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EDITORIAL

The most significant achievements in the field of natural sciences are reached in joint collaboration, where important roles are taken by biology and chemistry. Therefore publication of a Journal, displaying results of current studies in the field of biology and chemistry, facilitates highlighting of theoretical and practical issues and distribution of scientific discoveries.

One of the basic goals of the Journal is to promote the extensive exchange of information between the scientists from all over the world. We welcome publishing original papers and materials of biological and chemical conferences, held in different countries (after the process of their subsequent selection).

Creation of special International Journal of Biology and Chemistry is of great importance, because a great amount of scientists might publish their articles and it will help to widen the geography of future collaboration. We will be glad to publish also the papers of the scientists from the other continents.

The Journal aims to publish the results of the experimental and theoretical studies in the field of biology, biotechnology, chemistry and chemical technology. Among the emphasized subjects are: modern issues of technologies for organic synthesis; scientific basis of the production of physiologically active preparations; modern issues of technologies for processing of raw materials, production of new materials and technologies; study on chemical and physical properties and structure of oil and coal; theoretical and practical issues in processing of hydrocarbons; modern achievements in the field of nanotechnology; results of studies in the fields of biology, biotechnology, genetics, nanotechnology, etc.

We hope to receive papers from a number of scientific centers, which are involved in the application of the scientific principles of biology, biotechnology, chemistry and chemical technology on practice and carrying out research on the subject, whether it relates to the production of new materials, technology and ecological issues.

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Obtaining of surface-active substance sorbents based on acrylate-clay polymers

Abstract: In this work the problem of sewage treatment containing surface-active substance (SAS), using polymer-bentonite clay (BC) was discussed and sorbent synthesized. The sorption capacity of obtained polymer-clay composites in relation to surfactant in different environments and conditions was estimated. The used bentonite clay of the Manyrak deposit (East Kazakhstan region) was purified with the help the method of Salo by repeated washing with distilled water. Chemically cross-linked composite gels based on bentonite clay and polycarboxylic acids – poyacrylic (PAA) and polymethacrylic acids (PMAA) in ratio 1:10, 3:10 and 5:10 were synthesized with adding cross-linking agent methylene-bis-acrylamide (MBAA) 1 mole %, dinitrile of azo-bis-isobutyric acid (DAA) 0.5 mole % by weight of the monomer at a temperature of 70 °C for 2 hours. The kinetics of swelling of obtaining composites in solutions of and cationic surfactants – cetylpyridinium bromide (CPB), cetyltrimethylammonium bromide (CTAB) were studied; the influence of internal factors: the content of clay, concentration of surfactants, temperature and pH of the medium, on the swelling of composites in surfactant solutions was examined. These studies were carried out on a scanning electron microscope Quanta 3D 200i Dual system, Leica DM 6000 M (Switzerland) digital optical microscope for obtaining the morphological structure of dry and swollen samples of the obtained compositions, IR spectrometer «Satelitte» FTIR Mattson (USA), and Radwag AS 220/X (Poland) for measuring the density.
Key words: bentonite clay, polyacrylic acid, polymethacrylic acid, composite material, sorbent, ions of surface-active substance (SAS).

Introduction

The main reason of accumulation of surface-active agents in water objects, especially in the lower parts, is their resistance to biochemical oxidation. In turn, it reduces a possibility of self-purification of natural water resources and leads to secondary pollution of a water surface. Therefore surfactants belong to the group of the most dangerous and harmful substances which are found in sewage. Currently, protection of sewage from surfactants is an extremely important and global problem.

Requirements requested by polymer carriers are determined based on the forms and methods of testing. The most important condition is that their homogeneous and constituent components be co-located. To do this, it is important to select the component compositions correctly.

To obtain a composite carrier on the basis of polymer and clay, BC was selected from the East Kazakhstan region and polycarboxylic acid (PCA). Their choice as a composite composition was made for the following reasons:

1. Polycarboxylic acid refers to polyanions has a negative charge. If we rely on literature sources and the results of the research it is known that bentonite clay consists of negative particles, and this in turn means that both components have the same negative charge. If they have antipodal charges, then with electrostatic interaction a complex of salt will result and this would lead to the creation of insoluble compounds. This would destroy the homogeneity of the composition. And the same-named charged components of the composition are connected with each other by means of non-nucleon forces like hydrogen bonds and hydrophobic interactions. Such a system should retain the ability to swell and be homogeneous and interconnected in the ability to swell and be homogeneous and interconnected.

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2. Like bentonite clay, polycarboxylic acids (PCA) individually have functional groups (-COOH, -OH) capable of binding surfactants and hydrophobic groups. These qualities make it possible to assume that it is possible to bind surfactants and composite materials [1].

In this connection, in this work, the possibility of obtaining materials of composite carriers based on bentonite clay and polycarboxylic acids will be investigated. To determine the optimal conditions for the synthesis of bentonite clay-polycarboxylic acid composite gels (BC-PCA), the influence of various internal and external factors, such as the amount of bentonite clay (BC) the synthesis route, temperature and were studied in two surfactant solutions.

Materials and methods

To produce polymer-clay composite gels, domestic bentonite clay of the Manyrak deposit (East Kazakhstan region) and polyacrylic and polymethacrylic acid monomers were used, which were subjected to initial purification. The used bentonite clay was cleaned with the help of the method of Salo. Only after three washings the investigated clay is separated from large parts and impurities of sand, the content of these components reaches up to 48 % [2].

The chemical content of natural and purified bentonite clays determined by the diffraction spectral analysis (DFS-13) method is presented in Table 1. Based on the results, the clay studied, consisting of alumina and silicon oxides, refers to aluminosilicates. In this composition, the predominance of montmorillonite is evident.

Chemically cross-linked composite gels based on bentonite clay and polycarboxylic acids – poyacrylic (PAA) and polymethacrylic acids (PMAA) in ratio 1:10, 3:10 and 5:10 were synthesized. A cross-linking agent methylene-bis-acrylamide (MBAA) 1 mole %, dinitrile of azo-bis-isobutyric acid (DAA) 0.5 mole % by weight of the monomer was added. The polymerization was carried out in an ampoule lowered in a thermostat heated to 70 °C and isolated from the air by a laboratory film "Parafilm", at a temperature of 70°C for 2 hours. The completeness of the washing of the composite gels PAA-BC and PMAA-BC was controlled by a qualitative reaction to the double bond of $KMnO_4$ [3].

Table 1 – X-ray analysis of clay

Example of clay	Phase			
	Intensive		Amorphous, C^0	
	SiO_2 3.3 A^0	montmorillonite 4.6 C^0		
Natural	62.0	92.0	3.50	2.20
Purified	35.0	130.0	3.63	2.20

Results and their discussion

The composition and physicochemical parameters of the composite gels obtained are shown in Table 2. Based on the data of the table, one can observe a general pattern observed for all acrylate-clay gels, as the amount of bentonite clay in the composition increases, the yield of gels increases accordingly. Since, as the amount of bentonite clay increases, the bond between polycarboxylic acids and polymers increases, and as a result, a favorable condition is established for increasing the density and yield of the composite. The similarity of the ash content of BC-PAA and BC-PMAA gels may be due to the amount of bentonite clay in the composition. It is known that organic substances in the composition of the composite burn and remain inorganic substances. To be more precise, bentonite clay remains in the ash as unburned inorganic matter.

To obtain the exact composition it was interesting to obtain figures of acrylate-clay gels in a scanning electron microscope (SEM). Based on the obtained results, the size of the BC-PAA complex amounted to about 1-3 mm of the same world composition units [4].

Based on the data of the table, one can observe a general pattern observed for all acrylate-clay gels, as the amount of bentonite clay in the composition increases, the yield of gels increases accordingly. Since, as the amount of bentonite clay increases, the bond between polycarboxylic acids and polymers increases, and as a result, a favorable condition is es-

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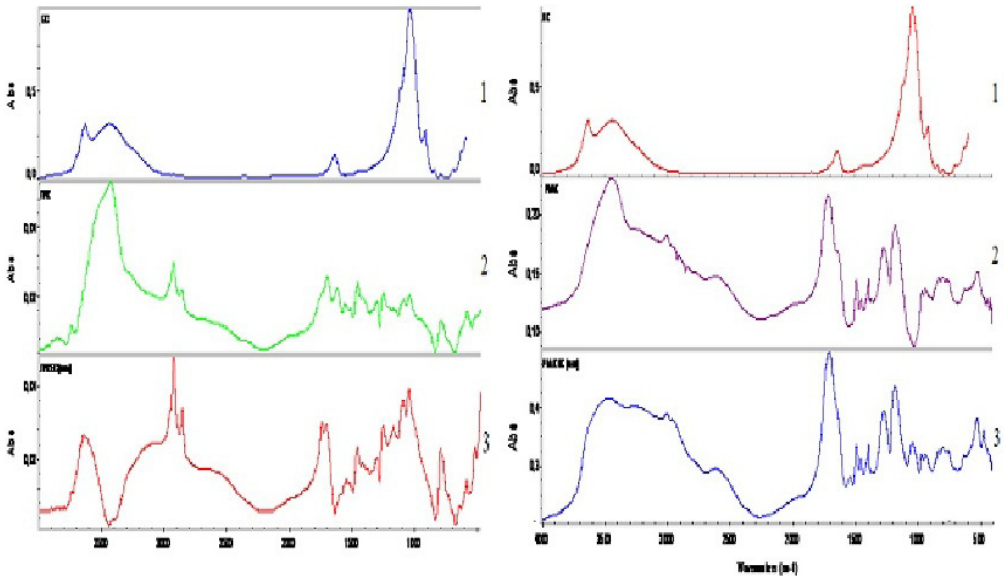
Table 2 – Physicochemical characteristics of gels

Composite	BC-PAA			BC-PMAA		
Composition, weight %	3:10	5:10	7:10	3:10	5:10	7:10
G, %	84.80	98.40	102.31	84.11	86.83	73.53
A^{α}, %	18.24	29.94	38.19	18.24	29.94	37.89
ρ, g/cm^3	1.34	1.361	1.37	1.49	1.54	1.56
S, %	7.06	3.70	1.20	12.32	9.70	7.70
j, %	2.80	2.13	1.93	3.59	3.15	2.89
G – yield of the fraction of the composite gel, %; A^{α} – ash content of composite gels, %; P – density of composite gel, g/cm^3; S – yield of the fraction sol, %; J – degree of crosslinking, %						

To confirm the composition of acrylate-clay BC-PCA gels, the IR spectrum was removed. The results of IR spectroscopy show the formation of the BC-PCA complex. In the spectrum, one can see the bands inherent in both carbon and bentonite clay (Figure 1). In the spectra of acrylate-clay gels, the vibration of carboxylate ions is prescribed in the interval 1705, 1699, 1706 cm^{-1}, 1539, 1540, 1549 cm^{-1}, the connection of the tetrahedron net of bentonite clay 3648 cm^{-1} bathochromic shift and in the form of a wide band 3650-2800 cm^{-1}. In all these bands, one can observe a significant increase in intensity proving the formation of hydrogen bonds. The Si-O-Si bond is prescribed in area 1044; 1092 cm-1, C-C (δ) 797, 795 cm^{-1}, and the Si-O bond in 5885, 516, 552, 468, 521, 416 (δ) cm^{-1}. A strand can be seen broad bands of increased intensity inherent in the hydrogen bond chelate type in the spectra of 3200-2500 cm^{-1}.



(a) (b)

Figure 1 – IR spectra of the BC-PCA; where: a) bentonite clay (1); PAA gel (2); BC-PAA gel (3) b) bentonite clay (1); PMAA gel (2); BC-PMAA gel (3)

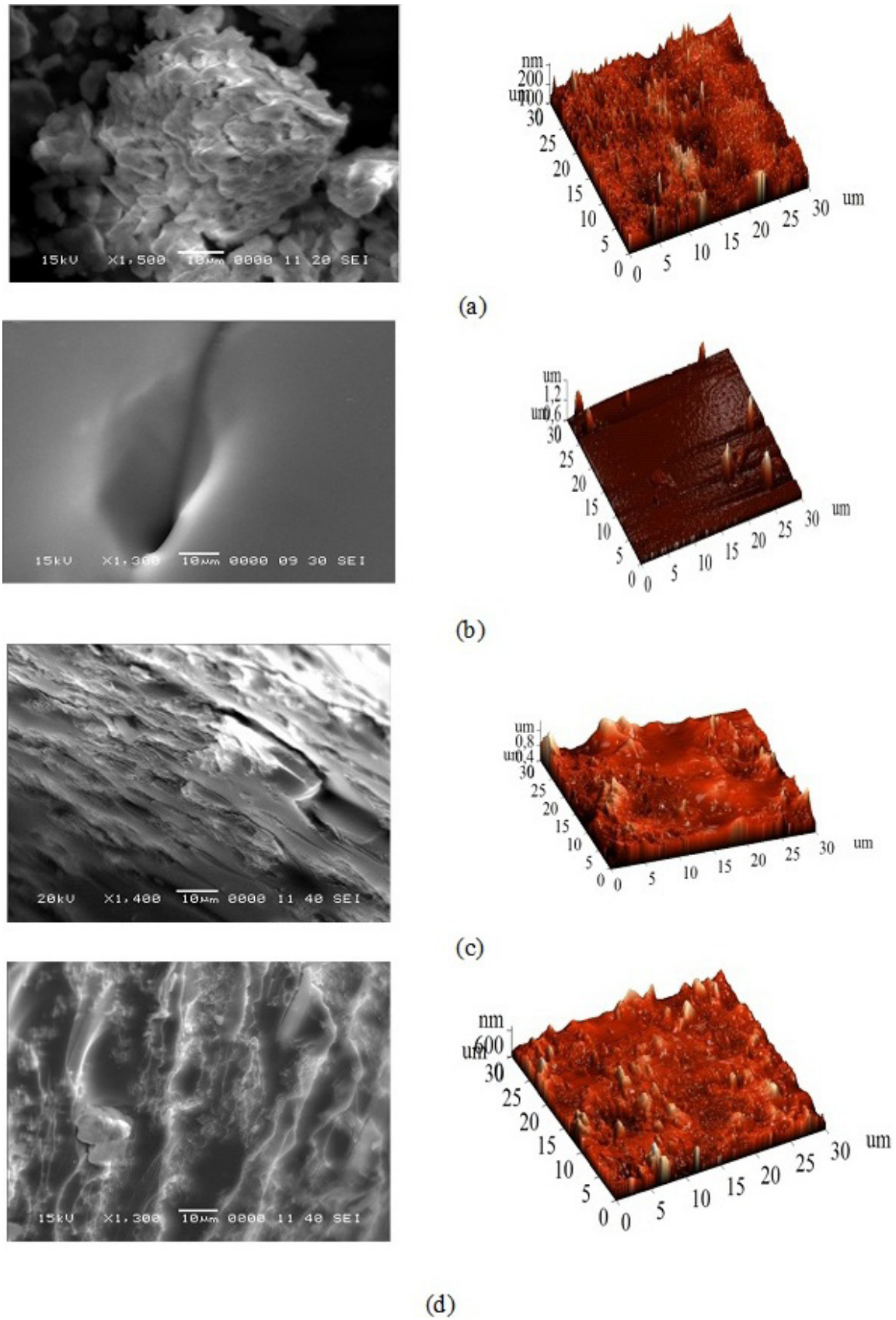


Figure 2 – Pictures of scanning electron microscopy and atomic-force microcopy; where:
BC (a); PAA (b); BC-PAA(c); BC-PMAA (d)

To obtain a difference in the surface structure of the obtained composite gels based on BC-PAA, pure gel PAA and BC. These differences can be seen in the pictures of the composition taken with an atomic force microscope. It is noticeable from the pictures that with the addition of bentonite clay, the surface of the gel becomes smooth, this indicates that the particles of bentonite clay penetrate the polymer and produce a uniform gel. The principle of the atomic force microscope is based on recording the force interaction between the surface of the sample and the probe, by recording the magnitude of the bend, one can obtain an image of the surface relief [5].

According to the results of the research, the components of the obtained composite BC-PCA gels together form a complex with the help of hydrogen bonds and are chemically crosslinked by cross-linking agent.

Before evaluating and regulating the sorption capacity of composite gels, one should know about the swelling of gels in a CPB and CTAB solution. Therefore, the degree of swelling of synthesized clay polymer compositions is determined by the methods of swelling equality[5]. Based on the results of the study, the effect of the pH of the medium on the swelling kinetics of competing gels in the CPB solution (Figure 3) can be seen that as the pH of the medium increases, the swelling of the composite gels increases significantly, because the degree of dissociation of the weak PAA depends on the pH medium. For example, for BC-PAA gels the swelling ratio at pH = 1 is about 10 g/g, and at pH = 11, it will increase to about 422 g/g.

Figure 4 shows the change in the swelling characteristics of composite gels as a function of temperature, as well as the change in the volume of bentonite clay in the composite. With the increase in the volume of bentonite clay, the swelling capacity of the composite decreases. The swelling capacity of pure bentonite clay in the CPB solution is significantly low, resulting in the properties of the composite in which the volume of bentonite clay is closer to the swelling of pure bentonite clay. For example, the degree of swelling for the composite BC-PAA gel [1:10] at 25 °C is about 119.03 g/g, and for the BC-PAA [5:10] gel, about 82.09 g/g. With increasing temperature, the movement of molecules in the CTAB solution increases and leads to an increase in swelling of the gel. At the same time, an increase in temperature leads to a weakening of the hydrogen bond between the composite and the CTAB, as a result of which the swelling properties increase. For example, at a temperature of 25 °C for BC-PAA G (1:10), the degree of swelling is 119.03 g/g, and at a temperature of 60 °C, the degree of swelling of the composite increases and is about 175.19 g/g. Thus, the composite gels obtained with a negatively charged cationic surfactant-CTAB through an electrostatic bond form a complex. For various internal and external factors, in particular, the volume of BC in the composition of the composite and the concentration of the CTAB solution, the pH of the medium and the relationship with the temperature change shows different swelling capacities.

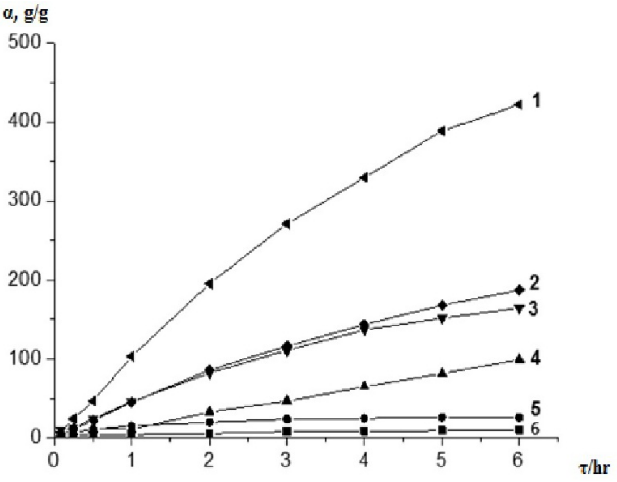


Figure 3 – Kinetics of swelling of composite gels at different pH values; where: τ= 6 hours; T = 25 ºC; BC-PAA (1:10); [DAA] = 0.5 %; CA = 1 %; pH = 11 (1), 9 (2), 7 (3), 5 (4), 3 (5), 1 (6)

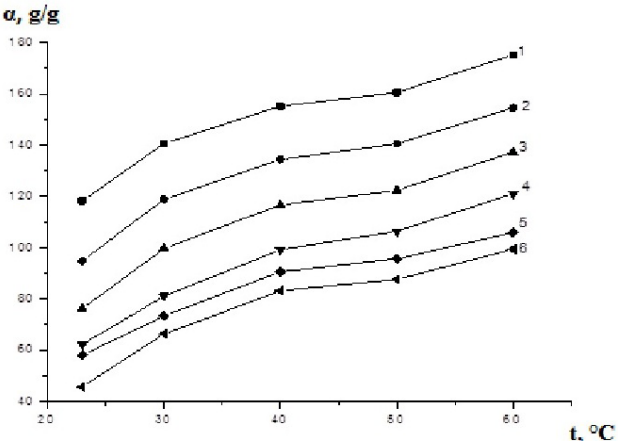


Figure 4 – Dependence of the swelling degree of compilation gels on temperature; where: τ= 6 hours; T = 25 ºC; [CTAB] = 1.10^{-4} M; BC-PAA [1:10] (1); [3:10] (3); [5:10] (5); BC-PMAA [1:10] (2); [3:10] (4); [5:10] (6)

Conclusions

Protection of sewage from surfactants is an extremely important and global problem.This situation determined the intensive development of serious scientific research into the study of the specific features of this type of pollution and the search for ways to prevent it.

The following conclusions were made to the results of the study:

1) acrylate-clay gels on the basis of bentonite clay and polycarboxylic acid (acrylic and methacrylic acids) were obtained by radical polymerization, optimal synthesis conditions were identified, physicochemical characteristics of the gels were determined; It was found that the components of acrylate-clay gels are linked together by hydrogen bonding and form a uniform, water-swellable polyelectrolyte gel, that the components of acrylate-clay gels are linked together by a hydrophobic bonds;

2) the kinetics of swelling of obtaining composites in solutions of and cationic surfactants – cetylpyridinium bromide (CPB), cetyltrimethylammonium bromide (CTAB) were studied; the influence of internal factors: the content of clay, concentration of surfactants, temperature and pH of the medium, on the swelling of composites in surfactant solutions was examined by the method of equilibrium swelling. The results of morphological structure studies were obtained.

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Characteristics of interaction of miRNA with mRNA of *E2F* transcription factors family genes

Abstract: Search of binding sites of 6266 miRNA with mRNA of genes of *E2F* transcription factors family was implemented. The mRNA of *E2F1* gene is associated with 13 miRNAs in 5′UTR, CDS and 3′UTR. The mRNA of *E2F2* gene has binding sites for 10 miRNAs. The binding sites of miR-1-875-3p and miR-760-3p are conservative in mRNA of *E2F2* gene of 18 mammalian species. The mRNA of *E2F3* gene contains binding sites for one miRNA in the 5'UTR, for two miRNAs in the 3'UTR and for other seven miRNAs in the CDS. The miR-7-19239-3p, miR-19-42772-5p, miR-3-9461-3p, miR-17-39416-3p can interact with mRNA of *E2F3* gene with energy more than -120 kJ/mole. The mRNA of *E2F4* gene has binding sites for six miRNAs in CDS, 5'UTR and 3'UTR. The mRNA of *E2F5* gene contains binding sites for seven miRNA located only in the CDS. The mRNA of *E2F6* gene has one binding site for miRNA in the 5'UTR, three in the 3'UTR. The mRNA of *E2F7* gene binds miR-14-34881-3p in the CDS. The predicted miRNA binding sites with mRNA of *E2F* gene family help to find associations of miRNAs with their target genes for the development of diagnostic methods of tumourigenesis. The following pairs can be used as associations of miRNA with target genes: miR-6511b-3p, miR-1-1714-3p and miR-6786-5p with mRNA of *E2F1* gene; miR-7-19239-3p, miR-19-42772-5p, miR-3-9461-3p and miR-17-39416-3p with mRNA of *E2F3* gene; miR-5-15026-5p and miR-20-44817-5p with mRNA of *E2F4* gene.
Key words: miRNA, mRNA, transcription factor, *E2F1-8* genes, tumourigenesis.

Introduction

The E2F family of transcription factors includes E2F1-E2F8 proteins, which play an important role in the animal cell cycle [1]. The E2F family of proteins divides by functions into transcriptional activators and repressors. Activators E2F1, E2F2, E2F3a accelerate the cell cycle, and E2F3b, E2F4, E2F5, E2F6, E2F7, E2F8 inhibiting cell cycle. Members of family form heterodimers that increases their stability. The balance between activators and repressors regulates the progress of the cell cycle [2]. Proteins of E2F family regulate transcription of cell cycle genes, negative regulators, checkpoints, proteins of apoptosis, nucleotide synthesis, DNA replication and DNA reparation [3]. A wide range of E2F participation in key processes of cell functioning dictates the need to explore the biological role of members of the E2F family. Some studies found E2F proteins involved in tumourigenesis.

In recent years it was studied the effect of miRNA expression on E2F family of genes in tumorigenesis [4-10]. It was shown the involvement of miRNA in the regulation of the expression of genes of *E2F* family in the cancer of stomach [15], esophagus [11], ovaries [17], colon [12], endometrium [13], lung [14], liver [16] and other; the change in the concentration of various miRNAs and the expression of *E2F* family genes with breast cancer [6-12]. Changes in miRNA concentration and expression of *E2F* family of genes have been studied for *E2F1* [18], *E2F2* [19], and *E2F3* [20, 21] genes. There are several publications for *E2F5* and *E2F7* genes [22-23]. The effect of miRNA on the expression of *E2F4* and *E2F6* has not been studied. In the works cited above, the direct effect of miRNA on mRNA genes of *E2F* family with the establishment of binding sites have not been studied. In connection with this it is needed to identify the influence of currently known 6266 miRNA on the expression of *E2F* family genes.

Materials and methods

Nucleotide sequences of mRNAs of E2F family genes were downloaded from GenBank (http://www.ncbi.nlm.nih.gov). We used the following abbreviations of species names: *Ailuropoda melanoleuca* –

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Ame, Bos taurus – Bta, Canis familiaris – Cfa, *Capra hircus – Chi, Chlorocebus sabaeus – Csa, Coturnix japonica – Cja*, *Cricetulus griseus – Cgr, Felis catus – Fca, Gorilla gorilla – Ggo, Heterocephalus glaber – Hgl, Loxodonta africana – Laf*, *Lipotes vexillifer – Lve, Macaca fascicularis – Mfa, Macaca mulatta – Mml, Macaca nemestrina – Mne, Monodelphis domestica – Mdo, Mus musculus – Mmu, Nannospalax galili – Nga*, *Nomascus leucogenys – Nle*, *Ovis aries – Oar, Pan paniscus – Ppa, Pan troglodytes – Ptr, Papio Anubis – Pan, Pongo abelii – Pab, Pteropus alecto – Pal*, *Rattus norvegicus – Rno, Rhinopithecus bieti – Rbi, Rhinopithecus roxellana – Rro*, *Saimiri boliviensis – Sbo, Sus scrofa – Ssc, Tupaia chinensis – Tch, Ursus maritimus – Uma.*

2565 miRNA were downloaded from miRBase (http://mirbase.org). Where as 3701 miRNA were taken from the publication of Londin E. et al. [24]. Nucleotide sequences of miRNAs were listed with our notation: miR-1-875-3p(cggcucugggucuguggggagc); miR-1-1714-3p(cggcggcggcggagcgcggg); miR-1-2558-3p(ccuucuucucccccaccccagc); miR-2-3313-3p(ggcggcggcggcggcggcggccccg); miR-2-4804-5p(ugagcaacacagugagacuccuuu); miR-3-9461-3p(cccggcagcgguggcagcgguag); miR-5-14523-3p(ucgcgcucgcugccuucucccc); miR-5-15026-5p(agccagggcaggccgggccuccg); miR-5-16438-3p(gcggcggcagcuggggcgggaa); miR-5-16871-5p(uaaaauuaauugcaguuuuugu); miR-6-17487-3p(cgcacacacacacacagacaccu); miR-7-19239-3p(gguggcggcggcggcuccgggcu); miR-8-24124-3p(gcuccugccuugccggagucug); miR-9-26166-3p(cuguccugccggcggccguggc); miR-10-5299-5p(cggcggcggccgccgcggg); miR-10-25954-5p(agggagccucuguuggggcuggaa); miR-11-18690-5p(cuggggggaggaggaagaggaga); miR-11-23098-5p(cugaggggcaggaggugggag); miR-14-34881-3p(cugggcuuguggggaccccugg); miR-16-36797-3p(ugaugcccucgcccucccuagu); miR-16-37595-3p(cgaccucggcccugcccuugca); miR-17-34996-5p(ugaacccgagaggaagagauugc); miR-17-36033-3p(ugccccgaccugaccccggcccucg); miR-17-38391-3p(ccuucuccuccucucccucccua); miR-17-39416-3p(gccucgccgccgccucugcugc); miR-17-42540-3p(cggcggcggcgcgccggguc); miR-18-39953-5p(ccgccccgccgcucccggcgcccc); miR-19-42593-3p(ccucccccuuuccaccccaguga); miR-19-42772-5p(gggccggcggcggcggcgccucu); miR-19-43065-3p(ucuguccaccuugcuucuucagg); miR-19-43662-5p(uggcuggaggagcuggggguguca); miR-20-44817-5p(ggcuagagcccgacgggggcccgg); miR-21-40861-3p(gucccccucucucccuuccccaa); miR-22-44137-3p(cucccugcagcggucagaggauc).

Binding sites for tested miRNAs were revealed using the MirTarget program [25]. This program defines the following features of binding: a) beginning of miRNA binding with mRNAs; b) localization of miRNA binding sites in the 5'-untranslated regions (5'UTRs), coding domain sequences (CDSs) and 3'UTRs of mRNAs; c) free energy of hybridization (ΔG, kJ/mole); d) schemes of nucleotide interactions between miRNAs and mRNAs. The ratio ΔG/ΔGm (%) was counted for each site, where ΔGm is free energy of miRNA binding with its perfect complementary nucleotide sequence. The miRNA binding sites located on the mRNAs have ΔG/ΔGm ratios of 90% and more. We also note the position of the binding sites on the mRNA, beginning from the first nucleotide of the 5'UTR of mRNA. The MirTarget program computes the interactions between the nucleotides of miRNAs and those of target gene mRNAs. It found bonds between adenine (A) and uracil (U), guanine (G) and cytosine (C), and G and U, as well as between A and C via one hydrogen bond.

In the interaction of miRNA with mRNA, the program allows one unpaired nucleotide only in mRNA, but not in miRNA, since it is bound to the RISK complex. Contrary to the hypothesis that miRNA binds with mRNA only in the 3'UTR, and interacts with mRNA only due to the "seed" of the site, the program takes into account the interaction of miRNA with mRNA over the entire length in 5'UTR, CDS and 3'UTR at the basis of physico-chemical properties of these molecules.

Results and their discussion

It was found that 13 miRNAs contacted with mRNA of *E2F1* gene. One miRNA of them is associated in the 5'UTR, five miRNA – in the 3'UTR and seven miRNA – in the CDS, which shows a clear preference for the binding of miRNA in the beginning of mRNA (table 1). The mRNA of *E2F1* gene has one binding site for miR-1913 arranged in the 5'UTR. Binding of miRNA in the 5'UTR has a biological significance, because it allows to miRNA stopping protein synthesis earlier, and do not waste energy on synthesis of abortive protein in the case of miRNA binding in the 3'UTR. The free energy of interaction of miR-6511b-3p, miR-1-1714-3p and miR-6786-5p with mRNA of *E2F1* gene is more than -115 kJ/mole, indicating a strong binding of these miRNAs and more effective suppression of E2F1 protein synthesis.

E2F2 gene consists of a smaller number of nucleotides and possibly therefore its mRNA has binding

sites only for ten miRNAs (table 1). There are no multiple binding sites for miRNAs. The mRNA of *E2F2* gene contains seven binding sites in the 3'UTR, three sites in the CDS and there are no sites in the 5'UTR. Among the mRNA areas, that having a miRNA binding sites, we prefer protein coding regions, which largely reflect the connection of a miRNA with gene function. Therefore, we chose miR-760-3p to determine how conservative this binding in the evolution of *E2F2* gene.

Table 1 – Characteristics of miRNAs binding with mRNA *E2F1, E2F2* genes

Gene *E2F1* miR-1913, 29*, -115, 90, 22; miR-6786-5p, 267, -115, 90, 21; miR-10-5299-5p, 290, -115, 95, 19; miR-X-44865-3p, 292, -115, 92, 20; miR-1-1714-3p, 381, -119, 95, 20; miR-17-36033-3p, 446, -129, 87, 25; miR-22-44137-3p, 764, -115, 89, 23; miR-16-36797-3p, 1382, -115, 93, 22; miR-6-17487-3p, 1642**, -113, 90, 23; miR-21-40861-3p, 2178**, -110, 90, 22; miR-4749-3p, 2322**, -108, 91, 20; miR-6511b-3p, 2326**, -121, 93, 23; miR-6813-3p, 2537**, -108, 91, 21
Gene *E2F2* miR-1-875-3p, 623, -115, 90, 22; miR-760, 624, -106, 93, 20; miR-4539, 1406, -113, 90, 22; miR-548m, 2091**, -93, 90, 21; miR-2-4804-5p, 4107**, -113, 90, 24; miR-5684, 4121**, -98, 92, 20; miR-1273g-3p, 4127**, -113, 96, 21; miR-1273f , 4160**, -96, 92, 19; miR-17-34996-5p, 4165**, -110, 90, 23; miR-10-25954-5p, 4482**, -119, 89, 24
Gene *E2F3* miR-7-19239-3p, 24*, -125, 89, 23; miR-19-42593-3p, 371, -115, 89, 23; miR-5-16438-3p, 457, -115, 87, 22; miR-17-42540-3p, 449, -115, 92, 20; miR-3-9461-3p, 461, -121, 89, 23; miR-11-18690-5p, 530, -110, 90, 22; miR-19-42772-5p, 553, -127, 90, 23; miR-17-39416-3p, 692, -123, 94, 22; miR-1-2558-3p, 3172**, -113, 90, 22; miR-5-16871-5p, 4430**, -93, 92, 22
Gene *E2F4* miR-5-15026-5p, 11*, -125, 91, 23; miR-5-14523-3p, 42*, -117, 92, 22; miR-6791-3p, 159, -108, 91, 21; miR-20-44817-5p, 534, -123, 89, 23; miR-11-23098-5p, 1745**, -110, 91, 21; miR-19-43662-5p, 1756**, -115, 89, 23
Gene *E2F5* miR-9-26166-3p, 66, -113, 90, 22; miR-8-24124-3p, 71, -115, 92, 22; miR-16-37595-3p, 84, -115, 90, 22; miR-6068, 103, -110, 90, 21; miR-7-19239-3p, 130, -125, 89, 23; miR-18-39953-5p, 163, -129, 90, 23; miR-6791-3p, 232, -108, 91, 21
Gene *E2F6* miR-19-43065-3p, 228*, -115, 92, 22; miR-151a-5p, 2212**, -104, 92, 21; miR-151b-5p, 2215**, -93, 96, 18; miR-17-38391-3p, 3023**, -115, 90, 23
Gene *E2F7* miR-14-34881-3p, 71*, -119, 93, 22
Note. miRNA (the number of binding sites); the beginning of binding site; the miRNA region: * – 5'UTR, ** – 3'UTR; the free energy change (ΔG, kJ/mole); the ΔG/ΔGm (%); length of miRNA (nt)

Data given in Table 2 show that heptapeptide TPHGPEG, encoded by the binding site of miR-1-875-3p and miR-760-3p, conservative in 18 animal species, which indicate the stability of miR-1-875-3p and miR-760-3p connection with the expression of *E2F2* gene in the process of long evolution. Binding sites of miR-760-3p and miR-1-875-3p were determined in the area of 15% from the beginning in CDS. These miRNAs binding sites were determined in mRNA of *E2F2* gene of rat, mice and, therefore, these animals can be used in an experiment of studying the action of miR-760-3p and miR-1-875-3p.

The mRNA of *E2F3* gene contains binding sites for 10 miRNAs, which have one binding site (table 1). The miR-7-19239-3p is bind in the 5'UTR, miR-1-2558-3p and miR-5-16871-5p in the 3'UTR and other miRNAs are bind in the CDS mRNA of *E2F3* gene.

The miR-7-19239-3p, miR-19-42772-5p, miR-3-9461-3p, miR-17-39416-3p can interact with energy more than -120 kJ/mole, which indicates a strong binding to mRNA of *E2F3* gene. However, not all miRNAs can be synthesized at one time in each cell. In order to suppress protein synthesis the miRNA concentration should be comparable with the concentration of mRNA, to reduce the number of free mRNA and cause inhibition of translation. Should be awared that about half of all miRNAs are derived

from introns, and are synthesized together with the host gene, which can not be expressed in a given cell at a given time.

The miR-19-42593-3p is linked in region of mRNA from 371 nt to 420 nt. This binding site of miR-19-42593-3p encoded oligopeptide AAV-VAAAAAA (table 3).

E2F4 gene contains binding sites for six miR-NAs. Two miRNAs bind in the CDS and two miR-NAs in 5'UTR and 3'UTR (Table 1). The free energy of interaction (ΔG) of miR-5-15026-5p and miR-20-44817-5p with mRNA of *E2F4* gene is equaled to or more than -120 kJ/mole, indicating a strong binding of these miRNA and more effective suppression of E2F4 protein synthesis.

The mRNA of *E2F5* gene contains binding sites for seven miRNAs located in the CDS. Binding sites of the following miRNAs encode oligopeptides indicated in brackets: miR-6068 (PPPQPPQ), miR-9-26166-3p (GQQAPAG), miR-8-24124-3p (QAPAGQG), miR-16-37595-3p (GQGQGQR), miR-7-19239-3p (APQPPPPP), miR-18-39953-5p (GGAGGGSS), miR-6791-3p (LLQEAKD). Tables 4-7 show the conservatism of these oligopeptides in the E2F5 protein.

Table 2 – Conservatism of TPHGPEG heptapeptide encoded by miR-760-3p and miR-1-875-3p binding site in mRNA *E2F2* gene

Region of E2F2	Object
APGTCLDA**TPHGPEG**QVVRCLPA	*Hsa, Ppa, Mml, Nle, Chi, Fca, Ptr, Oar, Pab, Rro, Cja, Ggo, Lve*
ASGTCLDA**TPHGPEG**QVVRCLPA	*Mfa*
APGTCLDA**TPHGPEG**QAVRCVPA	*Ame*
AAGTCLDA**TPHGPEG**QAVRCVPA	*Cfa*
ALGTCLDA**TPHGPEG**QIVRCVPA	*Rno, Mmu*
Note. In bold, a conservative heptapeptide encoded by miR-760-3p and miR-1-875-3p binding site	

Table 3 – Conservatism of decapeptide AAVVAAAAAA encoded by miR-19-42593-3p binding site in mRNA *E2F3* gene

Region of E2F3	Object
VTAGGGEG**AAVVAAAAAA.**SMDKRALL	*Hsa, Lve, Ptr, Mne, Pab, Nle, Bta, Csa, Oar, Cgr, Mmu, Pal*
VTAGGGEG**AAVVAAAAAAA**SMDKRALL	*Nga*
VTAGGGEG**AAAAAAAAAA.**SMDKRALL	*Mdo*
VTAGGGEG**AAVVAAAAAA.**SMDTAGSLL	*Ggo*
Note. In bold, a conservative decapeptide encoded by miR-19-42593-3p binding site	

Table 4 – Variability of decapeptide encoded by miR-6068 binding site in mRNA *E2F5* gene

Region of E2F5	Object
QGQGQR**PPPQPPQ**AQAPQP	*Hsa Ggo*
QGQGQR**PPPHPPQ**AQAPQP	*Nle*
QGQGQR**PQPQPPQ**AQAPQP	*Ptr Mml Csa*
QGQDQR**PQPQPPQ**AQAPQP	*Cja*
QGQGQR**PQPQPSQ**AQPPQQ	*Ame*
QGQGQR**PQPQQSQ**AQPPPP	*Lve*
QGQGQR**PQPPQPQ**PPQQPP	*Laf*
QGQGQR**PQPPPSQ**AQPPPP	*Ssc*
QGQGQR**PQ**A**Q**S**PQ**AQAPQP	*Rro*

Table 5 – Conservatism of decapeptide APQPPPPP encoded by miR-7-19239-3p binding site in mRNA *E2F5* gene

Region of E2F5	Object
QPPQAQ**APQPPPP**PQLGGA	*Hsa, Ptr, Mml, Csa*
QPPQAQ**APQPPPP**QQLGGA	*Ggo*
HPPQAQ**APQPPPP**PQLGGA	*Nle*
QSPQAQ**APQPPP.**LQLGGA	*Rro*

Table 6 – Conservatism of decapeptides encoded by miR-9-26166-3p, miR-8-24124-3p, miR-16-37595-3p binding site in mRNA E2F5 gene

Regions of E2F5			Object
miR-9-26166-3p	miR-8-24124-3p	miR-16-37595-3p	
AEPASS**GQQAPAG**QGQGQR	PASSGQ**QAPAGQG**QGQRPP	GQQAPA**GQGQGQR**PPPQPP	*Hsa*
AEPASS**GQQAPAG**QGQGQR	PASSGQ**QAPAGQG**QGQRPQ	GQQAPA**GQGQGQR**PQPQPP	*Ptr*
AEPASS**GQQAPAG**QGQGQR	PASSGQ**QAPAGQG**QGQRPP	GQQAPA**GQGQGQR**PPPHPP	*Nle*
AEPASS**GQQAPPG**QGQGQR	PASSGQ**QAPPGQG**QGQRPQ	GQQAPP**GQGQGQR**PQPQPP	*Mml*
AEPASS**GQQAPPG**QGQGQR	PASSGQ**QAPPGQG**QGQRPP	GQQAPP**GQGQGQR**PPPQPP	*Ggo*
AEPASS**GQQAPPG**QGQDQR	PASSGQ**QAPPGQG**QDQRPQ	GQQAPP**GQGQDQR**PQPQPP	*Cja*
AEPASS**GQQAPPG**QGQGQR	PASSGQ**QAPPGQG**QGQRPQ	GQQAPP**GQGQGQR**PQPQPP	*Csa*
AEPASS**GQQAPPG**QGQGQR	PASSGQ**QAPPGQG**QGQRPQ	GQQAPP**GQGQGQR**PQAQSP	*Rro*
AEPASS**GQQAPQG**QGQGQR	PASSGQ**QAPQGQG**QGQRPQ	GQQAPQ**GQGQGQR**PQPPQP	*Laf*
VLALRA**GQQAPQG**QGQGQR	ALRAGQ**QAPQGQG**QGQRPQ	GQQAPQ**GQGQGQR**PQPQPS	*Ame*
AEPGGS**GQPAPQG**QGQGQR	PGGSGQ**PAPQGQG**QGQRPQ	GQPAPQ**GQGQGQR**PQPQQS	*Lve*
AEPASS**GQPAPEG**QGQGQR	PASSGQ**PAPEGQG**QGQRPQ	GQPAPE**GQGQGQR**PQPPPS	*Ssc*

Table 7 – Conservatism of decapeptide LLQEAKD encoded by miR-6791-3p binding site in mRNA *E2F5* gene

Region of E2F5	Object
TTKFVS**LLQEAKD**GVLDLK	*Hsa, Ggo, Ptr, Mml, Cja, Uma, Fca, Pab, Tch, Ssc, Sbo, Ame, Csa, Rro, Lve, Laf, Mdo, Nga, Mmu*
TAKFVS**LLQEAKD**GVLDLK	*Bta*
TTNFVS**LLQEAKD**GVLDLK	*Nle*

E2F6 gene contains binding sites for one miRNA in the 5'UTR and for three miRNAs in the 3'UTR. Nucleotide sequences of miR-19-43065-3p binding sites in mRNA of *E2F6* gene are shown in Table 9. Binding sites of miR-19-43065-3p are completely homologous in *Homo sapiens, Pan troglodytes, Nomascus leucogenys, Pan paniscus* and there is only one nucleotide replacement in the remaining species. Therefore, for tens of millions of years, miRNA binding sites were remain, which indicates the stability of the process *E2F6* gene expression regulation by miRNA.

mRNA of *E2F7* gene binds to miR-14-34881-3p in the 5'UTR. The nucleotide sequences of binding site of miR-14-34881-3p in mRNA of *E2F7* gene are shown in Table 10. Binding sites of miR-14-34881-3p are completely homologous in *Homo sapiens, Rhinopithecus roxellana, Chlorocebus sabaesus, Papio anubis*. In mRNA of *E2F7* gene of the remaining species this miRNA has only one substitution of nucleotides. That is, for tens of millions of years, the binding sites of miR-14-34881-3p in mRNA of *E2F7* gene persist, indicating that the method of regulating the expression of *E2F7* gene by miRNA is stable.

The miRNA binding sites located in the 5'UTR were found only in monkeys. In other animals, these binding sites were strongly changed, or absent.

Identified binding sites in the protein-coding region of mRNA genes of *E2F* family have several characteristics. Some binding sites are conserved along with flanking sequences of amino acids (Tables 2, 3, 5, 6, 7). Other binding sites are more conservative than flanking sequences. The most common binding sites located between conserved sequences and the length of sites of multiple binding sites vary in mRNA of different animal species (Tables 4, 8). In this connection, the question arises whether the peptides coded by binding sites in the CDS of are any function other than the reflection of binding sites. In the case of a change in the length of binding sites and the corresponding oligopeptides up to their absence, they probably do not play a functional role other than miRNA binding. In the case of high conservatism of encoded oligopeptides and their flanking amino acids, probably these oligopeptides are necessary for the demonstration of function of the complete protein.

Таблица 8 – Variability of oktapeptide GGAGGGSS encoded by miR-18-39953-5p binding site in mRNA of *E2F5* gene

Region of E2F5	Object
PPPPQL**GGAGGGSS**RHEKSL	*Hsa, Ptr, Nle, Csa, Rro*
PPPPPL**GGAGGGSS**RHEKSL	*Ggo*
PPPQQL**GGAGGGSS**RHEKSL	*Mml*
PSQQQL**GGAGGGSS**RHEKSL	*Sbo*
PSQQQL**GGVGGGSS**RHEKSL	*Cja*
TPPPQF**GGVGGGSS**RHEKSL	*Hgl*
PPPPPL**GGGGGGSS**RHEKSL	*Lve*
PPQQPL**GGGGGGSS**RHEKSL	*Ssc*
PPPPQL**GGGGGGG-**RHEKSL	*Ame*
AAPPGN**GGGGSSS-**RHEKSL	*Mdo*
PPQQLA**GGGSS---**RHEKSL	*Tch*
ASCAPP**GAGSS---**RHEKSL	*Bta*
PSAALA**GGSS----**RHEKSL	*Mmu*
QPPRVR**GGSS----**RHEKSL	*Fca*
RSSGRR**GGSS----**RHEKSX	*Pab*

Table 9 – Nucleotide sequences of binding sites of miR-19-43065-3p in 5'UTR of mRNA *E2F6* gene

Nucleotide sequences	Object
GUGCUCGA**GCUGAGCGCGAGAGGGCGGGAGA**GCUCGUGG	*Has, Ptr, Nle, Ppa, Pab*
GUGCUCGA**GCU<u>GAGUGCGAGAGGGCGGGAGA</u>**GCUCGUGG	*Ggo*
GUGAUCGA**GCUGGGCGCGAGAGGGCGGGAGA**GCUCGCAG	*Rro, Rbi*
GUGAUCGA**GCUGGGCGCGAGAGGGCGGGAGA**GCUCGCGG	*Csa*
GUGAUCGA**GCUGCGCGCGAGAGGGCGGGAGA**GCUCGCGG	*Pan, Mml, Mfa*
GCGCUCGA**GC**UA**GGCGCGAGAGGGCGGGAGA**GCUCUCGG	*Cja*
Note. In bold, binding site of miR-19-43065-3p	

Table 10 – Nucleotide sequences of binding sites of miR-14-34881-3p in 5'UTR of mRNA *E2F7* gene

Nucleotide sequences	Object
UGCCCGGACG**CCGCGGGGU**CCCCGCCAGCCCAGGGCACUCGGC	*Hsa*
UGUCGGGACG**CCGCGGGGU**CCCCGCCAGCCCAGGGCACUCGGC	*Rro, Csa*
UGUUGGGACG**CCGCGGGGU**CCCCGCCAGCCCAGGGCACUCGGC	*Pan*
UGCCCGGACG**CCACGGGGU**CCCCGCCAGCCCAGGGCACUCGGC	*Ggo, Ptr, Ppa*
UACACGGACG**CCACGGGGU**CCCCGCCAGCCCAGGGCACUCGGC	*Nle*
UGUCGGGACG**CCGCGGGGU**CCCCGCCAGUCCAGGGCACUCGGC	*Mml, Mne, Mfa*
UGCCCGGACG**CCGCGGGGU**CCCA**GCCAGCCCAG**GGCACUCGGC	*Cja, Sbo*
Note. In bold, binding site of miR-14-34881-3p	

The nucleotide sequences of binding sites that located in the 5'UTR are flanked by conserved regions without changing in the length of miRNA binding sites (Tables 9, 10). On the basis defined in the present work different miRNA binding sites in mRNA of a gene family can be identified associations miRNA with mRNA which allow their use as diagnostic markers for different oncology diseases.

The mRNA of *E2F1, E2F2, E2F3* genes activate the cell cycle, and the probable cause is that they often demonstrate themselves as oncogenes, because they increase cell proliferation. We have identified an increased number of miRNAs, interacting with mRNA of *E2F1, E2F2, E2F3* genes, probably they work as increased protection against excessive fusion E2F1, E2F2, E2F3 proteins. Less ability of mRNA of *E2F4, E2F5, E2F6, E2F7, E2F8* genes to bind miRNA allows to maintain the required level of apoptosis.

Finding miRNA binding sites raises the question of the level of reliability of found sites. One effective way to establish the reliability of binding sites is finding of binding sites in orthologous genes and identification of orthologous miRNA. Location of binding site in the protein coding region facilitates its conservation in evolution, especially, if the corresponding oligopeptide plays an important role in the function of protein. Similar results were obtained earlier [26, 27].

From cited studies it is known that for all taken miRNAs their concentrations vary with the change in the activity (expression) of *E2F* family genes, none could significantly affect on mRNA, unless the miRNA concentration was much higher than the mRNA concentration. Unfortunately, authors of virtually all publications did not simultaneously control the concentration of miRNA and the concentration of the synthesized protein of the target gene. Therefore, we cannot say with confidence that if the gene expression changes along with the level of miRNA with a positive or negative correlation, then this gene is a target for miRNA. In addition to the direct action of miRNA on the expression of the target gene, miRNA affects on many transcription factors, which in turn can influence on the expression of many genes, including those studied simultaneously with the studied miRNAs.

Conclusion

The obtained results indicate that mRNA of *E2F* genes family bind with miRNA in different degrees. The mRNA of *E2F1, E2F2, E2F3* genes have the largest number of miRNA binding sites which accelerate the cell cycle. Probably therefore the expression of *E2F1, E2F2, E2F3* genes should be largely influenced by miRNA, to prevent an uncontrolled increase in cell proliferation, which is usually observed during tumourigenesis. The predicted miRNA binding sites with mRNA of *E2F* gene family help to find associations of miRNA with their target genes for the development of diagnostic methods of tumourigenesis. The following pairs can be used as associations of miRNA with target genes: miR-6511b-3p, miR-1-1714-3p and miR-6786-5p with mRNA of *E2F1* gene; miR-7-19239-3p, miR-19-42772-5p, miR-3-9461-3p and miR-17-39416-3p with mRNA of *E2F3* gene; miR-5-15026-5p and miR-20-44817-5p with mRNA of *E2F4* gene.

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Circasepran rhytyms of motion activity

Abstract: In this study the circaseptan rhythms of the motion activity of practically healthy people with an average level of locomotor activity were analyzed, engaged in mental work, of different ages and sex. We compared data of peoples, who have usual working week (5 working days per week) and a person who worked seven days per week, at the same pace, to determine the influence of the social factor. The statistically significant circaseptan rhythms with period between 6.4 and 7.0 days were found, with the internal, endogenous rhythm being in most cases more significant in relation to the external rhythm, which should be taken into account, for example, in the formulation of optimal individual schedule.
Key words: circaseptan rhythms, week, social factors, motion activity, people, period.

Introduction

In a wide range of biological rhythms, weekly rhythms, occupying an important place in our daily life, at first sight look like exogenous rhythms, passively responding to environment cycles, in this case, social cycles. Nevertheless, the scientific literature data presented that indicate the endogeneity of these cycles. So, for example, one of the founders of chronobiology, Jurgen Aschoff, styduing scientists of antiquity, who study biological weekly rhythms [1], mentioned Hippocrates, Aristotle and Galen. However, even before the ancient Greeks, before Hippocrates and Galen, the famous scientist of the East, Abu Ali Hussein ibn Abdallah ibn Sina, or Avicenna (980-1032), discovered that the week was an important unit of biological time. He showed that, as a rule, the duration of diseases, for example, with pneumonia until the era of access to sulfonamides and antibiotics, took 7 days before finding out whether the patient would survive or die. The studies of Hobart Reiman [2], Kurt P. Richter [3], and Eric Ask-Upmark [4], give incontrovertible proofs about the importance of the week in human pathology, circaseptan rhythms of the physiological functions of a healthy person are also known [5; 6].

About weekly variations in biology are oflen viewed as no more than a response to the social week. Whereas the social schedule can be a strong synchronizer of circaseptan rhythms, much evidence has accumulated illustrating that this component has a dual aspect, being partly endogenous while also responding not just to the social week but also to circaseptans in geomagnetics.

Materials and methods

In this study, we analyzed the circaseptan rhythms of the motion activity of practically healthy people with an average level of locomotor activity, engaged in mental work, of different ages and sex. We compared data of peoples, who have usual working week (5 working days per week) and a person who worked seven days per week, at the same pace, to determine the influence of the social factor. As the method of investigation, automated multi-day wrist actigraphy (AMI, New-York, USA) was chosen, as a parameter, ZCM (zero crossing mode) was used, which is the count of the number of times the accelerometer signal crosses 0 for each time period. The data were recorded every minute on the continuation of a long time interval (6-7 months). For the analysis of the methods of spectral analysis were used [7-9].

Results and their discussion

An analysis of a two-year, continuous record of a 51-year-old man (TK) working standard five days a week showed a highly significant weekly rhythm ($p < 0.001$) with the following characteristics: period 7.001 days [6.995; 7.008], the amplitude of 8.4592, the acrophase -0.52233 (Table 1).

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Table 1 – Chronostructure of ZCM circadian rhythms

No.	The cipher of the participant of the experiment, sex, age	Period, days	Frequency	Amplitude	Acrophase
1	FH, male, 93 years old	6.878 [6.858; 6.898]	0,006058	4.796	-0.75291
2	TK, male, 51 years old	7.001 [6.995; 7.008]	0.142834	8.4592	-0.52233
3	ZT, female, 42 years old	7.886 [7.854; 7.918]	0.005283	4.2042	-0.2973
		6.934 [6.844; 7.02]	0.006009	1.6821	-0.53751
		6.451 [6,43; 6.472]	0.006459	4.259	-0.01379
4	RK, male, 16 years old	7.097 [7.043; 7.156]	0.005871	23.596	-0.39953
		6.635 [6.601; 6.669]	0.006279	27.803	-0.72364

In other participants of the experiment, the motor activity showed the most pronounced (with maximum amplitude) rhythms with a period slightly shorter than 7 days, while also revealing a statistically significant component almost equal to the astronomical week.

Subject 3 (ZT) had three statistically significant rhythms with a weekly periodicity, of which the highest and most significant amplitude was for a cycle with a period of 6.45 [6.43; 6.47] days, i.e., shorter than a week, although the period close to the week at 6.93 days [6.84; 7.02] is also statistically significant and reflects the contribution of the social factor to the analyzed biological rhythm. The youngest participant in the experiment had the highest rates of motor activity and the highest amplitude, i.e. for him the differences in the days of the week were most pronounced (Table 1, Figure 1).

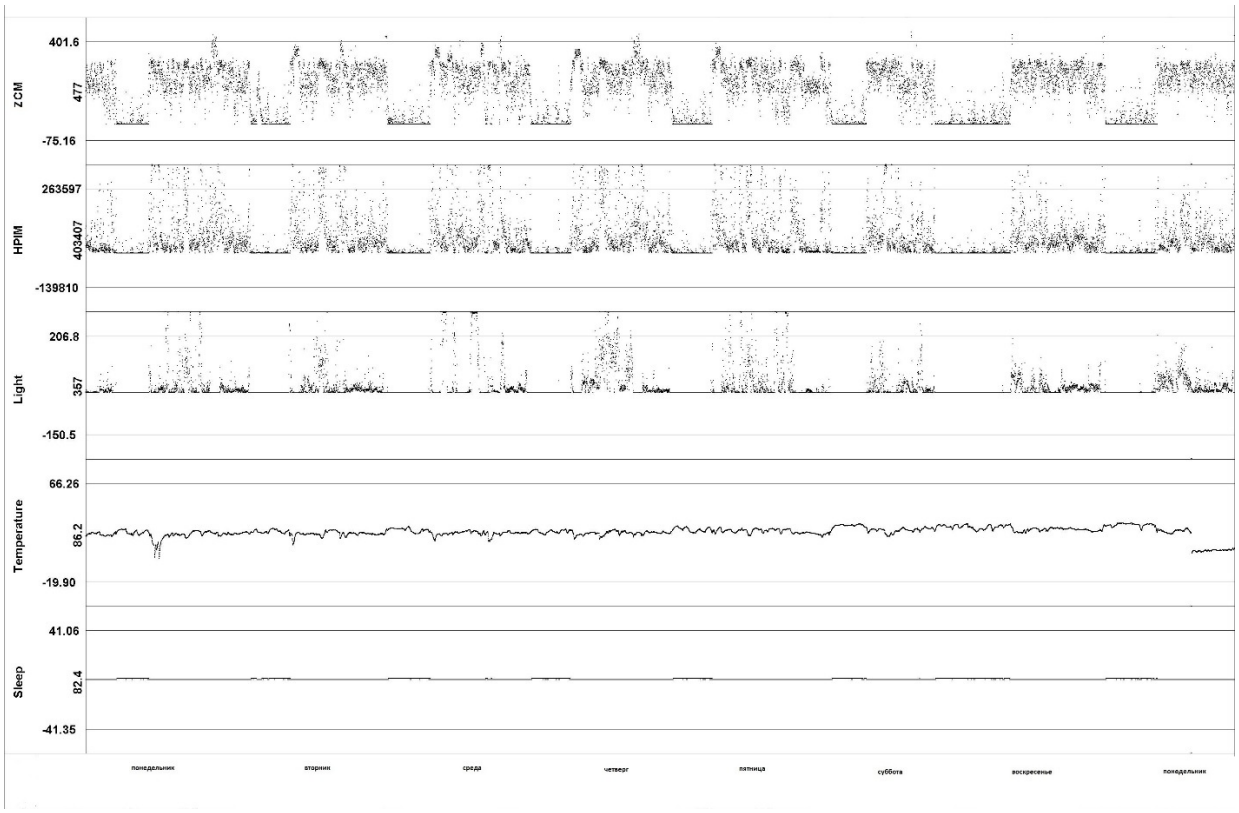

Figure 1 – Chronogram of motor activity during the week of one of the participants in the experiment (RK)

Subject 1 (FH) was the only one of the analyzed groups that worked without weekends, and not during the experiment only, but also for many decades, despite its advanced age. His biological week was predictable differ from the calendar week (somewhat shorter), but the other two participants having a training (RK) and working (ZT) schedule have also biological week, shorter than the astronomical one. The amplitude of the cycle for women and old man were low. Probably, the woman' motion activity at the weekend is related to household chores.

Changes as a function of age in the relative circaseptan-to-circadian prominence indicated a resurgence of the about-weekly variation in the elderly, Figure 2 [10]. The question may be raised whether this is a common feature of non-photic cycles, since a similar trend with age is found for the relative prominence of transyears versus the 1-year synchronized variation in blood pressure and heart rate [11].

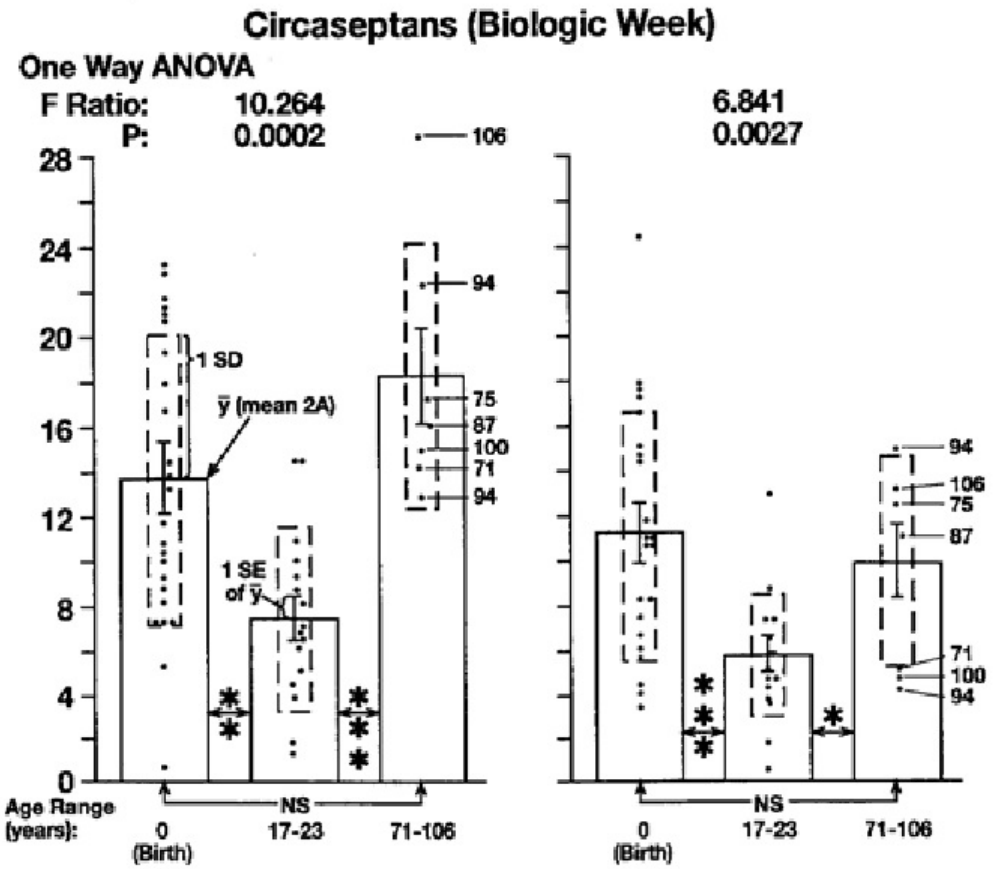

Figure 2 – Double amplitude of systolic (left) and diastolic (right) blood pressure is statistically significantly larger in the young and elderly than in mid-adulthood

Earlier, other authors [5; 6] showed a drift of the acrophase of the week, as well as the duration of the circadian rhythm cycle of 17-ketosteroid in the urine of a clinically healthy person. Data on urinary excretion of urinary hormones were collected daily for 10 years, periodically the cycle duration was synchronized exactly with the week, with a peak on Wednesdays or Thursdays. Periodically, the circaseptan acrophase of testosterone began to shift, and the period lasted longer than a week for several years, then the rhythm was characterized by a shorter period, the statistically most significant rhythm had a shorter period than exactly 1 week. The authors explain the periodic changes in the length of the cycles due to the influence of heliophysical factors.

A significant contribution of heliomagnetic factors to weekly rhythms of heart rate dynamics on some people was also reported earlier in the scientific literature [12]. The shortening of the cycle observed in our experiment is associated with the

endogenous circadian component, as well as the influence of external physical factors. Absolute domination of external heliophysical factors excludes the absence of other circadian frequencies in the spectrum of participant 1 (TK), except for a cycle of exactly 7 days. The influence of age and sex was manifested in the amplitude of the cycle, but not in its period.

Thus, in the dynamics of motion activity a statistically significant circaseptan rhythm was found, with the internal, endogenous rhythm being in most cases more significant in relation to the external rhythm, which should be taken into account, for example, in the formulation of optimal individual schedule.

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The importance of soybean (*Glycine max*) as a source of biologically valuable substances

Abstract: In the paper the biological valuable components of soybean are discussed. Soya is widespread product in the world. Soya is a prevention agent against of cardiovascular diseases, tromboembolosm. Consumption of soybean protein is decreased the content of cholesterol in blood, the risk of osteoporosis, promotes preservation of bones in the elderly. The useful futures of soybean are provided by the large content of protein, izoflavonoids, lecithin, micro- and macroelements and vitamins. High concentrations of biological active components in soybean allow using them in the pharmaceutical industry for production of drugs and dietary supplements. Phytopreparations like Inoclim, Estroel, produced by pharmaceutical companies on the basis of soybean extract, containing soybean isoflavonoides against menopausal syndrome are reviewed. Soybean isoflavonoids like genistine and daidestin have antioxidant, anticarcinogenic effect, normalize the function of the immune system and hemostasis The study of biological valuable components of Kazakhstan soybean varieties are required.
Key words: soybean, microelements, protein, izoflavonoids, lecithin.

Soya got a status of one of the most important crops as a source of protein, oil and nutraceuticals. The high content of isoflavonoids and folic acid has made this universal to use it for a healthy diet. Soy proteins are becoming increasingly important as a plant source for protein products with a high number of essential amino acids. The content of quality fats and polyunsaturated fatty acids is also important from the nutrichetic point of view [1]. Soy (*Glycine max*, Leguminosae) – is not only a valuable oil culture, but also as a feed for livestock and aquaculture. Soy is home to China, the main producers of soy products in the world are the USA, Brazil, Argentina and India. Soybean has been cultivated in China for more than 4000 years. Soy is a commercial crop and grown in 35 countries as the main seed of oilseeds [2]. On a global scale, 38% of the total soybean crop is grown in the US; in Brazil and – 25%, Argentina – 19%, China – 7%, India – 3%, Canada – 2% and Paraguay (2%) [3].

Soy is used as an important source of dietary protein and oil all over the world. Soy is of high nutritional value due to the high concentration of oil (18-25%) and protein (38-50%) and is a popular food all over the world [4]. Production and consumption of soy products is increasing every day in Western countries. In Asian countries, soy is used as a fermented and unfermented food product, such as soy sauce, Miso, natto, yoghurts, kinako, fresh protein, desserts, baby food and soy milk, which is further processed into tofu [5]. The main product of soybean is used as the primary source of protein for diseases, such as lactose intolerance and severe gastroenteritis in infants [6]. Mature soybean seeds contain approximately 35% protein, 31% carbohydrates, 17% fat, and 5% minerals [7].

Soy protein contains a significant amount of essential amino acids, that is, histidine, isoleucine, leucine, lysine, phenylalanine, tyrosine, threonine, tryptophan and valine, which are recommended for daily consumption as a balanced diet [8]. It is known that soy reduces the level of cholesterol in blood plasma [8] and is used in the prevention of cancer [9], improves bone density [10] and provides protection against bowel and kidney disease [11]. These properties are supported by the presence of isoflavonoids, saponins, protein and peptides in soybeans [12; 13]. Soy contains 35-40% protein, this includes globulins, 11S glycine and 7S β-conglycinin. These proteins contain all the amino acids necessary for human nutrition, which makes soy products almost equivalent to animal protein sources, but with less saturated fat

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and no cholesterol. Soy also contains biologically active protein components of hemagglutinin, trypsin inhibitors, α-amylase and lipoxygenases [14]. Soy is not only a high-quality protein, but now it is considered that it plays preventive and therapeutic roles for a number of diseases [15].

Soya contains about 19% oil, of which triglycerides are the main component. Soybean oil is characterized by a relatively large number of polyunsaturated fatty acids (PUFA) – 51% linoleic acid and 8% α-linolenic acid, stearic acid – 4, palmitic acid – 10, oleic acid – 23% of the total.

The oil also contains 1-3% phospholipids, ~ 35% phosphatidylcholine, ~ 25% phosphatidylethanolamine, ~ 15% phosphatidyl inositol, ~ 5-10% phosphatidic acid. Soybeans contain ~ 35% carbohydrates, polysaccharides, oligosaccharides, such as stachyose (4%) and raffinose (1.1%). Stachyose is a tetrose with galactosehaving structure of galactose-glucose-fructose, whereas raffinose is a triose with the structure of galactose-glucose-fructose [15]. When used as a dietary supplement to fiber, soluble polysaccharides are used to modify the physical properties of various products [16].

Soy is the best source of B vitamins compared to cereals, although B12 and vitamin C are not enough [14]. Soybean oil also contains tocopherols, which are natural antioxidants. Soy also contains 5% of minerals. It is relatively rich in K, P, Ca, Mg and Fe. Soy ferritin can extract a significant amount of iron [17].Traditionally, products based on soybeans have been used for many centuries in most Asian countries, and lately this food has been used.

Traditionally, soya bean products have been used for centuries in most Asian countries, and recently this food has been very popular in the western hemisphere [18]. Transgenic soybeans are included in agricultural technology to increase productivity mainly by reducing costs and, consequently, the cost of production. Soy is gaining momentum as a nutritious product, and is also becoming popular for nutraceuticals because it contains an essential amino acid and secondary metabolites such as isoflavonoids, saponins, phytic acids, phytosterols, trypsin inhibitors and peptides [19].

Soya as a functional ingredient influences lowering of cholesterol and the prevention of cardiovascular diseases, diabetes, bone strength and the prevention of cancer. It is believed that food based on soybeans can help lower cholesterol levels [7]. Transgenic soybean with α-tocopherol content by expression of the γ-tocopherol methyltransferase gene of the plant *Perilla frutescens* prevents oxidative damage to lipids during seed storage and germination [20]. The use of soybeans, which are good sources of calcium and protein and a simple way to help in maintaining strong bones and reduce the risk of osteoporosis. Studies show that it is isoflavones, genistein and dieldin in soybeans, prevent bone loss or bone destruction. In addition, protein in soy helps keep calcium in our bodies. Soy is the richest source of isoflavones (up to 3 mg/g dry weight) [21]. Isoflavonoids prevent various types of disease, such as bone fragility, cancer, cardiovascular diseases, menopause, diabetes and obesity [22-24]. Epidemiological and clinical studies of soy isoflavonoids have shown that soy consumption is associated with a reduced risk of breast cancer [25]. The influence of consumption of yellow soybeans, black soybeans (*Glycine max*) or beans (sword bean) (*Canavalia gladiate*) at the level of lipids and oxidative stresses in rats was evaluated. They suggested that consumption of various types of beans can inhibit oxidative stress in postmenopausal women, increasing antioxidant activity and improving lipid profiles [26]. In addition to isoflavones, soy contains other sub-classes of flavonoids, including flavonols, aurones, flavones, flavanols, chalcons, red and blue anthocyanin pigments. Folic acid, present in soybeans, has a synergistic effect in preventing loss of bone mass. It should be noted that the consumption of black soy has led to the greatest improvement in risk factors associated with cardiovascular diseases. Folic acid has a therapeutic effect in many other health disorders, such as anemia, poor absorption of nutrients, brain development in infants, treatment of Alzheimer's disease, age-related hearing loss, etc. Therefore, diets rich in soy, are a good source of this vitamin, can be useful for nutrition. The importance of polyphenols increases due to their dual role in the food industry as a stabilizer of lipids and in the prevention of diseases associated with oxidative stress. Polyphenols as natural antioxidants are able to inhibit lipid peroxidation and protect against damages caused by free radicals [27].

Soybeans, soy products and preparations based on soybeans (Figure 1) have found wide application for the treatment of menopausal syndrome due to the high content of phytoestrogens in them that have a unique selective effect on the β-receptors of estrogens, in contrast to endogenous estrogens and estrogens in the hormone replacement. It has been established from a number of studies that soy isoflavones are not only more effective in eliminating tides in women in menopause, but the effectiveness of soy isoflavones is comparable to that of hormone replacement therapy. In addition to influencing the neuro-

vegetative symptoms of menopause, soy isoflavones reduce the level of total cholesterol in the blood serum, reduce the level of low and very low density lipoproteins, and increase the level of high-density lipoproteins. In addition, according to some data, soy isoflavones exhibit an antithrombotic effect [28].

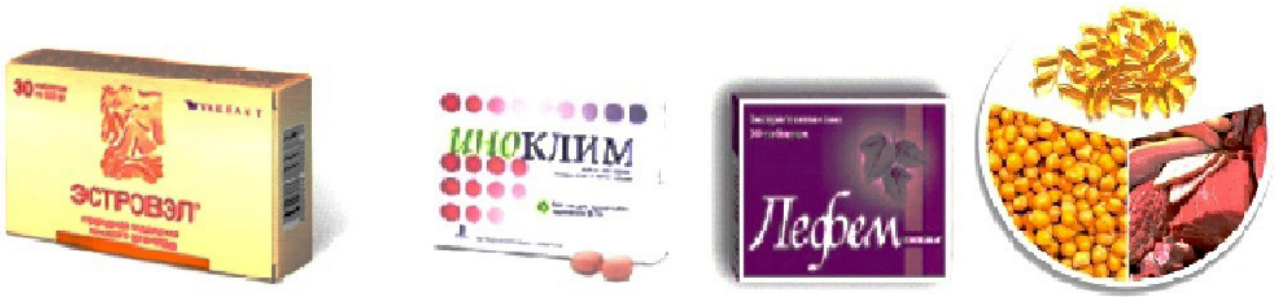

Figure 1 – Phytopreparations, containing soybean extract (http://climaxhelp.ru/drugs/fito/)

In the treatment of climacteric syndrome, hormone replacement therapy continues to be the main method of treatment. But many women have contraindications or prejudices to the use of hormonal drugs. In connection with this, it is urgent to search for alternative methods of treating climacteric syndrome, including herbal preparations. It has been established that bioflavonoids are able to inhibit, and in some cases stimulate a large number of enzymatic systems, both in experimental animals and in humans. Flavonoids have antioxidant, anticarcinogenic effect, normalize the function of the immune system and hemostasis. In this case, the toxic effect of flavonoids on human and animal cells is either absent or minimal, and has protective properties for breast cancer [30].

Laboratory Innotech Internacional (France) produces the drug "Inoklim". At its core the preparation contains soybean extract, rich in two important isoflavones: genistin and daidzein, recommended for the treatment of patients with menopausal syndrome [31].

The effectiveness and acceptability of "Inoklim" in relation to the frequency and intensity of symptoms of climacteric syndrome, as well as the tolerability and safety of this drug was studied.

The severity of menopausal syndrome was assessed using a questionnaire to calculate the Kupperman index (vasomotor symptoms, insomnia, nervousness, dizziness, general weakness, headache, rapid heartbeat), and a second questioning was conducted against the background of ingestion of "Inoklim".

The study shows the high effectiveness of soy isoflavones in the treatment of the pathological symptoms of the climacteric symptom. Against the backdrop of the application of "Inoklim" for 3 months in postmenopausal women with pathologic menopause, the general condition significantly improved, the severity of psychoemotional and vegetative-vascular disorders decreased. Evaluation of the effectiveness of the drug by patients was high.

Phytopreparation "Inoklim" possesses an estrogen-like action, it helps to prevent and reduce the intensity of symptoms of menopause (hot flashes, osteoporosis, and emotional instability), stabilize the condition, improve sleep. The drug has no side effects inherent in hormone replacement therapy. It includes soybean extract Novasoy, soy lecithin, fish gelatin and other auxiliaries.

Thus, the study allows to consider the "Inoklim" containing soybean extract, rich in two important isoflavones: genistin and daidzin, as a highly effective method of stopping the pathological manifestations of climacteric syndrome, as well as an alternative method of its treatment in the presence of contraindications to the use of hormone replacement therapy or in case of failure from taking hormonal drugs.

The Estroel phytopreparation contains a zymicifugacaramose extract of the root of wild yam, contains soy extract. In addition to plant extracts, this preparation contains indole-3-carbinol, extract of nettle leaves, boron, vitamin E, vitamin B6, folic acid, amino acids (5-hydroxytryptophan, D, L-phenylalanine). Estroel helps eliminate estrogen deficiency, reduce the intensity of tides, correct the psycho-emotional state, reduce the risk of estrogen-dependent tumors, normalize hematological parameters, immunocorrection, prevent osteoporosis, and eliminate vitamin deficiency [32].

Thus, soy is one of the promising crops as a source of important components for the pharmaceutical industry, necessary for maintaining human health. Soy is currently grown in many regions of Kazakhstan. Soy is grown in the Almaty region (Aksu, Sarkan and Alakol regions) [28], in the farms of Northern Kazakhstan [29]. This crop is profitable, as it has a high purchase price and is successfully used in crop rotation. The investment cluster program "MaJiCo – 2020" provides, along with other crops, an increase in soybean crops in Kazakhstan to 400 thousand hectares with production of 1 million tons of beans per year. The future research works by the estimation and extraction of biologically valuable components from Kazakhstani soybean varieties are required.

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Multiple premises for research-integrated blended education via mapping genetic resources

Abstract: Since the last century a special emphasis has been made on the species and crop diversity and their conservation, especially after several N.I. Vavilov's research expeditions. Institutional pre-requisites may have been seen from the pattern of the Belorussian collection which has been integrated recently to AEGIS initiative affiliated in turn with ECPGR (European Cooperative Programme for Plant Genetic Resources). The initiative comprises 650 institutions from 43 European countries engaged in promoting specific gene banks. Each institution is targeted to preserve and breed activities on a domestic valuable crop. National repositories summon up to adapting valuable crops to changing environment, production and consumer needs. On the other hand, the current trends lead to merged interdisciplinary MSc and PhD educational programs in mapping genetic resources domestically and internationally. Besides, current educational purposes of Bologna-linked universities worldwide demand to obtain and immediately imply highly competitive knowledge, consistent with growing trends of relevant accreditation, life-long learning, internationalization, further excellence of women in research and management, extending business-education partnerships, digital skills, support to innovative environment, proper employment of graduates and other factors. The above mentioned premises can be supported by modern GIS-technologies and versatile aerospace information, which supply more and more precise and reliable data on the state of agro-landscapes.

Key words: research-integrated blended education, mapping genetic resources.

Introduction

Current education needs impose new teaching formats via its modernization, and particularly massive online education, hands-on education, blended education, and therefore multisubject-"addicted" didactics. Historical, institutional and educational backgrounds put forward such a multidisciplinary educational program as mapping of genetic resources. Such program would facilitate subsequent multidisciplinary research including geoinformatics, genetics, plant breeding, agricultural science, bioinformatics, land and production management, digital management, space photography, mapping, computer modeling, IT technologies, employment analysis, charity policy, transnational student communications, and etc.

We propose the following question: Why such facet-like boundary programs should be developed regionally as across the continents? In the present paper we aimed to reveal the versatile backgrounds of such programs. Why such facet-like, boundary programmes should be developed regionally as across the continents? There may be versatile backgrounds we would like to concentrate at in current paper.

Historic pre-requisites

Plant genetic resources in general have been always under the scope of advanced science since the works of Linnaeus and Darwin. During the several research expeditions of N.I. Vavilov (who's 130-th anniversary has been celebrated as international forum in the institute named after him in November, 2017) special emphasis was made on plant diversity and conservation. Initially Vavilov focused on crop's fungal diseases [1] and subsequently the Research Institute of Experimental Agronomy have been established following the series of 1924-1929 expeditions encompassing Afghanistan, Africa, China, Japan, Korea, Mediterraneans, and Taiwan [2]. In 1856, the monk of an Augustinian Monastery, Gregor Johann

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Mendel, conducted experiments to study the transmission of hereditary traits on peas. As a result of the research, he made a series of biological discoveries, which he described in "Experiments on plant hybrids" in 1865. In his work, he noted that hereditary traits are not whole, as it was previously thought, but are transmitted by separate factors. Factors are found in cells in pairs and transmitted to the offspring through gametes. Now these factors are known as the genes [3]. In 1909, the Danish botanist Wilhelm Ludwig Johansen introduced the term "gene", and the American geneticist Thomas Ghent Morgan substantiated the chromosome theory of heredity in 2011 [4].

Investigation methods of plant evolution include hybridization and chromosome conjugation analysis in meiosis in hybrids (unrelated chromosomes do not conjugate) [5; 6]. An important method is the artificial re-synthesis of existing species by hybridization and the subsequent duplication of the chromosome number [7]. Significant role in the evolution of plants, including different crops (wheat, oats, cotton, potatoes, fruits, etc.) belongs to the effect of alloploidy [8]. Since the discovery of the action of the alkaloid colchicine, which appeared to prevent from the disjunction of paired chromosomes to the different poles of the cell, autopolyploidy is widely used to obtain new, valuable forms [9]. Completing methods of distant hybridization by cytogenetic studies, the researchers clarified the role of individual chromosomes (and their loci) in the inheritance of traits to further develop techniques that allow chromosome insertions of wild plants towards generation of valuable traits (e.g., resistance to rust) in cultivated plants [10]. Contribution of the nucleus and cytoplasm in the trait inheritance and development is investigated by applying a remote hybridization and analyzing the nature of the male cytoplasmic sterility used for obtaining heterozygotic forms. In plant genetics, apomixis and the phenomenon of self-incompatibility, i.e., the inability of plants to self-fertilize, as well as the genetic characteristics of self- and cross-pollen, vegetatively and apomictically reproduced forms are widely studied [11]. Modern plant genetics is increasingly saturated by ideas and methods of molecular biology (DNA hybridization, DNA-RNA hybridization, isozyme assays, etc.). Methods of population genetics and biometrics are used in plant genetics to distinguish genotypic and paratypic elements within general phenotypical diversity of traits in order to enhance the efficacy of conventional or molecular breeding [12]. All these methods are used to improve the economically valuable properties of crops: yield, resistance to unfavorable environmental conditions and diseases, a number of biochemical and technological features of the plant (or its seeds, fruits and rhizome), developmental features (wintering, early maturation, etc.).

Institutional pre-conditions

Ex-Soviet republics possessed a united collection of genetic resources based on the assemblage of a Vavilov Institute's of Plant Industry. It contains over 330 000 specimens of different crops. These accessions are being maintained to be further developed by 33 national supporting points. Since 2000 Belorussia is being engaged in collecting own crop stock by shaping the national genetic bank. This work financed by the Belorussian government and coordinated by the Research Arable Farming Institute in Zhodino. At present the collection enlists almost 50 000 specimens out of cereals (51%), leguminous (20%), fodder (12%), oilseed (8%), technical (2%), and vegetable crops (1%) [13]. The Belorussian collection has integrated recently into AEGIS initiative which is affiliated with European Cooperative Programme for Plant Genetic Resources (ECPGR). Altogether, 650 institutions from 43 European countries have elaborated a range of specific genebanks. Each genebanks is aimed to provide the conservation and breeding activities of a crop important for local agriculture (www.ecpgr.cgiar.org/aegis/). The Memorandum of Understanding of AEGIS came into force in July 2009. Total number of European collection of resources has reached 33 234. Among the national repositories the Plant Gene Resources of Canada (http://pgrc3.agr.gc.ca/) may be pointed as aimed to solve specific problems of Canadian agriculture and crop science. Its main task is to adapt valuable crops to changing environments, production facilities and consumer needs. This repository has transformed domestic breeding to become more flexible and consistent in meeting regular climate as antropogenic challenges [14].

One of these challenges is air pollution. Various negative chops and changes in the Earth's atmosphere are being registered mainly due to fluctuations in the contents of minor components of atmospheric air. There are two main sources of atmospheric pollution, natural and anthropogenic. A natural source is volcanoes, dust storms, weathering (erosion), wildfires, the decay of plant and animal residues [15]. Anthropogenic grounds of air pollution include facilities of the fuel and energy complex, transportation, a range of engineering enterprises [16]. By the year 1990 25.5 billion tons of carbon oxides, 190 million

tons of sulfur oxides, 65 million tons of nitrogen oxides, 1.4 million tons of chlorofluorocarbons (freon gas compounds), organic lead compounds, hydrocarbons, including carcinogenic (causing cancer) have been emitted to the air [17]. In addition to aerial concomitants, a large amount of solid particles pollutes the atmosphere, which is dusted and sooted. One of the greatest danger on the environment is the contamination by heavy metals [18]. Lead, cadmium, mercury, copper, nickel, zinc, chromium, and vanadium have become virtually permanent ingredients of the air of industrial centres. Particularly acute is the problem of air pollution by lead.

Global pollution of atmospheric air [19] affects the state of natural ecosystems, especially the green cover of our planet. One of the most visible indicators of the state of the biosphere are the forests and their well-being. Acid rains caused predominantly by sulfur dioxide and nitrogen oxides, evoke devastating damages of forest biocenoses. It is established that coniferous tree populations suffer from acid rains more than deciduous forests. Adaptation is one of the most important mechanisms supposed to increase the stability of biosystems including plants under changing conditions of a habitat. The better the living thing is adjusted to an environmental or inner factor, the more resistant it is to ongoing alterations [20].

The genotypically determined ability of the organism to modulate metabolism within certain limits depending on the action of the external environment is called the norm of reaction [21]. It is controlled by the genotype and is characteristic of all living organisms. Most of the modifications taking place within the norm of the reaction have an adaptive value. They correspond to changes in the habitat and provide better survival of plants under fluctuations in the condition of the environment. In this connection, such modifications have an evolutionary significance. The term "*reaction norm*" was introduced by W.L. Johansen in 1909 [22].

Educational trends

In a recent article [23] tendencies of Bologna-linked education were surveyed worldwide, and it has been emphasized that ongoing process of obtaining and immediate implying of highly competitive knowledge is not plausible without new prospects of education through the relevant accreditation, life-long learning, internationalization, excellence of women in research, business-education partnerships, distribution of digital skills, maintenance of innovation-tuned environment, decent employability of graduates and some other factors. So current education should get involved new ways of teaching via its modernization, and namely inducing massive online education, hands-on (i.e. experimental) education, blended (i.e. hybrid-form) education, and then multisubject-targeted didactics.

Thus, three forementioned backgrounds are giving a nudge to develop such multidisciplinary directions as mapping of genetic resources. On one hand, judging by abbreviated history of this specialty given above, it has already existed in more or less tangible form. The second conclusion is that it has already defined an institutional "shell" as a network of national and transnational gene banks and repositories. Finally, due to process of educational internationalization there are European and overseas heaps of research teams remaining out of the scope of this paper. However, there are no any transnational multidisciplinary programs of master or moreover doctoral education on this account.

GIS-based solutions for mapping genetic resources

The main task of research and educational institutions is the creation of maps as figurative-symbolic models reflecting the reality; where the solution depends on the use of standard and specific GIS technologies including new mapping techniques based on remote sensing. Geographic mapping is critical not only as automated reproduction of the cartography image, but also in terms of designing automated map implication thus automating the overall map studies. Graphic output devices allow to automate the process of map designing and utilization [24]. Cartographic images on the screen provide a number of advantages that are not possible in frame of conventional mapping: the ability to quickly build up different versions, transform coordinate systems, simulate 3-D images and dynamic videos, etc. This is a new tool for modeling the reality. In addition, an interactive way to combine various principles of processing, editing and proofing, manual generalization, taking into account the relationships of phenomena and objects, may assist in rising the effectiveness of using the experience and knowledge of the map designer [25].

The set of objective natural and social phenomena are indicated in a map, from a cartographic point of view, may be divided into five groups, depending on the nature of spatial allocation:

i, point localization (e.g. monitoring posts, businesses and cities on small-scale maps) for which the target is their exact locations and qualitative or quantitative characteristics;

ii, line localization (e.g. roads, pipelines, borders), display objects – locations, and their qualitative and quantitative characteristics;

iii, area localization, i.e. present on some parts of the mapping territory and absent on others (enterprises, cities and their parts on large-scale maps, specially protected natural areas) for which the distribution areas and qualitative or quantitative characteristics serve as the object of the map display;

iv, continuous propagation (atmosphere and its characteristics, rocks and their properties) for which the display object is not a fact, but the spatial variability of the qualitative or quantitative characteristics;

v, scattered distribution, individual display of which is impossible (biological species, crops of agricultural crops), the object of the show is the territory and the density of distribution.

Graphic means on ecological maps are the same as on maps of other subjects: extra-scale (iconic, alphabetic and digital), linear, area. They differ in shape, size, orientation, color, color saturation, and internal structure of the image [26]. The relationships of spatial allocation types of the cartographic phenomena, the nature of information and the applied graphic means supply with the methods of cartographic imaging. Ecological mapping implies the same methods of cartographic imaging as in other thematic areas. In this case the specificity is only in the content features of the cartographic phenomena [27-29]. Geoinformation technologies assume the application of the program-technical means of processing, transfer and analysis of the information while planning the agroforestry landscapes [30; 31].

Our resources allow us to analyze the agro-landscapes across the steppe, dryland and semi-desert zones. Application of GIS-technologies and aerospace information charts, and pictures for monitoring of the state of agro-landscapes provide their relevance and credibility. Use of GIS-technologies for monitoring, mapping and modeling of the agro-landscapes of the North-West Caspian region proved its high effectiveness. The total surveyed area exceeded 4.4 million hectares [30; 32-33]. This approach is being implemented in modern geoinformation research on long-term potential of Northern croplands in Kazakhstan [33].

Conclusions

In the previous chapters we introduced the importance of plant genetic resources, the role of higher education, and as a connection between them the GIS and remote sensing was also introduced, as a new and modern technology in both research and higher education. Why this approach should be implied as a pilot international educational program on mapping of genetic resources? What advantages are being seen in our opinion?

1. There will be a specific opportunity to issue and maintain double degree of European-Central Asian universities to be designed to combine general and molecular genetics with crop resources mapping and related investigations;
2. Experts with dual M.Sc. diploma in Genetics and Cartography will provide necessary “hookups” to modern agriculture, management of arable lands, biodiversity and trends in mutagenesis or monitoring over umpteen cases of environmental deteriorations;
3. Future graduates of that program would be able to run urban space management claiming to relieve life of cities, regions and districts;
4. Such knowledge-based education will certainly influence on quicker resolution of boundary and international conflicts via getting new knowledge and solving problems in multidisciplinary knowledge-based and interactively computed modes;
5. The program will enhance transnational alignment (lining) of educational and human resources: less developed universities could quickly grow to the level of those much better promoted, whereas stronger universities will be supplied with new young talents and teachers resources;
6. The program will lead to humanization of current science and technology: its multidisciplinary and challenging nature would broaden thinking dimensions of all the participants including teachers, researchers and students, to let them raise erudition, accelerate creativity, ability to build up teams and finding new options for worldwide employment, training and charity fairs;
7. Finally, such program will evoke multidisciplinary researches in the fields of geoinformatics, genetics, plant breeding, agricultural science, bioinformatics, land and production management, digital management, space photography, mapping, computer modeling, IT technologies, employment analysis, charity policy, transnational student communications, and etc.

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Preclinical study of "Microfit" probiotic preparation influence on internals of laboratory rats

Abstract: Histologic research is one of the most reliable methods of diagnosis of pathologies of organs and tissues. This method allows estimating both macroscopic and microscopic structural changes in organs and tissues of animals. Data obtained in the course of the pathomorphological research have fundamental value for studying toxic influence of preparations at the stage of preclinical research. Results of histologic structure of internals and tissues of laboratory Sprague Dawley rats are presented in this article. As a result of experiments it has been established that no side effects have been revealed at preparation administration to animals. "Microfit" biological preparation exerted no negative impact on functional activity of internals of an organism of rats, caused no allergic reactions. The macroscopic research of internals of all experimental animals revealed no pathology after autopsy. Pathomorphological research of the main organs and tissues confirms safety of the structure of tissues. Following the research results, within one month (30 days) of administration of the biological preparation, it has been established that in case of course intragastric administration of "Microfit" preparation to white Sprague Dawley rats in a conditional-therapeutic dose (30 mg/kg) and a dose exceeding the conditional-therapeutic dose by 10 times (300 mg/kg), the preparation has no toxic effect on condition of internals and tissues.
Key words: biological preparation, toxicity, histologic research, pathomorphological research, Sprague Dawley rats, conditional-therapeutic dose

Introduction

In recent years, pro-biotic preparations even more often began to be applied in complex therapy of a number of pathological states proceeding against the background of violation of the composition of normal microflora of a human body [1; 2]. Oppressing growth of undesirable microorganisms, a probiotics creates conditions for development of normal intestinal microflora; provides colonizational resistance, carries out digestive, synthetic, immunomodulation, detoxication functions [3; 4].

Introduction of new preparations in clinical practice is feasible only on condition of detailed studying of their specific pharmacological activity and safety at the stage of experimental (preclinical) research. Preclinical research of safety of a preparation aims identification of the possible damaging action on an organism of experimental animals and assessment of their safety. The research allows to reveal organs and body tissues most sensitive to substances of the studied preparation, and to estimate tolerance to use of the studied preparation at laboratory animals [5-7]. Therefore, development of new preparations and confirmation of their efficiency and safety for humans remains a very relevant task in preparation.

At assessment of general toxic action of a new preparation, experiments for determination of chronic toxicity on laboratory animals are carried out, as they allow assuming further possibility of work with this preparation. Histologic research of internals and tissues of experimental animals is important for creation of new preparations. There can be various allergic reactions of an organism caused by administration of this or that preparation, reducing its efficiency and therapeutic action considerably [8; 9].

In this regard, the purpose of this research is studying of influence of "Microfit" probiotic biological preparation based on various strains of *Lactobacillus*, extract of buds of balsam poplar and adsorbing substance on the condition of internals and tissues of laboratory rats.

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Materials and methods

Preclinical histologic research on studying of chronic toxicity of "Microfit" biological preparation have been conducted in the laboratory of toxicology and pharmacology of RSE on the REU "National Center for Biotechnology" under the Committee of Science of the Ministry of Education and Science of the Republic of Kazakhstan (CS MES RK). Experiments were carried out on white Sprague Dawley rats, with the initial weight of 180-240 g, received from the vivarium of RSE on the REU "National Center for Biotechnology" CS MES RK. 6 groups of rats have been created for experiments: two groups – control groups of males and females, the other four groups – experimental groups with 6 animals in each group.

"Microfit» preparation consists of lactic bacteria (*Lactobacillus casei, L.plantarum, L.sakei*), extract of buds of balsam poplar and an adsorbing substance (tagan sorbent).

"Microfit" biological preparation was administrated to rats intragastrically, daily, 7 times a week, in a conditional-therapeutic dose (30 mg/kg) and in the dose exceeding the conditional-therapeutic dose by 10 times (300 mg/kg) within 1 month. Animals receiving drinking water intragastrically in equivalent volume within 1 month served as control animals. Tests of "Microfit" biological preparation for administration taking into account the body weight of rats were prepared just before intragastric introduction for rats. For intragastric administration of "Microfit" biological preparation to laboratory rats, contents of a bottle were dissolved in drinking water. Control and experimental animals were managed in identical conditions.

The research was conducted according to the "Rules of carrying out preclinical research, medicobiological experiments and clinical tests in the Republic of Kazakhstan" [10]. The recommendations stated in "The guide to experimental (preclinical) studying of new pharmacological substances" [11; 12] were taken into account during the research. Treatment of animals complied with the ethical principles of good laboratory practice [13].

Upon termination of administration of "Microfit" biological preparation (in one month from the beginning of administration of the biological preparation), they removed internals of animals. For a microscopic research, they took heart, lungs, liver, spleen, kidneys, ovary/testicle. Internals from 3 animals from each of the studied groups were taken for carrying out a histologic research. The microscopy of tissue structures of internals was carried out on Axioskop 40 light-optical microscope, Carl Zeiss, Germany, at increase in 200. Coloring method: hematoxylin and eosine.

Statistical processing of the results was carried out with the use of "Statistica 6.0" software package, Microsoft Excel 97. Distributions were described by average (M) and a mean square deviation (SD) for all animals in the group. Intergroup differences were estimated against the nonparametric criterion Mann-Whitney U-test [14; 15].

Experiments were made according to the "Rules of the European Convention for the Protection of Vertebrate Animals used for Experimental and Other Scientific Purposes" [16].

Results and their discussion

In experiments on studying of chronic toxicity of "Microfit" biological preparation, heart, lungs, liver, spleen, kidneys, ovary/testicle were taken for a histologic research. After autopsy, macroscopically the internals had a usual arrangement, without pathology. The research of tissue structures of internals (heart, lungs, liver, spleen, kidneys, ovary/testicle) was conducted.

Microscopically, the tissue of a lung of a male rat from the control group is normal. The structure of tissue is kept, without pathological changes. Lumen of alveoluses is normal. Interalveolar partitions are plethoric, with diapedetic hemorrhages. Walls of bronchial tubes and bronchioles are of different caliber, normal. Integumentary epithelium with a focal desquamation. Peribronchial lymph nodes of normal structure (A).

The structure of lung tissue of a male rat receiving preparation in a dose of 30 mg/kg is kept, without pathology. Lumen of alveoluses is free. Interalveolar partitions are slightly edematous, plethoric, with single diapedetic hemorrhages. Walls of bronchial tubes and bronchioles are of different caliber, normal. Integumentary epithelium with centers of proliferation and a desquamation. In the lumen of a part of bronchioles – desquamated cells of epithelium (B).

The structure of lung tissue of a male rat receiving preparation in a dose of 300 mg/kg is kept, without pathology and anomalies. Lumen of alveoluses is free. Interalveolar partitions are slightly edematous, plethoric, with single diapedetic hemorrhages. Walls of bronchial tubes and bronchioles are of different caliber, normal. Integumentary epithelium with centers of proliferation and desquamation. In a lumen of a part of bronchioles – desquamated cells of epithelium (C). Histologic research of structures of lung tissues of male rats are presented on the Figure 1.

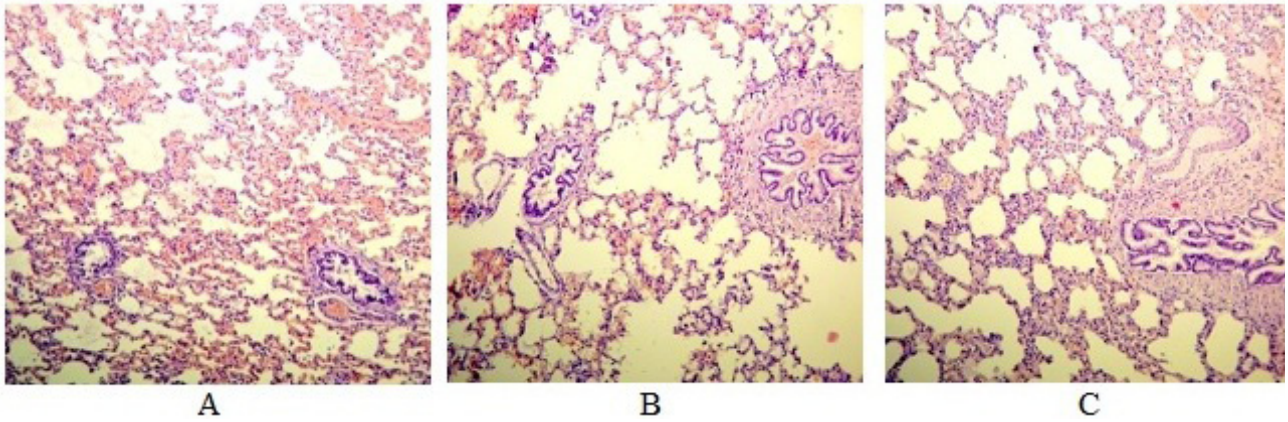

Figure 1 – Histologic structure of lung tissue of a male rat: A – control group;
B – influence of preparation in a dose of 30 mg/kg;
C – influence of preparation in a dose of 300 mg/kg. Coloring by hematoxylin and eosine.

Structure of heart tissue of a male rat from the control group and male rats from the group receiving "Microfit" in doses of 30 mg/kg and 300 mg/kg without deviation and pathology. Muscle fibers of auricles, ventricles and partitions are normal. Contracting and conveying cardiomyocytes are slightly edematous. Peri-muscularly – hypostasis, single erythrocytes. Vessels with the phenomena of uneven plethora. Lumen of coronal arteries is empty (Figure 2; A, B, C).

The structure of spleen tissue of a male rat from the control group and male rats from the group receiving "Microfit" in doses of 30 mg/kg and 300 mg/kg is normal and without pathology. Lymphoid follicles are normal, lymphocytes surround the central arteries in the form of "couplings". In reticular stroma, there are focal hemorrhages. In microhaemo-circulation vessels, there is uneven plethora. In the capsule there is a circulatory disturbance in the form of diapedetic hemorrhages (Figure 3; A, B, C).

The structure of liver tissue of control male rat is not damaged. The frame structure of hepatocytes is kept, moderated plethora of central veins and vessels of portal tracts. Portal tracts are small, insignificant lymphohysteocytic infiltration. The number of Kupffer and Ito cells in sinusoids is not changed. Phenomenon of uneven plethora in vessels. Normal cholangioles (Figure 4; A).

Lumen of central veins of liver of male rats receiving preparation in doses of 30 mg/kg and 300 mg/kg is slightly expanded. Hepatic segments, trabeculas and beams of usual structure. Periportal tracts and interlobular intervals are slightly expanded due to poor hypostasis. The number of Kupffer Ito cells in sinusoids is not changed, plethora is noted. Phenomenon of uneven plethora in vessels. Cholangioles of usual structure (Figure 4; B, C).

Structure of tissue of kidneys of a male rat from the control group and male rats receiving preparation in doses of 30 mg/kg and 300 mg/kg are kept, normal, without pathology and deviations. Renal glomerulus are equal, located evenly on the whole cortical layer. Intraglomerullar anses capillaires are unevenly plethoric. Lumen of proximal and distal tubules is free. Poor hypostasis in stroma. Diapedetic hemorrhages in the capsule. Epithelium of kidney pelvis with centers of desquamation (Figure 5; A, B, C).

Structure of testicle tissue of male rat from the control group and male rats receiving preparation in doses of 30 mg/kg and 300 mg/kg are not damaged, without pathological changes. Tissue of a testic is presented by numerous segments with existence of multiple equal testicular tubules containing homogeneous eosinophylic mass and squamous cells of epithelium in the lumen. Tubules are covered from within by the epithelio-spermatogenous layer located on the basal membrane with existence of 4-5 layers. The epithelio-spermatogenous layer is presented by two cellular differona: spermatogenous and supporting cells. Numerous Sertoli cells and interstitial Leydiga cells (Figure 6; A, B, C) are visible.

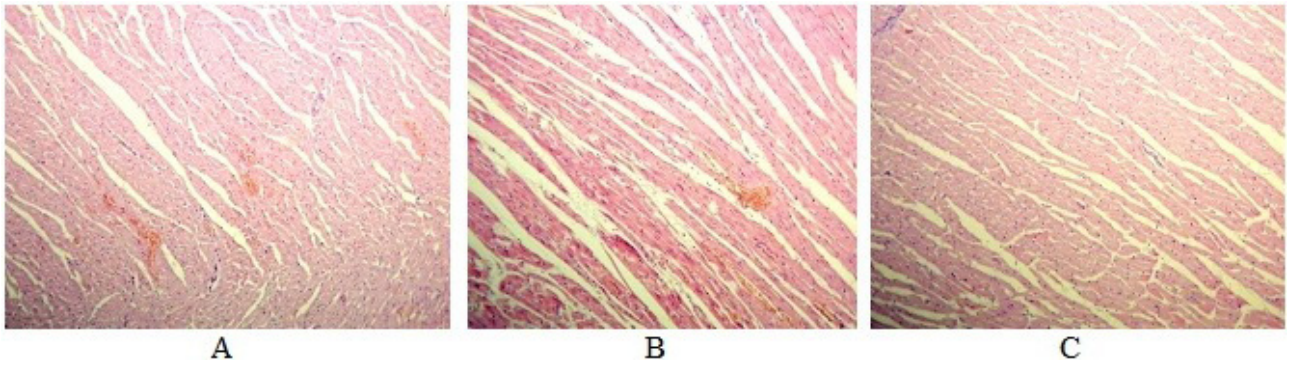

Figure 2 – Histologic structure of myocardium tissue of a male rat: A – control group;
B – influence of preparation in a dose of 30 mg/kg;
C – influence of preparation in a dose of 300 mg/kg. Coloring by hematoxylin and eosine.

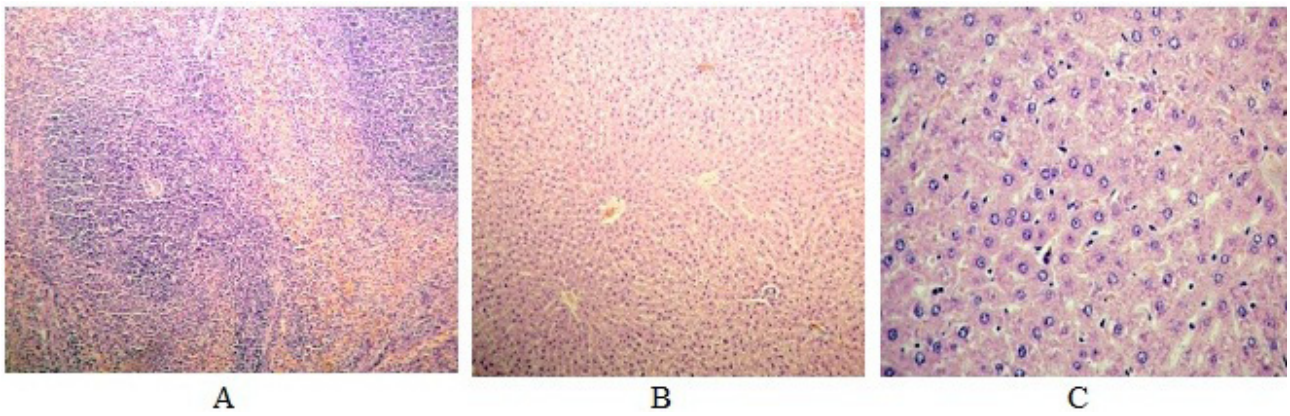

Figure 3 – Histologic structure of spleen of a male rat: A – control group;
B – influence of preparation in a dose of 30 mg/kg;
C – influence of preparation in a dose of 300 mg/kg. Coloring by hematoxylin and eosine.

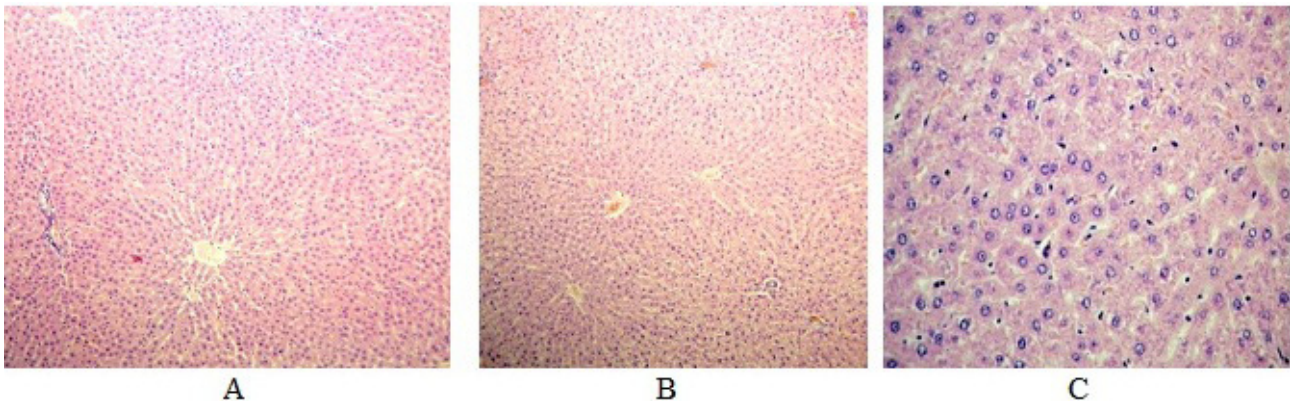

Figure 4 – Histologic structure of liver of a male rat: A – control group;
B – influence of preparation in a dose of 30 mg/kg;
C – influence of preparation in a dose of 300 mg/kg. Coloring by hematoxylin and eosine.

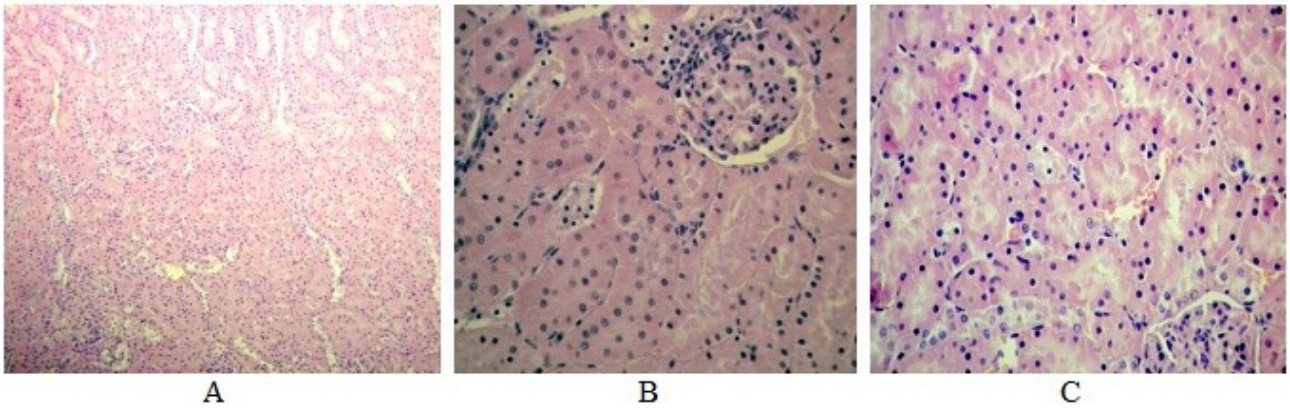

Figure 5 – Histologic structure of kidneys of a male rat: A – control group;
B – influence of preparation in a dose of 30 mg/kg;
C – influence of preparation in a dose of 300 mg/kg. Coloring by hematoxylin and eosine.

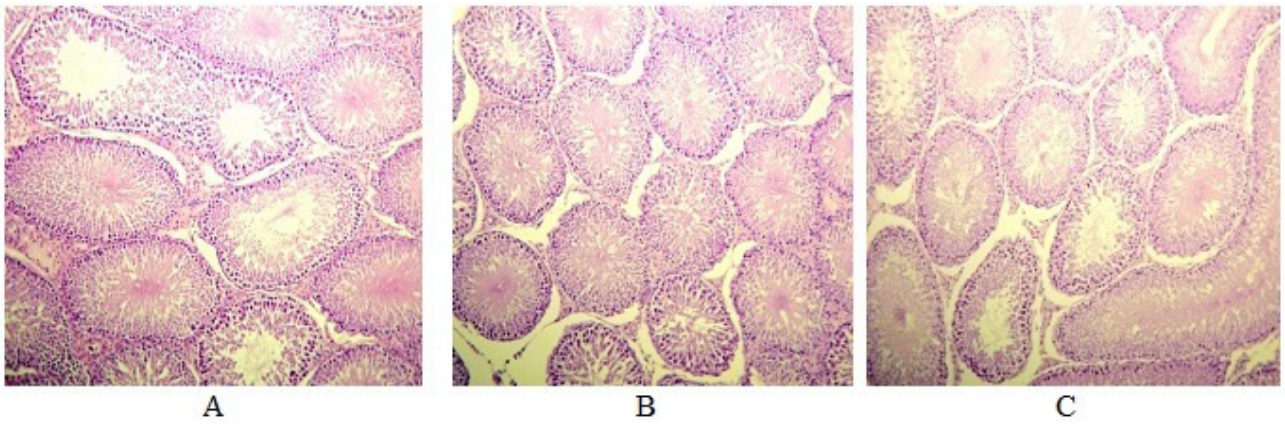

Figure 6 – Histologic structure of testicle of a male rat: A – control group;
B – influence of preparation in a dose of 30 mg/kg;
C – influence of preparation in a dose of 300 mg/kg. Coloring by hematoxylin and eosine.

Conclusion

As a result of studying of chronic toxicity of «Microfit» combined preparation, it has been established that its administration does not cause death of rats, does not damage the general condition of internals and tissues. At macroscopic research of heart, liver, kidneys, lungs, spleen, testicles/ovaries, no degenerate changes have been revealed at administration of two levels of doses (30 mg/kg and 300 mg/kg) of «Microfit» biological preparation. Macroscopically, all organs and tissues had the color, sizes and structure corresponding to reference values for this species of animals. The Patho-morphological research of the main organs and tissues confirms safety of the structure of tissues.

Thus, at course intragastric administration during 1 month in doses of 30 mg/kg and 300 mg/kg, the studied preparation exerts no impact on the state and morphology of internals and tissues of animals. Therefore, the results the patho-morphological of research have confirmed lack of toxic injuries of the vitals and tissues connected with administration of «Microfit» preparation.

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Heavy metals accumulation by the vegetation of the territory of the East Kazakhstan

Abstract: The objective of this work was study and assessment of the main regularities of distribution of forms of finding of the heavy metals: Cu, Zn, Mn, Co, Pb, Cd, in the plants of the territory of the east Kazakhstan. It was found that the same species of a plant accumulates the different number of HM on different types of soils. The vibration amplitude of content of the researched elements in species of the plants growing on various types of soils makes 1.1 – 6.3 times. Varying of the HM content in botanical plant families is in a small range. Zinc is characterized by a basipetal distribution along the morphological organs of plants, for the copper and manganese the acropetal distribution is characteristic. The coefficient of biological absorption of all elements was higher in plants of the family *Fabaceae Lindl.*
Key words: heavy metals, biogenic migration, accumulation, botanical families, coefficient of biological absorption.

Introduction

The east region of Kazakhstan includes the territories of the former nuclear test site and the areas of the reserve zone of the Abai Museum-Reserve (fig.1). Detailed studies in this area have not been carried out, therefore there is insufficient data on the background content of heavy metals in natural objects, including plants, which are used in most cases as a natural standard. Today the research of the content in the environment of toxic at high concentrations of substances is the largest social and economic issue. The most priority pollutants of the natural environment are heavy metals (HM), especially Pb, Cd, Zn, Cu. This is due to both the trends in the development of industry, and physiological and biochemical features of HM, their high level of toxicity and the ability to accumulate in living organisms.

Figure 1 – A map of Kazakhstan, highlighted in red – eastern Kazakhstan

 Printed in Kazakhstan

Very important and actual problem is the development of scientific bases for monitoring the content of HM in natural objects, including plants, of great scientific and practical interest. It is necessary to control the content of HM in the environmental objects of different regions, and first of all in plants that are the main source of most chemical elements for living organisms and a highly informative indicator of their level in the biosphere. The chemical composition of the plant is a result of the selective relationship of organisms to elements of content in the soil [1, 2]. In various geochemical conditions, the chemical composition and metabolism of plants, even in the representatives of one species, can differ significantly [3]. The plant specific features, soil type, concentration, form of HM finding, soil pH, its granulometric composition, organic matter content, cation absorption capacity in soil, availability of technogenic sources of ecosystem pollution has impact on flow of HM into plants [4-6]. The distribution of HM in the plant is in turn dependent on the physiological functions performed by the various organs of the plant, their morphological structure and the physiological functions performed by the chemical elements. Due to selective absorption, the chemical elements enter the plant in favorable for life proportions.

The work aim was determination of the regional background level of accumulation of HM by different species, morphological organs and families of wild vegetation of the study area.

Experimental

In this work the zonal typical plants of the steppe and desert-steppe zone were studied, in total 100 plant samples, 18 species from six families, were studied. For tests were taken samples of all of the genetic horizons of the soil profile. The samples of all of the genetic horizons of the soil profile were taken for investigations. Definition of macrocomposition of all tests of soils (pH, a humus, CO_2 of carbonates, granulometric composition) was carried out by standard methods. The content of heavy metals in the explored soils was determined on the KFK-3 device by a photocolorimetric dithizone method by G.Ya. Rin'kis's recipe [6-10]. The reproducibility of the method was equal to ± 4.2%. Selection of fractions of Pb and Zn was carried out by method of parallel extraction. All analytical data were processed by mathematical analysis and mathematical statistics in soil science according to E.A. Dmitriev [7].

Results and discussion

It has shown (Table 1), that the same plant species accumulates different amounts of HM on different soil types [7, 11-15]. The content of the investigated elements in plant species growing on different types of soils varies: copper – 1.1 – 3.5 times, zinc – 1.1 – 3.2 times, manganese – 1.1 – 2.5 times, cobalt – 1.1 – 2.0 times, lead – 1.1 -3.3 times, cadmium – 1.1 – 6.3 times. Differences in the accumulation of HM by the same species on different soil types are due to both the biological characteristics of plants and the ecological condition-differences in the content and bioavailability of the elements in the soils [12-14].

According to the results of the research, the content of HM in the plants of the botanic families studied is distributed in the following order of decrease (Table 2):

- on Cu: *Chenopodiaceae > Asteraceae > Cyperaceae > Poaceae, Limoneaceae > Fabaceae;*
- on Zinc: *Limoneaceae > Chenopodiaceae > Cyperaceae > Poaceae > Asteraceae > Fabaceae;*
- on Mn: *Cyperaceae > Fabaceae > Chenopodiaceae > Asteraceae , Limoneaceae > Poaceae;*
- on Co: *Poaceae > Fabaceae > Chenopodiaceae > Asteraceae , Limoneaceae > Cyperaceae;*
- on Pb: *Poaceae > Chenopodiaceae > Fabaceae > Asteraceae , Cyperaceae > Limoneaceae;*
- on Cd: *Asteraceae > Fabaceae > Limoneaceae > Chenopodiaceae > Cyperaceae, Poaceae.*

Varying the HM content in the various botanical families of plants is in a small range and amounts to an average: copper – 35.0%, zinc – 19.0%, manganese – 34.8%, cobalt – 46.7%, lead – 43.3%, cadmium – 51.5%. Due to selective absorption, chemical elements enter the plant in favorable proportions for life [8-10]. This is especially evident in various plant organs, where chemical elements have their specific function.

The distribution of HM content by plant organs is presented in Table 3. It has been found that zinc is characterized by a basipetal distribution over the organs of plants, for copper and manganese it is acropetal. Cobalt, lead, and cadmium are differently distributed over the morphological organs of plants. They are characterized by the greatest accumulation in the roots with a decrease in leaves and stems. The stems contain a minimum number of them.

Table 1 – HM content in the plant species growing on various types of soils

Type of soil	Cu	Zn	Mn	Co	Pb	Cd
Artemisia terrae-albae Krasch						
Ch_1	1.4/0.1	13.6/0.8	84.2/0.1	0.9/0.2	1.3/0.1	0.24/0.53
M_1	1.1/0.1	14.5/0.6	61.1/0.1	0.6/0.1	0.6/0.05	0.46/0.56
S	3.8/0.2	4.6/0.2	153.9/0.2	1.2/0.2	2.0/0.2	0.2/0.1
Carex melanostachya Bieb. Ex. Wiild						
Ch_1	1.9/0.2	11.8/0.7	146.5/0.2	0.7/0.1	1.6/0.2	0.44/1.02
M_1	1.7/0.1	13.2/0.7	118.2/0.1	1.2/0.2	1.2/0.1	0.07/0.08
Goniolimon speciosum (L.) Boiss						
Ch_1	1.0/0.1	15.2/0.8	89.1/0.1	1.4/0.2	0.4/0.04	0.64/1.49
S	1.6/0.1	16.4/0.8	155.8/0.2	2.3/0.3	0.4/0.04	0.73/0.37
Limonium gmelini (Willd) O. Kuntze						
Ch_1	0.7/0.1	15.2/0.8	84.3/0.1	0.6/0.1	1.0/0.1	0.3/0.7
S	2.0/0.1	14.8/0.7	132.2/0.2	0.7/0.1	1.2/0.1	0.32/0.16
Salsola tamariskina Pall						
Ch_1	2.9/0.2	15.1/0.8	107.5/0.1	1.0/0.2	1.1/0.1	0.43/1.00
S	4.0/0.3	16.6/0.8	133.8/0.2	1.8/0.3	2.6/0.2	0.46/0.23
Stipa capillata(L.)						
Ch_1	1.7/0.1	9.4/0.5	9.4/0.01	1.7/0.2	2.2/0.2	0.19/0.72
S	3.0/0.2	10.6/0.5	10.6/0.01	1.8/0.2	4.0/0.3	0.37/1.5

Note: Ch_1 – light chestnut normal soils, M_1 – meadow light soils, S – solonchaks; in the numerator – the content of the element in the plant, mg / kg, in the denominator – the coefficient of biological absorption (CBA).

Table 2 – The content of heavy metals in various botanical families of plants in the study area

Plant family	n	Cu	Zn	Mn	Co	Pb	Cd
Asteraceae Dumort. Asters	20	2.3±0.4 1.1-4.0 (53)	11.3±1.5 3.6-15.8 (42)	114.8±25.4 97.3-997.1 (70)	1.0±0.1 0.4-1.7 (44)	1.4±0.3 0.4-3.8 (64)	0.69±0.20 0.18-2.07 (90)
Chenopodiace-ae Vent. Chenopodiaceae	12	3.3±0.2 2.6-4.1 (18)	15.0±0.8 14.7-17.0 (13)	116.4±11.3 82.1-150.9 (24)	1.3±0.4 0.6-2.9 (69)	1.6±0.3 0.8-2.9 (51)	0.43±0.02 0.35-0.53 (15)
Cyperaceae Juss. Sedge	14	2.1±0.2 1.6-2.9 (24)	12.3±0.4 10.4-13.4 (9)	130.1±14.1 103.0-197.8 (29)	0.7±0.1 0.4-1.2 (39)	1.4±0.2 0.9-2.0 (30)	0.42±0.07 0.07-0.64 (45)
Fabaceae Lindl. Beans	18	1.6±0.1 1.1-2.0 (25)	10.7±0.7 7.8-14.1 (20)	128.4±13.9 91.2-188.7 (33)	1.5±0.2 0.8-2.6 (40)	1.5±0.1 1.0-2.2 (27)	0.56±0.15 0.12-1.63 (81)
Limoneaceae Lincz. Thrift	18	1.9±0.4 0.5-4.9 (66)	15.3±0.3 14.5-16.5 (6)	114.6±14.3 70.0-194.8 (37)	1.0±0.2 0.6-2.3 (55)	0.9±0.1 0.4-1.4 (44)	0.44±0.06 0.28-0.73 (42)
Poaceae Barnhart The bluegrass	18	1.9±0.2 1.4-3.0 (26)	11.5±0.8 7.7-15.9 (21)	11.3±0.6 10.3-13.8 (16)	1.6±0.2 0.6-2.3 (33)	2.0±0.3 1.2-4.0 (44)	0.42±0.05 0.19-0.73 (36)

Note: n is the number of samples; in the numerator – the arithmetic mean and its error, mg/kg; in the denominator – the range of variation, mg / kg, in parentheses – the coefficient of variation, %.

As can be seen from these series, the CBA of all elements appeared to be higher in the plants of the family *Fabaceae Lindl.* In general, for the area under study, it is characteristic that copper, manganese, cobalt, and lead are classified as a group of elements of average absorption by the level of biological absorption of plants; zinc, cadmium – to the group of elements of intensive absorption. For the latter, biogenic migration, apparently, can act as the main factor in the migration of these elements in the landscape.

Conclusion

It was found that differences in the accumulation of heavy metals by the same species on different types of soils are due to both the biological characteristics of plants and the ecological condition – differences in the content and bioavailability of elements in a particular soil. The content of the investigated elements in plant species growing on different soil types varies: copper – 1.1 – 3.5 times, zinc – 1.1 – 3.2 times, manganese – 1.1 – 2.5 times, cobalt – 1.1 – 2.0 times, lead – 1.1 -3.3 times, cadmium – 1.1 – 6.3 times. Varying of the content of heavy metals in botanical plant families is in a small range and amounts to an average: copper 35.0%, zinc 19.0%, manganese 34.8%, cobalt 46.7%, lead 43.3 %, cadmium – 51.5%. Zinc is characterized by a basipetal distribution according to the morphological organs of plants, and acropetal distribution is typical for copper and manganese.

Table 3 – The HM content in the organs of a common set of wild plants (n = 100)

Element	Root	Stalk (stem)	Leaf
Cu	2.6±0.3 0.5-6.3 (36)	1.8±0.3 0.5-6.3 (51)	1.7±0.3 0.5-4.1 (39)
Zn	11.8±0.7 3.4-15.8 (18)	13.9±2.8 3.5-26.6 (30)	15.1±1.0 2.7-21.2 (22)
Mn	135.7±23.7 8.6-677.6 (48)	83.5±15.2 6.3-274.7 (50)	78.4±6.7 10.0-189.0 (21)
Co	1.7±0.4 0.4-4.8 (62)	0.8±0.2 0.1-3.2 (69)	1.1±0.2 0.2-3.1 (43)
Pb	2.0±0.4 0.3-7.2 (51)	1.0±0.2 0.1-4.1 (58)	1.3±0.2 0.2-3.5 (39)
Cd	0.67±0.14 0,10-2.88 (58)	0.34±0.06 0.02-1.29 (56)	0.51±0.11 0.04-2.03 (54)

Note: n is the number of samples; in the numerator – the arithmetic mean and its error, mg/kg; in the denominator – the range of variation, mg/kg, in parentheses – the coefficient of variation, %.

Cobalt, lead and cadmium are characterized by the greatest accumulation in roots with a decrease in leaves and stems (stalk). The stems contain a minimum number of them. For copper, zinc is characterized by intense absorption by stems, less leaves, roots, the coefficient of biological absorption (CBA): $CBA_{Stalk\ (stem)} > CBA_{leaf} > CBA_{root}$; for Pb, Mn – $CBA_{root} > CBA_{stalk\ (stem)} > CBA_{leaf}$; for Co, Cd – $CBA_{root} > CBA_{leaf} > CBA_{stalk\ (stem)}$. By the value of CBA Cu, Co refers to the elements of medium biological capture and weak accumulation in plants; Zn, Mn, Pb – to elements of strong biological accumulation; Cd – to elements of vigorous biological accumulation. CBA of all elements was higher in plants of the family *Fabaceae Lindl.*

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Development of the composite materials based on N-(2-vinyloxyethyl)-N-(2-cyanoethyl) amine

Abstract: The novel cationic hydrogels based on N-isopropylacrylamide (NIPAAm) and N-(2-vinyloxyethyl)-N-(2-cyanoethyl) amine (VOECEA) were synthesized for the first time by radical copolymerization. The composition of copolymers were determined by using IR spectroscopy.

Key words: N-isopropylacrylamide, N-(2-vinyloxyethyl)-N-(2-cyanoethyl) amine, thermosensitive polymers, hydrophobic interactions , swellable copolymers thermosensitive, interpolymer complex (IPC).

Introduction

In recent years the main attention of researchers of the leading scientific centers is have interested so-called “clever” or “incentive – sensitive” the polymeric materials reacting to little changes of properties of environment (pH, temperatures, electric field, etc.).

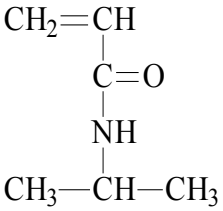
One of the most perspective in the scientific and practical relation versions incentive – sensitive materials are thermo sensitive polymers, which water solutions are characterized existence of the lower critical temperature of dissolution (LCTD) and experiencing phase transition at rather small variations temperatures [1]. Typically, such polymers are prepared using amphiphilic water-soluble monomers containing in their structure at the same time hydrophilic group and hydrophobic moieties such as, N-isopropylacrylamide, vinyl methyl ether or N-vinyl caprolactam [2].

The Kazakh National University. Al-Farabi was developed and successfully implemented other approach to the synthesis of new thermo sensitive polymers, based on radical copolymerization of hydrophilic and hydrophobic monomers.

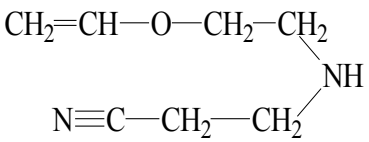
It opens the possibility to obtain soluble and cross linked polymers controlled over a wide range thermal sensitivity, perspective for use in different fields of electronics and biomedicine. This work in the actual field of research and dedicated to the creation and study of new polymers and linear mesh structures exhibiting a controlled sensitivity to changes in temperature and pH environments [3-5].

The purpose of work the obtaining composite materials of N-isopropylacrylamide and N-(2-vinyloxyethyl)-N-(2-cyanoethyl) amine, a study of their physico-chemical characteristics.

Experimental part



N-isopropylacrylamide



N-(2-vinyloxyethyl)-N-(2-cyanoethyl) amine

Synthesis of hydrogels

The syntheses of hydrogels of various compositions were performed by free radical crosslinking copolymerization at 60°C. Briefly, NiPAAm and VOECEA were dissolved in water. The concentration of the crosslinking agent, N, N-methylene-bis-akpilamid (MBAA), was 2.0 and 4.0 wt.% with respect to monomers. After being purged by the argon.

The reaction time depended on the concentration of the crosslinking agent, as well as on the NiPAAm/VOECEA comonomer weight ratio in the initial mixture and was in the range of 1 to 3 h. After the reaction was completed, the gels were cut into discs and immersed in water which was changed daily for a week, to remove unreacted reactants. The discs were dried at room temperature for a day and then at the temperature of 37°C to hydrogels (cm thick and cm in diameter). The samples were labeled as NiPAAm/VOECEA/MBAA 30/70/1, 50/50/1, 70/30/1.

Results and Discussion

FT-IR spectra of hydrogels with 1.0 wt.% of MBAA are presented in Figure 1. Figures show FT-IR spectra of homo- and copolymer hydrogels of different composition, both monomer content and crosslinking agent concentration.

The first three numbers in the sample labels correspond to the comonomer NiPAAm/VOECEA weight ratio, and the third one corresponds to the concentration of the crosslinking agent, MBAA.

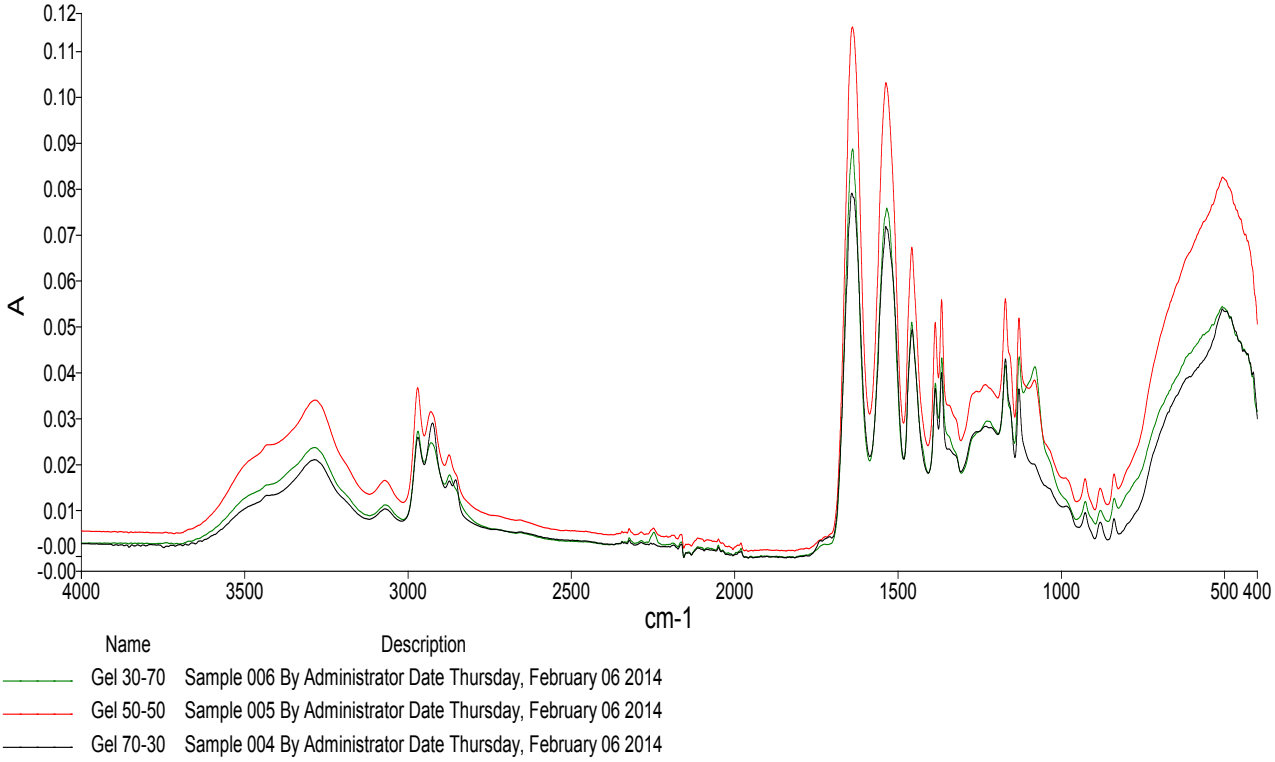
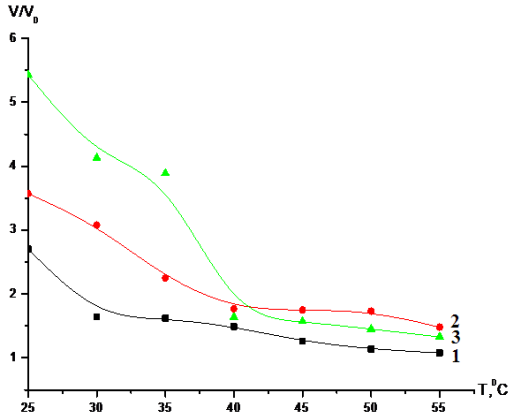


Figure 1 – FT-IR spectra of hydrogels: spectra of hydrogels with 1.0 wt.% of MBAA ((A)30/70/1; (B) 50/50/1; (C) 70/30/1;). The first two numbers in the sample labels correspond to the comonomer NiPAAm/VOECEA weight ratio, and the third one corresponds to the concentration of the crosslinking agent, MBAA

FT-IR spectra of hydrogels are similar. Each spectrum shows a wide band in the area of 3300–3100 cm−1 which corresponds to the C– O–C stretching vibration of carboxylic groups in VOECEA and N–H stretching vibration of NiPAAm. Stretching of C–H group from NiPAAm is also noticeable at 2976 cm−1. Peak at 1723 cm−1 originates from the vibration of the carbonyl group in N-(2-vinyloxyethyl)-N-(2-cyanoethyl) amine. Typical amide I band and amide II band of NiPAAm ap-

pear around 1650 cm−1 and 1540 cm−1, respectively. Two typical bands of C–H vibrations of nearly the same intensity at 1386 and 1379 cm−1 correspond to the stretching vibration of C–H bond of CH (CH3)2 groups. The band around 1174 cm−1 originates from the amide III band in P(NiPAAm). Band at 1207 cm−1 corresponds to C–O stretching of carboxylic groups in N-(2-vinyloxyethyl)-N-(2-cyanoethyl) amine. At 1400 cm−1 some C–O–H banding in plane is visible. Characteristic bands in the FT-IR spectra correspond to the absorption bands of hydrogels characteristic for homopolymers of poly(N-(2-vinyloxyethyl)-N-(2-cyanoethyl) amine) and poly(N-isopropylacrylamide) but are slightly shifted in relation to the wavenumbers of pure polymers because of the crosslinking reaction and the formation of the hydrogel polymer network.

We investigated swelling capacity of hydrogels in different environments of pH, as hydrogels on a basis [NIPAAM]: [VOECEA] of a positive charge.

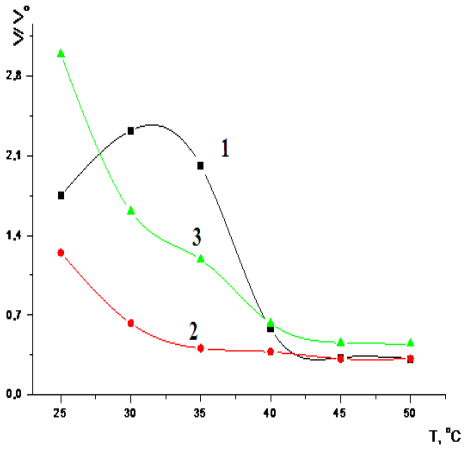


NiPAAm/VOECEA hydrogels with 1.0 wt.% of MBAA ((1)30/70/1; (2) 50/50/1; (3) 70/30/1;).

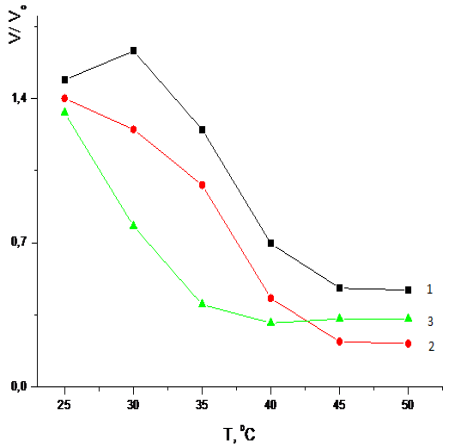
Figure 2 – Influence of the temperatures to hydrogels based on the NiPAAm/VOECEA.

Conclusion

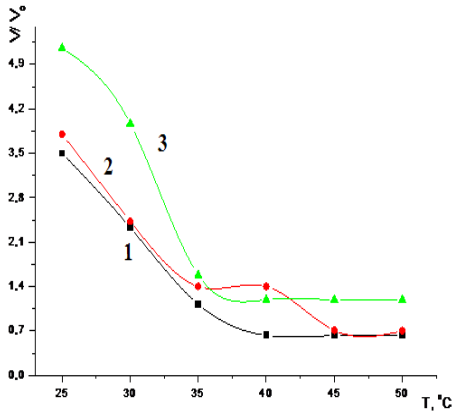
Thus, in this work has been synthesized cationic type hydrogels based on NIPAAM/VOECEA and has investigated physical and chemical properties of the new NIPAAM/VOECEA hydrogels. The syntheses of hydrogels of various compositions were performed by free radical crosslinking copolymerization and also has been investigated thermosensitivity of hydrogels. We have proved that, the above temperature the is lower swelling of copolymers.



(3)NiPAAm/VOECEA hydrogels with 1.0 wt.% of MBAA (30/70/1); pH = 4,0 (1); 7,0 (2); 9,0 (3); [CA] = 0,5%



(4)NiPAAm/VOECEA hydrogels with 1.0 wt.% of MBAA (50/50/1); pH = 4,0 (1); 7,0 (2); 9,0 (3); [CA] = 0,5%



(5)NiPAAm/VOECEA hydrogels with 1.0 wt.% of MBAA (70/30/1); pH = 4,0 (1); 7,0 (2); 9,0 (3); [CA] = 0,5%

Figure 3-5 – The behavior of hydrogels based on the NiPAAm/VOECEA depends on the temperatures in different environments of pH.

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Utilization of styrene copolymer lattices (DBSS/POE) as chemical admixture for mortar

Abstract: Copolymer emulsion lattices based on styrene (St) and butyl acrylate (BuA) was synthesized with composition ratio (5/ 5) using potassium persulfate/ sodium metabisulfite (KPS/ NaMBS) as redox initiation in the presence of a coemulsifier dodecyl benzene sodium sulfonate/ polyoxyethylene glycol monomethyl ether (DBSS/ POE). The effect of concentration of copolymer lattices on the physico-mechanical properties of mortar was investigated. The results showed that, as concentration of copolymer lattices increased, W/C ratio, setting time as well as water absorption decrease, while compressive strength increases.
Key words: copolymer, lattices, strength, workability

Introduction

Chemical admixtures are chemicals that add to cement, mortar as well as concrete to improve the physical and mechanical properties including W/C ratio, setting time, water absorption, chemically combined water, compressive strength,...etc [1-10]. Admixtures can be classified by functions as air-entraining, water-reducing, plasticizers, accelerating, retarding, hydration-control, corrosion inhibitors, shrinkage reducers, alkali-silica reactivity inhibitors, and miscellaneous [10-20]. Admixtures modified mortars and concrete such as polymer lattices, water-soluble resins, surfactants, epoxy and polyurethane have been widely used in the world [21-30]. In our laboratory, it is of particular interest to study the effect of polymers on the physico-mechanical properties of cement, mortar and concrete. Our previous work reported the copolymer latexes based on molar ratio of 2-hydroxy ethyl acrylate and 2-hydroxy ethylmethacrylate [31], acrylic acid and butymethacrylate [32], 2-hydroxy ethyl acrylate and 2-hydroxymethacrylic acid [33], and styrene and methacrylate [34, 35]. The results indicate that the latexes cause improvement in mortar properties compared with control samples without latexes. Negim et al [3] prepared copolymer emulsion lattices based on styrene and butyl acrylate in presence of potassium persulfate/ sodium metabisulfite (KPS/ NaMBS) as redox initiator system and a coemulsifier dodecyl benzene sodium sulfonate and polyoxyethylene glycol monomethyl ether (DBSS/ POE). The effect of copolymer lattices on physico-mechanical properties of cement pastes was investigated. The work was further extended to include the application of the obtained copolymer lattices with different dosages to modify the properties of mortar.

Materials and methods

Materials

Dodecyl benzene sodium sulfonate (DBSS) was used as anionic surfactant with a molecular weight of 348.48g/mole. The nonionic surfactants used were polyoxyethylene glycol monomethyl ether [POE) with a molecular weight of 5000.00. The chemical structure of the various surfactants is shown in Table 1.

The raw materials used in the present study are Portland cement clinker (PCC) and raw gypsum (G). Each of those raw materials was separately ground in a steel ball mill until the surface area of respectively 3650 and 2800 cm^2/g was achieved. The chemical composition of the raw materials is shown in Table 2. The mineralogical composition of the PCC sample is C_3S, 58.79 %; β- C_2S, 17.68 %; C_3A, 8.08 %; C_4AF, 9.72 %. The Portland Cement (PC) was prepared by mixing 96 % PCC and 4 % G (by weight) in a porcelain ball mill for one hour using 3 balls to ensure

complete homogeneity of the cement. The Blaine surface area of the cement sample was 3350 cm^2/g [35].

The fine aggregate used was sand with particle size ranging from 0.21mm to 0.53 mm and is free from organic or clay-like materials.

Table 1 – The chemical structure of surfactants

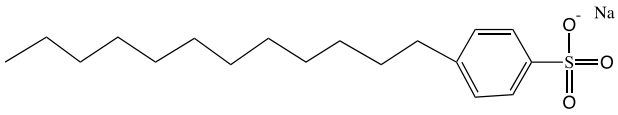
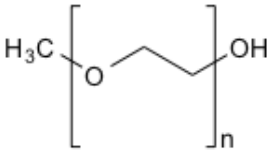
Surfactants	Symbol	Structure
Dodecyl benzene sodium sulfonate	DBSS	
Polyoxyethylene glycol monomethyl ether	POF	

Table 2 – The chemical composition of the raw materials, mass %

Oxides Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	L.O.I
PCC	21.48	6.03	4.22	64.29	0.68	0.39	0.21	0.11	1.32
G	0.58	0.14	0.11	30.08	0.13	45.36	0.07	0.09	22.16

Synthesis and characterization of copolymers

Copolymer emulsion latexes based on styrene (St) with butyl acrylate (St/BuA) was synthesized with composition ratios (5: 5) using potassium persulfate/sodium metabisulfite (KPS/NaMBS) as redox initiation system in the presence of a co-emulsifier 2% dodecyl benzene sodium sulfonate with 1.5% Polyoxyethylene glycol monomethyl ether (DBSS/POE) The preparation of copolymers and the methods of analysis (^{1}H NMR, rheological and morphological techniques) have been previously described in a previous investigation [3].

Mixing and testing

Mortar specimens of size 70 mm cube were prepared in three groups. The control mix (M0) consists of Portland cement (PC), sand and water. The proportion of cement to sand was 1:3 (by weight). In mixes M1, M2 and M3, prepared lattices with dosage 0.25, 0.5 and 1.0 % was added. However, the mix M0 is the reference without lattices.

The cement and sand were intermixed until homogeneity was achieved. Then the prepared lattices were added to the mixing water. This was then added gradually to cement/sand mixture to determine the water of consistency using Vicat apparatus [36, 37].

The resulting mortar was directly placed into 70 mm cube stainless steel moulds. The moulds were manually agitated for 2 minutes and then on a vibrator for another 2 minutes. The moulds were kept in a humidity chamber at 100 % R. H and a constant room temperature overnight, then demoulded and cured under water till the time of testing. Testing included compressive strength, water absorption and combined water and was conducted at 1 day, 3, 7 and 28 days. The determination of water absorption as per the specifications of BS 1881: Part 122[38], compressive strength, water absorption and combined water were described in a previous investigation by the authors [39].

Results and discussion

Water/Cement Ratio

The water / cement (W/C) ratio for cement pastes, concretes and mortars has a major on their properties including water absorption, workability and compressive [15, 2]. The effect of copolymer lattices dosages on W/C ratio of mortar mixes is shown in Figure 1. The results showed that W/C ratio of mortars is decreased with increasing dosage of copolymer lattices. Mortar mixed with M1, 0.25% gave lower W/C ra-

tio, 0.32 while mortar mixed with M3, 1.0% showed higher W/C ratio, 0.48. W/C ratio of mortars depends on many factors, such as type monomers, surfactants, type and dosage of lattices [5, 9, 22]. Furthermore, the W/C ratio of mortar mixed with St/ BuA lattices in presence of DBSS/POE is lower than those premixed with St/ BuA lattices in presence of DBSS/ PVA [34].

Workability

The addition of St/BuA lattices in presence of DBSS/POE to mortar mixes, improved the workability of mortar as shown in Figure 2. However, workability increased with increasing dosage of lattices. As expected, and in agreement with previously reported results by authors [30-34], workability increases with increasing dosage of lattices. in addition, the use of anionic surfactant in the preparation of lattices is highly detrimental to the workability of mortars and concretes. however, using lattices with nonionic surfactant improved the workability due to the steric repulsion forces [40].

Compressive strength

The results of compressive strength of mortars mixed with different dosages of St/BuA lattices are represented as a function of curing time in Figure 3. The results showed that the compressive strength increases for up to 28 days. However, the compressive strength of mortars increased with decreasing dosage of lattices. Mortar mixed with 0.25% lattice M1 gave highest compressive strength, while mortar mixed with 1% lattice M3 gave lowest compressive strength. The same behavior was reported by Negim et al. [35] when they studied the effect of lattices dosage in presence of DBSS/PVA on compressive strength of mortar. However, the compressive strength of mortar mixed with lattices in presences of DBSS/POE is higher than those premixed with lattices in presence of DBSS/PVA. This is attributed the formation of ether linkage between lattices and particles of cement and fine aggregate.

Water absorption

Water absorption of mortars mixed with lattices at different curing times is shown in Figure 4. The results showed that, the absorption reduces with the increase in curing time for all mixes. However, the water absorption increased with increasing dosage of lattice from 0.25%, M1 to 1.0%, M3. The decrease in water absorption is due to the formation of new linkage inside the pore structure of the hardened cement as in the study reported in Refs. [30-35].

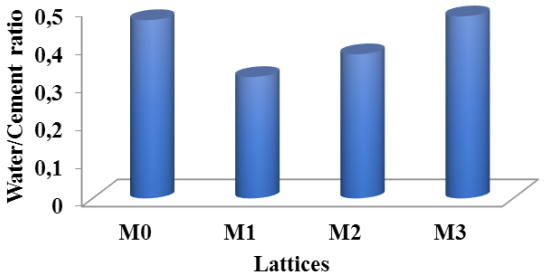


Figure 1 – The effect of St/BuA lattices on the water/cement ratio of mortar

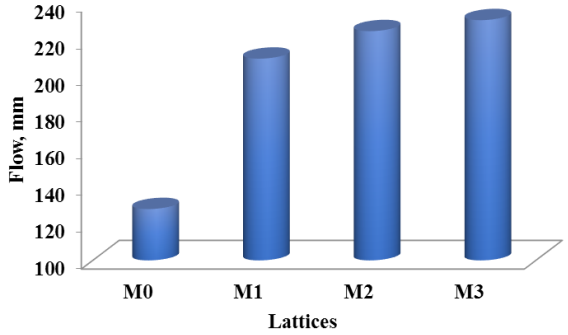


Figure 2 – The effect of St/BuA lattices on the workability of mortar

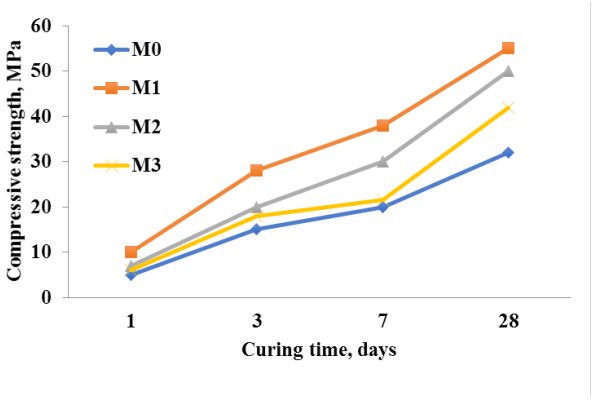


Figure 3 – The effect of St/BuA lattices on the compressive strength of mortar

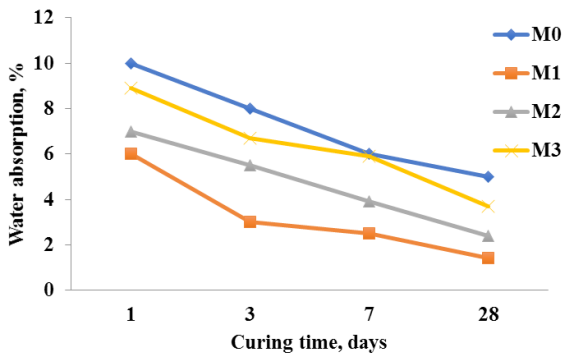


Figure 4 – The effect of St/BuA lattices on the water absorption of mortar

Conclusions

St/BuA lattices were prepared in presence of co-emulsifiers DBSS/POE and characterized by using FT-IR and ^{1}H NMR [3]. Mixing the mortar with different dosage of lattices decreased the water/cement ratio. Mixing the cement pastes with the copolymer lattices enhances the workability. The water absorption of the mortar premixed with the lattices decreases, while the compressive strength increases with decreasing dosage of lattices.

Acknowledgments

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UDC 541.128, 547.261, 665.612.3,
662.767, 66.023:088.8, 66.093.673

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Test of catalysts for purification of toxic gases of the motor transport and the industry

Abstract: The work aim was preparation and testing effective catalysts for reduction of toxic gases of the motor transport and industry. The laboratory flowing installation, the stationary diesel generator of brand 5GF-LDE with power of 5 kVA and the diesel engine – generator of Kama Automobile Plant truck running on diesel fuel were used for investigation. The full-sized catalysts were also used for the experimental – industrial tests of catalysts with JSC "EMG" (Kazakhstan) on flue gas of oil heating furnaces in order to reduce toxic emissions. Stability of the carriers and the active phases to poisoning by water vapour was researched. The tests showed high efficiency of the neutralization on NO_x- to 65%, C_xH_y-to 85.0-88%, CO-99.0-100%. The catalytic samples on the basis of Ni and Mn promoted by Pd (0.1%, 0.25%) and Pt (0.1%), provide high degree of transformation CO to CO_2, C_xH_y into CO_2 and H_2O, NO to N_2. Decrease in toxiferous emissions on the South-West Kamyshitovoye field was: on CO –100%, on NO -7.7%, on NO_x-7,7%, on SO_2 – 57.1%; on the "S. Balgimbayevo" field: on CO – 99.6%, on NO -20.4 %, on NO_x-19.6 %.
Key words: catalyst, exhaust gases, metal block carriers, diesel generator

Introduction

In general, emissions of pollutants and greenhouse gases into the atmosphere from industrial activities and transport are formed from the emissions of stationary and mobile sources. Road transport emissions relate to emissions from mobile sources and are determined by emissions of vehicle pollutants during their transport operations. The source of emission of harmful substances of a motor vehicle is the internal combustion engine installed on it. In the exhaust gases of the engine contain more than 200 toxic chemical compounds [1, 2].

Except direct negative impact on health of the person, emissions of the motor transport have greenhouse and ozone-depleting effect on the atmosphere of the earth. It is connected with the content in the fulfilled gases of the engine of the following substances: carbon dioxide CO_2, the main component in the exhaust gases of the engine, creating a greenhouse effect in the atmosphere (greenhouse gas); methane CH_4, ammonia NH_3 and nitrous oxide N_2O – greenhouse and ozone-depleting substances contained in the exhaust gases of the engine. The qualitative and quantitative indicators of the release of harmful pollutants with exhaust gases of vehicles during their transport work are ambiguous and depend on many factors: on the type of the used fuel, from the design, conditions and operating conditions of the engine, on the amount of the done work, on the type and characteristics of the car's movement. Protection of the environment from industrial and transport pollution poses to humanity demands to improve the synthesis methods of neutralizing catalyst and purification of gas emissions from harmful [3-5]. The most effective means of purifying of the exhaust gases of internal combustion engines of automobiles is catalytic method. It's known that as primary catalyst carrier for neutralization of off-gases of motor transport and the industry use a metal wire, a steel foil, a grid from stainless steel or from bronze, the granulouse carrier – in the form of balls or extrudates, the ceramic carrier from a spodumen, oxide or zirconium nitride, etc. However not all of them are capable to maintain the loadings received in use in actual practice operation (on the car and in the production conditions), and also to correspond requirements imposed to catalytic converters such as thermal stability, mechanical strength, gas-dynamic resistance, stable catalytic activity throughout the progressive time of operation. Monolithic blocks are the most suitable carriers of the catalysts used for the solution of environmental issues [6, 7]. The development of compositions and methods of preparation of a new generation of

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catalysts with low content of platinum group metals for complex purification of exhaust gases of motor transport becomes more relevant in the world due to the deteriorating state of the atmosphere, especially in the industrial cities, and the tightening of environmental standards [8-10].

The work aim was synthesis of efficient and stable catalysts of neutralization of exhaust gases of motor transport on the metal block carriers and their test in the laboratory and in actual use on natural gases of the stationary diesel generator of brand 5GF-LDE with power of 5 kVA at various loadings and on the diesel engine of Kama Automobile Plant (KamAP). It was also planned to applicate the full-sized catalysts for the experimental – industrial tests of catalysts with JSC "EMG" (Kazakhstan) on flue gas of oil heating furnaces in order to reduce toxic emissions.

Materials and Methods

Preparation of the laboratory and full-size examples is carried out by earlier developed technique [11-14]. The primary carrier of catalysts is made of heat-resistant steel foil (corrugated and rolled into a block) brands H23Yu5, H15Yu5 containing about 5% aluminum, of 50.0 microns thick. The washcoat is a suspension of aluminium salt or of aluminium salt with additives.

The laboratory tests were carried out at the mounted laboratory installation (fig.1) with a tubular reactor of integrated type. Installation consists of the cylinders (1) containing researched gases (hydrocarbons, carbon oxide, nitrogen oxide, nitrogen). In system air was moved, gases were moved from cylinders, then through ventile of thin adjustment (3) entered to rotameter (4) individually calibrated under each gas and needed for gas speed regulation intended which then moved to the mixer (6) where gases were mixed up and entered to a quartz reactor (7) with diameter10 mm. The reactor was heated with by tubular furnace, the temperature in which was measured by chromele-alumele thermocouple (9). The reactor temperature was fixed by potentiometer, temperature regulator (11), calibrated by e.d.p. of thermocouples.

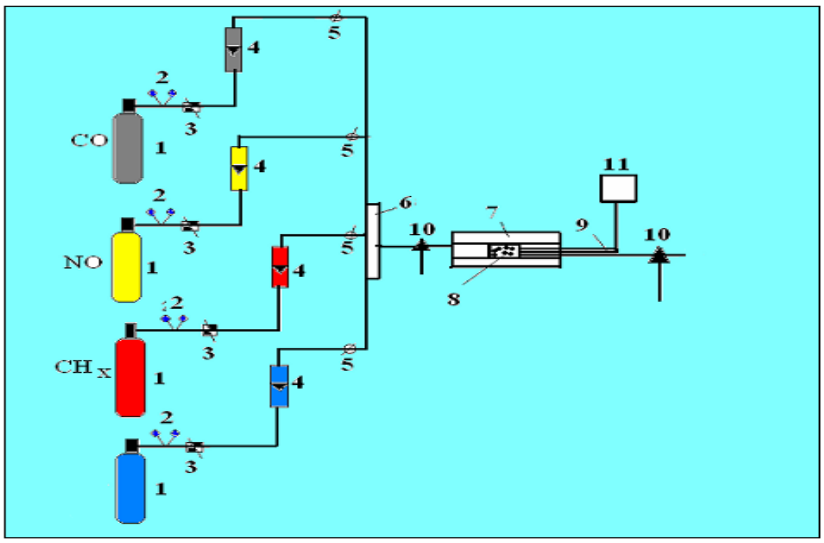


Figure 1 – Scheme of the flowing installation: 1- A gas bag; 2-Manometer; 3-Ventile of thin regulation; 4-Rotameter; 5-Crane; 6-Mixer; 7-Heating system; 8-Catalyst; 9-Thermocouple; 10-Selection of tests before and after the catalyst; 11 – Temperature regulator.

Gas mixture is prepared by giving into the mixer of hydrocarbons from a cylinder and compressed air from the line. Content of hydrocarbon in mix was 0.5 vol.%. Concentration of oxygen varied from 2.0 to 10.0 vol.%. The gas mixture was analyzed by GLC and OPTOGAZ gas analyzer before and after the reaction. The chromatographs "Crystal 2000M" and Chrom 3700 with a flame ionization detector were used. Time of analysis-20-30 min. Before testing, the catalyst sample was kept in the reactor for 30 min. in the flow of the reaction mixture at 500°C. Thereafter, the gas temperature was lowered to given values, and

was determined the conversion of CO, NO and hydrocarbons.

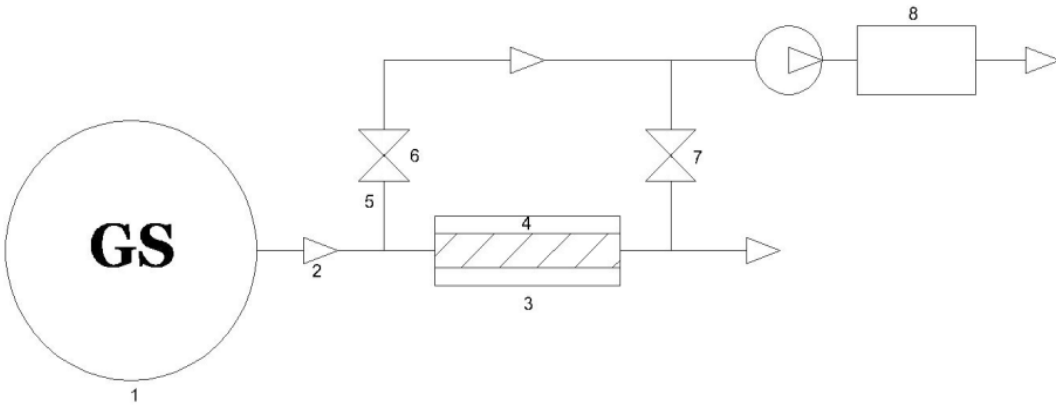
Characteristic of activity of the catalyst was the degree of conversion (α) of initial reagent (hydrocarbon, carbon monoxide, nitric oxide), defined by the formula:

$$\alpha = C\ init.\text{-}C\ fin./C\ init. \cdot 100\ \%,$$

where $C_{init.}$ and $C_{fin.}$- are the initial and final concentrations of a reagent in volume of a test.

The full-size samples of the block metal catalysts were used in the researches at the stand on the basis of diesel generator of brand 5GF-LDE with power of 5 kVA (fig.2, 3). The full-size catalyst samples had a diameter of 30.0 mm, a height of 90.0 mm. The catalyst was loaded into the gas-abstersive offshoot of the diesel generator. Temperature before and after the catalyst is determined with help of a chromel-alumel thermocouple outputted on the digital indicator. Gas mixture was analyzed by means of GLC and on a gas analyzer "Optogaz 500" before and after the reaction. The chromatographs "Crystal 2000M" and "Chrom 3700" with a flame ionization detector were used. Analysis duration was equal to 20-30 min.

Figure 2 – The catalytic unit (the stand) on the basis of diesel generator



1 – Diesel generator; 2 – exhaust pipe; 3 – catalytic reactor; 4 – catalyst sample; 5 – gas operated probe; 6, 7 – sampling valves before and after the catalyst; 8 – a gas analyzer.

Figure 3 – The general scheme of the bench on the basis of the diesel-generator

The full-sized catalysts were also used for the experimental – industrial tests of catalysts on the diesel engine of Kama Automobile Plant (KamAP). The object of a test – diesel engine – generator of KamAP of model 820.52-260- is completed with pistons of model 820.52-1004015-40 CB with the chamber of combustion in diameter of 80.0 mm, depth of 25.0 mm, cylinders heads of model 7406.1003040, turbo kompressors "Schweitzer" S2B/7624TAE with cases of turbines with A/R=1.0 and the complete set of the catalytic neutralizers which was elaborated by authors of this article. The neutralizer consists of 2 block catalysts on the metal carrier (fig.4) in diameter of 220 mm and height 90.0 mm everyone with the honey comb structure of channels. 0.1 weight. % Pt was used as an active component. The prepared catalyst was tested on the engine working on the diesel fuel with the characteristics: cetane number, not less – 49, density at 150°C-820-860, concentration of sulfur, not more than-500 ppm. In system of greasing oil "Lukoil Super" SAE15W40, APICF4 was used. As cooling liquid (freezing) water was applied. Defi-

nition of concentration of gaseous harmful emissions in the waste gases, including, nitrogen oxides (NO_x), total hydrocarbons (C_xH_y), carbon oxide (CO), was made by a multicomponent gas analyzer "Autotest – 02.03" of the I-st class. Calculation of specific emissions was carried out in view of power consumption at n=1500 rev/min., power consumption – 3.5 kVA, at n=2200 rev./min, power consumption – 11.2 kVA. Definition of harmful emissions in the exhaust gases on a minimal idle motion was carried out on the preliminary preheated engine in a mode of rated power.

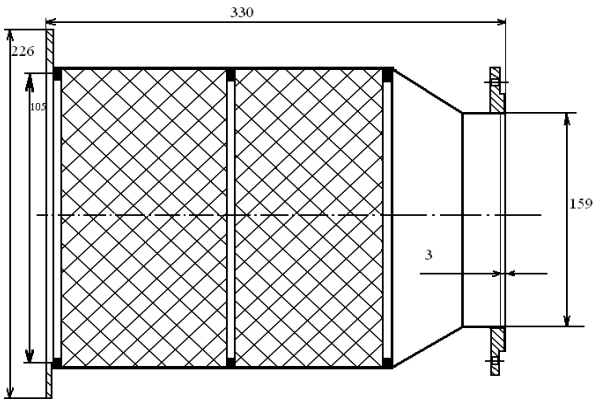


Figure 4 – Dimensions and the scheme of disposition of the catalytic neutralizer in the case

The full-sized catalysts on the block metal carriers were also used for the experimental – industrial tests of catalysts with JSC "EMG" (Kazakhstan) on flue gas of oil heating furnaces in order to reduce toxic emissions. Ready full-size catalysts on metal blocks entered on assembly where cylindrical corps were manufactured. In casings there are clamps for catalysts. Catalytic filters are installed directly on the pipe of waste gases of oil heating furnaces after the samplers before the catalyst (fig.5). In order to reduce heat transfer catalyst was wrapped with heat insulating mineral wool with reflective foil. In the course of operation of the furnace temperature of gases was determined before and after the catalyst by a mercurial thermometer and a temperature sensor of a gas analyzer. Concentration of toxiferous gases before and after catalytic filters was defined by a gas analyzer of MCI-150 of Bosh firm. Dimensions of the block filter is: for the furnace PTB-10/64: diameter – 410 mm, height 400 mm, for the furnace PT-16/150 – diameter -500 mm, height 400 mm, for the furnace PT-3.5 – 900 mm diameter, height of 400 mm. Temperature of off-gases on the S. Balgimbayevo field to the catalyst was in limits 350ºC.

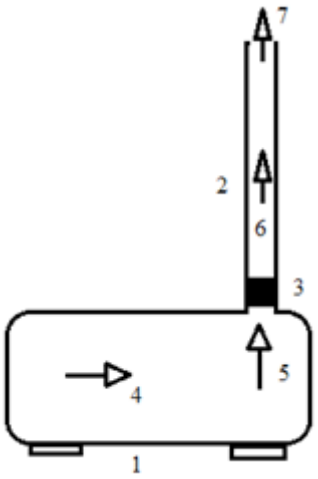


Figure 5 – Technological scheme of the installation and the functional principle of the catalyst in the furnace of oil heating: 1 – Furnace of oil heating, 2 – flue, 3 – catalytic neutralizer, 4,5 – stream of waste gases (CO, CH_x, NO_x) before the catalyst, 6,7 – the flow of gases after the catalyst (H_2O, CO_2, N_2).

Results and Discussion

The poisoning action of SO_2 in the process of cleaning of combustion gases was studied. XPS research of freshly prepared and waste (after the long-run tests of 50 hours) catalysts showed that the reason of decrease of the activity of the Pt-containing catalysts in the course of purification of products of combustion of fuel is associated to accumulation of sulfur compounds. Investigation of the activity of catalysts based on Pt, Pt + Pd, Pd on stability to SO_2 (0.1% in air for 10 hours at 350°C) showed that the catalyst activity is reduced at low test temperatures, but after calcination at 500°C with air blowing for 2 hours Pt catalyst activity is almost reduced and activity of the Pd-catalyst is reached to 80%.

Tests of full-sized samples of the catalysts were carried out on all modes of operation of the engine of the diesel generator (a no-load operation (idling), 1.0; 2.0; 3.0; 4.0 kVA). The results of triple tests of catalysts are presented in tab. 1, 2.

Catalysts based on palladium and platinum with a promoting additives were tested for thermal stability under load of diesel generator 3.0 kVA. During the 100-hour test with fractional neutralizers calcination at 600°C at an interval of 5 hours in a muffle furnace it was found that the introduced structural and textural thermostabilizing additives into the catalysts promote a sustainable activity (tab.3).

Table 1 – Reduction of the toxic emissions on the diesel generator with use of 3.0% catalyst on the basis of Mn and Ni oxides

Power consumption, kVA	The temperature of exhaust gases, °C	The content of toxic components in the exhaust gas, ppm					
		CO		C_xH_y		NO_x	
		Before catalyst	After catalyst	Before catalyst	After catalyst	Before catalyst	After catalyst
Idling (0)	25	0.036	0.035	65.0	60.0	13.2	13.2
2.0	260	0.030	0.00	81.0	20.0	17.4	10.8
3.0	300	0.021	0.00	89.0	3.5	19.0	7.6
4.0	425	0.014	0.00	111.0	10.0	23.0	8.0

Table 2 – Reduction of the toxic emissions of diesel generator by using a catalyst on the base of 0.2% Pd

Power consumption, kVA	Temperature of exhaust gases, °C	The content of toxic components in the exhaust gas, ppm					
		CO		C_xH_y		NO_x	
		Before catalyst	After catalyst	Before catalyst	After catalyst	Before catalyst	After catalyst
Idling (0)	25	0.033	0.033	67.2	55.1	14.5	14.1
2.0	533	0,03	0.002	79.6	62.3	17.8	8.3
3.0	573	0.02	0.00	92.1	6.4	21.0	6.4
4.0	698	0.015	0.00	107.0	4.2	22.6	7.0

Table 3 – Tests of thermal stability Pt- and Pd-containing catalysts on diesel generator

The catalyst	Exhaust gases	Initial degree of cleaning, %	Duration of testing, h.				
			5	10	25	50	100
0.1% Pt+Ni	CO	100	100	100	100	100	100
	C_xH_y	95.0	95.3	94.2	94.3	94.2	94.7
	NO_x	60.5	60.0	61.0	59.8	59.7	59.6
0.2% Pd+Mn	CO	100	100	100	100	100	100
	C_xH_y	90.0	90.2	90.0	88.7	88.8	88.4
	NO_x	48.2	42.9	48.1	48.1	46.8	46.4

It was found a presence of SO_3 and SO_2 in the exhaust gases of diesel-generator. On all the catalysts after the tests was observed the soot scurf, but least of all the carbon black content on zeolite-containing catalyst was presented. Also on the catalysts it was revealed phosphorus and less zinc oxide, apparently presenting in the diesel fuel in the form of organic additives. Nevertheless, the catalysts were resistant to poisoning by "poisons" contained in the exhaust gases. The most effective catalyst was a zeolite-containing carrier, promoted with Pt. Its effectiveness has remained constant for 50 h. of the diesel engine operation.

By the method of emission spectrum analysis the composition of the catalyst after 50 h. of operation on the diesel generator was studied. It was found the presence on the surface S, P, Zn, Ca, Mg. Probably, these elements were incorporated into diesel fuel oil to increase their performance. As a result of research of fragments of spent catalysts by the IR methods and an emission spectroscopy it was succeeded to define the possible content of elements, potentially dangerous to the catalyst, in exhaust gases flow (tab.4). Thus, the performed researches showed that the catalysts are subjected to the combined effect of the exhaust gases. According to data of electron microscopy and XPS the noble metal in the initial monodisperse catalysts are in an oxidized state with a uniform distribution of metal particles on the carrier and are characterized by high thermal stability. The main difference between the

synthesized catalysts is found at determining time of their warming up prior to reaction (200°C) in a stream of diesel exhaust gas in the mode of a no-load operation (420.0 rev/min). The studied catalysts may be arranged in a row: 0.1 weight of % of Pt (2 min.), % Pd-0.2 (4 min.), % Pd-0.1 (7 min.).

Table 4 – Impurities, potentially dangerous to the used catalysts, which are contained in exhaust gases of the diesel engine

Element	The finding form	Possible quantity, %	Assignment	Total amount of impurities passing through the catalyzate, g
S	SO_2-SO_3	0.04-0.4	impurity in fuel and oils	0.5-5.0
P, Zn	Zn dithiophosphate	0.1-0.2	corrosion inhibitors and antioxidants	0.4-0.6
Ca	sulfonates	0.3	detergents	-
Mg	phenates	0.1	detergents	-

As the result of the tests it was found that the most effective at all engine operating conditions was the catalyst containing oxides of nickel and manganese, activated by 0.1% of Pt. On quality of ecological cleaning of combustion gases the catalyst complies with the environmental standards of Euro-3. The catalytic samples on the basis of Ni and Mn promoted by Pd (0.1%, 0.25%) and Pt (0.1%), provide high degree of transformation CO to CO_2, C_xH_y into CO_2 and H_2O, NO to N_2.

Results of tests of the diesel engine-generator of KamAP (tab.5) equipped with the catalytic neutralizer of fulfilled gases which was elaborated by the authors of this article, show, that application the catalytic neutralizer of the fulfilled gases resulted in decrease in harmful emissions in comparison with the engine without neutralizer: on NO_x-33.0 %, C_xH_y – 82.0 %, CO-98.0 % (2200 rev./min.). On a mode of the minimal idling (800 rev./min.) efficiency of neutralizer has made on NO_x-59.0 %, C_xH_y-86.0 %, CO-99.0 %.

Results of neutralization of toxiferous emissions on the S. Balgimbayevo field are given in tab. 6. Catalytic filters were installed on several furnaces of heating of oil and water on the Southwest Kamyshitovoye field (Kazakhstan): on the PT-3,5 furnace with the forced feed of air and on 4 furnaces PT-16/150 with own pull of air. Decrease in toxiferous emissions on the South-West Kamyshitovoye field on the PT-16/150 furnace after the catalyst amounted to: on CO –100%, on NO -7.7%, on NO_x-7,7%, on SO_2 – 57.1%.

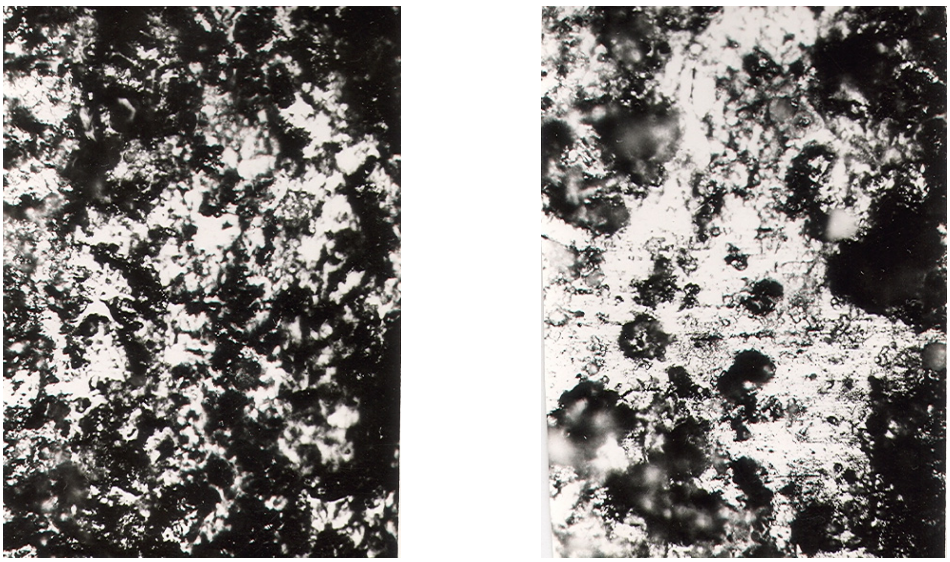
Table 5 – Tests of the full-sized catalysts for neutralization of toxic emissions of engine KamAP

Number of revolutions, rev./min.	CO, ppm			C_xH_y, ppm			NO_x, ppm		
	without neutralizer	with neutralizer	degree of cleaning, %	with out neutralizer	with neutralizer	degree of cleaning, %	without neutralizer	with neutra lizer	degree of cleaning, %
800	123	1.3	99	3182	445	86	128	75.25	59
2200	733	8	98	3728	671	82	118	79.06	33

Table 6 – Test of full-size catalytic neutralizers on furnaces of heating of oil on the "S. Bal-gimbayevo" field

The toxic components	The toxic gases content, ppm		The cleaning efficiency, %
	Initial, without neutralizer	after neutralizer	
CO	1,280.0	5.0	99.6
NO	49.0	39.0	20.4
NO_x	51.0	41.0	19.6

X-ray phase analysis and EM (electron microscope EM-125 K) physical and chemical researches of catalysts show that the prepared oxide catalysts represent spinels with a cubic lattice with $NiMnO_4$ peaks 2Å, 52Å, 148Å, 203Å. There were also revealed low-intensity reflexes of alumina (160Å, 256Å), in the catalysts on the base of manganese are formed the particles which are finely dispersed, uniformly distributed on the surface of the carrier. X-ray analysis showed Pd and Pt scattering spectrum, which indicates a high dispersion of the metal (fig.5). Pt particle sizes are 7-8 nm, Pd-11 nm.



a b

Figure 6 – The nanosized particles (300, 000 magnification) : a – Pt, b – Pd

Conclusion

Thus, the catalysts supported on metal block carriers for cleaning of exhaust gases of motor transport were developed and tested in the laboratory and in real operating conditions of vehicles of motor transport. Stability of the carrier and the active phase of the catalysts supported on metal blocks to poisoning by water vapor is investigated. At poisoning by water vapor of catalysts promoted with Pt they are activated again under heating at T=300°C under a stream of dry air for 4 hours. In the presence of steams degree of transformation of nitrogen oxide on the catalysts which are not promoted by Pt decreases to zero whereas the catalysts promoted by 0.1% of Pt (wt.) kept higher activity during 50 h of an experiment. The full-size catalysts with various active phase on metal block carriers were tested on natural gases of the stationary diesel generator of brand 5GF-LDE with power of 5 kVA at various loadings. The prepared catalysts at 200°C and above provide high performance in bench tests. The most effective at all engine operating conditions was the catalyst containing oxides of nickel and manganese, activated by 0.1% of Pt. Full-size catalyst samples were tested on truck of KamAP running on diesel fuel. Thanks to the use the catalytic converter exhaust emissions are reduced (in comparison with the engine without catalyst) on NO_x-33.0%, C_xH_y-82%, CO-98% (at 2,200 rev/min). At a minimum idling mode (800 rev/min.) the efficiency of the neutralizer was on: NO_x-59%, C_xH_y-86%, CO-99%. Decrease in toxiferous emissions on the South-West Kamyshitovoye field on the PT-16/150 furnace after the catalyst amounted to: on CO –100%, on NO -7.7%, on NO_x-7,7%, on SO_2 – 57.1%. Decrease in toxiferous emissions on the "S. Balgimbayevo" field: on CO – 99.6%, on NO -20.4 %, on NO_x-19.6 %.

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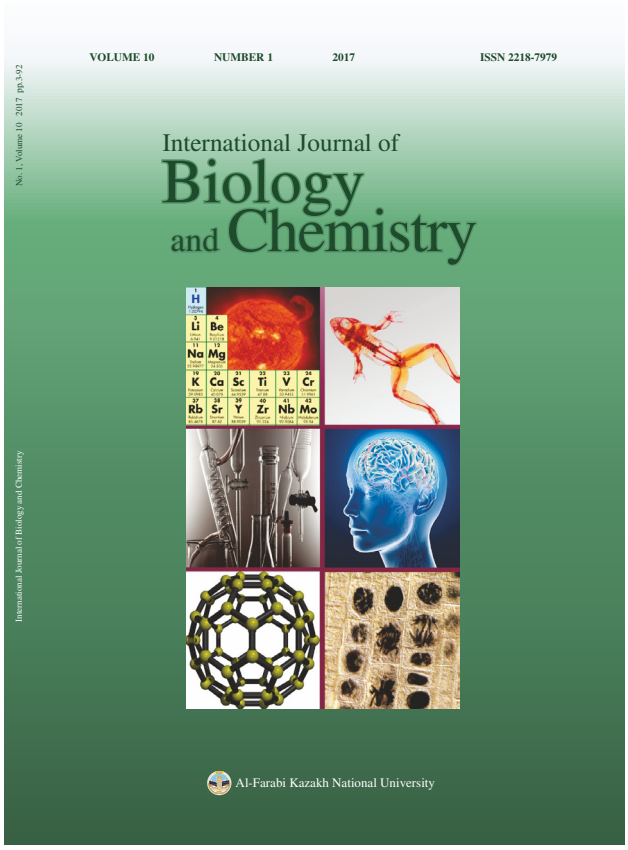

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