsequent use in the degradation processes of several mycotoxins aimed at disinfection of raw materials and products.

To develop these stable forms of enzymes, we used the same approach as previously was applied for the hexahistidine-tagged organophosphorus hydrolase (His_6-OPH) degrading organophosphorus pesticides [3–6]. To start with, the Lomonosov supercomputer (developed at Lomonosov Moscow State University) [7] was applied to calculate possible modes of interaction of a number of polyelectrolytes with selected enzymes that could modify various mycotoxins, namely: Zn-dependent neutral protease (1npc), resorcylate decarboxylase (2dvx), aflatoxin oxidase (AFO) (5yfd), and carboxypeptidase A (1yme).

Polyglutamic acid (PLE_{50}), polyaspartic acid (PLD_{50}), as well as their block copolymers with polyethylene glycol (PEG-PLE_{50}, PEG-PLD_{50}, PLE_{50}-PEG-PLE_{50}) were chosen for computer calculations, since they showed the best results earlier in the study devoted to the formation of EPCs with His_6-OPH [3]. Succinylated gelatin (a drug under the brand name Gelofusin) was used as negative control, as it had shown the most tight and strong interaction with His6-OPH, which led to a strong blockage of the active centers of the enzyme, resulting in the loss of enzymatic activity [3].

The smallest effect on the protease at pH 7.5 was observed for PLE_{50}, PLD_{50}, and PEG-PLD_{50}, while PEG-PLE_{50}, PLE_{50}-PEG-PLE_{50}, and succinylated gelatin somehow succeeded in blocking the active centers of the enzyme dimer molecule. Under similar conditions, decarboxylase was covered up only by succinylated gelatin, which blocked three of the four active centers of the tetrameric enzyme.

The active center of AFO, on the contrary, was not blocked only by PLE_{50}. It should be noted that the cavity of the active center of this enzyme is a through tunnel, and therefore the blocking of both ends (‘entry’ or ‘exit’) of this tunnel equally affected the enzyme activity.

The best polymer counterparts for carboxypeptidase A were PLE_{50}, PLD_{50}, PEG-PLD_{50} and PLE_{50}-PEG-PLE_{50}, and the worst – PEG-PLE_{50} and succinylated gelatin.

The results indicated that the most versatile polymer for preserving the enzymatic activity of all studied enzymes is PLE_{50} at pH 7.5. So, this it could be further applied for stabilizing these enzymes and preparing enzyme-polyelectrolyte complexes which are capable of efficient catalytic degradation of various mycotoxins mixtures.

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Technology for cleaning internal surface of tanks from adhered solid chlororganic polymers

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In the 90s of the last century, activated carbon impregnated with mercury chloride ($HgCl_2$) was used as a catalyst in the industrial process of polyvinyl chloride (PVC) production. Starting-up procedures and emergency shutdowns in the PVC production cycle are usually accompanied by formation of zones of local temperature peaks in the polymerization reactor. This can lead to the formation of solid mercury residues containing polymer deposits on the inner surface of reactor. While implementing the procedure of bringing former facilities in the safe state, a problem of cleaning polymerization reactors and tanks from unrecoverable chlororganic polymers arises. One of the promising approaches for solving this problem is hydro-cavitation (HC) cleaning procedure.

To determine the HC-cleaning process main technological parameters values, an experimental study has been carried out which includes the following steps:

- determination of adhesive strength values between unrecoverable PVC residues and steel at different temperatures;
- establishing the HC-jets pressure force dependence, affecting on the surface being cleaned, from the distance between the surface and the cut of the HC-nozzle;
- determination of the minimum required contact time between HC-jet and surface being cleaned for complete removal of unrecoverable PVC residues in one run.

It has been established that cleaning process takes a single run under the following conditions: HC-jet pressure of 20 atm, the distance between the nozzle exit and the surface to be cleaned of 5 mm and the nozzle linear speed in the range of 50–75 mm/s. Additionally, it has been shown that pretreatment of solidified chlororganic polymer compounds for 5 minutes with water at 100°C more than 7 times reduces their integrity and strength.

Basing on the results of the experimental studies, a pilot industrial mobile unit which allows cleaning the inner surface of industrial tanks from unrecoverable residues of chlororganic polymers has been designed and successfully tested.

Drying-incapsulation technology for treatment of wastewater contaminated with heavy metals

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Chemical facilities are known to generate a large amount of wastewaters, including those containing heavy metals in both water-soluble and water-insoluble forms. Significantly polluted water effluents can’t be discharged into the sewer or biological treatment plant and are usually sent to purification unit. Purification (neutralization) of such wastewater is a quite complicated and expensive technological task due to its multistage design and the requirement for a large number of tanks. Furthermore, a solid precipitate forms during the wastewater treatment process, which must either be disposed off or the conditions for its safe long-term storage must be ensured.

In order to reduce capital and operating costs, we have studied the continuous process of convective spray drying of wastewater with its simultaneous encapsulation in a fluidized bed. Wastewater containing mercury(II) chloride was used as an object of the study. $HgCl_2$ was present both in the dissolved form and in the form of a water-insoluble metal-containing polymer complex (solid particles ~0.25 mm in size). Wastewater was sprayed and dried directly in the chamber of the dryer-encapsulator, and the precipitated solid phase continuously produced sites of granulation-encapsulation. Molten ceresin was used as a binder and encapsulator, being fed under pressure into the fluidized bed through the nozzles, installed into two zones of main apparatus: initial and final encapsulation. Two-step granulation-encapsulation procedure provides the absence of the initial solid phase material on the surface of the final product. The resulting dry product is continuously discharged from the apparatus and the exhaust gas, after its purification on the bag filter, is directed into ventilation system.

It was found that the temperature in the fluidized bed should be maintained in the range from 60 to 70°C. More than 80% of the discharged dry product consisted of granules with the size of ≥ 0.5 mm. The resulting product is found to be waterproof (swelling was not observed at the temperature of 40°C during 72 h).

Thus, the proposed method provides an efficient treatment of wastewater contaminated with heavy metals, while the treatment can be carried out in a single apparatus with obtaining dry, loose, waterproof product which is suitable for long-term storage and inert to the environmental exposure.

Hydrogen chloride emission reduction in flue gases during thermal neutralization of mineral materials contaminated with toxic organochlorine compounds

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Currently, there are more than 150 objects of accumulated environmental damage in the Russian Federation, with the total contaminated area of ~4,500 hectares. There are several objects in this list, among others, that are related to former large-scale facilities which had been earlier producing toxic organochlorine compounds, as well as landfills for their burial. The rehabilitation of such territories is planned to be carried out within the framework of both regional and federal targeted programs. The basic technological method for making these territories safe is thermal neutralization of contaminated industrial objects. One of the main disadvantages of this method is hydrogen chloride formation during combustion of organochlorine compounds, which can lead to premature corrosion of technological equipment.

In our attempts of searching for technological solutions to reduce hydrogen chloride emission in flue gases, we’ve studied the thermal neutralization process of bulk mineral materials (mixture of soil and milled red brick) contaminated with trichloromethyl-bis(p-chlorophenyl)methane (DDT) and hexachlorocyclohexane in concentrations of 25.23 mg/kg and 13.17 mg/kg, respectively. In the course of the study, the contaminated bulk mixture was sequentially placed into drum dryer and furnace, heated by flue gases through external chambers enclosing the dryer and furnace bodies, so sequential drying and calcination was realized. To neutralize the hydrogen chloride formed, slaked lime (reagent) was sprayed into the volume of the dryer in the direct-flow mode by means of a pneumatic device. Flue gases were exhausted from the furnace and fed into the gas purification system, then the thermally treated bulk mixture was cooled and discharged.

It was found that the reagent sprayed must be in the form of particles with the size of less than 30 microns, and the mass ratio of the reagent: contaminated building materials/soils should be in the range of 0,11–0,2. The total residence time of the treated mixture in the drum dryer and furnace equals to 1 h in the temperature range from 200 to 750°C, which provides the complete thermal neutralization. Under these conditions, the concentration of hydrogen chloride in the exhaust flue gas showed almost 4-fold decrease, which can significantly reduce the capital and operating costs of the flue gas treatment system. Patent for the invention is successfully obtained [1].

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Fiber heat insulation waste recycling in laminated high-temperature composites with phosphate binder

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Fiber heat insulation materials (FHIM) provide highly effective thermal protection as they combine a low thermal conductivity and volume weight, the resistance to thermal shocks, etc. The use of FHIM allows to raise the productivity of heat aggregates, to reduce the cladding cost and decrease the fuel consumption.

A technology is known for producing fiber plates for heat insulation cladding which generally uses a roll material breaking up followed by item formation in the presence of a binder that provides the improved strength of prepared composites. However, the heat insulation layer replacement is accompanied by the formation of a waste which contains bound fibers, which poses a problem of its utilization.

The aim of the study was to work out a method for utilization of the spent fibrous insulation material in the composition of sandwich type where upper and lower layers were fiber material blankets with mainly one-way fiber position, while the interlaying of this sandwich construction was a composite binder on the base of spent heat insulation fibers and aluminoboronphosphate binder (ABPB).

It is noteworthy that using phosphate binders does not necessarily requires preliminary high temperature burning. Besides, obtained units are characterized by low shrinkage. Phosphate binders are homogeneous metastable water solutions of phosphate compounds which harden spontaneously as a result of their transformation under heating, pH change, hardener adding or desiccation. At the same time, a large number of new colloidal formations on a fiber surface emerges after that they are gradually transformed into crystal form, which raises the unit strength up to several times.

Waste based on basalt, mullite-siliceous and chromium-mullite-siliceous fibers was used. It appeared reasonable to remake fiber waste not containing a binder by repulping in water followed by release from excess water. The obtained moist mass was mixed with ABPB.

The optimal method for treatment of mineral fiber layers was used to improve adhesion of an outer layer with a composite binder without a considerable FHIM fluffing. Composites were obtained by hot pressing under pressure of 12 MPa and treatment in microwave oven for 5 min.

A lubricating agent was used in a mineral fiber production impeding the fiber moistening. A surfactant addition provided preparation of the material based on mullite-siliceous fiber having the strength which was up to 30% higher. It could be explained by the activation of fiber surface after the lubricant removal and by the closer contact of ABPB with fibers.

To determine the optimal binder composition, the ABPB content was varied from 10 to 80%. It was determined that mullite-siliceous and chromium-mullite-siliceous fibers required 62–70 wt% ABPB (in relation to fiber waste mass) with simultaneous lubricant addition.

Binder-containing FHIM wastes are usually badly repulped in water. So, it prevents obtaining a homogeneous composite binder. Accordingly, the effect of mechanical treatment of wastes (attrition, impact) on morphological peculiarities of the obtained materials was studied. During dispersing fibers, fragments were formed with a large content of powder fraction; the attrition gave the higher quantity of fine-dispersed particles. As a result, the particles were equally distributed in terms of composite binder volume and more deeply penetrated into fiber layers with the subsequent improvement in flexural strength of the end products.

Thus, we have developed a method for preparation of laminated heat insulation materials of sandwich type containing a composite binder produced from fiber waste and aluminoboronphosphate concentrate binder.

Medical and biological hydroxyapatite based concepts for solving chemical safety problems

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Currently, synthetic constructions comprising both organic and mineral components are of great interest for the development of bone substitute materials. In reconstructive surgery, composites containing hydroxyapatite and natural biodegradable polymers such as gelatin, have become widespread [1].

Hydroxyapatite (HAP) is basic calcium phosphate $Ca_{10}(PO_4)_6(OH)_2$, which is the main component of bone tissue (45–70 wt. %), dentin (72 wt. %), tooth cement (71 wt. %), and tooth enamel. However, environmental and economic aspects of its production, as well as the problem of effective immobilization of bioactive substances on the surface of HAP, remain unresolved.

A promising approach for solving this problem has been proposed by creating dispersion systems of HAP in a reactor of a rotary pulsation apparatus. Using this apparatus, a method of non-waste production of HAP for medical purpose was developed [2]. Additionally, the developed procedure allows using the wash waters from the purification step as a mineral complex additive enriched with nitrogen, phosphorus, and calcium for feeding agricultural plants.

A procedure for obtaining HAP of desired structure intended for preparing compositions used in therapeutic and preventive practice is well known [3]. Colloidal silver characterized by high antibacterial activity is used as an adsorbate. The formed composition of nanosized HAP and colloidal silver demonstrates higher antibacterial activity as compared to unmodified HAP, and also provides good adsorption properties of the HAP nanoparticles which can be used to solve problems related to elimination of chemical contamination consequences.

Thus, the biochemical investigations of HAP are inevitably accompanied by the development of chemical safety ensuring approaches in the context of identification and disposal of hazardous chemicals in the environment.

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Propolis as a native environmental indicator

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Due to the growth and development of industry as well as the intensive use of chemicals in agriculture, control over anthropogenic pollutants' release into environment has gained an increased relevance and high socio-economic importance. Taking into account the trophic chains, heavy metals belong to the group of the most hazardous pollutants, which can enter the human body and cause health damage and pathological processes.

Various natural entities are discussed as the most selective and informative indicators of accumulation and migration of heavy metals within the ecosystem. One of the most suitable potential indicators is propolis, a well-known bioactive complex produced by honeybees by mixing wax, pollen, salivary secretions, and collected natural resins [1]. The chemical composition of propolis is affected by natural and climate conditions and the type of bee flora. However, there are three groups of substances, the most commonly found in propolis, i.e. polyphenols, waxes and mechanical impurities. Deposition of heavy metals, such as cadmium and lead in propolis, is heterogeneous and depends on the concentration and composition of each group of propolis ingredients.

The aim of this study was to quantify the total/differential content of cadmium and lead in various propolis samples as well as to interpret the results obtained.

The propolis samples were collected in the Penza region (sample No. 1) and the Altay region (sample No. 2) in 2018 and analyzed. Propolis separation using n-heptane and ethanol was carried out in a Soxlet apparatus. According to the recorded change in the mass of the propolis samples, the material balance was drawn up (Table 1).

Table 1. Material balance of propolis samples after extraction

Sample	Part of propolis, wt.%		
	Polyphenols	Waxes	Mechanical impurities
1	30.0 ± 0.1	62.0 ± 0.1	8.0 ± 0.1
2	72.5 ± 0.1	22.5 ± 0.1	5.0 ± 0.1

The content of cadmium and lead in the resulting samples was determined by atomic absorption spectrophotometry (Table 2).

Table 2. Content of heavy metals in propolis samples and propolis ingredients, mg/kg (X ± Sx)

Group of substances	Indicator			
	Cadmium		Lead	
	Sample 1	Sample 2	Sample 1	Sample 2
Polyphenols	0.006 ± 0.002	0.003 ± 0.001	0.150 ± 0.004	0.020 ± 0.008
Waxes	0.070 ± 0.01	-	2.370 ± 0.003	0.110 ± 0.001
Mechanical impurities	0.014 ± 0.002	0.009 ± 0.002	0.380 ± 0.002	0.060 ± 0.001
∑	0.090 ± 0.014	0.012 ± 0.003	2.900 ± 0.009	0.190 ± 0.01

The highest total content of cadmium and lead was found in propolis sample No. 1. It was established that heavy metals accumulation takes place mainly in the waxes and impurities of the propolis samples, which can be explained by the chemical composition of these ingredients involving proteins, lipids, inorganic substances, as well as foreign objects. Cadmium in the wax part of the propolis sample No. 2 was not found, probably due to the lack of substances prone to its deposition, or complete dispersion of cadmium in the environment at the time of samples collection. Lead was found in both samples and in all groups of propolis ingredients of the samples studied, taking into account that its migration routes depend significantly on the development of the trophic chain as well as the influence of man-made factors.

Thus, the quantitative content of heavy elements in propolis and their distribution in propokis ingredients, depending on the locations of sample collection, have been determined. The obtained results clearly indicate that certain components of propolis can be effectively used in environmental monitoring of heavy metal levels.

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Radiation safety of the Absheron Peninsula area

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Recently, radiation safety has been added to the scope of long-known safety issues in the oil industry. It is common knowledge that technological processes of oil production and treatment have a negative impact on the environment and lead to its contamination with various chemical compounds. In addition, over the past 20 years, the deposition of salts with a high content of natural radionuclides in oil field equipment has become a relevant problem.

Natural radionuclides in the environment exist in a dynamic equilibrium, which can be disturbed by complex natural phenomena or the consequences of human economic activity. The contamination of oil and gas with radionuclides of terrestrial origin occurs in two ways. The first one is due to the fact that oil deposits are often associated with uranium-rich shale. The concentration of uranium in a shale can reach 1000 g/t or more. The porous sandstones lying below contain brines in which ^{226}Ra and related by-products are gradually dissolved. These products then enter the overlying oil and gas deposits and contaminate them with radionuclides. The second contamination route is due to the diffusion of ^{222}Rn into the oil layers. The lifetimes of ^{222}Rn decay products are measured in seconds and minutes, for example, ^{210}Pb (22.3 years) and ^{210}Po (138 days). These nuclides, along with radium, are the main pollutants of oil and gas [1].

At the start of the exploitation of drilled wells, oil and gas come in dry form, but then water begins to mix with their flow forming an emulsion or aerosol. This stratal water contains dissolved inactive sulfates and carbonates of Cu, Sr and Ba. Radium is always present in the stratal waters of oil and gas deposits in the form of watersoluble chlorides. When extracting oil or gas, due to sulfate imbalances, radium chlorides turn into practically insoluble sulfate compounds in fresh water, which are deposited in the form of sediments on technological equipment. The possible reasons for this fact – the temperature decreases of the extracted fluid as it moves from the bottom of the well to the wellmouth, the use of water that is incompatible with stratal water in terms of its chemical composition, etc.

Analysis of the available scientific and technical information shows that this phenomenon cannot be avoided at the current level of oil production technology development [2]. Obviously, the formation of sediments with a high content of natural radionuclides on technological equipment poses a potential threat of personnel radiation exposure and environmental pollution. Sources of radioactive contamination are also natural radionuclides occurred in the Earth's crust and brought to the surface as a result of oil production, i.e. ^{238}U, ^{232}Th, and ^{40}K. The level of radioactive contamination of field and technological equipment is determined, first of all, by the isotopes ^{226}Ra and ^{228}Ra contained in the associated stratal waters of oil deposits. Radioactive substances accumulate in the internal cavities of the equipment in the form of salt deposits, the density of which is in the range of 3.0–3.9 g/cm^3. The main component of these deposits is radiobarite $Ba(Ra)SO_4$. The specific activity of such sediments can reach $1.5 \cdot 10^7$ Bq/kg.

The increased concentrations of radionuclides are also observed in heavy oil filtration and gas separation products, that accumulate in filters, separators and settling tanks. Sediments on the walls of oil and gas field equipment are usually more radioactive than sludges. Moreover, oil and gas production waste also contains toxic heavy metals, i.e. cadmium, lead, zinc, and mercury.

The environmental situation on the Absheron Peninsula can be considered as unfavourable, or even critical. The biosphere of the Absheron Peninsula has been under relentless anthropogenic pressure for more than 100 years. Irrational use of natural resources and processing of raw materials, environmentally incorrect placement of multibranch industrial facilities, poor transport interchange, improper disposal of solid and liquid wastes have turned the territory of the Peninsula into a totally contaminated zone [3].

In terms of industrial production, Absheron is the largest industrial region of the Republic of Azerbaijan. It accounts for more than 70% of gross industrial product, about 60% of total onshore oil production, all oil refining, almost all petrochemical industry, over 80% of mechanical engineering and metal processing, and about 30% of the electricity generated. The Absheron Peninsula urgently needs to restore the stability of its ecosystem. More than 150 mineral deposits are being exploited on the Absheron Peninsula with severely damaged environment in the vicinity. In total, ~16,000 hectares of its territory are contaminated with oil and oil products. The radioecological situation in this region is relatively safe (in general, the natural radioactive background of the peninsula, composed of weakly radioactive sedimentary rocks, varies within 6 μR/h). However, local and spatial areas have been identified with radioactivity exceeding the permissible background in tens, or even more times, as a result of anthropogenic activity. This mainly refers to the oil field, where oil production waste has accumulated over time. In addition, in the villages of Ramana and Yeni Suraxani two iodine plants are located that contaminate the territory with radioactive isotopes.

Environmental protection and creating favorable level of well-being are global problems of our time. Ensuring radiation safety of the population requires urgent measures related, first of all, to the purifying of contaminated areas, the decontamination of equipment used, as well as safe and environmentally sound disposal of radioactive waste. In addition, radioactive sludge and drilling fluid waste can be repumped into wells under high pressure.

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Monitoring water bodies polluted with toxic organic substances

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It is known from the literature, that ~6 million tons of oil and oil products are discharged into the world ocean every year [1]. This results in the water pollution, in particular, with organic compounds, moreover, many of these compounds are toxic, for example polycyclic aromatic compounds.

In this research work, water samples polluted with organic compounds were analyzed. The samples were collected from two areas of the Absheron Peninsula in Azerbaijan: the Guneshli Field and the Caspian Sea in the Hovsan region. Qualitative analysis of water samples was carried out using a gas chromatograph with a flame-ionizing detector FID 6890 (Agilent, USA) and a ZB-1 column (Phenomenex, USA).

The contents of organic compounds in these samples were determined and a mass chromatographic analysis was performed, the results are presented in Table 1.

Table 1. Organic compounds content in water samples from Guneshli Field and Hovsan territory

Polycyclic aromatic hydrocarbons, μg/l	Guneshli Field	Hovsan
Fluorantene	0.010	0.015
Benz[a]anthracene	< 0.011	0.004
Chrysene	0.023	0.012
Benzo[b + j + k]fluoranthene	0.012	0.031
Benzo[a]pyrene	0.013	0.015
Indeno[1,2,3-cd]pyrene	< 0.012	< 0.014
Benzo[ghi]perylene	< 0.010	< 0.012

As can be seen from the table, water samples from the Hovsan territory were found to have a higher level of pollution with polycyclic aromatic hydrocarbons. This can be probably explained by the presence of a chemical plant in the immediate proximity of the sample collection site.

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Disposal of bio-sludge of industrial enterprise wastewater treatment facilities (exemplified by Kazanorgsintez PJSC)

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The operation of water and wastewater treatment facilities leads to generation of increasing quantities of sewage sludge and deposits in any industrial region. Due to the presence of ecotoxicants and their poor water-giving properties, the issues of wastewater sludge processing are of great ecological and economic importance, since the high content of contaminating organic substances, pathogenic bacteria, viruses, helminth eggs, and associated water contributes to secondary pollution of the environment in the storage sites. On the other hand, a significant increase in the cost of elimination of negative environmental impacts has recently been observed, including those for solid waste management [1]. Therefore, the problem of processing of precipitation of domestic and industrial wastewater is more urgent than ever before.

A rational way out of this situation is creating such a process of sludge processing that will allow their use as secondary raw materials for the production of marketable products and, thereby, increase the profitability of the treatment facilities. To date, the task of utilization of wastewater sewage sludge has been put forward among the priority tasks requiring urgent and radical solutions.

The aim of this work is to develop an organic mineral soil structure-forming additive for non-agricultural land.

The structure-forming additive is used for the reclamation of depleted and degraded soils which are contaminated with various pollutants and not included in agricultural circulation lands.

The following tasks are expected to be solved in this research:

1. Studying toxic properties of bio-sludge treatment facilities;
2. Development of technological aspects of obtaining an organic mineral structure-forming additive;
3. Development of optimal conditions for its use.

The object of study is a bio-sludge of wastewater stored at silt sites of treatment facilities of Kazanorgsintez PJSC industrial enterprise (Kazan, Russia).

According to the chemical composition, the sediments of biological treatment facilities are a mixture of mineral and organic substances with an ash content of 41–70%. The main components are the necessary macro- and microelements, which determine the fertilizer value of the structure-forming agent, including nitrogen, phosphorus, potassium, calcium, zinc, magnesium, manganese, boron and others. The following heavy metals are also present in the form of trace impurities in the product: chromium, lead, mercury, copper, cadmium, among others.

Taking into consideration the state sanitary regulations and standards 2.1.7.573-96 “Hygienic requirements to wastewater and sewage sludge use for land irrigation and fertilization”, we have developed technical requirements for the composition of the proposed commercial products - organic mineral soil structure-forming additives (table 1).

The structure-forming additive is a dark pasty mass with a specific odor, obtained as a result of wastewater sewage sludge exposure and drying in natural conditions on silt sites of biological treatment facilities.

Table 1. Average composition of organomineral structure-forming additive

Indicator	Structurant	Regulatory requirements
Moisture, % no more	65–80	82
Dry matter, % at least, including (mg/kg no more):	20–35	20
Plumbum (Pb)	200	1000
Arsenicum (As)	20	20
Hydrargyrum (Hg)	1	15
Cadmium (Cd)	30	30
Niccolum (Ni)	50	400
Chromium (Cr^{3+})	100	1200
Manganum (Mn)	500	2000
Zincum (Zn)	200	4000
Cuprum (Cu)	650	1500

It is important that the content of heavy metals in the structure-forming additive should not exceed 4000 mg/kg [2].

Taking into account the current requirements of environmental protection, it is recommended to apply such conditions of storage, transportation and use for the proposed product that exclude its entering open water bodies. In addition, it is prohibited to apply the structure-forming additive for soils in the territories of water protection and conservation zones, and also to use it for remediation of soils with the increased content of heavy metals (the content of heavy metals in the soil of the territory proposed for reclamation should not exceed 0.7 MPC level specified in the regulatory documentation) [2].

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Cytotoxic effect of nanostructured silver particles on primary human fibroblasts

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The rapid progress and development of modern nanotechnologies for the synthesis of nanostructured silver particles (NSPs) is of great importance in various fields of science and technology, including food, cosmetic and medical industries [1, 2]. The safety of their usage depends on their cytotoxic effect on human body.

The aim of this research was to study the cytotoxic effect of NSPs on primary human fibroblasts and establish the dose concentrations that are safe for cells.

Materials and methods.

Test substances. 0.025, 0.125, 0.25, 0.5, and 1.0% aqueous solutions of NSPs were prepared from 'Colloidal silver Concentrate in water dispersion' (Technical specifications 9185-008-17572054-15) with an initial concentration of NSPs C_0 = 507.6 mg/l (hereinafter referred to as 'CS Concentrate'); surfactant sodium dioctyl sulfosuccinate $C_{20}H_{37}NaO_7S$ was used with an initial concentration of 40.0 g/l [3].

Cellular model. Two lines of primary human fibroblasts were used as a model: a) normal fibroblasts; b) fibroblasts infected with *Mycoplasma* sp.; c) transformed HeLa cells.

Test procedure. The laboratory experiment was performed *in vitro* in three stages. During the first and the second stages of experiments, in few hours after seeding the cells of two lines of primary human fibroblasts, the tested substances were introduced into the growth medium. Cells were cultured for 8 h in the presence of test substances, fixed with freshly prepared paraformaldehyde and stained with DNA-binding DAPI fluorochrome. The cytotoxicity of the tested substances was assessed by calculating the proportion of dying cells. During the third stage of the experiment, a monolayer of HeLa cells in the wells of a 6-well culture plate was obtained to test the toxic properties of surfactant that was a part of the 'CS Concentrate'. The 0.3% aqueous solution of surfactant without NSPs in it, similar to the content of surfactant in 0.25% aqueous solution of 'CS Concentrate', was prepared. The growth medium was changed to a fresh one in the growth plate and portions of the resulting 0.3% aqueous surfactant solution of 2.5, 5.0, 10.0, 20.0 and 50.0 μl were added. HeLa cells were then incubated in the medium for 1 h, 1 and 2 days.

Test results. The results of the experiments showed that:

- 1 and 0.5% aqueous solutions of NSPs of ‘CS Concentrate’ introduced into the growth medium were found to be toxic for primary human fibroblast cells after 24 h, since they caused cell lysis and necrosis;

- introduction into the growth medium of 0.25, 0.125 and 0.025% aqueous solutions of NSPs ‘CS Concentrate’ after 24 h was non-toxic and had no toxic impact on primary human fibroblasts. Cells retained their normal morphology and proliferation ability;

- introduction of 0.25 and 0.025% aqueous solutions of SNPs ‘CS Concentrate’ into the *Mycoplasma*-infected cell growth medium suppressed the growth and killed *Mycoplasma* sp. cells;

- HeLa cell death was not detected after incubation of HeLa cells in a medium with 0.3% aqueous surfactant solution for 1.0 h, 1 and 2 days of monitoring. Consequently, the content of 0.25% aqueous solution of ‘CS Concentrate’ and 0.3% aqueous solution of surfactant did not cause cytotoxic effects that could lead to the death of HeLa cells.

Conclusions. Studying the cytotoxic effect of NSP-preparations in water dispersion on primary human fibroblasts allowed to establish the facts of dose dependence of the use of ‘CS Concentrate’ as a modifying additive to the nutrient medium, and the safe dose of its use in food, cosmetic and medical products was determined.

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Impact of nanostructured silver particles on cytokinetic parameters of cultured cells

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The extensive implementation in various fields of science and technology of synthesized nanostructured silver particles (NSPs) requires a comprehensive thorough study of their application in developed cosmetics, food and medical preparations for external and internal use. Given the impressive potential of applications of NSPs, an important task arises to study the possible toxic effects of NSPs, which can be related with cytokinetic parameters of human cells.

The research focused at establishing a safe dose concentration range of NSPs for human cells has been conducted earlier at “Inbiopharm”, Semenov Federal Research Center for Chemical Physics, and Belozersky Institute of Physico-Chemical Biology [1–3].

The aim of this experimental research was *in vitro* studying the impact of NSPs introduced into the growth medium of normal human fibroblasts on the state of the cell population by measuring two cytokinetic parameters – mitotic and apoptotic indexes with subsequent setting a safe dose for this type of cells.

Materials and methods

Test substances: 0.15, 0.25, 0.5% aqueous solutions of NSPs were prepared from ‘Colloidal silver Concentrate in water dispersion’ (Technical specifications 9185-008-17572054-15) with an initial concentration of NSPs $C_0 = 507.6$ mg/l (samples were assigned Preparation 1, Preparation 2, Preparation 3, respectively).

Cellular model. A line of primary human fibroblasts was used as a model: normal fibroblasts (10th-14th passages).

Test procedure. Cells were cultured on cover glasses in a DMEM medium with the addition of fetal calf serum (HyClone) and an antimicrobial and antifungal reagent (Gibco) for five days until a sub-confluent monolayer was formed. The biological effects caused by the presence of NSPs in Preparations were tested by adding aliquot suspensions of Preparations 1–3 to the cell growth medium at concentrations of 0.5, 1.0, 5.0, 10.0 and 15.0 µl per 1.0 ml of the medium. The control cells were cultured in the medium without the addition of Preparations 1–3. The cells were incubated in the presence of tested Preparations for 24 h. After one hour, cells were analyzed to detect possible rapid toxic effects; 24 h after applying the tested Preparations 1–3, cells were fixed with 3.7% formaldehyde solution on Phosphate buffered saline (PBS) (15 min), permeabilized plasma membranes with 0.5% Triton X-100 solution on PBS, stained with DNA-binding DAPI fluorochrome (0.5 µg/ml) and placed in Mowiol medium for preserving stained cells. To analyze the effect of Preparations 1–3, the state of the cultured cell population was determined by measuring two cytokinetic parameters – mitotic and apoptotic indexes.

Test results

Microscopic analysis of cells performed one hour after transplanting into a medium containing test Preparations 1–3, did not reveal any violations in the interphase and mitotic cells structure as well as in dynamics of population growth. Microscopic analysis performed 24 h after the cell incubation in the medium containing Preparations 1–3 showed that the tested preparations in the studied NSPs dose concentrations did not cause a toxic effect on cultured cells basing on two cytokinetic parameters – mitotic and apoptotic indexes.

Conclusions

The results of *in vitro* studying the impact of NSPs on the cytokinetic parameters of cultured cells, revealed no cytotoxic effects on the population of cultured normal human fibroblasts basing on two cytokinetic parameters – mitotic and apoptotic indexes for the tested Preparations 1–3 with a content of 0.5, 1.0, 5.0, 10.0 and 15.0 µl of NSPs per 1.0 ml of the growth medium.

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Antimicrobial activity of nanodisperse silver based compositions with supramolecular structure in aqueous solutions

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Over the last decade, "Inbiopharm", a Russian innovation company, in collaboration with the scientists and experts of Semenov Federal Research Center for Chemical Physics has been actively conducting research for the development of social projects in creating breakthrough nanotechnologies, nanomaterials, and bioengineering systems for environmental safety as well as for prevention and treatment of diseases. Based on the mastered original bio-nanotechnologies [1–4], a number of environmentally safe new-generation products with high biocidal activity towards a variety of microorganisms have been developed.

The aim of the experimental study was to determine antimicrobial properties of experimental samples of preparations with a supramolecular structure based on a colloid mixture of complex compounds containing stabilized nanostructured silver particles (NSPs) or a hydrosol of silver cations (HSCs) in aqueous solutions.

Materials and methods

Test substances: six variants of experimental samples of preparations with a concentration of 3.5 mg/l silver containing a complex of low-molecular weight biologically active substances (Preparations 1–6). The tests of the samples were carried out by diffusion into agar using international collection bacterial test strains. The following test strains of microorganisms were used as test cultures to determine the antimicrobial activity of drugs: 1). Gram-positive bacteria: *Staphylococcus aureus* INA 00761 (MRSA), *Micrococcus luteus* NCTC 8340, *Mycobacterium smegmatis* mc^2 155; 2). Gram-negative bacteria: *Pseudomonas aeruginosa* ATCC 27853.

Determination of antimicrobial activity. To determine the antimicrobial activity by the method of diffusion in agar, the modified agar medium No. 2 Gause of the following composition was used (%): glucose – 1, pepton – 0.5, trypton – 0.3, NaCl – 0.5, agar – 2, the rest is tap water; pH 7.2–7.4. The molten medium was poured into Petri dishes in the amount of 15 and 25 ml and after solidification the surface of the agar was washed with a suspension of daily bacterial agar cultures with a titer of 10^7 cells. Holes were made with a sterile drill in hardened agar. The test solution was pumped into the wells in the amount of 100 or 130 µl, respectively. Petri dishes were incubated at 37°C within a day (strains *S. aureus* INA 00761, *M. luteus* NCTC 8340, *P. aeruginosa* ATCC 27853) or three days (*Myc. smegmatis* mc^2 155). The level of antimicrobial activity was evaluated by the shape and size of the diameters of the growth inhibition zones of the tested strains around the wells.

Test results. All six versions of the tested experimental samples exhibit antimicrobial activity, since they inhibit the growth of bacteria *S. aureus* INA 00761, *M. luteus* NCTC 8340, *Myc. smegmatis* mc^2 155 and *P. aeruginosa* ATCC 27853. Zones of bacterial growth inhibition in the agaric medium have an unusual shape in the form of rays or lobes radiating from the wells. In one case, Preparation 5 had a zone of bacterial growth inhibition in the form of a ring, which was characteristic of antimicrobial compounds, but in some cases, it was a ring with a slightly wavy edge.

Conclusions. To carry out comprehensive prevention of viral and bacterial diseases, “Inbiopharm” company has currently registered in the Russian Federation the range of modern health-improving products including: dietary supplement, a local blocker of viruses, bacteria and fungi “SEREBRO-AC” (SILVER-AC); Tonic spray with antimicrobial action “Serebrianyi Strazh” (Silver Guard); cosmetic skin tonic “Era Vodoleia” (Era of Aquarius); body gel with antimicrobial action “Serebrianyi Krot” (Silver Mole), protective products based on a concentrate of silver cations in water dispersion “Aquivon-Eco” and “Aquivon-Hydro”.

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Determination of glyphosate in beekeeping products by HPLC with fluorescent detection

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Currently, monitoring pesticides in environmental objects and food products is extremely relevant. One of the most widely used herbicides are preparations based on glyphosate, i.e. (N-(phosphonomethyl)-glycine). These products are marketed by manufacturers as low-toxic and safe pesticides. However, it was found that glyphosate increased the probability of developing cancer and could negatively affect mental and reproductive health [1].

N-(phosphonomethyl)-glycine is a systemic herbicide of continuous action from the group of inhibitors of the biosynthesis of aromatic amino acids. The possibility of its impact on non-target organisms, for example, bees, can’t be excluded. Thus, it was reported that glyphosate accumulated in beekeeping products (honey, bee bread, propolis) [2]. Apparently, the herbicide can reduce the immunity of bees due to the destruction of beneficial bacteria in the digestive organs, which negatively affects the development of larvae and results in a decrease in the bee population [3].

The lack of officially approved methods for the determination of glyphosate in beekeeping products in Russia hampers monitoring its residual amounts and, therefore, can enable entering the herbicide into human body through the trophic chains. Thus, the determination of glyphosate in the waste products of honeybees is an urgent task.

We have developed an analytical HPLC-based procedure for determination of glyphosate in beekeeping products involving extraction of glyphosate with a mixture of solvents, derivatization with 9-fluorenylmethyl chloroformate (FMOC-Cl) followed by fluorescence detection of the resulting product under reverse phase HPLC. The lower limit of the determined content of glyphosate is 0.05 mg/kg with a standard deviation not exceeding 0.05.

The advantages of the developed technique are simplicity, rapidity and low consumption of organic solvents used, which corresponds to the basic ideas of ‘green chemistry’.

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Effect of nitrogen-containing pesticides on physical and chemical indicators of grape varieties

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Azerbaijan is one of the leading grape producer and exporter countries. The vineyards areas have almost doubled in recent years, particularly, in the agro-industrial complex of the Ganja-Gazakh zone, and this zone is still the main grape-producing region of Azerbaijan. However, the range of pesticides used in vineyards has also significantly expanded recently.

In agriculture, a broad variety of pesticides are used to protect plants. Some pests and diseases have grapevine as their favourite host and the vineyard – as preferred environment, so an intensive pesticide treatment is usually required to meet quantitative production standards [1–3]. A pesticide is any substance used in agriculture to destroy, repel, or control certain forms of plants. Pesticides include herbicides to destroy weeds and other undesirable vegetation, insecticides – to control a wide range of insects, fungicides used to prevent mold and mildew growth, disinfectants – to prevent the spread of bacteria, and compounds used to control mice and rats.

The objects for research were two local grape varieties: Tabriz (white) and Medrese collected in 2018 in the grape areas of two different regions of Azerbaijan: Gazach and Shamkir, respectively. When studying physical and chemical composition of the grape must and wine materials, the following parameters were determined as the main quality indicators: sugar content, as well as content of ethyl alcohol and titratable acids, and pH values.

The pesticide test objects were the following nitrogen-containing pesticides applied in the studied regions: tebuconazole, azoxytrobin, and difeconazole. Determination of the residual amount of the pesticides was carried out by chromatography and mass spectrometry methods.

The results of the analyses are presented and the effects of nitrogen-containing pesticides on the grape quality are discussed in terms of excessive use of nitrogen- containing pesticides in the vineyards.

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Determination of organic pollution of atmospheric air in Baku using moss bioindicators

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Biomonitoring using moss as an indicator of air pollution with heavy metals and a variety of toxic chemical compounds could be applied as a useful approach for assessment of atmospheric pollution of large cities [1, 2].

To determine the content of toxic organic substances in the air of the Khatai and Narimanov districts of the city of Baku, the researchers of the department of environmental chemistry of Baku State University conducted an analysis of persistent organic pollutants and studied their content in the air. For this purpose, biomonitoring of atmospheric air of these regions was carried out using moss transplants Moss *Sphagnum girgensohnii* Russow. The analysis was performed with the help of an Agilent 6890N gas chromatograph with an Agilent 5975 mass selective detector.

Large amounts of polycyclic aromatic hydrocarbons – naphthalene, azulene, acenaphthene, chrysene, phenanthrene, anthracene, fluoranthene, pyrene, benzanthracene, benzo[a]pyrene, phenols, nitrobenzene, dibenzofuran, pyridine, phthalates, toluene, alkylbenzene – were found in the atmospheric air of the above regions along with benzene, ethanol, benzaldehyde, acetophenone, benzoic acid, formamides, furans, furfural, organic acids, etc. These organic compounds are known for their toxicity and it seems likely that they have got into the atmospheric air of the investigated areas during oil refining procedures and from exhaust gases of motor vehicles.

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Determination of heavy metals in atmospheric air of the city of Baku

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Air pollution is one of the most important global environmental problems causing severe damages to human health and ecosystems. The urban atmosphere is usually subjected to large emissions of anthropogenic contaminants produced by both stationary sources and mobile sources related to traffic. Trace elements are widely dispersed in the environment and their interactions with different natural components result in toxic effects on the biosphere. The transport and distribution of trace elements have already aroused the interest of the researchers [1].

A moss bag technique was employed in Baku for the first time and was demonstrated to be a useful, inexpensive, and accessible biomonitoring method for evaluation of air pollution with airborne metals. A total of 37 elements were revealed in 21 moss bags (*Sphagnum girgensohnii*) exposed for three months and analyzed by two complementary analytical tools: instrumental neutron activation analysis and atomic absorption spectrometry. Multivariate statistical analysis was performed and provided determination of the enriched geochemical bounded elements. The concentrations obtained were compared with the values published in the literature. It is noteworthy that the ratio of a specific metal versus the total concentrations were found to be relatively high, i.e. Pb (3.9%), V (4.9%), Al (5.5%), Sb (10%), Th (11.5%), Na (11.5%), and I (14.8%) [$C_{metal}/C_{total} \cdot 100$]. Substantial concentrations for seasalt elements Na and I were encountered at locations in the vicinity of salty lakes and reservoirs. The extent of contamination was calculated for the studied elements using pollution and enriched indices. Metal pollution index was measured which allowed identification of four peak area that can represent a significant hazard to the human health and the environment.

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Organic mineral fertilizer based on solid domestic waste and natural resources

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Accumulation, storage and recycling of domestic waste is one of the acute environmental problems resulting in pollution of the atmosphere and soil. The solution to this problem should be based on developing safe recycling technologies for waste disposal and search for possibilities to use domestic waste as secondary raw material.

Use of solid domestic waste as a raw material for production of fertilizers of organomineral composition can be considered as one of these solutions. Depending on the climatic zone and seasonal changes, solid domestic waste may contain 30–60% of food waste. The organic part content of food waste can be up to 70%.

In nature, organic waste is biologically decomposed and poses no danger. However, as solid domestic waste contains helminth eggs and pathogenic microorganisms, this waste poses a significant risk for human health. For this reason, before using raw domestic waste for fertilizing the soil, it must be disinfected at temperatures above 50°C [1].

The authors proposed a procedure for obtaining a fertilizer with both organic and mineral ingredients, in which inorganic inclusions (stones, glass, metal objects, plastics etc.) are preliminarily extracted from solid domestic waste; then, organic components (food waste, paper, wood) are crushed and treated with Azerbaijan geothermal waters containing H_2S, which comes out of the bowels at a temperature of 55–75°C; followed by mixing the resulting the mass with grinded phonolite. The obtained mass is kept in an oven at 100–110°C for 1.5–2 h, and neutralized with shell rock to pH = 6.5–7.5.

Spent organic component of solid food waste has the following chemical composition (% of dry mass): organic part – 56–73; nitrogen – 0.7–1.7; phosphorus – 0.5–0.7; calcium – 3.91–5.6; sulfur – 0.2–0.3; carbon – 28–34. Humidity is 33–48% of total mass, pH = 6.5–7.5.

Geothermal waters collected from the source of the Leric district (Azerbaijan) coming from a depth with a temperature of 55–75°C and containing dissolved hydrogen sulfide at the concentration level of 28–31 wt%, have been used for disinfection of the raw material. In accordance with the classification accepted in hydrogeology, the water of this source is classified as hydrocarbonate type in terms of predominant anion, and calcium typy – in terms of predominant cation, and has the following chemical composition (wt%): CaO

– 51– 97; MgO – 1.3– 31.42; Fe_2O_3 – 0.3– 0.5, K_2O – 1.2– 1.4; Na_2O – 0.5– 0.7; CO_2 – 38–48. Before using geothermal water, the concentration of hydrogen sulfide is brought to 10–15%.

When obtaining the fertilizer, a local phonolyte of the Azerbaijan deposit with medium SiO_2 content has been added to the mixture, with the following chemical composition (wt%): SiO_2 – 59–79; TiO_2 – 0.85; Al_2O_3 – 16.98; Fe_2O_3 – 3.25; FeO – 2.76; MnO – 0.09; MgO – 2.51; CaO – 1.69; Na_2O – 1.93; K_2O – 9.6; P_2O_5 – 0.55.

To neutralize the resulted pulp, a local shell rock of the Absheron Peninsula coastal area with a porosity of 27–31%, water absorption of 0.9–1.2% and the following composition (wt%) has been used: CaO – 51–57; MgO – 1.33; CO_2 – 38–48; Al_2O_3 – 2.4; Fe_2O_3 – 0.3; K_2O – 1.2; Na_2O – 0.5.

Example 1. 100 g of organic component of solid domestic waste is placed in a 600–800 ml container, 5 ml of geothermal water with 15% H_2S content is added, the mixture is stirred for 10 min, then, 15 g of grinded phonolite is added. The resulting mass is placed in the oven and incubated at 100°C for 1.2 h. The hydrolytic destruction of organic compounds in the waste is carried out. The formed mass has pH 3.2. The mass is cooled down and left to mature for 30–40 min.

The process of maturation completes the process of destruction of the original solid waste as well as the release of carbon dioxide formed during food fermentation and hydrolytic destruction. At the end of the maturation process, crushed shell rock is added to the resulting mass while stirring, and adjusting pH of the medium to 6.5.

After granulation, the obtained fertilizer contains (wt %): N – 0.55; P_2O_5 – 0.45; K_2O – 6.1; H_2O – 2.6; MgO – 1.66; Na_2O – 0.93; CaO – 9.2; Al_2O_3 – 9.9; SiO_2 – 17.81; other oxides – 2.1.

Thus, the proposed method makes it possible to dispose solid domestic waste using its organic component – a source of nitrogen, phosphorus and potassium. Using phonolite will increase the content of potassium as an important element for soil fertilizing, while processing food waste with geothermal waters will disinfect and eliminate the undesired microflora without additional energy consumption.

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Designing an experiment to study evaporation of hazardous chemicals in workrooms

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The idea that an experiment may be planned dates back to ancient times. However, only at the beginning of the 20th century methodological foundations of the scientific organization of experimental research were laid. The theory of experimental design began to develop especially rapidly after the appearance of the pioneering works of D. Box and C. Wilson in 1951. A large contribution to the development of optimal experimental design methods was made by domestic researchers: V.V. Nalimov, V.I. Denisov, V.G. Gorsky and others [1–3].

To solve scientific, industrial and technological problems successfully, a modern research engineer needs to have competencies in the field of the theory of mathematical statistics, practical skills in planning an experiment, and methods of statistical processing of experimental data.

As an example of using the experimental planning tools, we are considering here the results of the study, the purpose of which was to assess the influence of the air parameters in the working room (temperature, humidity) on the evaporation intensity of a hazardous chemical substance (HCS) spill.

The experiment was conducted on a facility that allowed to vary the temperature and humidity. The multiplicity of air exchange in the facility corresponded to indicators for industrial premises as described in the standard documentation SNiP 2.04.05-91. Measurements of the concentration of HCS vapors in the air were made in accordance with the developed experimental design. Two factors were taken into account: temperature and air humidity. In accordance with the full factorial experiment, the variation of factors was carried out at three levels [4]. Isopropyl alcohol was used as HCS model.

The dependence of the concentration of HCS (Y) vapor on the temperature (X_1) and humidity (X_2) of the air in the working room was described by a general regression model.

According to the results of the experiment, a mathematical model of the evaporation process of the cold water has been developed, describing the dependence of the concentration of the cold water vapor on the temperature and humidity in the working room:

$$Y(X_1, X_2) = 4{,}96 + 1{,}72 \times X_1 + 0{,}51 \times X_2 - 0{,}79 \times X_1 \times X_2$$

Figure 1 shows the 3D-image of the response surface calculated from the results of processing the experimental data.

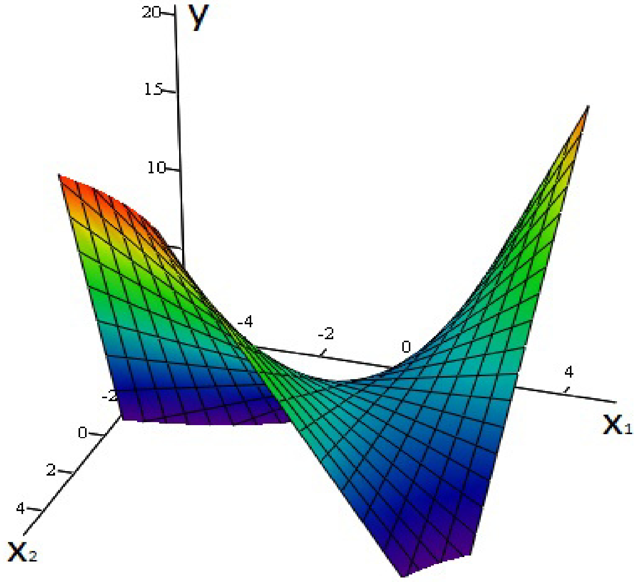

Fig. 1. Dependence of HCS vapors concentration on temperature and air humidity in the working room

The obtained dependence makes it possible to assess the level of air pollution with HCS in the temperature and humidity range specified for workrooms. A comparison of the concentrations calculated with the help of the model with the permissible level of air pollution (MPC of the working area air) will allow us to assess the risk of inhalation exposure to airborne substances for working personnel in local emergency situations. These results can be applied for a reasonable assessment of occupational risk in chemical industry.

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Database of hazardous chemical substances and processing equipment for decision-making support system for ensuring chemical safety

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Risk assessment of the negative impact of hazardous chemical factors on public health and environment is an important task in the operation of enterprises in the Russian Federation.

In this regard, information support of specialists involved in ensuring industrial and environmental safety of hazardous production facilities is one of the urgent concerns. To solve this problem, it is proposed to provide information support in this field at a qualitatively new level using modern information technologies based on the creation of decision support systems. When hazardous production facilities (HPF) are functioning, such systems provide data on the substances, materials and reliability characteristics of equipment which can be used for creating databases to predict and ensure the safety of chemical processes:

- database of hazardous chemicals substances and materials;
- database of chemical technological equipment;
- database on reliability and safety of HPF.

The relevance of the work is outlined in the objectives of state policy in the field of chemical safety along with the ways of their implementation, as defined in [1].

The database of hazardous chemicals and materials, including new ones, is envisaged to cover the following information:

- data on chemicals and materials whose hazard is due to their physicochemical properties (explosives; compressed substances; gases liquefied and dissolved under pressure; substances flammable in various aggregate states of matter; components of an aerosolized products; self-decomposing, self-heating and pyrophoric substances; emitting flammable gases in contact with water; oxidants and organic peroxides; corrosion-prone metals, etc.);
- data on chemicals and materials whose hazard is due to their toxicological properties, i.e. posing hazard to the human body (having acute toxicity for the body; causing damage (necrosis) or skin irritation; causing serious damage or irritation of eyes; having a sensitizing effect; having selective toxicity with a single and/or multiple (prolonged) exposure to target organs and/or systems;

mutagens; carcinogens; reprotoxicants and substances that are hazardous upon aspiration);

- data on on chemicals and materials whose hazard is due to their ecotoxicological properties, i.e. posing threat for environment (with acute and/or chronic toxicity for aquatic environment, soil, groundwater, depleting the ozone layer, etc.).

The technological equipment database includes characteristics of the main and auxiliary technological equipment of HPF operating at the subjects located on territory of the Russian Federation, and is intended for accounting within the state information system in the field of chemical safety, in terms of neutralizing chemical threats, preventing and minimizing chemical risks, improving the protection of the population and the environment from the negative impact of HPF, preventing and eliminating the consequences of chemical emergencies, including: replacing physically worn-out equipment and obsolete technologies with more modern ones (with reducing the volume of potentially hazardous chemicals used, using less hazardous chemicals or substances in a less hazardous state), as well as designing objects with the lowest level of complexity and less sensitive to unauthorized actions.

Thus, the proposed informational software package for management decision-making support will allow to provide the most prompt and optimal measures to ensure the safety of public health and recommendations for various decision-makers to reduce risks aimed at mitigation of negative impacts of production of chemicals on public health and environment.

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Sorbent for oil spill liquidation based on polyurethane foam filled with plant and polymer waste

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Nowadays, oil and petroleum products are considered as one of the most of harmful pollutants of the environment. Active exploration and production of increasing amount of oil have been continued for more than two centuries. In general, oil production is increased in direct proportion to population growth and demands for operation of various equipment.

It is widely understood that it is easier to prevent emergencies, accompanied by oil spills than to deal with their consequences. In this regard, an urgent need arises to improve methods for cleaning different surfaces from contamination of oil, in order to mitigate anthropogenic stress on the environment and reduce the cost of the appropriate purification procedures.

This work deals with the relevant task – to develop a novel effective sorbent for oil spill cleanup on the basis of polyurethane foam, plant, and polymer waste.

The object of the study was a sorbent obtained from a polyurethane foam, filled with generally available and cheap cellulose-containing plant waste and polymer waste.

The benefits of using the developed sorbent include not only its high oil capacity, but also a possibility to solve two problems at once – recycling and reducing cost of the sorbent. Additional advantage of this sorbent is its environmental safety.

The filler content is 20–35%. Less filler content is impractical, because it does not significantly reduce the cost of sorbent. The higher filler content of more than 35 wt% leads to a decrease in the absorption capacity of the matrix. We have developed a range of sorbents based on different kinds of the abovementioned waste with high enough oil capacity values varying from 8,2 to 12,8 g/g. The most effective sorbent is made using chopped rice straw, its absorptive oil capacity reaches ~13g/g.

The recovery of the absorbed oil can be performed by the spin or centrifugation with subsequent reuse. Such a possibility was demonstrated by the example of our similar sorbent filled with buckwheat hulls [1–5].

Therefore, the developed sorbent produced from plant and polymer waste was found to have sufficiently high sorption properties. At the same time, we have additionally solved the problem of utilization of waste cellulose and polymer production.

The resulting material can be used for the collection of liquid petroleum products and organic substances in the spill to clean up oil-polluted water areas, soils, septic tanks, storm water, etc. from hydrocarbons and their derivatives, crude oil, light and heavy grades of fuel, and other oil typess on water and land.

The sorbent has the following advantages:

- hydrophobic (will not absorb water) and oleophilic properties (absorbs oil);
- versatility of absorption (absorbs oil and oil products, mineral and vegetable oils, chemical products, etc.); has a high rate of recovery after the absorption; it does not sink even in saturated (fully saturated) form; has a super-fast sorption;
- easy handling due to low density;
- easy removal of absorbed material by pressing or centrifugation;
- high heat of combustion (more than 6000 kcal/kg);
- non-toxicity to humans, aquatic fauna, flora and fauna;
- the ability to be used as a filter material for purification water environments from oil and liquid petroleum products, both on local and general treatment facilities, as well as for purification of gas emissions into the atmosphere;
- the possibility of using the sorbent material as insulation, soundproofing, finishing and packaging materials;
- it can be produced from available raw materials and in any geometric shape (in the form of granules, mats, booms, pillows, etc.). In addition, its life time is unlimited.

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Determination of metaldehyde in atmospheric air

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Intensive use of chemicals in agriculture leads to increasing pollution of the atmospheric air with a large amount of various chemical compounds, including pesticides. In this regard, the development of sensitive, accurate and easy-to-use procedures for determination of pesticides in the air is a relevant issue.

Metaldehyde is one of the widely used pesticides applied as a molluskocide for controlling slugs in crops of vegetable, fruit, flower, berries, grapevine, etc. Approximately safe level of impact of metaldehyde in the atmospheric air of populated areas is 0.003 mg/m^3. The known technique for determination of metaldehyde in atmospheric air (Procedural Guidance 4.1.2283-07) is based on determination of metaldehyde derivative using gas chromatography with a thermionic detector.

This technique is complicated due to the fact that derivatization of metaldehyde with 2,4-dinitrophenylhydrazine takes considerable time.

The accuracy and reproducibility of analysis results depend on the quantitative results of the depolymerization reaction and the absence of acetaldehyde loss due to its high volatility. In addition, toluene is used in preparation of metaldehyde derivatives, which is a highly toxic compound.

The aim of this work was developing a highly sensitive procedure for determination of metaldehyde in atmospheric air without the derivatization step. The procedure design was carried out using a gas chromatograph with a flame ionization detector.

The experiments involved establishing optimal conditions for air sampling, the conditions for sample preparation for analysis and chromatography conditions. Air sampling of air is conducted as follows. Air is passed through a blue ribbon paper filter placed in a filter holder, at a speed of 20 dm^3/min for 15 min.

A paper filter with a taken sample is transferred to screw-on vials, 10 cm^3 of acetone is added, and the vials are shaken for 15 min. The extraction is repeated thrice. The combined acetone extracts are poured into a flask to distill off the solvent. The solvent is distilled off to a volume of 0,1–0,2 cm^3 at a water bath temperature not exceeding 30°C. The remaining solvent is removed in a stream of air. The dry residue is dissolved in 1.0 cm^3 of acetone and analyzed under the following chromatographic conditions:

- capillary column DB-5, 30 m long, 0.32 mm in diameter, 0.25 μm granularity;

- the initial temperature of the column thermostat is 70°C (1.0 min), then the temperature is raised to 190°C at a speed of 50°C/min (1.0 min) followed by rising the temperature to 300°C rises at a speed of 30°C/min (1.0 min);
- detector temperature – 290°C;
- evaporator temperature – 160°C;
- the speed of the carrier gas (helium) – 4.0 cm^3/min;
- air supply speed – 300 cm^3/min;
- hydrogen flow rate – 30 cm^3/min;
- charge gas (helium) speed – 20 cm^3/min;
- volume of injected sample – 2 mm^3;
- sample input mode – splitless;
- linear detection range – 1.0–20.0 ng;
- approximated retention time of metaldehyde – 2.6 min.

Calibration solutions with concentrations in the range of 0.5–10.0 μg/cm^3 are used for analysis. The metaldehyde content in the air sample is calculated by the formula:

$$X = C \times V / Vt,$$

where C is the concentration of metaldehyde in the chromatographic solution, which is taken from the calibration graph in accordance with the size of the chromatographic peak, μg/cm^3; V is the volume of the extract prepared for chromatography, cm^3; Vt is the volume of air sample collected for analysis and brought to standard conditions.

The sensitivity of the method for the sampling of 300 dm^3 of air is 0.0017 mg/m^3. The error of the analysis performed with the use of the proposed procedure is 15.9%.

Thus, the conducted study allowed us to develop a procedure for determination of metaldehyde in atmospheric air, which is characterized by high sensitivity, the absence of the derivatization step, with the reduced error and possibility of simplifying the analysis.

Simultaneous determination of fludioxonil and fluxapyroxad in water by high-performance liquid chromatography

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The widespread use of pesticides in the cultivation of agricultural plants leads to pollution of soils, groundwater and food products. Accordingly, there is an urgent need to develop sensitive and accurate techniques for determining pesticides in various environmental objects, particularly, in water.

Fludioxonil and fluxapyroxad are known as broad-spectrum fungicides. They are used both individually and in combination, enhancing each other’s action. The development of an analytical procedure that provides simultaneous determination of these two substances in one sample will reduce the time of the analysis and its cost.

The aim of this work was to develop a procedure for simultaneous determination of fludioxonil and fluxapyroxad in water.

To perform the studies, we used a high performance liquid chromatograph Agilent 1260 equipped with a diode array detector and Hypersil BDS C18 chromatographic column of 150 mm long and 4.6 mm in diameter. The conditions for sample preparation and the conditions of chromatographic detection were established during developing the method.

Sample preparation was carried out as follows. A sample of pre-filtered water with a volume of 100 cm3 is placed in a separatory funnel with a capacity of 250 cm^3, 2 g of sodium chloride are added and mixed until its complete dissolving. Then, 30 cm^3 of methylene chloride are added and extracted for 30 min. After the phases are completely separated, the lower layer of methylene chloride is filtered through a layer of anhydrous sodium sulfate (with layer thickness of 1.0–1.5 cm) into a concentrator flask with a capacity of 100 cm^3. The extraction is repeated using 30 cm^3 of methylene chloride. Combined filtrate is evaporated to dryness by a rotary vacuum evaporator at a water bath temperature not exceeding 40°C. The dry residue is dissolved in 1 cm^3 of acetonitrile and analyzed under the following chromatographic conditions:

- mobile phase: a mixture of acetonitrile with water in a ratio of 60 : 40 by volume;
- flow rate of the mobile phase – 0.7 cm^3/min;
- column temperature – 25°C;
- detection wavelength – 233 nm (for fluxapyroxad), 265 nm (for fludioxonil);
- the volume of the introduced sample is 25 mm^3.

Identification of substances is carried out by retention time, while the quantitative determination is performed by the method of absolute calibration by peak areas. The retention time values for fludioxonil and fluxapyroxad upon chromatography were 7.076 and 7.512 min, respectively.

The concentration of fludioxonil and fluxapyroxad in a water sample (X, mg / dm^3) can be calculated by the formula:

$$X = C \times V / V1,$$

where C is the concentration of fludioxonil and fluxapyroxad in the chromatographic solution, taken from the calibration graph in accordance with the size of the chromatographic peak area, μg/cm^3; V is the volume of the extract prepared for chromatography, cm^3; V1 is volume of the analyzed sample, cm^3.

The lower detection limit determining fludioxonil in water is 0.001 mg/dm^3, fluxapyroxad – 0.001 mg/dm^3. The maximum permissible concentration of fluxapyroxad in water is 0.006 mg/dm^3, fludioxonil – 0.1 mg/dm^3. The main advantage of the developed procedure is the ability to simultaneously determine the concentrations of fludioxonil and fluxapiroxad in water, which significantly optimizes the analysis.

Effect of gamma radiation on hydrocarbon mixtures

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Studying gamma radiolysis of saturated and unsaturated hydrocarbon mixtures at various concentrations makes it possible to draw conclusions about the nature of the main radiation-chemical processes. This information is of great practical importance because of the danger of fuel with unstable properties.

In fuels containing a large amount of unsaturated hydrocarbons, the irradiation process is usually accompanied by increase in coking behavior and color deteriorations. The processes that have arisen as a result of the radiolysis continue for a long time after the cessation of irradiation, which can lead to changes in the composition of the fuel. Changes in the structure of liquid organic fuels are physically manifested in changes of their viscosity and density. The amount of decomposed hydrocarbon increases with increasing total radiation dose. As a result, at ambient temperature, the performance properties of petroleum fuels deteriorate. The relationship between the chemical composition of the fuel and its stability is not well understood.

The experiments conducted by the authors are focused on studying the effect of ionizing radiation on changes in the physicochemical properties of petroleum hydrocarbons. We studied several kinds of operational performance of fuel under static conditions in the usual manner before and after irradiation.

The results of the experimental studies on radiation resistance of various oil products have been previously described in the papers [1–7]. Taking into account an opportunity to develop new technological processes with the use of radioactive energy, it is necessary to study the effect of various types of radiation on hydrocarbons and oil products. A fuel stability is understood as the ability of the fuel to maintain its chemical structure under operating conditions under exposure to temperature changes, ionizing radiation and under the influence of metals. It is necessary to provide a radiation resistance of fuels without significant changes in their physical and chemical properties.

In this work, the impact of ionizing radiation on mixtures hexane-hexene was investigated. Laboratory studies were carried out on ^{60}Co gamma source at a dose rate of $P = 0.10$ of Gy/s at absorbed doses in the range of $D = 34–103$ kGy. Impact of ionizing radiation on changes in structural composition of the mixtures hexane-hexene in static conditions was investigated. Density, viscosity, iodic numbers of hexane-hexene mixtures were determined before and after irradiation at various absorbed doses. The results obtained indicate that the presence of olefin compounds can be the main reason for low stability observed for hydrocarbon fuels and can lead to impairing liquid fuel performance.

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Modelling of technological unit of low-tonnage multi-product scheme for production of N-phenyl-β-naphthylamine and 4,4’-bismalenimidodiphenylmethane

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One of the distinguishing features of low-tonnage production schemes is the possibility of obtaining several types of products using the same technological equipment. The creation of universal reactor plants that allow the implementation of various chemical processes is a necessary step in optimizing costs of production organization, thus, the goal of this work is to model technological units capable to produce a wide range of products, which is an issue of high relevance.

The subject of the development is a system of devices consisting of a reactor R1, a heat exchanger HE1 and a separating flask SF1 (Fig. 1), designed to implement technological processes for the production of two products: N-phenyl-β-naphthylamine and 4,4′-bismaleinimidodiphenylmethane. The versatility of the unit is ensured by the special design of separating flask SF1, which allows the aniline vapors condensed in the HE1 heat exchanger to be returned to the reactor R1 in the case of synthesis of N-phenyl-β-naphthylamine [1] and to remove water formed during the reaction as an azeotrope mixture with toluene during the formulation step of 4,4'-bismaleinimidodiphenylmethane [2].

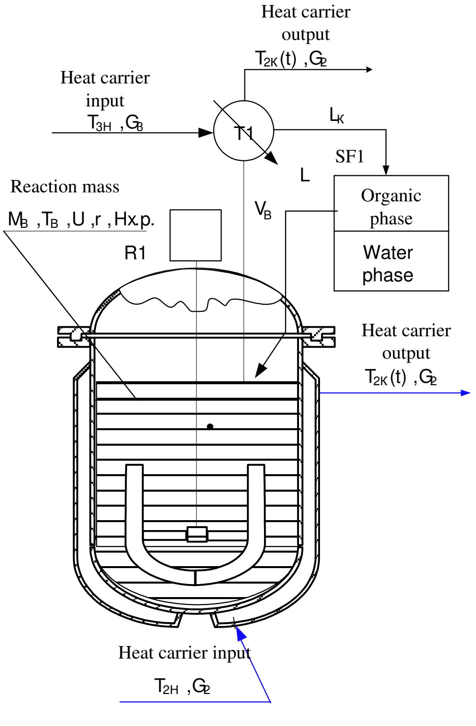

Fig. 1. Scheme of material flows of the reactor unit

The general equation of material balance for the reactor R1, taking into account the equimolarity of the reaction, has the following form (1):

$$\frac{dM_B}{dt} = -V_B + L \qquad (1)$$

where M_B is the amount of reaction mass in the reactor, mol; V_B – the molar flow of the vapor phase, mol/s; L – the fluid flow from the separating flask, mol/s.

The equations of the component-wise material balance are given below (2):

$$\frac{dx_{B,i}}{dt}=\frac{1}{M_B}\left(\left(-V_B y_{B,i}-a_i\cdot U_B\cdot r+L\cdot x_{L,i}\right)-\left(\frac{dM_B}{dt}x_{B,i}\right)\right),\ i\in\left[1;NC_R\right]_r$$

$$\frac{dx_{B,i}}{dt}=\frac{1}{M_B}\cdot\left(\left(-V_B y_{B,i}+a_i\cdot U_B\cdot r+L\cdot x_{L,i}\right)-\left(\frac{dM_B}{dt}x_{B,i}\right)\right),\ i\in\left[NC_R+1;NC_P\right]_r \qquad (2)$$

$$\frac{dx_{B,i}}{dt}=\frac{1}{M_B}\cdot\left(\left(-V_B y_{B,i}+L\cdot x_{L,i}\right)-\left(\frac{dM_B}{dt}x_{B,i}\right)\right),\ i\in\left[NC_P+1;NC\right],$$

where $x_{B,i}$ is the content of the *i*-th component in the liquid phase of the reactor, molar fractions; $y_{B,i}$ is the content of the *i*-th component in the vapor phase of the reactor, molar fractions; a_i is the stoichiometric coefficient of the *i*-th component of the reaction; *r* is the chemical reaction rate in the liquid phase of the reactor, mol/(m^3× s); U_B is the volume of the reaction mass, m^3; $x_{L,I}$ is the content of the *i*-th component in the organic phase of the separating flask, molar fractions; NC_R is the number of reagents; NC_P is the number of reaction products; *NC* is the total number of components. After preparation of 4,4′-bismaleinimidodiphenylmethane is finished, the fluid flow from the separating flask *L* is assumed to be 0.

The heat balance equation for the reaction mass in the reactor can be expressed as follows (3):

$$\frac{d\left(M_B h_B\right)}{dt}=-H_{x.p.}\cdot U_B\cdot r+L\cdot h_{L.}-V_B\cdot H_{B.}+K_B\cdot F_B\cdot\left(T_2-T_B\right), \qquad (3)$$

where h_B is the enthalpy of the reaction mass, J/mol; h_L is the enthalpy of the organic phase of the separating flask, J/mol; H_B is the enthalpy of vapor in the reactor, J/mol; $H_{x.p.}$ is the thermal effect of the reaction, J/mol; K_B is the heat transfer coefficient, W/(m^2×K); F_B is the heat transfer surface, m^2;T_B is the boiling point of the reaction mass in the reactor, °C; T_2 is the heat carrier temperature in the coil and jacket, °C.

Using the developed mathematical model, it was possible to determine the optimal conditions for the processes of obtaining N-phenyl-β-naphthylamine and 4,4'-bismaleimidodiphenylmethane, which provided achieving the maximum yield and the required quality of the target products.

This work was financially supported by the Ministry of Industry and Trade of the Russian Federation.

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Special aspects of risk assessment during elimination of accumulated environmental damage objects

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Currently, the priority tasks to ensure the environmental safety of the Russian Federation include the elimination of objects of accumulated environmental damage, which include territories, buildings and structures contaminated as a result of preceding economic activities, as well as waste disposal facilities.

To this end, there is an urgent need to develop technologies for decontamination or recycling of accumulated toxic waste, liquidation of sludge tanks, dismantling of dangerous buildings and structures, reclamation of contaminated land, etc.

Accidents can occur at every stage of technological processes, due to fires, explosions, and the release of toxic substances from the equipment. In addition, a technological process can cause adverse effects even in normal operating conditions. The danger in such conditions may be associated with the systematic release of pollutants into the air, which can lead to a negative impact on public health and the environment [1].

The justification of the technological process safety should be based on the use of science-based criteria that allow to quantify the degree of danger of technological decisions made [1, 2].

Quantitative risk indicators are proposed to be used as such criteria since they objectively characterize the possibility of occurrence of adverse events during the operation cycle of a production facility [1].

To assess the hazard of the technology for the liquidation of accumulated environmental damage objects, a comprehensive system of quantitative risk indicators has been developed (Figure 1).

The proposed system of criteria allows to determine the degree of hazard of the selected technology for the personnel and population under the conditions of the normal operation of technological process and in the case of accidents. The criteria system is intended for assessing the acceptability of the technological solutions made at the stage of production design and when choosing the safest process for its industrial implementation.

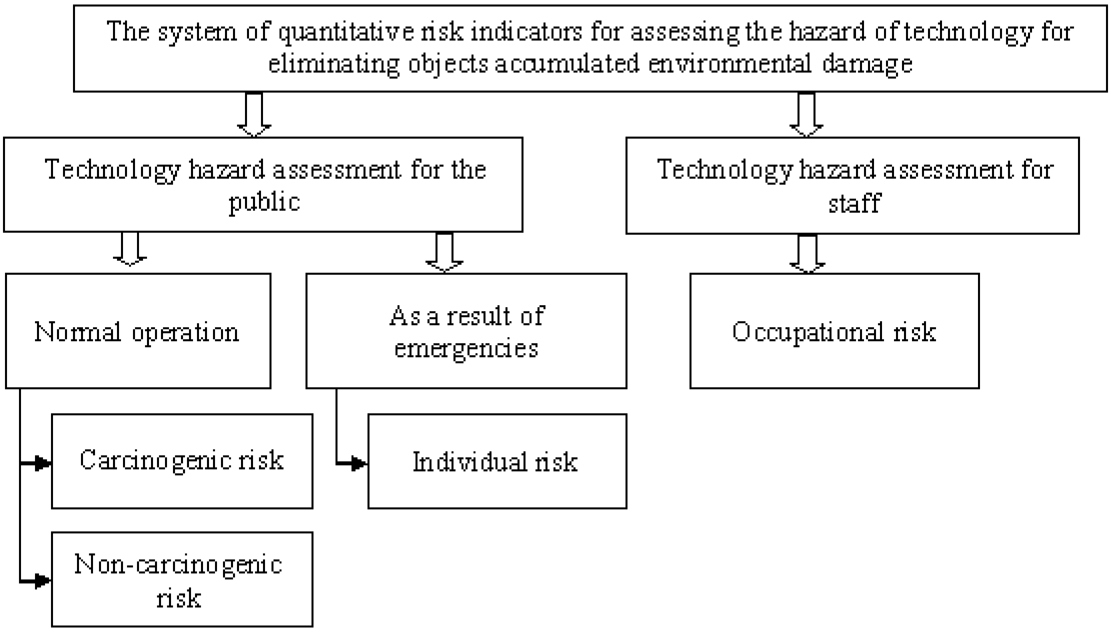

Fig. 1. The system of quantitative risk indicators

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Utilization of A-2u composition in standard boiler units

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A hydrocavitation method [1] has been developed for the discharge of explosive charges from A-IX-2.

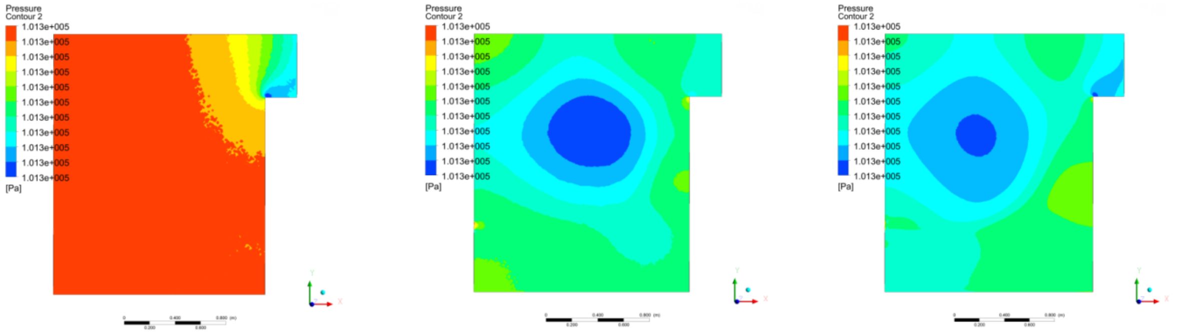
Limitations in the application of this method are associated with a large flow rate, complexity of wastewater treatment, and a short storage period (up to 5 days) of the resulting explosive composition – A-2u due to its low stability [2]. On the expiry of this period, the A-2u must be destroyed.

Modification of the A-2U composition was carried out, which increased the storage period up to 1 year [3]. Due to the limited demand for the composition, it is proposed to use it as fuel in regular boiler units [4] in places where they are stored and disposed of.

The combustion rate of the modified A-2u has been calculated in the conditions of operation of the furnaces of boiler units. The combustion time of pellets of the modified composition with a diameter of 6 mm at atmospheric pressure and a temperature of 1000°C (typical conditions for layer combustion furnaces), is calculated to be about 0.1 s.

Modeling of the process of co-combustion of standard fuel and the modified A-2u composition has been carried out at different values of its mass flow rate (m_{ex}) using the multi-purpose software system of finite element analysis ANSYS [5] for the KE-2,5-14C boiler.

Figure 1 shows the distribution of pressure in the furnace for co-burning brown coal and A-2u with different values of the mass flow of pellets A-2u, with the load of the boiler on coal 25%.



a $m_{ex} = 0$ kg/h b $m_{ex} = 36$ kg/h· per 1m^3 c $m_{ex} = 126$ kg/h· per 1m^3

Fig. 1. Pressure distribution in the boiler furnace KE-2,5-14 C. a – 100% load of coal boiler; b, c – 25% load of boiler with brown coal and different mass flow of granulated A-2U (m_{ex})

Calculations have shown the possibility of safe co-combustion of the modified A-2u with brown or hard coal in KE-series boilers with a maximum uniform flow rate of A-2u from 36 to 90 kg/h per 1 m^3 of the firebox.

The following conclusions can be drawn from the results of this study:

1. The energy characteristics of the modified A-2u composition have been evaluated and the possibility of using the developed modified A-2u composition as a boiler fuel has been shown.

2. The calculation of the combustion rate of the modified A-2u is carried out. The combustion rate is 2–3 cm/s at a temperature of 1000°K and a pressure of 10^5 Pa.

3. Modeling of the combustion process of the modified A-2u in the form of granules and water suspension in combination with solid fuel in the furnace of the KE-2,5-14C boiler unit using the finite element analysis program ANSIS is performed. It is possible to burn modified A-2u in the form of pellets or in the form of a suspension together with brown or hard coal in boilers of the KE series with a steam capacity of 2.5 to 25 t/h with a maximum uniform flow rate, respectively, from 36 to 90 kg/h per 1 m^3 of the firebox without changing the maximum pressure in the firebox, in comparison with the mode of burning coal at full load of the boiler. This proves the possibility of using the A-2u composition as a component of boiler fuel in places where ammunition is stored and disposed of, in regular boiler units.

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Pyrolysis processing of hazardous technological waste

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One of the priority tasks in ensuring the chemical and environmental safety of the Russian Federation is elimination of local sources of pollution. These sources often arise spontaneously, and it seems unreasonable to build stationary plants for their processing. To solve such local problems, it is rational to use mobile installations that can move to the required place as the problem arises.

The team of Penza State Universty, Penza within the framework of the Federal target program "National system of chemical and biological safety of the Russian Federation (2009-2014)", approved by Government resolution No. 791 of October 27, 2008, designed and manufactured a non-volatile mobile complex for environmentally friendly destruction of a wide scope of hazardous solid waste, which has successfully passed the governmental tests (Fig. 1).

Fig. 1. Pyrolysis plant

The processing technology provides for sequential thermal oxidative pyrolysis (gasification) of unsorted waste in a thermal decomposition chamber with external heating and afterburning of the gas phase with a coke residue. At the same time, the content of harmful substances in the atmospheric air and in the coke residue does not exceed the standard values of the MPC. The coke residue is discharged periodically as it accumulates.

The degree of hazard of waste and processed products was determined experimentally judging by the negative impact on biological objects (bioassays) [2].

The following types of waste were processed in the course of the pilot operation of the pyrolysis plant:

- Sand contaminated with spent engine oils (sand – 80%, oil – 20%): specially made model mixture. Hazard class: II (highly dangerous).
- non-commodity paper and cardboard residues produced by wastewater treatment facilities of the factory «Mayak» (city of Penza, Russia). Waste pollution includes contamination with soil, dyes, and microbiological organisms. Hazard class: III (moderate dangerous).
- Chlorine-containing waste of OAO Khimprom enterprise (Volgograd, Russia) ("White Sea" landfill sludge») – solid or pasty mass from gray to purple color with a characteristic smell of organic volatile liquids. Granulometric composition: 0–50 mm. Main mineral components: $CaCO_3$, $CaSO_4$, $CaCl_2$, $Ca(OH)_2$, SiO_2. The content of organic pollutants ranges from 1.10 to 7 mg/kg and includes: 1,2-dichloroethane, chloroform, carbon tetrachloride, trichloroethylene, and toluene. Hazard class: II (highly dangerous).

After pyrolysis processing, the biological hazard class of the coke and ash residue was determined along with the degree of waste processing.

The calculation of the degree of processing (K_{proc}) was performed using the equation [3]:

$$K_{proc} = \frac{\sum\limits_i M_{i0} - \sum\limits_i M_{icoke-ash}}{\sum\limits_i \alpha_i M_{i0}} \cdot 100\% ,$$

where is $\sum\limits_i M_{i0}$ is mass of the waste processed at the pyrolysis plant;

$\sum\limits_i M_{icoke-ash}$ is mass of coke and ash residue of waste of hazard class I–IV;

α_i is mass fraction of organic pollutants in the initial composition ($\alpha = 1$ for waste obtained after wastewater treatment of the factory «Mayak»).

All types of products obtained using pyrolysis plant are classified as compounds of hazard class IV (low-hazard). The processing rate was 95%.

Thus, we have developed, manufactured and tested the waste processing complex, which is a mobile energy-autonomous system that provides the efficient pyrolysis processing of household and industrial waste. According to its operational characteristics, the mobile complex corresponds to the level of the best world analogues.

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Comprehensive soil rehabilitation technology

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It is a widespread situation when environmental engineering surveys at large industrial facilities reveal contamination of technogenic soils with both organic and inorganic pollutants. While making a decision of choosing a rehabilitation technology, an integrated approach should be used. The studies carried out made it possible to propose the following comprehensive soil rehabilitation technology, which is based on a combination of thermal treatment and leaching procedures (Fig. 1).

In accordance with the scheme, soil contaminated with organic pollutants is treated in a furnace of the thermal neutralization unit (at the temperature varying in the range from 700 to 850°C), while volatile contaminants are oxidized in the high temperature zone (at the temperature of more than 1200°C) for several seconds. The dust and fly ash collection from the flue gases is carried out by means of cyclone or bag filter. Then the flue gases are purified by passing through sanitary column (absorption method) followed by wet electrostatic precipitator. The resulting wastewater is transferred to the water treatment station of the leaching unit, and after purification they are returned into the cycle of irrigation.

At the leaching unit, the soil is laid uniformy in height on a specially equipped site, which includes a waterproofing base, drainage layer, a prefabricated collector with a well and a water treatment station, with the base of the site tilting towards the prefabricated collector. The leachate obtained during the leaching process is collected in the well and then delivered to a water treatment station, where it is purified from contaminants using one of the generally accepted methods (adsorption, ion exchange, baromembrane) or combination thereof. Purified water is sent back into the cycle of leaching.

The neutralized soils are returned to the places of their withdrawal.

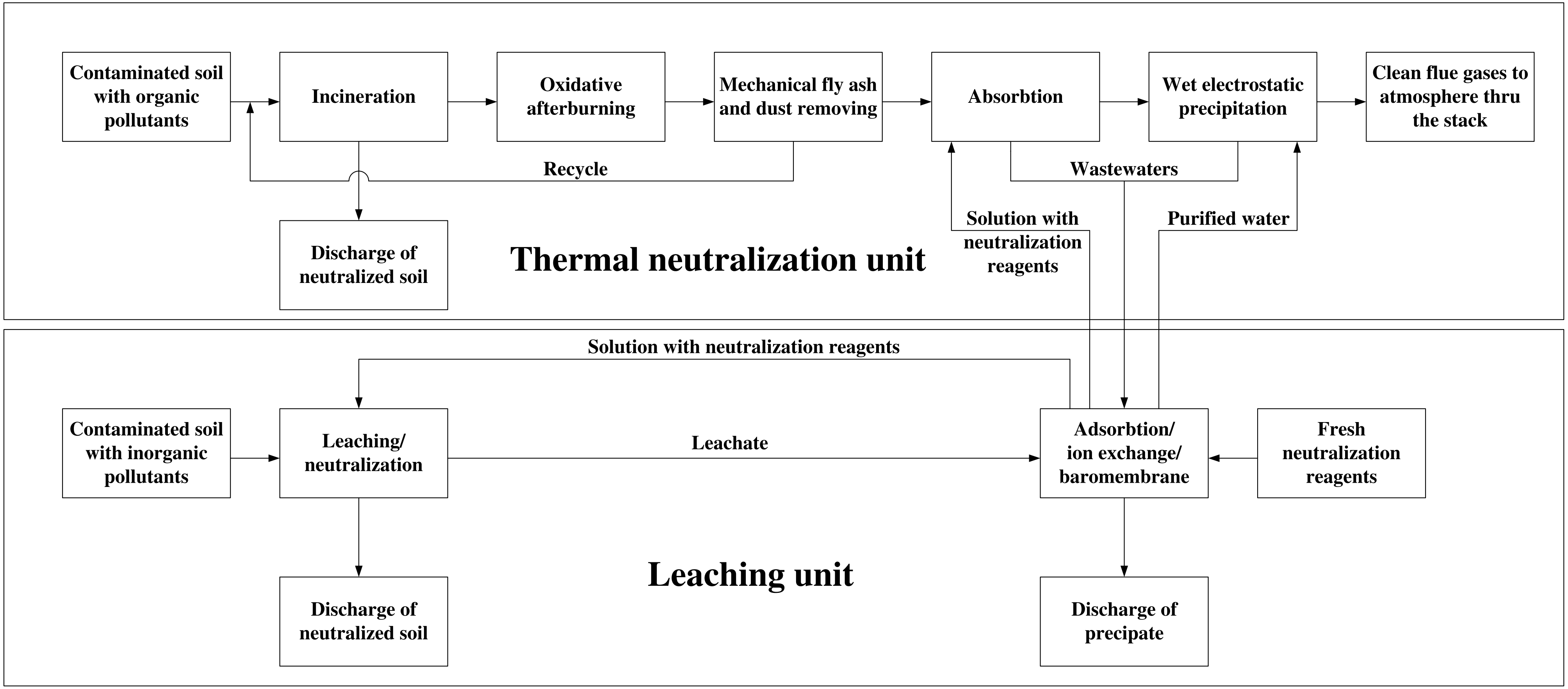

Fig. 1. Principal scheme of neutralization process of contaminated soils

Concept of creating small-scale import-substituting chemical productions in conditions of environmental regulatory system reform

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In the context of the Russian Federation state reform of the environmental regulatory system and in accordance with the concept of implementation of the best available technologies (BAT) which is adopted as the main mechanism for implementing state policy in the field of environmental safety, special attention at the development stage should be paid to resolving issues related to determining the level of harmful impact of newly introduced technologies on the environment with its minimizing to regulatory level values corresponding to BAT. It’s of utmost importance since the production of basic organic chemicals is legally classified as a field of application of BAT [1] and is related to the category I objects in terms of the negative impact level on the environment (significant impact) [2].

A technology can only be considered as the best available one if it complies with a combination of five criteria:

a) it demonstrates the lowest level of negative impact on the environment per unit of time or the volume of manufactured products (goods);
b) it is characterized by economic efficiency of implementation and operation;
c) it uses resource- and energy-saving methods;
d) it has a reasonable implementation period;
e) its technological processes are industrially implemented at two or more facilities in the Russian Federation that have a negative impact on the environment and are related to the scope of BAT [3].

In order to fulfill the legislative requirements for technologies, the researchers of the Federal State Unitary Enterprise “State Research Institute of Organic Chemistry and Technology” have applied a systematic scientific approach during the organization of production processes, which allows achieving the required level of development and almost complete compliance of the created small-scale import-substituting chemical productions with BAT criteria.

The main technological decisions regarding selection of the production method were made according to the results of a comparative assessment of possible methods of obtaining a target product according to such criteria of the effectiveness of chemical technological processes as material and energy capacity, availability of raw materials, waste formation, complexity of equipment design, corrosivity of media, the presence of special requirements for materials for manufacturing technological equipment, and cost. Next, the researchers carried out a feasibility study and evaluated the level of manufacturability and environmental friendliness of the decisions made, the level of costs for the organization of production and the level of technological and environmental safety. The data obtained were used to quantify new technologies for production of organic substances in accordance with the principles of the BAT [4]. Then, the stage of decision-making came, converting decisions into raw data for designing production and implementation of design solutions.

Applying the system analysis methods ensured that the final decision was optimal and balanced, and made it possible to develop and implement resource- and energy-saving, low-waste technologies of small-scale production that met modern requirements of industrial and environmental safety. A distinctive feature of small-scale chemical productions organized by Federal State Unitary Enterprise “State Research Institute of Organic Chemistry and Technology” is their uniqueness and novelty of the procedures for obtaining target products. As an example, we can cite the development of technologies for producing two target products, i.e. a functional additive for rubber goods – an antioxidant N-phenyl-β-naphthylamine (Neozone D) [5] and a regulator of polymerization of monomers diisopropylxanthogendisulfide (Diproxide) [6].

This work was financially supported by the Ministry of Industry and Trade of the Russian Federation.

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Biogas disposal complex generating methane-based automobile gas fuel

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In the last decade, an active research of alternative types of fuel, including motor fuels, has been performed, which can provide a safe and sustainable solution to the priority environmental problems. The increased growth of interest in gas as a motor fuel is explained not only by its economic indicators, but also by higher energy and environmental characteristics compared to petroleum fuels. Gasification of transport in Russia is carried out in accordance with the Decree of the Government of the Russian Federation No. 767-r dated 05/13/2013 “On the expansion of the use of natural gas as a motor fuel”. Despite the huge resources of natural gas, Russia is only in the top 20 of countries in terms of natural gas-fuel vehicles due to the lack of gas engine corridors and the necessary gas station networks along the busiest highways.

An important and relevant direction outlined in the “Energy Strategy of Russia for the Period until 2035” is the use of renewable energy sources and local fuels. Biogas is one of such sources, and biogas ingredient – methane is the main component of gas motor fuel.

In Moscow and Moscow region, biogas is produced at a variety of facilities, as a result of microbiological fermentation of organic waste and has the following average content (% vol.): in biogas facilities operating at “Federal Scientific Agroengineering Center VIM”: CH_4 – 51.2%, CO_2 – 45.3%, H_2S – 0.034%; in gas of digesters of urban treatment facilities (Mosvodokanal) CH_4 – 62.5%, CO_2 – 26.2%, H_2S – 0%; in landfill gas of municipal solid waste (MSW) landfills (Kulakovsky landfill, Moscow region) CH_4 – 53.1%, CO_2 – 44.7%, H_2S – 0.028%. However, its direct use as a gas engine fuel ($CH_4 > 85\%$, $CO_2 < 3\%$, $H_2S < 10$ мг/м^3) [1] is impossible without preliminary purification of hydrogen sulfide and carbon dioxide which are harmful to the engine. Methods for removing H_2S and CO_2 from gas mixtures are known, but they are resource and energy consuming.

Purification, storage and transportation of biogas for the purpose of its subsequent use as the motor fuel can be performed by conversion of its components to gas hydrates under certain thermobaric conditions. It was found that all hydrophobic gases, including the main components of biogas and volatile liquids, are capable of forming gas hydrates. The equilibrium thermobaric conditions of hydrate formation for individual gases [2] and the conditions for the destruction of gas hydrates were determined, both in flow-type installations and in closed systems [3]. The production of gas hydrates from water and biogas can be provided by simple maintaining the necessary pressure and temperature parameters in the hydrate forming reactor. One of the options for producing gas hydrates may be implemented by using the following steps:

- loading prepared water into the reactor;
- biogas purging;
- biogas pressure rise up to 6–11 MPa;
- cooling followed by hydrate formation at +2…+6°C;
- cooling to –1…–18°C (freezing).

The technology for transporting methane in gas hydrate form is the safest approach. When the temperature in the reactor is raised, gas hydrates are successively destroyed with the release of gaseous pure methane, followed by carbon dioxide, then – hydrogen sulfide.

Studying and analyzing the patterns of formation and decomposition of gas hydrates allowed us to formulate the technical appearance of a complex facilities for utilization of biogas into methane-based gas engine fuel. The complex includes: a gasholder of a biogas plant or landfill gas of the MSW landfill; technical module for producing gas hydrate, including a thermobaric tank, compressor station, heat pump for cooling a hydrate former; a node for transporting gas hydrates; gas hydrate processing section by raising the temperature; unit for consumer acceptance of marketable products (methane, carbon dioxide, hydrogen sulfide).

The work is carried out according to the plan of research of the Ministry of Education and Science, and with the financial support of the Russian Federal Property Fund in the framework of scientific project No. 18-29-25042mk.

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Polyelement composition of snow cover pollutants in impact zones of metallurgical enterprise

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The operation of industrial enterprises frequently leads to release of great number of pollutants into the environment. The emissions of pollutants into the air first of all directly affect the body of humans and animals, then, these substances settle on the soils and plants, resulting in negative impact on human health and environmental safety.

The increasing rate of environmental pollution requires regular analysis for detection of toxic chemicals in the atmosphere, soil, and also in the snow in winter.

There is a broad variety of methods for assessing the state of atmospheric air, but one of the most acceptable is studying snow cover. This method is a relatively cheap and can be an informative indicator of industrial pollution in winter. The concentration of impurities in the snow reflects their content in the atmosphere and indicates the source and mechanism of aerosol formation at the site under investigation [1].

The aim of this research was to study air pollution in the 30-km zone of the city of Lipetsk (Russia) as the area exposed of possible harmful effects caused by metallurgical plant – PJSC NLMK Lipetsk.

Ferrous and non-ferrous metallurgy enterprises are known as the main contributors to atmospheric air and environmental pollution with heavy metals (HM). NLMK group of companies is the largest steel manufacturer in Russia. Monitoring the effects on environment of the industrial enterprise PJSC NMLK Lipetsk was carried out. The object of study was snow cover [2].

The study revealed 9 HM chemical pollutants (Fe, Cr, Zn, Mn, Ni, Co, Pb, Cu, Cd). It is worth mentioning that the content of the water-soluble HM-fraction in the snow cover was at microconcentrations level, however, their content in the near 4–6 km zone was 2–10 times higher compared to the background, which indicated a low solubility of the solid precipitation fraction, on the one hand, and increased technogenic load on the snow cover of the near zone, on the other.

The main influx of metals was found to occur at a distance of up to 9 km from the source of emission. Further, when moving away from the city center, the concentration of metals begins to decrease and at a distance of 23 km from the plume, values close to background are observed (Fig. 1). The greatest dust load is located in the eastern direction, which can be explained by the wind rose in this region.

The level of total HM-contamination is moderate (250–450 mg/m^2) in the near impact zone (4–6 km) and low in the rest of the surveyed area (100–250 mg/m^2). At the same time, the near impact zone is characterized by a high level of inflow of HM. In the rest of the surveyed area, except for the background areas, an average level of inflow of HM (mainly, iron) has been observed, which indicates a rather high degree of anthropogenic load on the snow and soil cover.

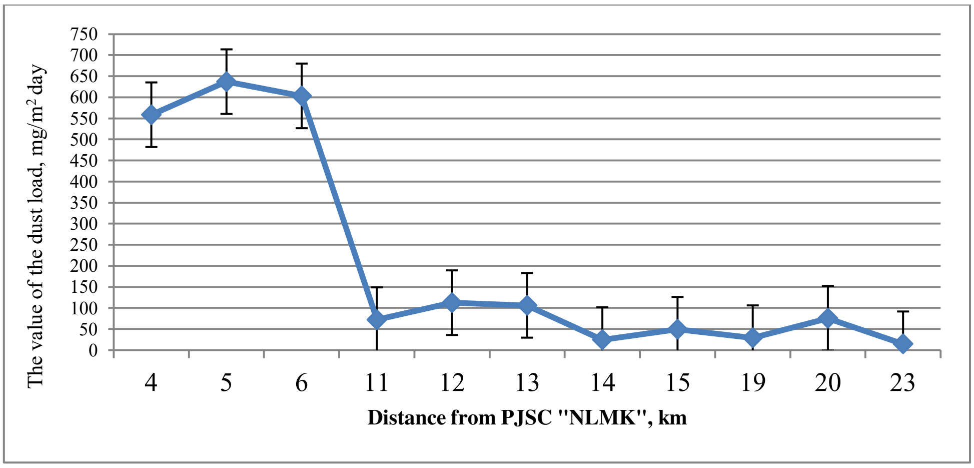

Fig. 1. Effect of distance on amount of dust load in the area of location of PJSC “NLMK”

Finally, the cationic and anionic composition of snowmelt melt water was determined, and no excess of the MPC-level established for drinking water was found (Table 1).

Table 1. Cationic and anionic composition of liquid snow fraction in the impact zone of PJSC “NLMK”, mg/dm^3

№	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	SO_4^{2-}	NO_3^{-}	NO_2^{-}	NH_4^{+}	Cl^{-}
1	19.7±0.3	1.5±0.1	0.6±0.1	0.4±0.0	6.9±1.4	16.6±3.6	0.07±0.01	0.15±0.05	8.9±1.4
2	4.5±0.1	1.5±0.2	0.6±0.0	0.2±0.0	5.6±1.1	3.5±0.8	0.02±0.00	0.06±0.02	1.8±0.3
3	2.2±0.0	0.3±0.1	0.4±0.0	0.2±0.0	4.9±1.0	1.4±0.4	0.02±0.00	0.3±0.11	1.8±0.3
4	21.±0.2	0.3±0.1	1.8±0.0	1.2±0.1	16.7±3.3	5.3±1.2	0.02±0.00	0.07±0.03	3.5±0.6
5	4.9±0.0	0.7±0.0	1.0±0.0	0.2±0.0	5.2±1.0	2.3±0.7	0.01±0.00	0.32±0.11	2.3±0.4
6	6.9±0.1	0.9±0.0	0.7±0.0	0.3±0.0	7.1±1.4	2.1±0.6	0	0.08±0.03	0.9±0.1
7	17.1±0.1	2.5±0.0	1.3±0.0	0.6±0.0	10.6±2.1	2.0±0.6	0.38±0.05	0.05±0.02	3.4±0.5
8	9.6±0.1	0.7±0.1	1.1±0.1	0.3±0.0	10.8±2.2	3.2±0.7	0	0.05±0.02	2.3±0.4
9	3.4±0.0	0.2±0.0	0.5±0.0	0.2±0.0	14.9±3.0	2.4±0.7	0	0.06±0.02	1.2±0.2
10	6.5±0.1	0.5±0.0	2.1±0.1	0.3±0.0	8.4±1.7	6.2±1.4	0.08±0.01	0.56±0.19	7.4±1.2
11	2.4±0.1	0.2±0.1	0.3±0.0	0.2±0.0	8.0±1.6	2.2±0.7	0	0.12±0.04	1.1±0.2

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Novel technological approaches to catalytic hydrogenation of fats

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Novel high-efficient fiberglass woven catalysts (FGWC) for hydrogenation of vegetable oils and fats have been developed. The search for new approaches to hydrogenation processes of solid vegetable fats, as well as new structures and forms of catalytic materials, was carried out in order to reduce the consumption coefficients of catalytically active metals in relation to the mass of the carrier and to the mass of the hydrogenated oil. Another important goal was to reduce the cost of procedures for purifying hydrogenation products from catalyst impurities and products of their dissolution. These problems have been successfully solved by using in hydrogenation processes novel catalysts made from fiber-glass woven materials, which are designed from compositions of silicon and aluminum oxides and other oxides in the form of a net containing Ni, Pd, Pi, Cu, Cr, Co and other active in hydrogenation metals-fillers deposited on the surface of the abovementioned fabrics [1, 2].

Experimental studies of hydrogenation processes of vegetable oils (sunflower, rapeseed, soy, etc.) were carried out in a laboratory reactor with a volume of 200 cm^3 in order to obtain salamas (solid fat obtained by hydrogenation of liquid fats) as a final product. The quality of the obtained salamas should meet the requirements of real margarine production. The processes were carried out by pumping oil through a fixed layer of fibrous catalyst with agitators of various design, including FGWC-fixed ones [3, 4].

The decay coefficients of catalytically active metal are decreased up to 0.005 wt.% relative to the weight of carrier, and up to 0.001 wt.% relative to the weight of hydrogenated oil without compromising the quality of final product, i.e. the degree of hydrogenation and the ratio of *cis-* and *trans*-isomers. This is due to the difference in interaction of FGWC and traditional granulated catalysts with the liquid phase of the hydrogenated oil. In the case of FGWC, the developed surface of the fibrous element is formed not from a poorly accessible network of micropores in the catalyst granules, but by the total surface of a set of thin elementary fabric fibers with a deposited catalyst that actively works even with small amounts of catalytically active metals (Ni, Pd, etc.).

A fibrous carrier made of silicon and/or aluminum oxides firmly holds the catalytically active metal in its matrix providing its low residual content in the hydrogenated oil, i.e., high product quality. Unlike conventional porous oxide catalysts with polycrystalline granules, the proposed fibrous catalysts with a similar chemical composition are in an amorphous (glassy) state. This effect is due to the factor of non-equilibrium phase state of the carrier, whose surface properties are strongly affected by the liquid reaction medium,\ due to the increased holding ability of the glassy matrix with respect to catalytically active metal. As a result, it became possible to completely eliminate the physiologically hazardous metal – Ni from the composition of the final product.

FGWC catalysts were fixed on cylindrical frames of the reactor working in hydrogen atmosphere with agitator screws located inside the frames. The catalytic ‘cartridge-diffusers’ formed in this way [5] were run in the circuits of hydrogen-saturated liquid media circulating inside the reactors.

The proposed schemes of design of nodes for catalyst arrangement are simple to manufacture and can be easily implemented in existing salamas production reactors with low costs for their reconstruction and short time for installation and dismantling of the catalytic material [6]. The reactors of the proposed design can operate both in periodic and continuous modes, which provides conditions for a significant increase in the productivity of the existing equipment without attracting capital expenditures. The advantages of the proposed method for obtaining hydrogenation products of vegetable oils and fats make it possible to considerably simplify the process of catalyst separation (filtration on a large-cell filter or sedimentation). The expensive and complex manufacturing step of deep filtration of powdery Ni-containing catalyst has been excluded from the technological chain. This would reduce the cost of hydrogenated fat by ~20–30% and solves the environmentally relevant issues associated with the accumulation and treatment necessity of spent Ni-containing catalyst powder.

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Development and implementation of new generation of universal import-substituting fiber-glass woven catalytic materials for enterprises of chemical, metallurgical, oil-refining and food industry of Russian Federation

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The report summarizes information on versatile catalyst systems developed as a result of our scientific and engineering collaboration with some Russian and European scientific and industrial enterprises is provided here. The catalysts are based on silica fiber-glass amorphous matrices doped with metals and manufactured as finished articles with various types of woven structure. The main features of these fiber-glass woven catalytic (FGWC) systems, i.e. their structure, the phase state of the matrix, the manufacture and activation methods, design of the catalytic reactor, production process, and the ways of application give good reasons to consider FGWC as a new separate class of catalysts. As compared with traditional catalyst materials, these new catalysts are highly efficient in neutralization of industrial gas emissions, for example in the contact steps of nitric and sulfuric acids production; in catalytic processing of hydrocarbons; in water purification from nitrate and nitrite pollutants, in catalytic heat generation processes, etc. The successful development of these novel catalyst systems is based on non-traditional concept of an essential role of the branching-chain mechanisms in heterogeneous catalysis developed previously. Results of practical application of the novel catalysts in chemical industry are also presented here.

This type of versatile catalyst systems was created to solve a specific industrial problem, namely, to find the ways of suppressing the surface migration, mobility and sublimation loss of a platinum catalyst in catalytic combustion reactions (in particular, at the ammonia conversion step during the production of nitric acid). The catalytic systems with characteristics suitable for this task were developed on the basis of silica glass-fiber cloth materials activated by metal ions implanted into the glass-fiber amorphous woven matrix of the support. Further laboratory studies and industrial tests showed that this type of catalytic systems can be quite efficient in many other existing and newly developed industrial processes. It is expected that the FGWC catalysts would be able to replace the conventional bulk granulated and pelletized catalytic materials in industrial practice. The FGWC element is an article woven from silica glass fibers with an amorphous phase composition (SiO_2 content is 55–98 wt%) looking like a canvas or a grid, activated by the catalytic components chosen out from the defined group of metals (Pt, Pd, Ag, Cr, Ni, Mn, Co, etc.). The metal composition and content are determined in accordance with the requirements of each particular catalytic process [1–4].

The FGWC elements with platinum or palladium content of 0.01–0.1 wt.% show high activities in the oxidation of ammonia, comparable with the activities of standard catalytic platinoid gauzes (in which the platinum weight is about three orders of magnitude higher than in FGWC). At present, selectivity of FGWC systems is slightly lower than that of the platinoid metallic gauzes (85–90% vs. 95%), which currently allows to apply FGWC packages in ammonia conversion reactors only in combination with a platinoid package. However, even this combined pattern has reduced the weight of platinum metals in the reactor catalyst package by 20–50% and provided a 2-fold decrease in the platinum metals loss (0.06 g of platinum per ton of the acid produced vs. the conventional value of 0.12 g). This catalyst package structure is now used in the industrial reactors of some nitric acid production plants. It may be expected that FGWC packages in the foreseeable future would replace the traditional catalyst packages made of platinioid gauzes, which have been actually used in nitric acid production as the only version, throughout its history. To solve this fundamental problem, it is necessary to improve two parameters of FGWC: (i) to increase the selectivity from 85–90 to 95%; (ii) to increase the long-run thermal stability from 750 to 850°C. Developers now have at their disposal comprehensive conceptual and engineering approaches to improve these characteristics of FGWC [5–7].

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Development of sensors of potentially hazardous gases based on micro- and nanosized powders, as well as bulk structures obtained as a result of high-temperature SHS, LJS, SLS and their combinations processes

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The report describes gas-sensing properties of spinel ($NiFe_2O_4$, $CoFe_2O_4$) and orthorhombic ($LaFeO_3$) ferrites as well as cubic nickel–zinc stannates $Zn_{2-x}Ni_xSnO_4$ (with x = 0, 0.8) and some Ti-substituted transition metals oxides, prepared by self-propagating high-temperature synthesis (SHS), as well as nanosized powders of nickel ferrite ($NiFe_2O_4$) and nickel oxide (NiO) obtained by levitation-jet synthesis (LJS). The gas response of the materials was investigated towards a number of gases (ethanol, ammonia, propane, CO, ethane, ethene) at a variety of operating temperatures. A good gas response was found in the case of cubic nickel–zinc stannates as well as lanthanum orthoferrite with excellent selectivity for ethanol, as well as nanosized nickel oxide, whose characteristics in terms of gas sensitivity significantly exceed those of similar commercial products.

$Cr_{2-x}TixO_3$ powders (x = 0.2 and 0.3) were also synthesized in the heterogeneous combustion mode of condensed systems with additional heat treatment at 800–900°C. Optimal concentrations of titanium provided surface segregation of Ti-atoms. The synthesized materials $Cr_{1.8}Ti_{0.2}O_3$ and $Cr_{1.7}Ti_{0.3}O_3$ showed satisfactory sensitivity to ethanol vapors. Materials treated at 900°C contained enlarged agglomerates, which significantly affected the porosity of the sensor film. This resulted in decreased electrical conductivity compared to the materials annealed at 800°C. Sensitivity of all the sensors was increased by 10–20% in humid air (at 50% humidity). The results indicate that oxygen regeneration on films of the SHS product $Cr_{1.8}Ti_{0.2}O_3$ occurs faster under the influence of humid air than in dry air.

Tests for gas-sensing properties were also carried out for the following powderized compositions of SHS produced complex oxides (relative to gas): $BaSnO_3$ (NO); $YFeO_3$ and $LaFeO_3$ (C_2H_5OH); $CdFe_2O_4$ (C_2H_5OH; CO; H_2); $SrTiO_3$ and $BaTiO_3$ (CO_2; H_2O); $YBa_2Cu_3O_{7-x}$ (NO; NO_2, etc. The gas sensitivity of spinel and orthorhombic ferrites ($NiFe_2O_4$, $CoFe_2O_4$, $LaFeO_3$), as well as cubic nickel-zinc stannates $Zn_{1-x}Ni_xSnO_4$ (x = 0; 0.8) was studied in relation to CO, ammonia, ethanol, propane, ethane, etc. at operating temperatures of 350–600°C. Concentrations of all the tested gases were within the limits comparable to their concentrations in natural conditions, and the gases were able to dissolve in artificial air. All the materials studied had n-type electrical conductivity which provided gas sensitivity at operating temperatures of 350–600°C excepting $LaFeO_3$, which had p-type electrical conductivity. All the sensors showed satisfactory sensitivity to ethanol at concentration of 20 ppm. The best Gp index (2.62) at the optimal operating temperature of 550°C was demonstrated by $LaFeO_3$ orthoferrite. In the case of Zn_2SnO_4 and $Zn_{1.2}Ni_{0.8}SnO_4$, the responses were significantly higher in magnitude (~2 ppm or less) compared to the other sensors (9–20 ppm). Sensitivity of these two sensors towards ammonia at a concentration of 50 ppm is almost twice exceeds the sensitivity of ferrite sensors. The increased sensitivity of Zn-containing sensors is probably due to the open and porous micro-structure of the films of these sensors.

Additionally, another type of novel technologies is considered – selective laser sintering/melting (SLS/M) and SHS-assisted selective laser sintering/melting (SHS-SLS/M) 3D printing from powder blends which represent a current trend in the design of functional and functionally graded structures and parts (FGS/P) including micro electromechanical systems (MEMS). Meanwhile, direct laser sintering of micro- and nanosized particles turned to be a complex technological challenge since sintering into larger aggregates leads to the loss of service ability. At the same time, 3D (*X*-*Y*-*Z*) print technology seems highly applicable to designing 'nanosized core/polymer shell' composites without agglomeration and aging but with retaining options for their controlled release if needed. For this reason, the creation of 3D polymer-matrix nanocomposites (PMNC) by laser sintering using a mixture of polymer powders with nanoparticles is much more convenient since the melting point of polymers is markedly lower than that of metals and/or their oxides.

The above composites also open up new horizons for the development of 4D (*X*-*Y*-*Z*-*t*) print technology. Our approaches to realization of 4D SHS-assisted selective laser sintering/melting (SHS-SLS/M) and selective laser sintering/melting (SLS/M) processes using blends of polymer powders with functional micro- and/or nanoparticles as starting materials are also presented. Such processes can be applied for production of self-assembling solar cells, self-restoring catalytic systems, 'smart' prostheses, and micro/nano electromechanical systems, including structures, which may be used for production of gas-sensing devices.

Monitoring of polluted soils: impact of agricultural system on content of heavy metals and pesticide residues in soils

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The monitoring of polluted soils, as a part of the pedological (soil science) monitoring, was elaborated on the basis of the periodical agrochemical mapping carried out every 5 years and on the long-term observations of field experimental stations. The purpose of this study was periodical evaluation of the fertility status of agricultural soils, to assess soil losses of humus and nutrients, the content of heavy metals and pesticide residues, and other physical and chemical parameters. The analysis of the content of heavy metals and pesticide residues in soils was carried out by the Soil Quality Monitoring Center of the State Hydrometeorological Service. Soil samples were collected from 20 key-polygons located in the all pedoclimatical zones. The mobile forms of heavy metals (copper, zinc, lead) and the residues of organic-chlorinated pesticides (alpha-HCH, beta-HCH, gamma-HCH, 4,4′-DDE, 4,4′-DDD, 4,4′-DDT) were determined using atomic absorption spectrophotometry and SOLAAR apparatus.

The uncontrolled application of fertilizers and pesticides or even the cultivation of agricultural plants on previously polluted soils causes nutritional disturbances, irreversible phenomena that deteriorate the quality, compromise the vegetal production, accumulate elements and substances above the limits allowed for users. In most situations, heavy metal pollution of plants occurs more intensely due to the negative effects caused by occasional high emissions of sulphur and nitrogen oxides. The maximum permissible content (MPC) of the heavy metal mobile forms values in the soils was found to be ($mg \cdot kg^{-1}$): Cu – 3, Zn – 23, Pb – 6. According to the obtained results, the content of the heavy metal mobile forms in the soils does not exceed the MPC and cannot be dangerous for environment.

Pesticides used in agricultural technologies in the past, some insecticidal and herbicidal substances are persistent, so, their residues are still present in soils and plant products. In previous years, they were completely abandoned and replaced with organochlorine insecticides (based on hexachlorocyclohexane (HCH) and p,p'-dichlorodiphenyl-trichloroethane (DDT)) as well as organophosphorus pestisides (ethyl- or methylparathion, malathion, mevinphos) due to their high persistence and permanence in soils and plant production.

The determination of pesticide residues in soils of Moldova was suspended in 1970. However, the high degree of pesticide resistance and the high migration capacity generated the need to monitor the content of DDT and its metabolites in soil and environmental components. The dynamics of the degradation of these residues is necessary to be monitored through a special monitoring system. The herbicides applied for weed control have cumulative effects over time and quantitative levels of their residues in soils, which ultimately determines the effects of permanence including plant phytotoxicity. Applied to soil, herbicides interact with this polydisperse system, participating in a variety of processes that result not only in the effective action of weed control, but also in large amount of residues that have remnant effects on plants. These soil-herbicide interactions have several actions: absorption binding to clay minerals and soil humus, volatilization of non-absorbed substances, smoothing of remaining quantities in soil solution, decomposition by biodegradation, inactivation or activation [1, 2].

The MPC for ΣDDT and ΣHCH in soil is 0.1 mln^{-1}. The limits of the determination are: alpha-HCH, beta-HCH, 4,4′-DDE, 4,4′-DDD – 0.0004 mg·kg^{-1}; γ-HCH – 0.0001 mg·kg^{-1}; 4,4′-DDT – 0.0008 mg·kg^{-1}. The results of pesticide determination revealed that the ΣDDT and ΣHCH content in the investigated soil samples was insignificant and did not exceed the MPC. The contents of the DDT ranged from 0.0013 mln^{-1} (0.01 MPC) to 0.0604 mln^{-1} (0.60 MPC). Most of the total ΣDDT content in the soil belongs to its metabolite DDE. The maximum of HCH content in soil was 0.0012 mln^{-1} (0.01 MPC) with α-HCH and γ-HCH isomers predominated. The β-HCH isomer content was lower than the detection limit of the instrument used (< 0.0004), except for one sample (typical chernozem post-irrigated with wastewater from livestock complexes), which contained 0.008 mln^{-1} of the compound.

To decrease the polluting effect, it is preferable to use pesticides with the most efficient content of active substances and with the shortest time of their retention in the environment (including soils). It is necessary that pesticides used in successive treatments (especially widespread in viticulture and fruit orchards) would be capable of decomposing in soils from one treatment to another, without accumulation of polluting residues.

Overall, heavy metal and pesticide residues content in soils of Moldova was found to be low and did not exceed MPCs. The use of pesticides and uncontrolled fertilizers should be regulated to the extent that the content of the residual substances is correlated with levels of risk to humans and animals. Therefore, the following specific indicators must be known for each pesticide product: no-effect dose, tolerated daily dose, tolerable residue quantity, residue limit, maximum permissible limit, acceptable daily dose for the individual, tolerance level, maximum permissible contamination limit and the maximum daily dose allowed for humans. The depollution (remediation) measures should be aimed not only to remove hazardous sources, but to include all measures for restoring the affected agrochemical indices and returning soils to their basic property – fertility, since harmful effects, in most cases, are due to cumulative action of sources and pollutants, and only fertile soil can be resistant to harmful and degrading effects of pollution.

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Influence of organic waste composition on characteristics of biohydrogen production by dark fermentation

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The utilization of organic waste and the depletion of non-renewable energy resources are currently one of the most pressing problems of mankind. Obtaining biohydrogen in the process of dark fermentation (DF) makes it possible to take advantage of both the production of renewable energy and sustainable waste management. Along with the formation of biohydrogen, metabolites accumulate during DF, such as organic acids and alcohols, which can be used to produce products with high added value (e.g., biofuels, chemicals, biopolymers, and bioplastics) [1]. Organic matter (OM) in waste consists of three main biodegradable components: fats, proteins and carbohydrates. Their ratio is one of the fundamental characteristics for the DF process. Despite the fact that carbohydrates give the highest hydrogen yield, the presence of other components can contribute to the DF process due to a better balance of macro- and microelements and providing microorganisms with the necessary nutrients for cell growth.

In this work, we conducted a comparative study of the yield of biohydrogen and the accumulation of metabolites in the DF of simple substrates imitating proteins, fats, carbohydrates, their mixture, as well as a number of complex substrates under the same conditions (pH control at 5.5, thermophilic mode (55°C) , activated sludge from the local wastewater treatment plant as an inoculum, absence of active mixing). A distinctive feature of the work was that the inoculum was not subjected to any pre-treatment (e.g., heat-shock) to better reflect large-scale processes in which, during the processing of real non-sterile organic waste in the reactor, autoselection of the microbial community most adapted to the given conditions takes place. Table 1 lists the substrates used in the work, their component composition and the main characteristics of the DF process. The maximum hydrogen content in biogas (60.4%) and the specific hydrogen yield (138 ml H_2/g OM) were observed during DF of starch. The yield of hydrogen from proteins (peptone) and fats (sunflower oil) was 28–33 times lower than from carbohydrates (starch). Statistical analysis using Spearman's correlation coefficients showed that the carbohydrates make the largest contribution to the specific yield and hydrogen content in biogas (Fig. 1). At the same time, a statistically significant positive correlation was observed between the protein content and the accumulation of acetate, as well as the ratio of acetate to butyrate. The theoretical yield of hydrogen is 4 and 2 mol/mol glucose with the formation of acetate and butyrate as a metabolite, respectively [2]. Thus, enhanced accumulation of acetate in the presence of proteins can judge some positive effect of proteins on the DF process. However, most of the acetate could be formed due to the non-hydrogen producing Stickland reaction, the main pathway for the degradation of amino acids [3]. Apparently, the formation of H_2 from proteins followed the path of oxidative deamination of the amino acid, as evidenced by the statistically positive correlation of valerate and protein/carbohydrate ratio (Fig. 1).

Table 1. The main characteristics of dark fermentation process

Substrates	Potato Starch	Sunflower oil	Peptone (enzymatic)	Mixture starch/oil/ peptone	Feed-stuff for pigs	Dog food	Activated sludge
Carbohydrate : Protein : Fat mass ratio	224 : 9.0 : 1	1 : 1.6 : 38.9	5.7 : 227.9 : 1	7.8 : 5.4 : 1	19.0 : 8.4 : 1	8.7 : 4.5 : 1	5.7 : 9.0 : 1
H_2 in biogas, %	60.4	36.0	14.9	51.0	52.9	31.9	13.8
H_2 yield, ml H_2/g OM	138	4.9	4.1	59.5	43.6	63.3	16.2
H_2 yield, mmol H_2/g carbohydrates	6.16	0	0	4.51	4.36	6.82	4.66

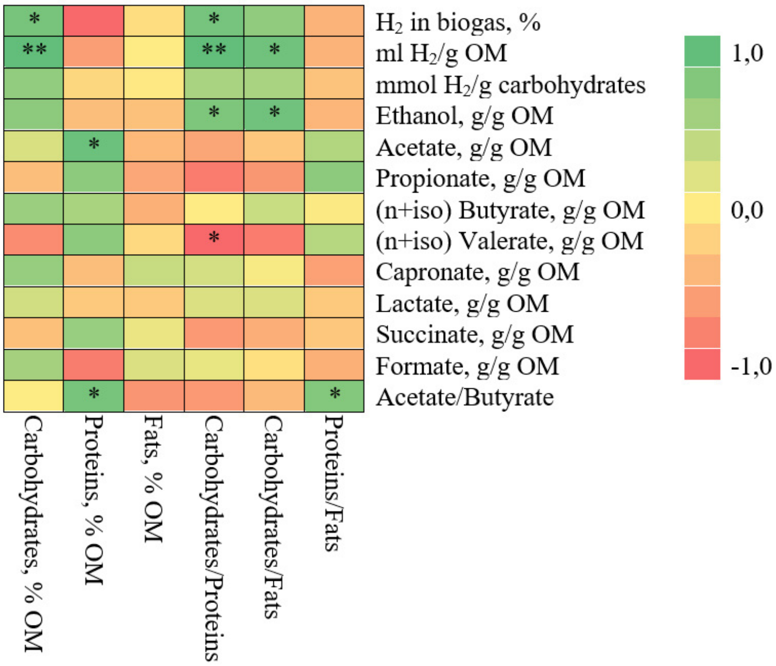

Fig. 1. Heat map of Spearman correlation between the component composition and characteristics of DF. Statistically significant values are indicated by the symbols: ** $P < 0.01$; * $P < 0.05$.

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Prediction of damaging factors and environmental risk management for transportation of petroleum products by road

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Assessment of the threat to the life and health of people as well as environmental risks caused by the emergency spills of road-transported petroleum products is of great importance and should be conducted with correct substantiation of the initial parameters for the formation of the accident damage effects. Thus, the area of the petroleum product spill is determined not only by the amount of flammable liquid that has leaked out, but also by the physical and chemical infiltration properties of the underlying surface. Scenarios of accident escalation and the level of possible environmental threats depend even more on these factors.

The literature analysis of the issue has shown that the empirical initial data is often highly uncertain and the experimental values obtained need preliminary processing when used in in full-scale tests to assess input factors for the formation of the oil spill damage effects [1, 2].

The following tasks were set out in this work:

1. Study of the main parameters of formation of damaging factors taking into account the physical and chemical properties of petroleum products, the underlying surface structure, environmental parameters, scenario diversity of transport routes and elements of the theory of similarity and scaling theory.
2. Development of a model of action/inaction of road users as an accident escalation factor.

The object of the study was the situation with road transportation of petroleum products on the route Moscow Oil Refinery – Zhukovsky Airport. Two hazardous sites were selected; thermal and pressure damage factors were calculated for the emergency spill of TS-1 kerosene and AI-95 gasoline from a fuel truck taking into account possible soil penetration and weather conditions [3–5].

Conclusions:

1. The existing methods for calculating the damaging factors have been developed on the basis of empirical data obtained in experiments with much smaller quantities of substances than those involved in the accident. Simple extrapolation of these data results in a discrepancy between the calculated and actual accident consequences data. It is reasonable to assume that applying the similarity theory to calculations of this type avoids deviations in the results; this area requires further research.
2. It has been shown that the type of underlying surface of a spill affects the final value of the accident damaging factor but this effect requires further investigation.
3. The value model of the impact of road users' action/inaction on the escalation of a tank accident has been proposed.

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Novel safe technology of N,N-dithiodimorpholine synthesis

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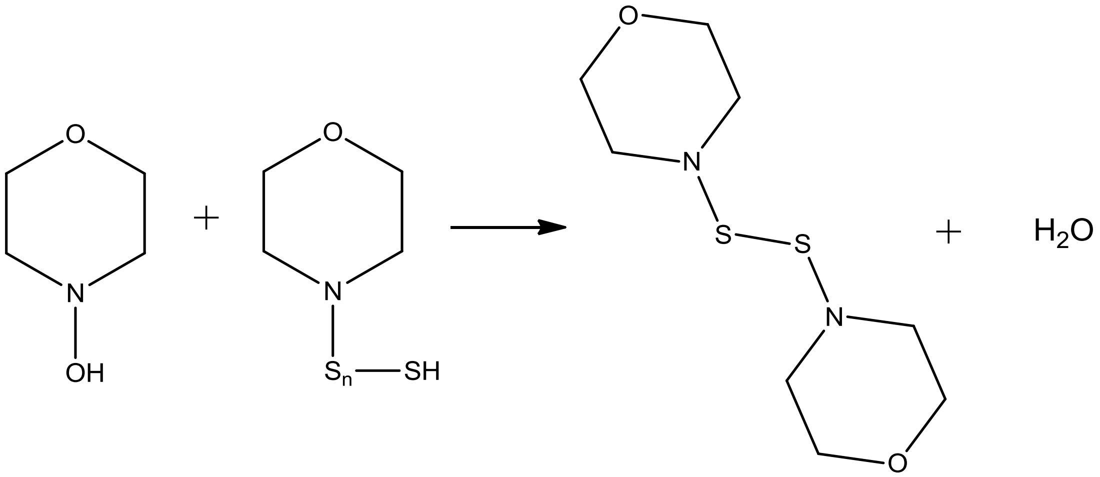
Creating operationally and environmentally safe chemical manufactures is one of the crucial tasks in chemical technology of organic substances. The existing technology of N,N-dithiodimorpholine (DTDM) synthesis doesn’t meet the specified safety requirements. Chlorine gas is employed at the step of dithiodichloride synthesis (one of intermediates DTDM preparation procedure). This reagent makes DTDM manufacture hazardous. In addition, significant amount of sodium hydroxide aqueous solution is applied at the DTDM preparation step, leading to the formation of the appropriate volume of water-alkaline waste, which needs careful neutralization.

We suggest a novel safe technology of synthesis of DTDM (and also some other N,N-dimorpholineoligosufides) which is based on electrophylic amination of 1-(N-morpholine)polysulfanes with N-hydroxymorpholine in the presence of copper compounds catalysts.

The new procedure of N,N-dithiodimorpoline (DTDM) synthesis involves the reaction of electrophilic amination reagent with 1-(N-morpholine)polysulfans as follows:



We applied N-hydroxymorpholine as aminating reagent, which could be easily synthesized by reaction of morpholine with the carbamidic hydrogen peroxide complex in polar organic solvents media, as described in our previous studies [1] and [2]. The main advantage of the presented method is application of the carbamidic hydrogen peroxide complex to produce aminating regent. Hydrogen peroxide is unstable in environment and easily decomposes into oxygen and water. Carbamide is directed to carbamidic hydrogen peroxide complex regeneration step, the solvent is recycled.

1-(N-morpholine)polysulfanes are synthesized by reaction of sulfur with an excess of morpholine, which is used as the solvent.

Interaction of 1-(N-morpholine)polysulfanes with N-hydroxymorpholine occurs in presence of copper compounds catalyst. The catalyst is separated from the reaction mixture by filtration. DTDM is isolated by solvent evaporation. Solvents and excess of morpholine are recycled.

The proposed approach to DTDM synthesis is more safe and low-waste forming as compared to the known DTDM preparation technology and represents significant interest not only in terms of technological safety but also as an example of “green” chemistry approach.

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Environmentally friendly approaches for modernization and eco-restructuring oil refining industry

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The chemical industry is the industrial backbone of all industrialized countries and economies. Currently, the main raw materials for chemical industry are petroleum, natural gas, and coal. However, oil and gas refining are the main sources of energy and industrial emissions. It should also be noted the relatively low level of environmental friendliness of the technological processes of hydrocarbon processing. The oil refining industry is a key element in the chemical industry. Significant transformation is now taking place in the oil refining industry under the influence of global megatrends. New processes are developed and implemented which are based on clean chemical technology. The demand for novel environmentally friendly products and processes is driven by social factors related to the environment, sustainable development, chemical safety, health and green energy that permeate the global economy [1].

Environmentally friendly approaches for modernization and eco-restructuring of the oil refining industry are based on the implementation of the principles of green chemistry and sustainable development [2]. Thus, deep purification of oil fractions from sulfur compounds can be performed using the promising method of oxidative desulfurization with an environmentally friendly oxidizing agent - hydrogen peroxide. Moreover, organic sulfur compounds are converted into oxidized forms such as sulfones under the mild conditions in the presence of H_2O_2, molybdates and formic acid [3]. Oxidized sulfur compounds are removed by extraction followed by bioconversion to sulfide simultaneously with biogas production using immobilized biocatalysts. Renewable waste may be added as a raw material to bioreactor for biogas producing [4, 5].

Analytical methods based on bioindicators (such as luminescent cells of photobacteria) and biological detection methods (for example, based on determining the concentration of intracellular adenosine triphosphate) may be used for continuous monitoring of toxicity of all hydrocarbon processing and waste [5, 6]. When implementing the proposed environmentally friendly integrated approaches with nitrogen-containing extractants (N,N-dimethylformamide, N-methylpyrrolidone), the possibilities of reducing the sulfur content in the gasoline fraction to the EURO-5 standard have been demonstrated.

Oil fractions purified by deep eco-efficiently oxidative desulfurization can be used in chemical industry for the production of high quality goods [2].

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Development of mathematical model (CFD-model) of MDI-production process

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Isocyanates are known as one of the most popular products of chemical industry, as they are applied as raw materials for production of different types of polyurethanes. In addition, isocyanates are valuable intermediates in the fine organic synthesis of pesticides and other biologically active substances. Moreover, isocyanates are attractive in terms of market perspective, but their production is hindered by a number of problems related to the fact that intermediate products are highly toxic and explosive substances, which means that ensuring safety on an industrial scale will require significant investments. To date, the Russian domestic market consumption of is fully satisfied due to imports, therefore, this area of research is of high relevance for national researchers.

MDI (Methylene diphenyl diisocyanate) is a widely used as polyurethane component throughout the world. This work is devoted to the development of a mathematical model of MDI-production reactors to find optimal operating conditions of the synthesis process. The modeling process has been divided into two parts. The first part includes modeling the entire reactor system in the ChemCAD software environment in order to obtain the overall equipment characteristics and process conditions; the second part of the simulation process includes CFD (Computational Fluid Dynamics)-modeling in Ansys DesignModeler software packages, and this stage allows analysis of the hydrodynamic regime inside the mixing reactor.

The process of obtaining MDI was simulated in the ChemCAD software package and involved:

1. Kinetic Reactor (KREA) for reaction of triphosgene with methylenedianiline (MDA) to produce carbonyl chlorides and MDA hydrochlorides;
2. Kinetic Reactor (KREA) for conducting the dehydrochlorination process and obtaining the target MDI-product.

First of all, the MDI-synthesis was simulated in a displacement reactor in the temperature range from 130 to 190°C to construct concentration profiles along the length of the reactor in an isothermal mode while maintaining the temperature in the reactor using a high-temperature coolant. The next stage of laboratory piloting was performed to conduct a subsequent adequacy check of the model. To this end, the material balances of the two MDI-reactors were simulated under different temperature conditions to obtain the maximum yield of the target MDI-product.

The second phase of this work was CFD-modeling, the object of which was a reactor-separator with the conversion of carbonyl chloride to the target MDI-product. The three-dimensional model of the reactor was created using the ANSYS DesignModeler software.

Thus, a mathematical description of the process for producing MDI in the reactor was developed, which was implemented as a part of computational fluid dynamics (CFD). A three-dimensional model of the reactor with a stirrer was created and the corresponding computational grid was generated. Using the developed model, a series of computational experiments were conducted in reactors with different mixing device designs.

The work was supported by the Ministry of Science and Higher Education of the Russian Federation (Federal Target Program No. 075-15-2019-1856, Unique project identifier RFMEFI60719X0315).

Production of carbon-based sorbents as an alternative method for utilization of forest chemical industry waste

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Currently, regeneration of lignin-containing waste is one of the important problems of the forest chemical industry[1]. One of the most promising trends in waste processing industry is production of sorbents using lignin-containing waste as raw material, for example, production of activated carbon and lignin based sorbents [2] and granulated active coals [3].

Authors propose a novel procedure for sorbent production based on carbonation of lignin-containing waste regenerated by producing microcrystalline cellulose.

Carbonization of lignin-containing waste was carried out on a bench-scale unit of thermogravimetric analysis with a reactor made of heat-resistant steel, equipped with a connection for inert gas supply and removal of steam-gas mixture into the condensation and combustion system.

The obtained coal was crushed for further briquetting. The briquettes were then ground to a fraction with a particle size in the range from 0.5 to 2.5 mm. This resultant coal had a higher bulk density and mechanical strength than the coal produced directly after carbonization.

The crushed coal was then activated in the rotary tube reactor of the bench unit under the following conditions: the activating agent – water vapor, the temperature of activation – 970°C, the duration of activation at given temperature – 40, 60, and 80 min (Table 1).

Table 1. Summary of activation data for carbon-based sorbents

Sample code	Mass of coal before activation, g	Mass of coal after activation, g	Activation time, min	Yield of active carbon, %	Burn rate, %
AC 1	10.677	9.873	40	92.5	17.9
AC 2	6.873	5.797	60	84.4	45.7
AC 3	11.252	5.633	80	50.1	49.9

These obtained samples were further evaluated for their iodine sorption activity (Table 2).

Table 2. Summary of adsorption activity of activated carbon samples

Indicator	Sample code		
	AC 1	AC 2	AC 3
Iodine adsorption activity, %	40.64	81.92	74.86

The experimental results on testing adsorption activity indicate a possibility of using the obtained sorbents at water treatment facilities for decontamination from inorganic impurities.

Thus, this study has confirmed a good potential of carbon-based sorbents production as an alternative method for utilization of waste of forest chemical industry along with their possible application in water treatment technologies.

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Portable test kit purposed for 1,1-dimethylhydrazine detection in working area and environment

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The space-rocket industry generates a negative impact on the environment and human health. The control of releases of hazardous rocket fuels at the level of maximum allowable concentration is a task of prime importance. One of the most hazardous substances is rocket hydrazine fuel or 1,1-dimethylhydrazine (DMH), which is a highly toxic organic compound and is classified as carcinogenic [1].

Typically, DMH control in liquid media is carried out by using test strips [2] and a portable bleeding device (PBD) [3]. DMH concentration in air can be determined by means of indicator tubes [4] and the passive chemical indicators. DMH identification on solid-phase surfaces and leak localizations are performed using the detecting element [5] and aerosol.

The $K_4H_4[Si(Mo_2O_7)_6$ potassium tetrahydro-12-molybdosilicate agent (THMS) is usually used in all the above mentioned testing equipment as a DMH chromogenic indicator. The testing accessories change colour from light-yellow to dark-blue, when DMH is identified, which is accompanied by formation of bright molybdene blue dye-stuff. THMS shows a competitive advantage in sensitivity, color saturation, ability to keep efficiency at low temperatures as opposed to the formerly known indicators, such as 4-pyridine aldehyde; bromothymol blue; silver salts; 4-(dimethylamino)cinnamic aldehyde; T Safranin phosphorotungstate, malachite green; 4-chloro-5,7-dinitrobenzofurazan, 4-(dimethylamino)benzaldehyde, molybdenum-phosphoric heteropoly acids, and cobalt salts.

We have developed a portable kit (see Fig. 1) equipped with the DMH testing accessories that allow for:

- the operational and weighted-average assessment of the ambient air;
- the analysis of cleansing aqueous solutions and fuel slippages;
- the sanitary-and-chemical control in working areas.

The testing accessories sensitivity equals to 0.5 MPC (Maximum Permissible Concentration).

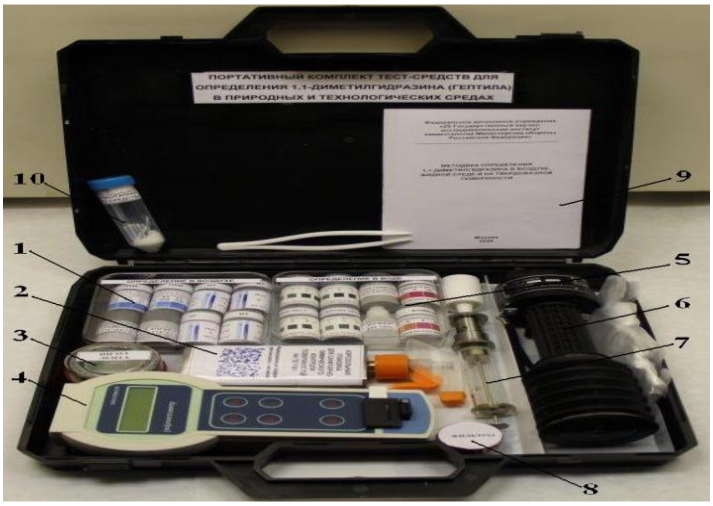

Fig. 1. Physical configuration of portable test kit intended for 1,1-dimethylhydrazine detection in the environment:
1 – Boxes with indicator tubes for air analysis;
2 – Indicator spray can for surface analysis;
3 – Detecting element for fuel leak detection;
4 – ECOTEST 2040 mini-reflectometer c/w remote cassettes;
5 – Boxes with indicator tubes for analysis of aqueous solutions;
6 – AM-0059 bellows-type aspirator;
7 – Portable bleeding device for TS;
8 – Filters for PBD;
9 – Measurement procedure description;
10 – A kit case for test accessories.

The portable 1,1-dimethylhydrazine detection kit has been tested at the following facilities: in test labs of propellants, in the propellant stocks, at the facilities when carrying out DMH related operations. The testing accessories allowed for control maintenance over the air DMH-pollution source and the level of DMH-pollution in working areas and the environment. The portable kit is proposed to be used as a part of complex labor safety monitoring system that ensures safety of the operation stuff when dealing with liquid rocket fuel components.

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Sensory properties of phosphorus-containing oxide layers on titanium formed by plasma-electrolytic oxidation

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Currently, a promising trend in development of electroanalytic sensors is the creation of novel metal oxide based sensors along with the detailed study of the known ones due to their high mechanical strength, chemical resistance, low cost, high temperature resistance, miniaturization and ease of use [1].

This paper presents the results of synthesis and investigation of the pH- and phosphate functions of phosphorus-containing oxide layers on titanium formed by plasma-electrolytic oxidation (PEO) method which involves formation of oxide layers on the surface of metals and alloys under the action of electric spark and microarc discharges in the anode region [2].

Oxide films on titanium were formed by PEO at a current density of $i = 0.05$ A/cm^2 for 5 min in an aqueous electrolyte containing 0.15 mol/l KH_2PO_4.

According to X-ray phase analysis, the resulting coatings contain titanium dioxide exclusively in anatase modification of. According to energy dispersive analysis, PEO-layers contain carbon, oxygen, phosphorus, and titanium.

The behavior of PEO-electrodes in the direct pH metric study was investigated in the pH range of 1.68–11.91. The behavior of the formed PEO-electrodes depended on pH of the buffer solutions. In the pH range from 2 to 7 (sections 1, 4 in Fig. 1) the studied phosphorus-containing oxide layers on titanium exhibited pH-sensitivity with an angular slope of the electrode function ~40 mV/pH (when changing pH from 2 to 12) and ~53 mV/pH (when changing pH from 12 to 2). In the pH range from 7 to 12, the phosphorus-containing electrodes were practically inert (sections 2, 3 in Fig. 1), which is consistent with the data described in [2]. According to these authors, this is due to the presence of phosphate groups embedded in the coating during the PEO process in the oxide layers.

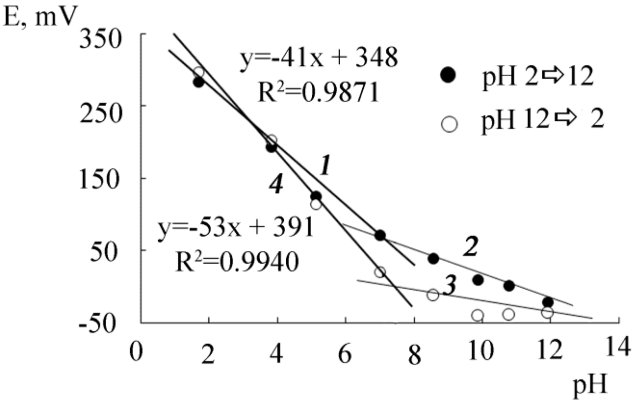

Fig. 1. Dependence of E potential on pH value for the PEO-electrode

Figure 2 shows the results of studying the phosphate function of the obtained PEO-electrodes. It can be seen that the interval of the electrode function *E*-(pPO_4^{3-}) covers the range from 2 to 4, while the linearity of the function $E = a$-b($pH_2PO_4^-$) is preserved in the range from 1 to 5 with an approximation coefficient $R^2 = 0.9913$. The slopes of the electrode functions are small in both cases but it is impossible to make conclusions about how close they are to the Nernst value. This is due to the fact that different forms of phosphorus-containing ions exist in the studied solutions.

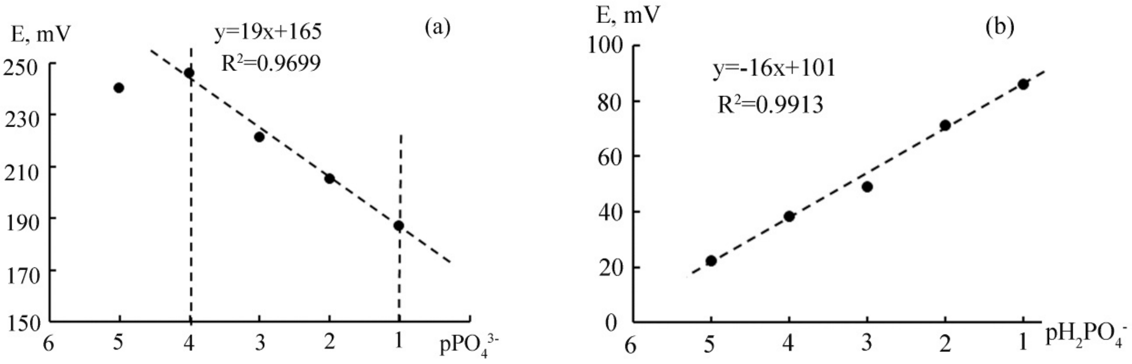

Fig. 2. Dependencies of *E*-(pPO_4^{3-}) (a) and *E*-($pH_2PO_4^-$) (b) for the PEO-electrode

Thus, in this work, it is shown that phosphorus-containing PEO-layers on titanium have polyfunctionality, therefore, they can be used as potentiometric sensors towards different ions.

The study was supported by the Russian Foundation for Basic Research, project № 18-03-00418.

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Chemical utilization of furfural waste

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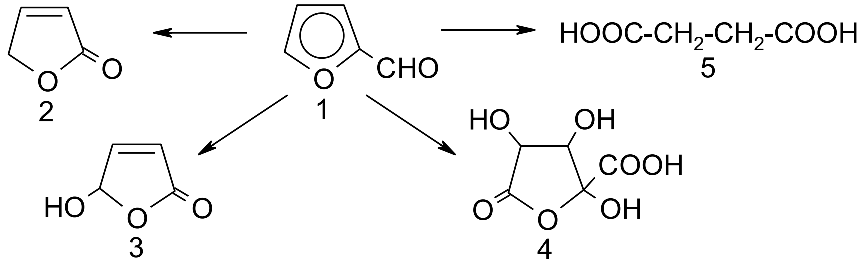
Furfural (**1**) is a product of chemical processing of agricultural and forestry waste. It is also formed in a noticeable amount in heat-treated food products [1]. There are known methods for isolating aldehyde **1** from various types of products [2], but this raises the urgent problem of recycling this neurotoxic substance.

A highly effective approach for chemical utilization of furfural based on the reactions of its oxidation with aqueous hydrogen peroxide was developed at Kuban State Technological University [3]. A detailed study of the influence of various factors on these reactions allowed us to identify principles for controlling directions of the oxidation reactions and yields of the target oxidation products. Basing on these data, a methodology for the directed synthesis of functionally substituted furans, furanones, hydroxyfuranones, carbon acids and their derivatives has been developed [4, 5] yielding the products **2–5** which are of the great practical importance.



Compounds **2–5** and compositions derived therefrom were found to be biologically active substances with a significant growth-regulating and anti-stress effect on various crops. The compounds are safe for the environment and can be applied in very low concentrations.

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Safe preparations for plant production based on 5-hydroxymethylfurfural waste

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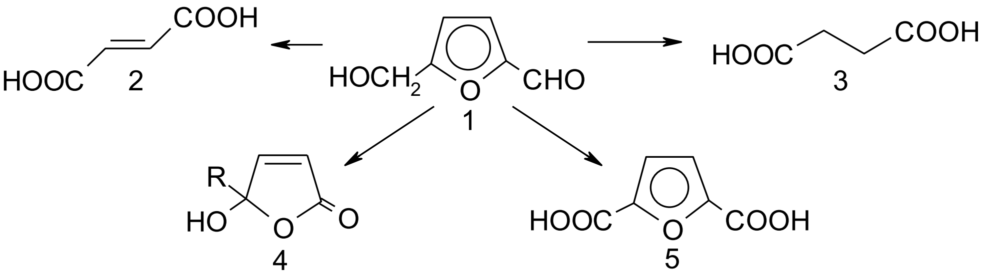
A novel plant growth regulator providing a significant increase in the sowing qualities of winter wheat and improving the resistance of seedlings to drought has been created. The method of its synthesis is based on a low-cost, commercially available process of chemical modification of 5-hydroxymethylfurfural (**1**) which is a highly toxic waste of food production [1]. The process is based on the oxidation of aldehyde **1** using a system including hydrogen peroxide and a vanadium catalyst [2]. Modifications of the regulator selectively increasing individual sowing characteristics of wheat have been developed.

The new preparation is vastly superior to such known highly effective commercial growth regulators as Furolan, Universalniy and Gibberellin in terms of the most important indicators (germination energy, length and weight of seedlings, germinating capacity, resistance to drought, and environmental safety).



The high efficiency of the new growth regulator is apparently due to the presence of compounds **2** and **3** in its composition which are involved in the biological Krebs cycle, as well as to the relevant physiologically active products **4** and **5**. The proposed approach can provide significant benefits from the use of the preparation at low doses of its consumption.

The developed method opens the way for industrial utilization of aldehyde **1** waste.

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Development of quality express method for determination of synthetic dyes in food products using liquid anion exchanger

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Synthetic dyes (SDs) are widely used in food industry because of their high stability, wide variety of assortment and low cost. However SDs can have negative impact on human health, therefore, their content in food products is regulated by Sanitary and Hygienic requirements. SDs are completely forbidden to use for some category of products including food for baby nutrition, wines, juices, etc. As a rule, high performance liquid chromatographic methods (HPLC) are used for monitoring of the content and presence of SD in food. These methods are time-consuming and require expensive equipment. While extraction methods of analysis are quick, do not require additional equipment and also can be used for analysis of SDs. The aim of this work was to develop high quality extraction express method for determination of SDs in food products (wines, juices, syrups, beverages) using liquid anion exchanger.

The distribution of 16 anionic synthetic dyes (E 102, E 104, E 110, E 122, E 123, E 124, E 127, E 128, E 129, E 131, E 132, E 133, E 142, E 143, E 151, E 155) was studied in the systems:

- an aqueous solution of SD – chloroform solution of trioctylmethylammonium chloride (TOMAC); chloroform solution of trioctylamine (TOA);
- an aqueous solution of SD – toluene solution of TOMAC; toluene solution of TOA.

In our work we used 10^{-4} M aqueous solutions of SDs prepared in wide range of pH (from 2.0 to 8.5). The determination of the content of SDs in the phases was carried out by photometric method. The distribution coefficients (D) and extraction rates (R, %) were calculated.

It was found, that TOMAC forms a stable uncharged complex with SD in the studied pH range, which is easy transferred to organic phase, with maximum D values for TOA achieved at pH 2–3. In the range of concentrations of TOA and TOMAC extractants from $2 \cdot 10^{-3}$ M to $5 \cdot 10^{-2}$ M the values of D of dyes ranged from 1 to 150, the values of R varied from 15% to 99%, while chloroform solutions of extractants were more effective than toluene solutions. When the concentration of extractants is higher than 10^{-2} M, the SD is quantitatively extracted into the organic phase. In summary, a quality express method was developed for determination of SDs in liquid foods, such as juices, syrups, wines and beverages using anion exchanger (10^{-2} M solution of TOMAC in chloroform). TOA can be used as SD extractant from food products of complex composition, while SDs can be completely reextracted at pH > 8–9. Two stage-extraction leads to removal of hydrophobic and hydrophilic components from the matrix.

Criteria for assessing impact and determining contribution of particulate matter with a dispersity of 10 and 2.5 microns to additional cases of morbidity and mortality

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The development of effective measures to protect the population from the harmful effects of particulate matter and to ensure the sanitary and epidemiological well-being of the population is a relevant task. It requires not only an objective hygienic assessment of the content of fine particulate matter with a dispersion of 10 microns (PM_{10}) and 2.5 microns ($PM_{2.5}$) in the atmospheric air, but also improvement of methods for assessing the impact of PM_{10} and $PM_{2.5}$ on public health.

Among the existing methodological approaches to assessing additional cases of morbidity and mortality from exposure to fine particulate matter of differentiated fractions, two main assessment methods are recommended by the World Health Organization (WHO) and widely used in the European Union, Canada and the USA, i.e.:

- methodology for assessing the growth of the relative risk value or the percentage change in the analyzed health indicator per standard unit of concentration PM_{10} and $PM_{2.5}$ (10 $\mu g/m^3$);
- methodology for assessing the increase in daily mortality per standard unit of concentration of PM_{10} and $PM_{2.5}$ (10 $\mu g/m^3$).

In the Republic of Belarus, the list of criteria for assessing additional cases of morbidity and mortality due to short-term exposure to PM_{10} and $PM_{2.5}$ includes indicators substantiated by epidemiological studies and the following WHO recommended indicators: the relative risk of an increase in daily mortality from respiratory and cardiovascular diseases; an increase in the number of hospitalizations with respiratory diseases; the increased use of bronchodilators; an increase in the incidence of bronchitis; a change in life lung capacity and less significant respiratory symptoms with increasing concentration of PM_{10} and $PM_{2.5}$ at 10 mg/m^3 in the air within a short period of time.

The following criteria for assessing additional cases of morbidity and mortality during chronic exposure to PM_{10} and $PM_{2.5}$ are highlighted: an increase in the incidence of pneumonia, acute bronchitis in children and adolescents, chronic bronchitis among people aged 25 years and older; increase in the appeal for emergency medical care, appeal for heart diseases, respiratory diseases; an increase in mortality from respiratory diseases and cardiovascular diseases.

A complex relationship ‘exposure level – response’ is used to assess the disease burden for the following five factors: acute lower respiratory tract infections in children under 5 years of age; chronic obstructive pulmonary disease in adults over 25 years old; lung cancer in adults over 25 years old; coronary heart disease in adults over 25 years old; stroke in adults over 25 years old.

It should be noted that the values of the potential risk to public health from acute exposure to PM_{10} and $PM_{2.5}$ in urban areas vary from 1.2% to 4.3% – an ‘acceptable’ risk level. The level of potential risk to public health from chronic exposure to PM_{10} is 3.7% (‘acceptable’ level), from exposure to $PM_{2.5}$ – 5.9% (‘satisfactory’ level). When it comes to the conditions of acute and chronic exposure to PM_{10} and $PM_{2.5}$ in urban areas, the values of hazard indices are characterized as ‘low (minimum)’, which corresponds to the background levels of morbidity. The highest values of the hazard index for acute and chronic exposure to $PM_{2.5}$ are found to be 0.61 and 0.63, respectively.

According to the analysis of the criteria for assessing additional cases of morbidity and mortality associated with the chronic exposure to particulate matter PM_{10} and $PM_{2.5}$ used in the EU, Canada and the USA, the most informative criteria are: the relative risk of reduced forced lung capacity and forced volume exhalation in adults and children; an increase in the incidence of pneumonia, acute bronchitis in children and adolescents, chronic bronchitis in people aged 25 years and older; an increase in fast medical assistance, including assistance for heart and respiratory diseases; an increase in mortality from diseases of the respiratory system and the cardiovascular system.

Modern approaches to organized surfactant-based nanosystems for organophosphorus compounds decomposition

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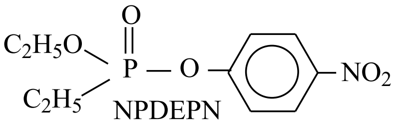
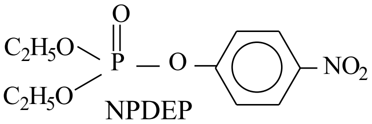
Conversion of considerable amounts of toxic compounds into environmentally harmless products requires, first of all, the safe and inexpensive solvent. In this regard, water is the solvent of choice which meets the Green chemistry requirements. A great many of chemical war gases, slowly degradable pesticides, herbicides, etc., are the hydrophobic esters of phosphorus(V), hence, their decomposition involves dephosphorylation and hydrolysis processes. Since the toxic phosphorus esters are generally water insoluble, aqueous surfactants can serve as a reaction media for decomposition of these substances. Among new synthetic surface active compounds, the Gemini surfactants (GS) are of special interest as host molecules. These unique compounds feature a number of unusual physico-chemical properties: extremely low critical micelle concentration, high adsorption efficiency, solubilizing ability, etc. The economical attractiveness of Gemini surfactants lies also in the fact that such surfactants provide more high acceleration of esterolytic reactions at a lower surfactant concentration and regulation of rates and directions of the chemical processes. The Scheme presents the main approaches to the development of highly efficient oxidative-nucleophilic systems.

The first approach involves the investigation of alkaline hydrolysis of two organophosphorus compounds (NPDEPN and NPDEP) as the model analogues of ecotoxicants with a structure of cationic surfactants. Wide possibilities in structure modifications of cationic moiety of the head group, spacer, alkyl 'tail', and examination of 'surfactant structure - property – micellar effects' relationships form a basis for the development of simple in composition and economically attractive systems. By comparison, the half-life of NPDEPN transformation into the reaction products at pH = 10.0 in water amounts to nearly 800 min and ~30 min in the cetyltrimethylammonium bromide (CTAB) solution, whereas in GS micelles (I) the half-life is as little as 4 min.


NPDEPN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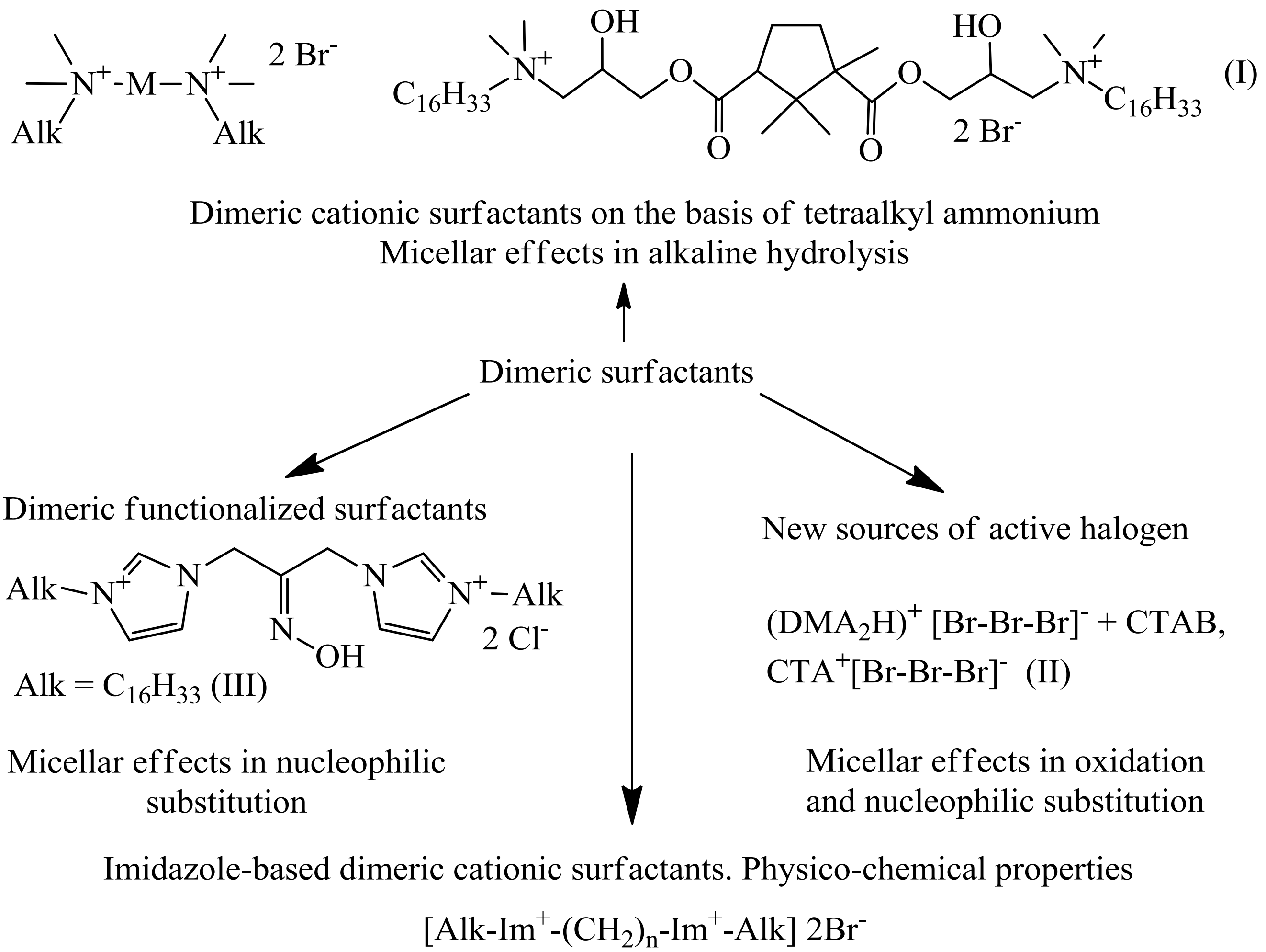

(I)

Dimeric cationic surfactants on the basis of tetraalkyl ammonium

Micellar effects in alkaline hydrolysis

Dimeric surfactants

Dimeric functionalized surfactants

Alk = $C_{16}H_{33}$ (III)

Micellar effects in nucleophilic substitution

New sources of active halogen

$(DMA_2H)^+ [Br\text{-}Br\text{-}Br]^- + CTAB$,

$CTA^+[Br\text{-}Br\text{-}Br]^-$ (II)

Micellar effects in oxidation and nucleophilic substitution

Imidazole-based dimeric cationic surfactants. Physico-chemical properties

$[Alk\text{-}Im^+\text{-}(CH_2)_n\text{-}Im^+\text{-}Alk]\ 2Br^-$

Scheme. General approaches to development of highly efficient oxidative-nucleophilic systems

A radically different approach to the development of a wide diversity of (oxidative-nucleophilic) systems for decomposition of ecotoxicants is based on careful investigation of compounds with reactive counter-ion dibromobromate $[Br\text{-}Br\text{-}Br]^-$, both in water and micellar solutions. Peculiarity of such surfactants lies in the fact that they can simultaneously serve as the sources both the nucleophilic (BrO^-) and oxidizing (HOBr) species, thus providing the advantages of organized nanosystems. The step of nucleophilic decomposition of NPDEPN can be significantly accelerated with $\tau_{1/2}$ for (II) reduced to ~20 s.

And, finally, the functionalized nano-sized assemblies show promise for the development of the systems, whose efficiency – similarly to enzyme analogues – is several orders higher ($\tau_{1/2}$ (III) ≈ 4 s) than that of non-functionalised counterparts.

The use of the approaches under consideration could provide high decomposition rates of low-reactive electrophilic substrates under mild conditions (temperature, pH, low concentrations).

Lanthanum-based conversion coatings on zinc-plated surface

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The corrosion resistance of galvanic zinc protective coatings can be improved by using chromate treatment processes. The resulting conversion chromate films inhibit corrosion processes on the surfaces of these metals and, in addition, have the ability of self-recovering after mechanical damage of the film.

Chromate solutions, such as the chromate coatings per se, are highly toxic due to the presence of hexavalent chromium ions. For this reason, their use is limited or completely prohibited by the appropriate regulations in the European Union and the Eurasian Economic Union countries, as well as South Korea, China, and other countries (Directives 2000/53/EC, RoHS and WEEE).

A series of technologies is described in the literature that apply chromium-free functional coatings, however, the composition of solutions and process parameters are not disclosed by the authors. A possible alternative to chromate treatment can be passivation processes in cerium and lanthanum-containing solutions [1–7]. There are some published research articles describing such coatings, but the composition of solutions and the operation parameters are also not given.

Thus, the present work is devoted to the development of the processes for the deposition of lanthanum-containing coatings as an improved alternative to the chromate treatment.

Taking into account the available literature information, solutions were prepared starting from the nitrate salt of cerium [$La(NO_3)_3 \cdot 6H_2O$] and hydrogen peroxide (H_2O_2) as an oxidant.

The experiments carried out made it possible to determine the optimum concentration range of the solution components in which cerium-containing coatings were formed. It was established that the concentration range of 9–15 g/l of lanthanum nitrate and 10–20 ml/l of hydrogen peroxide in the solution provided formation of homogeneous continuous coatings on the galvanized surfaces with a protective capacity of 60–70 sec.

Experiments revealed that at the solution temperature of less than 35°C, unsatisfactory coatings with low protective ability were formed, while the solution temperature above 50°C resulted in nonuniform coatings with deteriorated appearance and reduced protective ability. Taking into account these results, a range of solution temperatures of 35–50°C was found to be optimal. It was revealed that the coating formation at the temperature of 50°C and the pH value of 1.8–3.5 was completed within 120 sec, while the protective ability of coatings during this time reached the maximum and then almost did not change.

The coating thickness was determined by ellipsometric method. It was found that the thickness of coatings increased during first two min followed by stabilization at 135 nm.

It was shown that the protective ability and appearance of conversion lanthanum-containing coatings did not depend on the nature of the zinc substrate. Coatings formed on zinc precipitated from acidic, weakly acidic or alkaline electrolytes were characterized by approximately the same protective capacity. In order to explore the possibility of operating coatings under high-temperature conditions (thermal shock), the samples were heated for 1 h at the temperature of 160°C. It was found that the protective ability of lanthanum-containing coatings after thermal shock did not change, while the protective ability of chromate coatings, as expected, decreased to 12 sec.

Corrosion tests (ASTM B117) of the resulting lanthanum-containing coatings in a salt fog chamber were carried out. It was established that the time before the appearance of the first white corrosion centers on lanthanum-containing coatings was 25 h, which correlated with the period of 24 h as required by the ISO 9227 standard for colorless chromate coatings.

Thus, it has been shown that the developed lanthanum-containing passivation coatings on electro-galvanized steel parts are comparable to colorless chromate coatings in terms of their corrosion resistance and protective ability.

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New approaches for comprehensive protection of skin of rescuers and firefighters from chemical and thermal damaging factors

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One of the most urgent tasks of ensuring chemical safety is the development and improvement of personal protective equipment to provide protection of the staff of chemically hazardous facilities and emergency rescue units from chemical and thermal damaging factors arising during fire extinguishing and emergency rescue operations. The present work is devoted to creating specialized materials providing protection of the human skin from r simultaneous or successive exposure to toxic chemicals of the 1st and 2nd hazard classes in a wide range of concentrations (from dozens of maximum permissible concentrations up to the concentration of saturated vapors, aerosols and liquid phase), as well as heat fluxes from burning objects with the flux densities varied in the range from 5 to 40 kW/m^2.

We have shown a possibility of providing specialized protection for rescuers and firefighters, as well as the personnel of emergency rescue services by using individual protection equipment of both filtering and insulating types on the basis of materials and packages of materials with a complex layered structure, with heat-reflecting, thermo- and fire-resistant components on the external side of the package or a single package, and barrier impermeable or membrane vapor-permeable inner layers, heat-insulating and absorbing components in the depths of the packages. Options of the layered materials were obtained using different technologies in the form of prototypes, experimental and serial samples.

Using our own industrial base and production facilities of related companies combined with the application of innovative approaches and technologies, we have developed and created high-performance reliable protective clothing in the form of coveralls and filter-type suits, insulation-type suits and spacesuits that can provide protection for users in various emergency situations at chemical hazardous facilities.

Several modifications of filter-type protective suits have been designed to protect rescuers and firefighters against vapors and aerosols of toxic substances, provide wind and moisture protection, as well as protection against thermal damaging factors. The main characteristics of these suits are as follows:

- weight of the suits 2.5–3.0 kg;

- time of protective action of the material package against vapors of aerosols and chemicals of the 1st and 2nd hazard classes at concentrations in the range of 10–100 MPC – at least 6 h;
- protection ratio – 1 ... 3;
- resistance to open flame – at least 5 s;
- resistance to heat flux of 14 kW/m^2 – not less than 180 s,
- thermal protection at heat flux of 5 kW/m^2 – not less than 30 s;
- water resistance – at least 1 m of water depth.

In cooperation with one of the leading manufacturers in this field – the Special Equipment Factory JSC "PTS" (Russia), we have developed various versions of personal protective equipment of the insulating type with increased tightness made of new layered polymer fabric materials with barrier layers, as well as other protective suits of different types and levels of protection. The "PTS" factory has also produced a whole line of aggressiveproof fire- and heat-resistant, and heat-reflecting protective clothing made of laminated polymer fabric materials developed by our team.

The main characteristics of the developed products are as follows: weight of upper overalls varies between 4.0 and 7.0 kg; time of protective action against vapors and aerosols of chemicals of the 1st and 2nd hazard classes – at least 4 h; stability and thermal protection against heat fluxes with density of 5–14 kW/m^2 at thermal exposures of 60–180 s depending on purpose, heat resistance of some products – up to 40 kW/m^2.

Transfer of green technologies for producing NO_2 into small-volume industry

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Nitric oxide is a useful reagent widely applied in organic and inorganic synthesis [1], i.e. in reactions of oxidation, nitration, Kyodai-nitration, synthesis of anhydrous nitrates of metals, smokeless powder, nitrosyl sulfuric acid, glucuronic acid, etc. Existing methods for the synthesis of NO_2 are laborious, in some cases they use hardly accessible reagents and produce a lot of waste.

We have developed a new approach to obtain NO_2 based on the reaction:

$$CH_3COOH + 6\ HNO_3 = 6\ NO_2 + 5\ H_2O + CO + CO_2$$

using available reagents which allows regeneration of the utilized solvent (sulfuric acid). Following the developed synthetic scheme (Fig. 1), dry liquid or gaseous NO_2 of high quality can be produced.

The method can be applied for a large scale synthesis (up to 1.5 kg of NO_2 can be obtained using the laboratory glassware equipment).

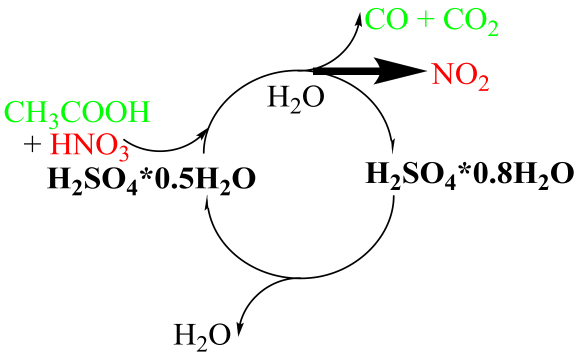

Fig. 1. Cycle of production of NO_2

Fig. 2. Generator of NO_2

Moreover, this reaction has been implemented for the industrial purposes: we designed a new chemical apparatus - generator of NO_2 with the productive capacity 1 kg/h (Fig. 2). This generator (20 foots containership MSUU 3410046) was successfully delivered to Saudi Arabia from the territory of the Republic of Belarus in transit through Lithuania and Germany.

In addition, we have designed a factory where NO_2 can be produced with the productive capacity of 5 kg/h.

The green technological method for producing NO_2 is environmentally friendly compared to the traditionally used electrochemical methods, and such generators can help to solve the OSCE (Organization for Security and Co-operation in Europe) problem associated with the need to utilize a large tonnage of produced NO_2. This device is a promising example of transferring laboratory technology to the small-capacity industry to solve the problem of time-efficient production of high-quality NO_2 without need to store large stocks of the product.

The method of producing NO_2 is an object of intellectual property (Eurasian patent No. 033307) [2].

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Investigation of benzene and chlorobenzene chlorination process in order to obtain *para*-dichlorobenzene

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The creation of modern aerospace and other special equipment, as well as microelectronic products is impossible without the use of heat-resistant polymers and the appropriate polymer composite materials. One of the most important heat-resistant specialty polymers is polyphenylene sulfide (PPS). The direct preparation of PPS is typically carried out by the interaction of *para*-dichlorobenzene (*p*-DCB) with sodium sulfide in a solvent medium. Thus, the organization of industrial production of PFC requires its provision with *p*-DCB.

It's important to emphasize that *p*-DCB is not industrially produced in Russia as an independent product.

In this regard, it has become necessary to obtain reliable research data on the parameters of the chlorination of benzene and chlorobenzene with the predominant production of *p*-DCB, as well as to lay the foundations for development and implementation of the process of separating *p*-DCB from the reaction mixture.

The main method for producing DCB is chlorination of chlorobenzene (or benzene) with gaseous chlorine in the presence of a catalyst [1] (equations 1–4):

$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$ (1)
$C_6H_5Cl + Cl_2 \rightarrow$ p-C6H4Cl_2 + HCl (2)
$C_6H_5Cl + Cl_2 \rightarrow$ o- $C_6H_4Cl_2 + HCl$ (3)
$C_6H_5Cl + Cl_2 \rightarrow$ m- $C_6H_4Cl_2 + HCl$ (4)
$C_6H_4Cl_2 + Cl_2 \rightarrow C_6H_3Cl_3 + HCl$ (5)

Chlorobenzene is formed at the first step (equation 1). When the benzene conversion reaches 20%, chlorobenzene begins to react with chlorine gas to form a mixture of *ortho*-, *meta*-, and *para*-DCB, as well as trichlorobenzenes (equations 2–5). The rate of DCB formation varies depending on the concentration of chlorobenzene in the reaction solution. As it increases, so does the rate of reactions for the formation of DCB isomers. During the formation of DCB, *para*- and *ortho*-isomers prevail, the ratio of which can be regulated by various technological methods.

An important practical task of this study was to increase the yield of the target product (*p*-DCB) and suppress the side reactions of deep chlorination.

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Analysis and assessing feasibility to produce detonation carbon structures

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At present, the military bases and arsenals of the Russian Federation Ministry of Defense are packed with hundreds of ammunition, having the last limitation storage term, while using them in fixed direction may result in a great risk of unplanned exploding. Storing the obsolete technical equipment and ammunition demands both the significant budget costs, and a great number of staff, and most importantly, increases social tension in the places of storing and exposes the people’s life and health to risk. All this stuff indisputably necessitates its neutralization [1, 2].

However, utilization of the explosives and ammunition is a complex technical and economic problem, it requires a comprehensive solution to many issues, the main of which are the tasks of creating safe, environmentally friendly and economically sound technologies for the extraction of explosives (explosives) from ammunition and their recycling.

The easiest way is to destroy the unrequired ammunition on special landfills undermining, but the most advisable and more environmentally friendly and economically safe solution is to dispose of them with the maximum use of their constituent components - stored explosives.

The most progressive direction of their subsequent use is obtaining detonation mixture containing carbon nanostructured objects. The priority is to find the most rational technical appearance of promising facilities for the synthesis of detonation nanostructures, development key technologies for the preparation of explosives and purification of the resulting product, as well as studying feasibility of implementing a system for the integrated disposal of ammunition with obtaining nanostructured materials of energy-intensive synthesis, technologies and materials.

In this work, scientific and technical studies on the properties of carbon nanostructures and the processes of their formation have been performed. The main trends and specific features of the related technology creation have been determined for obtaining nanostructured objects with focus on the improvement of physicochemical properties of promising composite materials and coatings on their basis. The optimal initial conditions and the vector of further research are selected.

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Electrically conductive composites with segregated structure based on various polymers and reduced graphene oxide

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At present, the production of polymer composite materials with a segregated structure (uneven distribution of the electrically conductive filler) is one of the most promising methods for producing electrically conductive polymer composites. The interest in composites with a segregated structure is due to the possibility of achieving high values of electrical conductivity with a sufficiently low loading of an electrically conductive filler. A special attention is paid to composites with graphene or graphene-like materials used as an electrically conductive filler. Firstly, this is due to the fact that graphene has unique mechanical and electrophysical properties. Secondly, its precursor, graphene oxide (GO) is transformed from dielectric into conductive material containing graphene with a large number of structural defects and residues of oxygen-bearing groups.

In this work, we studied the effect of the polymer matrix on the electrically conductive and mechanical properties of such composites. Composites were obtained by applying GO from water-alcohol dispersion onto the surface of particles of a polymer matrix powder, followed by removal of the liquid phase and GO reduction with hydrazine vapors at 100°C, and hot pressed. Polyvinyl chloride (PVC), poly(vinylidene fluoride-co-tetrafluoroethylene) (P(VDF-TFE)) and ultra-high molecular weight polyethylene (UHMWPE) were used as polymer matrices.

It was shown that in the case of using the non-polar UHMWPE matrix, the composition electrical conductivity was significantly lower than that based on polar PVC and P(VDF-TFE) at the same filler level. However, regardless of the matrix used, the proposed approach provided an increase in conductivity by more than 8 orders of magnitude compared to that of pure polymer, at the filler level of only 0.25 vol.%. It was found that even 1 wt.% of the filler content had a critical impact on the glassy polymer matrix of PVC resulting in the yield strength decrease by 77% compared to pure polymer, and the elastic modulus decrease from 17 to 5.7%. A reinforcing effect was observed with P(VDF-TFE) matrix, since the filler content of 1 wt.% led to an increase in the elastic modulus by 17%. The mechanical properties of the segregated structure composites based on UHMWPE changed insignificantly throughout the entire filler content range. The method for preparation of electrically conductive composites with a segregated structure is universal and can be used for a wide range of different polymers. This work extends the understanding of the possibilities of using such materials for applying in chemical safety field and industry for the removal of electrostatic electricity as well as in production of non-metallic microelectronic devices.

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Methodological approaches to assess hazard for public health and environment of chemicals and their mixtures handling on the territory of the Russian Federation

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Chemicals of different applications and origin handling on the territory of the Russian Federation can be hazardous for public health and environment due to their physicochemical and toxicological properties. Currently, there is lack of regulatory documents in the country that can reliably assess the hazard of these substances for public health and environment. Existing regulatory documentation needs to be revised for the purpose of harmonization of laws and regulations of the Russian Federation with the European Union guideline regulatory document in this field “Globally Harmonized System of Classification and Labeling of Chemicals (GHS) [1].

In this regard, it is important to create and implement a set of methods based on risk management mechanism in the production of chemicals:

- methodology for assessing chemicals handling on the territory of the Russian Federation for their hazard for population and environment (hereinafter - Method 1);
- methodology for assessing chemical mixtures handling on the territory of the RF for their hazard for population and environment (Method 2);
- methodology for assessing risk of multi-media exposure to chemicals and their dose loadings (Method 3).

Method 1 is based on an integrated approach involving identification and classification of the hazardous chemicals using new models and tools for analyzing the risk of chemical exposure for public health and environment. The identification of chemical substances (CS) is currently carried out in accordance with GOST 12.1.007-76 [2]. This document is a part of the national system of occupational safety standards and is applied only to the air of the working area. It does not take into account physicochemical and full toxicological properties of CS that are hazardous for the environment. Hazard identification is the first step in the risk assessment procedure which has a screening character and provides identification priorities for studying CS, their spreading in the environment and routes of entering human body.

Raw materials and finished chemical products handling on the territory of the country, as a rule, are multicomponent chemical mixtures. Identification of chemical products is carried out in accordance with GOST R 57443-2017 [3]. Classification of chemical products by their effects on human body and environment is carried out in accordance with the state standards [4–7] and has some limitations. The main difficulty in assessing hazards of multicomponent mixtures is the lack of necessary information on the nature of the combined effects of the ingredients. Therefore, Method 2 should be focused at assessing the chemical hazard of multicomponent mixtures, basing on physicochemical and toxicological properties of their components. Method 2 includes mathematical modeling for predicting relevant properties which are not available from literature and databases.

Method 3 includes mathematical models of migration, transformation, selective bioaccumulation of CS, etc. in the environment, estimates the doses of CS that affect human health (dose loadings), methods for determining the total doses and the risk of exposure to CS. Method 3 takes into account the physicochemical properties of CS with the possibility of the formation of toxic degradation products, which determines the ability of CS to be transported from one component to another, transformed, and spread over significant distances considering different routes of exposure: inhalation, oral or epidermal. This step is called “exposure assessment” and represents one of the most important steps of the risk study. Assessment of the dose-effect relationship establishes a relationship between the acting dose of CS and the cases of harmful effects on the exposed population based on a priori data. It takes into account the ability of CS to be redistributed between environmental components (air, water, soil), transform, form toxic degradation products having negative impact on human health along with various routes of exposure.

The final step of calculating the total risk value is the final part of the risk analysis and the initial phase of risk management. At this step all the data obtained in the previous steps are integrated, an assessment of the magnitude of the risk and analysis of the data reliability degree are carried out.

Thus, the developed methodological approaches implemented in information-analytical system for risk assessment, will allow the identification and hazard assessment of CS and their mixtures, simulate the behavior of CS in various environmental components, and provide quantitative assessment of risks to public health and environment.

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Training complex for personnel aimed at providing safe operation of potentially hazardous production facilities

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Hazardous production facilities (HPF) are classified as having high or extremely high hazard in terms of risk, thus, an industrial safety management system (ISMS) is required to be developed and implemented [1]. This system is a set of interrelated organizational and technical measures carried out by an organization in order to prevent accidents/incidents at the HPF, and to localize and eliminate the consequences of such accidents. ISMS should provide identification, analysis and forecasting of accident risks along with planning and implementation of measures reducing the risk of accidents at HPF.

Modern chemical production with high-tech equipment requires high professional skills of personnel of the hazardous production facilities providing safe and trouble-free operation of chemical-technological production, including knowledge of the requirements of the main regulatory documents [2–5]. In accordance with the requirements of [6, 7], the safety management system is meant to use various technical tools (simulators, training grounds, etc.). One of the most effective methods for improving personnel skills is the development of training complexes using computer simulation, which allows organizing training and practicing the necessary actions imitating possible emergency situations that may arise during the operation of HPF.

A training complex has been developed at Federal State Unitary Enterprise "State Research Institute of Organic Chemistry and Technology", intended for improving skills of personnel operating at HPF, including those using chemicals from lists 1–3 of the chemicals appendix to the Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on their destruction. The complex is based on specialized computer simulators (SCS) with the software capable to simulate chemical technological processes that are operated on real-life HPF. The developed approach and the proposed methodology make it possible:

- to develop structural mnemonic diagrams of HPF technological processes;
- describe the physicochemical basis of technological processes;
- identify with the help of structural logic diagrams the key characteristics of chemical technological processes as objects of control and the ability to control and manage them;
- create databases on chemical technological equipment; hazardous substances and their properties; possible emergency situations and scenarios of their development; forces and means for their localization and liquidation, etc.;
- create educational tasks using the existing capabilities of the developed

special software;

- manage the developed models of chemical technological equipment using interactive computer models based on the developed mimic diagrams in order to develop skills for identifying and eliminating malfunctions, incidents and necessary actions in the implementation of possible emergency situations.

In addition to the general functionality, SCS provide mathematical modeling of technological processes, including workflows of flammable and combustible liquids, explosive and flammable substances, vapor-gas media, finely divided solid products, separation and mass transfer processes, mixing, grinding, packaging processes, heat transfer processes, chemical processes.

The main elements of the structure of the SCS are the automated workplace of the trainer (an instructing person) and instructed managers, specialists and employees of HPF. The most effective are interactive simulators, reflecting a virtual copy of the workplace with an adequate way of functioning of the equipment, simulating the flow of basic processes and possible deviations, leading to emergency situations. The input data for launching the interactive model are: type of production; type of task (training or control event); instrumentation of chemical process; type of malfunctions, incidents or possible emergency situations in order to work out the necessary decisions.

The development of the training complex is expected to reduce the probability of emergencies arising from improper handling of hazardous substances and technological equipment, to increase the level of personnel readiness for emergency situations minimizing negative impact on the environment and human health.

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Hazard analysis of modern construction and finishing materials

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The air environment of modern workrooms has a multi-component chemical composition that depends on the degree of atmospheric air pollution as well as the level of internal sources of pollution, which primarily include products of polymer degradation materials that are components of finishing and construction materials.

The quality of the air environment of working premises is very important for working personnel who spend in such a rooms all the working day, thus, it can affect their well-being, performance and health, even at relatively low concentrations of a large number of different substances. In addition, such substances do not affect the human body independently, but in combination with a variety of factors: temperature, humidity, electromagnetic fields, etc. If a combined effect of these factors comes into contradiction with the hygienic requirements, the internal environment of working premises may become one of the significant risk factors for professionally caused diseases.

Numerous studies have shown that polymer materials, wood chipboard based on phenol-formaldehyde and urea-formaldehyde, fiberglass, paint coatings, etc. play an important role in the formation of working rooms’ air environment. Construction and finishing materials are sources of migration into the air of various hazardous chemicals that have a harmful effect on human health: phenol, formaldehyde, ammonia, styrene, isoprene, sulfur dioxide, toluene, butanol, and others [1].

Development of the production and application of composite wood materials (CWD) - plywood, wood chipboard (WCB), oriented strand-board (OSB) and wood-fibre board (WFB), based on urea, melamine and phenol formaldehyde resins, in civil and industrial construction, construction of transport facilities (aviation, railway, marine, etc.) and manufacture of furniture, put forward increased safety requirements for the air environment pollution of working rooms with formaldehyde, methanol, phenol and ammonia.

Currently, more than 80 substances have been identified in indoor air that differ in their hazard to humans, the level of recorded concentrations and the frequency of their presence in idoor air. Among these, 26 compounds are identified as the most significant hazardous volatile chemicals. The migration of these substances from furniture finishing materials into the air of working rooms should not exceed the permissible levels listed in the Technical Regulation "On Safety of Furniture Products" [2].

Prolonged staying of employees during the working day (6–8 h) in the workrooms with high content of a combination of hazardous chemicals in the air can cause an increase in the level of occupational diseases. The key point in assessing occupational risk is to establish a relationship between exposure to a risk factor (a hazardous chemical substance that has entered the body) and its impact on the health of the employee. Quantitative assessment of such effects can be made using toxico-kinetic models that allow calculating the content of hazardous chemical substances in the body of workers at any time with possible repeated inhalation effects [3].

For these purposes, the InhTox software package has been developed, which includes a database of hazardous chemicals and analytical subsystem. The software package allows to simulate the toxicokinetics of a hazardous chemical substances with daily repeated inhalation exposures and calculate the risk assessment of possible inhalation injuries of personnel of chemical objects.

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Sorption recovery of arsenic by industrial inorganic sorbents when cleaning solution of copper electrolyte

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Recovery of arsenic from spent copper electrolyte solutions purified from copper is a relevant issue. As a rule, the spent sulfate solution of the copper electrolyte obtained after the electrolytic separation of copper contains 5–15 g/l As in the form of arsenite and arsenate ions. At the first step of the purification, arsenic is usually separated by the reagent method; the residual concentration of arsenic in this case usually exceeds the Maximum Permissible Concentration (MPC = 0.05 mg/l). Consequently, it would be advisable to carry out post-treatment of solutions from this impurity to the MPC level by sorption method to address the issue of arsenic recovery.

At present, inorganic sorbents are widely used to purify drinking water and some technological solutions with a low arsenic content. The area of their use is limited to a pH range of 4–9 and low salt concentrations. However, their advantage is low cost as compared to ion-exchange resins. A technology is known using granular titanium phosphate for this purpose (with molar ratio P(V) : Ti(IV) = 0.7–1.4), where sorbent regeneration is carried out by means of sulfuric acid solution at elevated temperature [1]. An alternative procedure is described [2], where As is extracted using heat-treated brucite, while the authors of the other approach [3] have extracted As by sorption on titanium dioxide. Another approach [4] uses the non-regenerable fibrous sorbent PANION 140 (containing FeOOH nanoparticles in a polyacrylonitrile fiber matrix) for this purpose. A variety of inorganic sorbents offered by world leading manufacturers are characterized by the use of iron(III) hydroxide in the form of granules with a developed surface area. The available sorbent grades include Byoxide E33, FerrIX™ A33E, EVERZIT As, AdsorpAs®); regenerated sorbents contain iron(III) hydroxide immobilized in a polymer matrix (Putofine PFA 300E, FO36 hybrid sorbents). The extraction of arsenic using iron(III) hydroxide predominantly proceeds by the chemisorption mechanism [5].

In this work, we have studied the sorption extraction of arsenic from an industrial solution of spent copper electrolyte with As content of 9.55 g/l, after its purification by precipitation of arsenic with lime milk in the presence of additives. The solution used contained 13–15 g/l of $(NH_4)_2SO_4$ along with the following impurities (mg/l): Fe 0.8–1.0, Ni 0.3–0.4, Cu 2.8–3.5, As 0.4–1.0; the pH of the solution was 6.98. Inorganic sorbents Byoxide E33, EVERZIT As, and FO36 were used. It was been established that the sorbent Byoxide E33 had the best characteristics for the extraction of As. Its arsenic capacity varied in the range of 17–40 mg As/kg for the ratios solution volume : sorbent weight = 50–150 ml/g. The residual concentrations of As and Cu, Ni, Fe impurities in the purified solution were less than the corresponding MPC values. The consumption of Byoxide E33 sorbent was 1.7 kg at an initial concentration of As in the solution of 0.5 mg/l (0.5 g/m^3) after filtering the solution through a fixed bed of sorbent to clean the solution with a volume of 1 m^3 to the MPC. It is noteworthy that the physicochemical properties of the applied sorbents make it possible to use them in standard sorption filters with a fixed bed of sorbent.

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Production and use of highly hazardous pesticides in Russia and some countries in Eastern Europe, Caucasus and Central Asia: trends and perspectives for transition to safe alternatives

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The global community is increasingly aware of the risks to human health and the environment posed by use of highly hazardous pesticides (HHPs), the effects of which can undermine human health and affect future generations. HHP poisoning ranges from seemingly mild symptoms to much more severe, which can lead to chronic disability or death.

The first comprehensive study on the production and use of HHPs in Armenia, Kazakhstan, Russia, Ukraine and Uzbekistan has shown an alarming trend in increasing use of these highly hazardous chemicals.

Russia. At the beginning of 2020, the State Catalogue of Pesticides and Agrochemicals Allowed for Use in the Territory of the Russian Federation contained 652 pesticide formulations (individual and mixed by active ingredient) [1]. This is considerably more than had been allowed for use in previous years. At the same time, it is emphasized that 106 pesticides (by active ingredients) used in Russia are included in the list of highly hazardous pesticides according to the Pesticide Action Network (PAN) criteria [2]. Of these, 38 HHPs have not been registered or are banned in different countries [3]. Besides, it is noted that the long-term use of HHP in Russia has led to the contamination of agricultural land and forests with harmful substances. Ensuring environmental safety is complicated by the lack of effective state supervision over the safe handling of pesticides and agrochemicals in agricultural production.

Armenia. More than 60% of pesticides permitted by Armenian legislation belong to HHPs. One third of them are classified by WHO and the International Agency for Research on Cancer as carcinogens or possible carcinogens. This is alarming information within a context of increased cancer diseases and related mortality in Armenia. Most of imported pesticides come from China and India and the quantity is increasing annually.

Kazakhstan. As of March 2019, 1021 pesticide trade names have been registered and are in use in Kazakhstan, of which 386 (38% of the total) contain one or more active ingredients from the HHP list, herewith 25 compounds (20%

of the total) of the 74 active ingredients from the HHPs are banned in other countries but continue to be used in Kazakhstan.

Uzbekistan. The use of 59 HHPs is permitted in Uzbekistan, 34 of which are banned in other countries, but continue to be used in Uzbekistan.

Ukraine. The analysis showed that as at December 2019 [4] about one third (1,125 formulations) of pesticides and agrochemicals allowed to use in Ukraine contain 1–3 active ingredients from the HHP list. The total number of the active ingredients belonging to HHP in preparative forms of pesticides and agrochemicals is 83, 41 of which are already prohibited in other countries, but continue to be used in Ukraine.

These studies have resulted in recommendations to reduce and eventually eliminate HHPs in Eastern Europe, the Caucasus and Central Asia. Information on safe substitution of HHPs, including the use of ecosystem-based approach and traditional knowledge in agriculture will contribute pesticide-free initiatives in these countries. Parties to the Stockholm Convention on persistent organic pollutants, for example, have banned endosulfan, one of the HHPs, replacing it with safe alternatives and an ecosystem-based approach to agricultural pest management [5]. Another example is the initiatives of many countries to eliminate the use of glyphosphate [6], which has a potential to cause adverse health effects. Lessons learned from this process could be collected by the regional focal points of the Stockholm Convention on persistent organic pollutants and then shared with the national authorities to facilitate the switch from HHPs to safer alternatives.

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Using SERS sensors in various schemes of immunochemical analysis

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Identification of various classes of chemicals and mixtures in environmental objects is an urgent task of modern analytical chemistry. The use of standard analytical methods based on the chromatographic separation of chemical compounds, followed by determination of the separated components by spectral detectors (mass, IR, atomic emission spectrometers), is one of the most reliable ways to solve it. An alternative identification approach is based on methods that use selective procedures with respect to the substance being determined. Immunochemical analysis (ICA) plays a special role here. The advances of modern immunology allow to produce antibodies to a wide range of substances (pesticides, drugs, etc.) [1]. So, ICA is very attractive tool for solution of many analytical problems and now it is widely used in various fields of chemistry, biology and medicine [2].

It is often necessary to obtain analytical results directly at the sampling site, i.e. *in situ*. In this regard, various ICA variants have been developed, among which the use of SERS (Surface-enhanced Raman spectroscopy) sensors which occupies a special place. The use of immunoreagents with well-recognized SERS spectra markers provides high reliability of identification of the obtained immune complexes, and the developed portable SERS spectrometers make it possible to use highly sensitive ICA in the field conditions. The SERS sensor is usually a silicon wafer with a plasmonic material immobilized on its surface. In most cases, such surface is formed using silver or gold nanoparticles [3] obtained by physical or chemical methods [4].

For this study, a technology for the production of SERS sensors by the chemical method has been developed. It includes the modification of silicon wafers, the synthesis of a silver sol and immobilization of the nanoparticles on the prepared substrate. Thus obtained SERS sensors showed good reproducibility of the results and promise for their use in quantitative analysis [5]. In modern ICA, three main groups of solid-phase methods for antigen determination can be distinguished: direct, sandwich and several modifications of competitive method [6].

In the direct method, the desired antigen is adsorbed onto the surface of the substrate, unoccupied areas are blocked by a neutral protein, the so-called blocking agent, then antigen-specific antibodies are added and an immunochemical reaction is carried out. After washing unbound components, “Antigen-Antibody” (Ag-Ab) complexes are detected due to the presence of a marker in antibodies, in our case, TRITC (tetramethylrodamine isothiocyanate) acted as such. The signal intensity is directly proportional to the amount of antigen in the analyte.

In the sandwich method, binding antibodies, that capture the antigen from the analyte, are adsorbed onto the substrate then labeled antibodies are added. After washing the unbound components the immune complexes are detected. Again, the signal intensity is directly proportional to the amount of antigen in the analyte.

In the competitive method, binding antibodies are adsorbed onto a substrate, similar to that of the sandwich method. After blocking of the nonspecific adsorption sites, antibodies interact with the antigen in the analyte followed by washing, then, the substrate is immersed in the solution of labeled antigen. After washing unbound components, Ag-Ab complexes are detected. In this case the signal intensity will be inversely proportional to the concentration of antigen in the analyte. This type of immune analysis is the most suitable for the determination of low molecular weight antigens.

To study the possibility of using the obtained SERS sensors in each of the described methods, we used as an antigen phytohemagglutinin of *Phaseolus vulgaris* beans (PHA), which was applied to the experimental zone. To detect the Ag-Ab complex labeled with TRITC, antibodies to PHA were used at a concentration of $1.7 \cdot 10^{-6}$ M. In blank experiments labeled antibodies were applied to both regions of the substrate in the absence of antigen. The results are presented in the table.

Table. Application data for SERS sensors in various ICA schemes

№	Method	Concentration PHA, M	Iexp*, units	Icon*, units	I exp/I con
1	Direct	$1.5 \cdot 10^{-7}$	700	500	1.4
2	Direct (blank)	0	500	500	1
3	Sandwich	$1.5 \cdot 10^{-7}$	2000	1100	1.8
4	Sandwich (blank)	0	1000	1100	0.9
5	Competitive	$1.5 \cdot 10^{-7}$	300	600	0.5
6	Competitive (blank)	0	700	800	0.88

*Iexp, Icon – SERS signal intensivity of experimental and control zones, respectively

The data presented show the reliable positive signal differences between the experimental and control zones for direct and sandwich schemes. At the same time, there is the reliable negative signal difference between experimental and control zones for the competitive scheme. These results indicate that proposed method for creating a plasmon surface provides perspective SERS sensors that can be used in various immune analysis schemes.

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Monitoring of hazardous chemicals in atmospheric air by equilibrium steam analysis

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The state of atmospheric air at industrial facilities is strictly regulated. Currently, Russia has hygienic standards for maximum permissible concentration (MPC) of harmful substances in the air of the working zone [1], which regulate maximum occasional and average daily concentrations of harmful impurities in the atmospheric air. They are used to prevent the accumulated effects of harmful substances on the human body, prevention of chronic intoxication, and development of dangerous diseases leading to death.

However, relatively few maximum permissible concentrations of hazardous substances have been established for soils, unlike the atmosphere and the hydrosphere. Depending on the direction of mutual transitions of harmful substances from soil into other natural environments, four types of maximum permissible concentrations for harmful substances in soil are determined. The transition of chemicals from soil into the atmosphere is characterized by migration air hazard indicator ($K_{\text{migration soil-air}}$) [2]. The study of volatile components of petroleum products contained in soils can provide data on stable characteristics of the long-term state of the atmosphere, and should be carried out along with direct measurements of concentrations of harmful substances in the air of the working zone.

Studying volatile components of petroleum products found in soils requires specific analysis methods. One of the effective techniques is the analysis of equilibrium steam (vapor phase analysis). This work is devoted to the study of the composition of the vapor phase, which is in dynamic equilibrium with the soil and is regulated by the dynamics of the flow of volatile components from the liquid phase of the soil to the equilibrium vapor. For this purpose, the inverse form of the distribution coefficient used in vapor-phase analysis is used [3]:

(1)

where $K_{distributionG/L}$ is the inverse value of the coefficient of distribution of components between the liquid and vapor phases,

C_L – concentration of the component in the liquid phase,

C_G – concentration of the component in the vapor phase.

Quantitative values of the distribution coefficient between the vapor and liquid phases were obtained by analyzing the equilibrium vapor on the example of artificial mixtures of hydrocarbons and a set of non-hydrocarbon components. Two mixtures of components were made up. The first mixture contained alkane, cycloalkane and aromatic hydrocarbons. The second one – additionally to the hydrocarbons, contained acetone, butanol-1, and butyl acetate. The composition of the liquid phase of these mixtures, as well as the composition of the equilibrium vapor obtained at different degassing temperatures, was studied by capillary gas-liquid chromatography.

It was found that the values of the distribution coefficients of the hydrocarbons' mixture generally decrease with an increase in the boiling point of the components. At the same time, comparing the values of the distribution coefficients for components with similar boiling points, it can be noted that relatively high values of the distribution coefficients are fixed for cycloalkane and aromatic hydrocarbons in comparison with aliphatic hydrocarbons. Thus, relatively high values of distribution coefficients have been recorded for benzene, cyclohexane, toluene, and *o*-xylene. This is especially noticeable when conducting vapor-phase analysis at 100°C. The results indicate that the distribution of components between the vapor and liquid phases is influenced not only by the boiling points, but also by the chemical structure of the components.

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Utilization of toxic organic pollutants of water resources using oxidoreductases immobilized on biopolymers

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Phenol and its derivatives are extremely toxic water pollutants that can cause disorders of the central nervous system, eye mucous membranes, respiratory tract, skin, and exhibit a carcinogenic activity [1]. The most effective methods for phenol utilization can be classified mainly in two categories: destructive (thermal oxidation, electrical oxidation, hydrolysis, and chemical oxidation) [2] and regeneration techniques (extraction purification, distillation, rectification, adsorption, ion exchange purification, reverse osmosis, ultrafiltration, etherification, polymerization, polycondensation, biological purification and conversion of phenols into low-soluble substrates) [3]. In spite of the wide range of the existing phenol utilization methods, most of them do not provide full removal of contaminants from the water and require significant costs for the organization of purification processes.

Horseradish peroxidase (C.E. 1.11.1.7) is an enzyme extracted from the root *Armoracia rusticana*. This enzyme can oxidize organic compounds by the hydrogen peroxide generating free radicals which further oligomerize to the insoluble quinones [4]. To decrease the process cost and avoid the use of high amount of peroxidase, another oxidoreductase enzyme – glucose oxidase (C.E. 1.1.3.4) can be used [5].

To obtain the peroxidase extract, 5 g of *Armoracia rusticana* root was ground and mixed with 50 mL of phosphate buffer solution (pH = 7.0) and stirred continuously for 1 h. Then, the mixture was centrifuged at 5000 rpm for 20 minutes and filtered using a microporous filter. The centrifugate was stored in a refrigerator at a temperature of 3 ± 1°C.

Microspheres from sodium alginate were synthesized for enzyme immobilization. The synthesis was performed as follows: 10 mL of 1.5 wt. % sodium alginate solution was dropped into the 100 mL of 1.5 wt. % calcium chloride solution. The microspheres with a diameter of 2–2.5 mm were obtained. The microspheres were withstood in the solution for 2 min and, then, were washed with distilled water.

For enzyme immobilization, the alginate microspheres were withstood for 12 h in 50 mL of the solution consisted of 0.394 g of carbodiimide and 0.144 g of N-hydroxysuccinimide. Then, the microspheres were washed with water, treated with the enzyme extract for 6 h and washed with water. The biocatalyst was stored in a refrigerator at a temperature of 3 ± 1 °C.

The activity of the synthesized biocatalysts was estimated in the reaction of oxidation of phenol and 4-chlorophenol in a glass batch reactor in the presence of hydrogen peroxide and 4-aminoantipyrine. The biocatalyst activity was determined by measuring changes in the absorbance at 506 nm. The absorbance was recalculated into the reaction product concentrations using the molar absorption coefficient (for phenol – 0.275 $L\cdot mmol^{-1}\cdot cm^{-1}$; for 4-chlorophenol – 0.335 $L\cdot mmol^{-1}\cdot cm^{-1}$). A linearization of the Michaelis-Menten equation in the Lainuiver-Berk coordinates ($1/V_0 - 1/C_0$) was performed basing on the product concentration dependence on time. The kinetic parameters for the enzyme extract and the synthesized biocatalyst (maximum reaction rate V_m, Michaelis constant K_M, catalyst activity) were calculated (Table 1).

Table 1. Kinetic parameters of synthesized biocatalysts

Biocatalyst	V_m, $mM\cdot s^{-1}$		K_M, mM		Activity, U/mg	
	phenol	4-chlorophenol	phenol	4-chlorophenol	phenol	4-chlorophenol
HRP	0.054	0.048	0.93	0.51	1.07	1.25
HRP-GOX	0.051	0.050	1.06	0.65	0.95	1.12
ALG-HRP	0.012	0.009	1.24	0.68	0.35	0.58
ALG-HRP-GOX	0.011	0.085	1.33	0.71	0.31	0.53

HRP – horseradish peroxidase; GOX – glucose oxidase; ALG – alginate microspheres

Thus, the results indicate that the synthesized biocatalyst can effectively oxidize phenol and 4-chlorophenol at concentration levels up to 2 mmol/L. The immobilized enzyme exhibits about 25–30% of the activity of the native enzyme. The decrease in the activity can be explained by heterogenization and mass transfer limitation for the substrate molecule access to the catalyst active sites. In spite of the activity decrease, the developed biodegradable biocatalysts can be used repeatedly with a minimal loss in the effectiveness. The experiments showed a saving of up to 75% of the initial biocatalyst activity after 10 cycles of reuse.

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QSAR analysis of toxicity of organic compounds toward *Daphnia magna*

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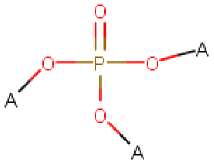
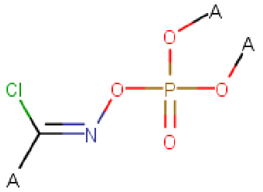
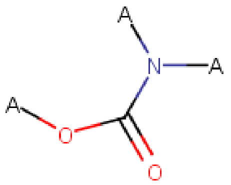
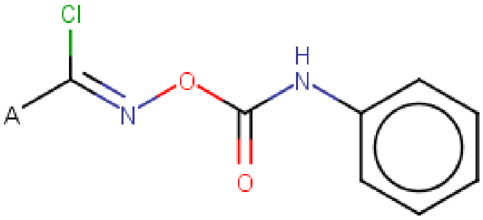
Since many organic substances used in agriculture and industry, penetrate into an aquatic medium, it is very important to estimate the ecotoxicological parameters of the existing compounds and the compounds to be developed in relation to aquatic organisms [1]. QSAR (quantitative structure – activity relationship) methods can provide significant assistance in decreasing the financial and time costs in estimating the hazard of chemicals [2]. The existing acute toxicity QSAR models for aquatic organisms comprehensively study a molecular structure using various statistical approaches. The diverse information obtained using QSAR models is of interest for researchers. However, the proposed QSAR models have limited application in some cases. For example, many QSAR models have no structural interpretation, which does not allow rational molecular design of compounds with an acceptable degree of toxicity to be performed [3, 4].

The aim of this work was to conduct QSAR analysis of the acute toxicity of organic compounds toward *Daphnia magna* at an exposure period of 24 h. The samples described in detail in [5, 6] served as initial data for constructing QSAR models.

When developing QSAR models, we used 2D simplex descriptors, the support-vector machine (SVM) and gradient boosting (GBM) methods. Adequate QSAR regression models were developed, the interpretation of which allowed us to describe quantitatively and rank well-known toxicophores and to refine their molecular environment by revealing the structure derivatives of the fragments, which significantly contribute to the acute toxicity (LC_{50}) of organic compounds toward *Daphnia magna*. Table 1 gives examples of some well-known toxicophores and their detailed molecular environment. Based on the results of interpretation of the regression models, we performed molecular design (modification) of highly toxic compounds with the aim of reducing their harmful effects.

Table 1. Summary of molecular interpretation of regression models

Known toxicophore	Structural fragments detailing the molecular environment of well-known toxicophores
 phosphate	 1-Chloroethylideneamino phosphate
 carbamate	 methylideneamino N-(3-chlorophenyl)carbamate

A is the site of attachment of a fragment to the rest of the molecule

We also developed acceptable QSAR classification models to reliably predict the manifestation of the specific or nonspecific toxicity of organic compounds toward *Daphnia magna*. The interpretation of these models made it possible to determine the structural fragments and the physicochemical characteristics of the molecules that are responsible for the manifestation of one of the mechanisms of toxic action.

The online version of the OCHEM expert system (https://ochem.eu) and the HYBOT descriptors [7] were used for a comparative QSAR investigation.

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Dusty gas movement in separating chamber of direct-flow cyclone

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The efficiency of cyclone equipment almost entirely depends on the nature of the gas movement in the separating chamber of the apparatus. Therefore, the accuracy of description of the gas phase velocity field largely determines the magnitude of error in estimating the degree of purification of dusty flows. The aim of this work was to obtain dependencies for all components of the gas velocity in the separating chamber of the direct-flow cyclone [1], the scheme of the cyclone is shown in Fig. 1.

The swirler 1 with the help of blades 2 creates a strongly twisted gas flow in the separating chamber. In this case, the dust particles, moving in a spiral, are thrown to the walls of the chamber and removed from the flow, and then through the pipe 4 - and from the apparatus. The purified gas leaves the cyclone through the outlet pipe 3.

In terms of hydrodynamics, the swirler is considered as a poorly streamlined body. As is known [2], at sufficiently high gas velocities, an intensive turbulence region (trace) with high values of transfer coefficients is formed behind such bodies. In the outer current region, outside the turbulent trace, the gas moves in a spiral, dragging the particles with it. In the track area, the longitudinal velocity profile is almost homogeneous. At relatively low dust concentrations, it is natural to assume that the presence of particles in the flow has little effect on the gas velocity field. Considering the velocity component fields to be axisymmetric and stationary, we can write the equations of motion in cylindrical coordinates as follows:

—— —— ——; (1)

—— —— ——; (2)

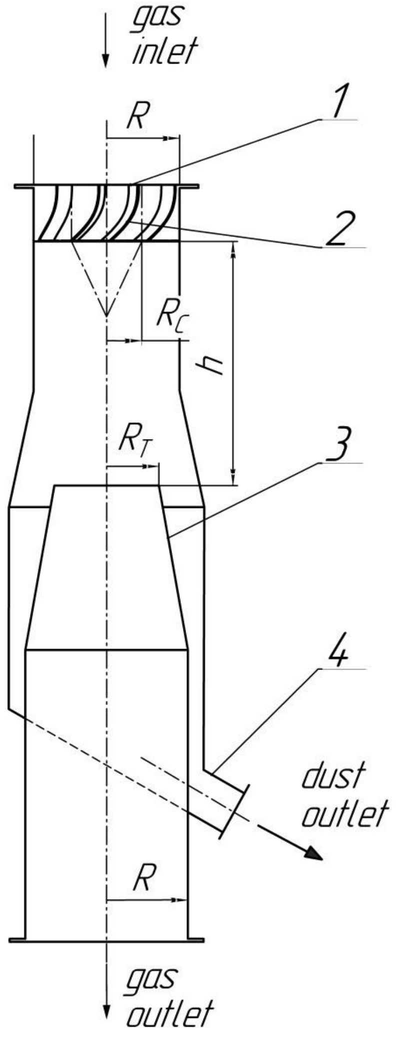

Fig. 1. Cyclone flow diagram

$$w_r \frac{\partial w_z}{\partial r} + w_z \frac{\partial w_z}{\partial z} = -\frac{1}{\rho}\frac{dp}{dz}. \qquad (3)$$

Here $w_r\ (r,z)$, $w_\varphi\ (r,z)$, $w_z\ (r,z)$ – are the radial, tangential and axial components of the gas velocity, respectively; $p(z)$ – is the pressure. Let's make up boundary conditions for equations (1)-(3). The condition of non-leaking of gas through the wall is the following:

$w_r\ (r,z) = 0$ at $r = R$ at any z. (4)

The tangential component of the gas velocity $w_\varphi\ (r,z)$ at $z = 0$ must be equal to the projection of the full gas velocity vector V on the tangential direction when the flow descends from the swirler blades, i.e $w_\varphi\ (R_c,z) = V \cos \beta$, where β – is the angle between the vector V and the tangential direction at the edge of the blades (the angle of twisting the flow). The condition for the longitudinal component of the velocity $w_z\ (r,z)$ arises from the constancy of the gas flow Q at any value of the coordinate z:

$$Q = \iint_S w_z(r,z)ds = const \qquad (5)$$

where S – is the cross section of the flow area. It results from this condition that the longitudinal component of the velocity depends only on the radial coordinate: $w_z = w_z(r)$. Then it follows from the equations of motion that the other velocity components are functions only of the coordinate r.

Taking into account the assumptions made and their consequences, equation (2) can be easily solved. Its solution satisfying the boundary condition formulated above is a hyperbolic function:

$$w_\varphi(r) = \frac{R_c V cos\beta}{r} \qquad (6)$$

Equation (1) allows us to determine the profile of the radial component of the gas velocity:

$$w_r(r) = R_c V cos\beta \sqrt{\frac{1}{r^2} - \frac{1}{R^2}} \qquad (7)$$

The component of the gas velocity along the z axis is determined from the equation (3). Its solution satisfying condition (5) is the function:

$$w_z(r) = \frac{Q}{\pi R^2} + A(\frac{2}{3}R - \sqrt{R^2 - r^2}),\ \text{где}\ A = \frac{R\Delta p}{\rho h R_c V cos\beta} \qquad (8)$$

The obtained solutions make it possible to determine the dependence of the gas velocity field in the separating chamber on its geometrical parameters R, R_c, h, the twist angle β and the gas flow rate Q.

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Treatment of oil polluted water by using polyurethane filled chitin

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The process of globalization leads to the rapid development of industry. This puts forward a high demand for using energy sources such as oil petroleum. As a result, an increasing amount of oil spills is observed along with pollution from this energy source, especially oil pollution in the water environment. Oil pollution not only negatively affects living organisms in the water bodies, but also adversely affects the water transport, the economy, the tourism, and it is also one of the routes of loss of the valuable source of energy [1]. Therefore, it is would be reasonable to remove the oil pollution from the water and to regenerate lost oils.

Currently, there is a lot of procedures commonly used to solve this serious problem. In particular, the use of adsorbents is considered one of the most effective methods. However, adsorbents for treatment oil polluted water are relatively expensive. Thus, creating an adsorbent with high efficiency in cleaning up the oil pollution and, at the same time, a reasonable price, has been the leading trend of research of scientists in recent years. To solve this problem, we have developed a combination of the expensive and effective synthetic sorbent - polyurethane foam (PUF) with the cheap natural material – chitin.

We applied filling PUF with 10% chitin (relative to the total mass of the components A and B of the PUF) with particle size 1–3 mm (PPU10M) which is reported as the most effective way for the foaming formation during the production of sorbent and oil adsorption [2]. The effects of absorption time and adsorbent consumption on the adsorption capacity have been evaluated on the samples of river water and seawater [3]. The research results indicate that the type of water does not affect the oil adsorption capacity. Therefore, the studied adsorbent can be widely used to remove oil pollution in various water systems. The results also show that the optimum adsorption time is 60 min for both types of water. The sorbent consumption is estimated to be 1g per 25g oil with the oil capacity of 13.41 g/g after 60 min adsorption.

The reuse of the adsorbent after the sorption process leads to decrease of the amount of solid waste and, at the same time, significantly reduces the cost of the process of removing oil pollution. The processes of mechanical regeneration by the squeeze method and the chemical regeneration by using toluene have been studied. The results show that in the mechanical regeneration procedure, the PPU10M adsorbent can be used up to 20 cycles with the regenerated oil efficiency up to 87%. The chemical regeneration method has a significantly higher degree of oil recovery with amounts of the regenerated oil up to 97%.

However, its reusability is limited to 10 cycles. This result shows that the use of an adsorbent produced from the combination between two materials: chitin and polyurethane foam, for the process of treatment of the oil pollution not only significantly reduces the cost of acquiring adsorbents, but also reduces the amount of the solid waste resulted from the adsorption process.

In addition, we have studied the problem of recycling solid waste after adsorption. To limit the discharge of solid waste into the environment, as well as reduce the use of raw materials, the wastes after the adsorption process can be used as a filler in the synthesis of adsorbents. The addition of the spent sorbent into the composition of the sorbent in the amount of 5, 10 and 15% of the mass has been investigated. It has been found that the material containing 5% of the spent adsorbent has the higher the oil capacity (up to 12.48 g/g) in comparison to the materials containing 10 and 15% of the filler.

The obtained results show that the material based on chitin and polyurethane foam is a promising adsorbent for removing oil pollution from water. It has high enough sorption ability and can be used in the different water environment. Moreover, it is characterized by high reusability and recyclability. Thus, the combined adsorbent based on chitin and polyurethane foam can be considered environmentally friendly, which is suitable for the practical use to clean up oil pollution from the water.

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Alkylated derivatives of resorcinarenes for binding of toxic metal cations

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An enormous attention is being paid to the issues of environmental pollution by heavy metals. Due to the increasing scale of anthropogenic impact on the environment, many heavy metals have been included in the international lists of pollutants requiring constant monitoring. Anthropogenic emissions into the environment result in the continuous accumulation of heavy metals in the body organs and tissues of animals and plants, which in turn leads to contamination of food products obtained from these raw materials. Heavy metals such as lead, zinc, cadmium, copper, and mercury are the most frequently found in many food products, soil and water.

To solve the problem of heavy metal contamination, a variety of organic complexing agents has been proposed for extraction of heavy metals with their subsequent quantitative analysis. In the present work, the efficiency of metal (Pb, Zn, Cd, Cu, Hg) binding by alkylated derivatives of resorcinarenes has been studied.

Thermodynamic and kinetic data on formation of complexes of heavy metal cations with resorcinarenes of new type are presented. It has been shown that the complexation process is exothermic, which confirms the coordination mechanism of metal binding. A study of the kinetics of the process reveals that the complex formation proceeds with high selectivity within a short contact time of a heavy metal solution with the solution of resorcinol. An increase in sorption time leads to the formation of thermodynamically stable coordination metal complexes suitable for quantitative determination by spectral analysis methods.

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Method of reducing workload on aspiration system in production of dusty carbon black

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Carbon black is a highly dispersed product which is widely used as a reinforcing filler in the production of rubbers for improving their physical and chemical properties, as a black pigment in the production of printing inks and other paint and varnish materials, as well as a filler for plastics and cable sheaths to provide specific properties of these materials [1].

Currently, more than 96% of the produced carbon black is obtained by the furnace method by pyrolysis of liquid hydrocarbon raw materials. As a result, carbon black aerosol enters inertial dust collectors, mainly cyclones, where particulates are separated from the gas stream. However, these facilities are very small in size, and as a result, the efficiency of carbon black capture in cyclones usually does not exceed 75%. This circumstance leads to the necessity of applying efficient high-load systems for pre-capture and aspiration, which are very expensive to maintain and occupy significant production space [2].

Analysis of existing constructions of inertial dust collectors that provide maximum efficiency of carbon black capture to reduce the workload on the pre-capture systems and especially aspiration, has led to conclusion that, in terms of engineering design, the usage of devices with counter swirling flows (CSF) instead of cyclones is the most optimal decision, including the imposition of high-intensity ultrasonic fields.

The separation capacity of CSF devices reaches 0.4 microns, and the efficiency of capturing particles of > 5 microns in size, runs up to 100%, which allows them to be repaid in 3–6 months of their usage.

Practical experience of using cyclones to capture carbon black shows that only 15% of the gases from their incoming quantity are sucked through the dust hopper, while the efficiency of capture is reduced to zero. The capacity of CSF devices with respect to gas can vary within the range of 0.50–1.15 of its nominal value without significant reducing the efficiency of capture. This is explained by the predominant impact of secondary gas parameters on the efficiency of capturing, since maintaining of these parameters means that the circumferential speed of the swirling flow of the dusty gas remains unchanged [3, 4].

Comparative calculations of the widely used cyclone SC-CN-34 for capturing carbon black versus the proposed CSF device with 60000 m^3/h capacity related to dusty gas, showed that the following design characteristics were optimal taking into account permissible fluctuations in production conditions:

1. Cyclone SC-CN-34-3600 with a dust hopper with the following parameters:

- capture efficiency 60–75%;
- coefficient of hydraulic resistance 1100;
- weight with a hopper of 10.5 t (without a hopper of 9.2 t).

2. An assembly of two parallel working devices CSF-1000×2 with a common dust hopper with the following parameters:

- capture efficiency of 90–95%;
- coefficient of hydraulic resistance 100;
- weight with a hopper 4.1 t (one unit without a hopper 1.4 t).

Thus, the results of calculations confirm the scientifically substantiated choice in favor of CSF devices, since their usage in the production of carbon black allows to reduce the workload on pre-capture system and especially on aspiration system up to 20–30% of the target product, which has the 3rd substance hazard category. At the same time, this approach allows to reduce the metal content and energy costs of production, increasing its environmental friendliness and economic feasibility of the process.

The work was carried out with the financial support of Omsk Carbon Group.

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Development of bactericidal materials based on polylactide and polyhydroxybutyrate fibers

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The development of polymer modifications of biologically active compounds is an important area of chemical technology and is aimed at the synthesis of polymer materials with biomedical properties. Metal complexes with porphyrins are used as homogeneous autooxidation catalysts for a number of nutrients. This process involves the intermediate formation of cytostatic reactive oxygen species (superoxide anion radical, peroxide and hydroxyl radicals, hydrogen peroxide). Polymer fibers of nanoscale size are the most promising carriers for functional low-molecular weight substances (particles). One of the best procedures for producing such fibers is electrostatic molding or electroforming from polymer solution (EF). The main advantages of EF include the relatively low cost of equipment, the simplicity of instrumental equipment, the variability in the conditions for producing fibers, as well as the possibility to apply different types of fibers and fiber-based products. The use of a number of natural polymers, such as polylactide and poly-(3-hydroxybutyrate), provides additional benefits in the development of fiber and matrix systems for environmental and biomedical applications. They are biocompatible and at the same time exhibit controlled biodegradation properties without generating toxic products.

In this work, new materials based on polylactide (PA) and poly-(3-hydroxybutyrate) (PHB) fibers and tetraphenylporphyrin metal complexes (MTPP, M = Fe, Mn) were obtained. Ultrafine fibers with the addition of 1, 3, and 5 wt% of MTPP (relative to the polymer content in the solution) were prepared by the method of EF solution in chloroform on a single-capillary set-up EFV-1 (Russia). The morphology of fibrous materials was investigated by electron microscopy on the Hitachi TM-1000 scanning electron microscope (Japan). Biocidal activity was determined by diffusion into agar containing a test culture, by determining the diameter of bacterial growth inhibition zones. Test cultures of *Staphylococcus aureus* P209 and *Escherichia coli* 1257 were used in experiments with various dilutions of the drug. Test cultures of microorganisms were grown on meat-peptone agar at 37°C for 24 h, then washed out from fibrous material and placed in agar-wells with a diameter of 3 mm. Crops were incubated for 24 h at a temperature of 37°C and zones of growth inhibition of test cultures were counted.

Depending on the characteristics of the molding solution and the electrical spinning process parameters, it is possible to obtain fibers of different diameters, densities and various geometric shapes. A significant number of spindle-like thickenings was observed for the initial PA and PHB, mostly caused by violation of the stationary polymer solution flow regime (beating, pulsation, etc.) due to insufficient conductivity of the molding solution, or its non-optimal viscosity. For a single fiber, a sequence of cylindrical fibers with a diameter of 1–3 µm and spindle-like elements with a maximum diameter of ~10 µm and a length of 20–30 µm were observed. When 1% MTPP was added to the molding solution, the average diameter of the cylindrical elements of such fibers slightly increased by 2-4 µm, but the spindle-like structures almost completely disappeared. Only a few local thickenings on the fiber were noted. This effect is most likely associated with an increase in the electrical conductivity of the molding polymer solution in the presence of the polar MTPP molecules. Further increase in MTPP concentration in the molding solution resulted in the complete disappearance of the thickenings on the fibers. Thus, metal complexes of tetraphenylporphyrin, along with their biocidal activity, also increase the electrical conductivity of the molding solution and can be used as a technological additive.

Biological tests of nonwoven materials have shown that fibers containing MTPP are active against bacterial test cultures, causing the death of 85–100% of colonies. This shows the feasibility of creating disinfectants based on polymers and metal complexes of porphyrins with respect to opportunistic and pathogenic microorganisms.

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Antimicrobal fibrous materials containing metal particles or complex of enzymes with antibacterial agents

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Today, the emergence of bacterial strains with multiple antibiotic resistance has become a problem of major concern. Accordingly, the development of special protective materials with a minimum inhibitory concentration of antibacterial components exhibiting high antimicrobial activity is an extremely urgent and important task for researchers and engineers. The possibility of introducing metal nanoparticles exhibiting antimicrobial activity into composite fibrous materials is the basis for the development of new means for individual and collective protection [1]. The use of combined mechanisms of antimicrobial action on bacterial cells of various modern antibiotic agents in combination with enzymes that hydrolytically inhibit the formation of antibiotic-resistant pathogens populations when introduced into fibrous materials can provide the creation of new protective agents. The search for new technological methods to obtain the most effective samples of such protective fibrous materials is a modern promising trend in the development of this area of research [2].

To develop such protective agents, synthetic polymers and copolymers were screened to choose fibrous materials with high adsorption and absorption capacities in relation to various metal nanoparticles and enzyme nanocomplexes with antimicrobial agents [3–6]. The most interesting results were obtained using polyamide fiber.

It has been shown that both composition and method for manufacturing materials significantly affect the controlled properties of the fibers. In addition, the method and conditions for the functionalization of fibers by introducing antibacterial components determine the antimicrobial activity of the end-products. Analysis of methods for producing nanodispersed systems for the functionalization of fibrous materials has revealed that electrochemical method is appeared to be the most suitable for the arc discharge in a liquid medium (water or an organic solvent), accompanied by corrosion of the metal electrode and the formation of nanoparticles. This method allows to flexibly control the qualitative and quantitative parameters of the resulting nanodispersed systems.

An important condition for providing stability of the resulting organosols and hydrosols is the prevention of aggregation and flocculation of the obtained and accumulated nanoparticles, since instability can lead to a decrease in their bactericidal properties when introduced into fibrous materials. To improve the stability of the obtained nanodispersed systems, surfactants and other effectors can be introduced into the initial solvent.

Thus, it has been established that the introduction of nanocomplexes of enzymes into the fibrous materials with known antibiotics, characterizing by different chemical structures and properties, in combination with different antimicrobial peptides leads to the complete preservation of their antibacterial action with the requirement that physicochemical characteristics of the fibrous materials themselves do not create diffusion problems for antimicrobial actions catalyzed by these complexes.

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Polymer compositions for protective clothing

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A special garment providing a barrier against harmful toxic substances penetration through body surface is one of the main means of protection for workers in the chemical industry. However, the suits made from materials with high barrier properties (for example, completely encapsulated suits) can cause discomfort and overheating of a person during the performance of his labor functions [1]. The design of textiles and clothing, ensuring compliance for environmental requirements, capable of maintenance of thermo-physiological comfort, possessing the necessary protective, mechanical, ergonomic, hygienic properties is a relevant task in the development of personal protective equipment.

Textile structure, thickness, fiber composition, composition of special finishing coatings – are indicators, which influence the properties of materials [2, 3]. The goal of this research was to study optimal ratios of the components of polymer compositions applied for protective coatings of textiles for chemical industry workers special garment. The content of the main ingredients in the coating composition is an important factor affecting the properties of the textile. The area of factors definition is of great importance in the experimental search for the optimal content of substances.

A variety of factors determine composition of the coating for protective materials, i.e. a range of various substances depending on the product end use and the nature of the polymer components, the additives to provide special functions, the method of finishing, etc. One of the approaches to increase the filtering properties of textile materials is the addition of sorbents, particularly, metals oxides. In this work, we have proposed to use both an aqueous dispersion of polyurethane and an aqueous dispersion of acrylic component as the main constituents of a polymer mixture in order to fix the sorbent on the textile surface. Polyurethane is one of the most widely used polymers for textiles coating. The reasons for selection of this materials are sufficient strength, flexibility, elasticity, good washing resistance, good adhesion to textile materials, chemical and abrasion resistance [2, 4]. Acrylic copolymer is also widely used for textile coating applications due to its strength, good adhesion, water resistance properties without deterioration of the textile appearance [2, 5].

Mechanical properties of the coated material samples have been tested in the preliminary experimental studies. A cotton fabric with a mass of 140 g/m^2 as textile substrate was used. The strength properties of the textiles are found to increase as a result of coating procedure. Particularly, breaking load of coated textile samples increased by 24% on the warp and by 9% on the weft compared to the original sample [6]. The thickness and stiffness of the textiles increased with the increase of the concentration of polymer binders in the coatings. This effect has a negatively impact on ergonomic and technological properties.

Looking forward, the objective of further research is to optimize the ratio and concentration of the main components, and to determine the final quantitative and qualitative composition of the coating for the protective clothing textile.

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Determination of PAHs content in waste waters

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Polyaromatic hydrocarbons (PAHs) are known as one of the most hazardous pollutants entering surface water of natural water bodies with effluents and wastewater from the enterprises of oil refining, oil shale industry, wood chemical industry, coke chemical industry, dyestuff industry, hydrolysis industry, etc. Oil refining, catalytic and thermal cracking processes produce wastewater contaminated with polyaromatic hydrocarbons, which are highly hazardous for the environment. This problem is of particular relevance in the Caspian countries, since wastewater entering the Caspian Sea can cause a serious seawater pollution [1].

Moreover, organic compounds such as polycyclic aromatic hydrocarbons are a global environmental problem as they can cause inflammation and skin cancer. It is known that there are two types of anthropogenic hydrocarbon sources: petrogenic and pyrogenic ones [2]. Petrogenic sources include crude oil and hydrocarbon compounds of petroleum origin. Pyrogenic sources of hydrocarbon compounds are formed as a result of incomplete combustion of organic substances such as oil, wood, coal, etc.

To analyze the quality of these waters, we collected three samples from the Refinery sites (Baku city, Azerbaijan) and used analytical methods to study the content of PAHs in the wastewater [1]. The analysis of the samples was performed on a HP6890 gas chromatograph with HP5975 mass selective detector, GC-MS (Agilent, USA) equipped with a ZB-5 column (Phenomenex, USA). The specifications of the ZB-5 column are as follows: 5% diphenyl – 95% dimethylpolysiloxane copolymer, length – 60 m, inner diameter – 0.25 mm, film thickness – 0.25 μm. The volume of the injected sample is 1 μl. A mixture of deuterated polycyclic aromatic hydrocarbons: naphthalene-d8, phenanthrene-d10, pyrene-d10, chrysene-d12 and perylene-d12 was used as an internal standard for calculating the results of chromatographic analysis.

The results are presented in Table 1. As can be seen from the table, a very high amount of PAHs has been found in the analyzed samples of the Refinery (Baku), which exceeds the maximum permissible concentration (MPC) for these compounds in wastewater. The MPCs of polyaromatic hydrocarbons are ranged from 4246 to 709168 μg/l for different kinds of water. For example, the amount of naphthalene is extremely high and, therefore, such polluted waters can be considered as highly hazardous for flora and fauna of aquatic ecosystems [3, 4].

Table 1. PAH amount in the кefinery waste water samples

Type of PAHs	Sample 1	Sample 2	Sample 3
	μq/l		
naphthalene	910367.1	157103.5	60277.4
acenaphthylene	1600.5	2363.7	62.9
acenaphthene	18759.5	10234.5	441.8
fluorene	55745.2	62869.3	1472.5
phenanthrene	100445.8	74629.4	2662.1
anthracene	7873.0	4262.2	187.1
fluoranthene	3299.0	2645.5	141.9
pyrene	31433.6	27274.8	1746.0
benz[a]anthracene	7214.1	2375.1	400.0
chrysene	13814.0	5966.4	728.0
benzo[b]fluoranthene	1167.0	530.5	60.9
benzo[k]fluoranthene	515.3	171.3	32.9
benzo[a]pyrene	1654.6	455.3	108.6
indeno[1,2,3-cd]pyrene	565.1	154.5	30.5
benzo[ghi]perylene	661.5	100.6	37.0
dibenz[ah]anthracene	960.0	184.1	69.3
Total content of 16 PAHs	**1156075.3**	**351320.6**	**68458.9**

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