# ҒЫЛЫМИ ЗЕРТТЕУДІ ШОЛУ
# ОБЗОР НАУЧНЫХ ИССЛЕДОВАНИЙ
# REVIEW OF RESEARCH

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## Institute of Organic Synthesis and Coal Chemistry: the present state and development prospects

The article is an overview of the research carried out in the LLP «Institute of Organic Synthesis and Coal Chemistry of RK» in recent years. The application of methods of ultrasonic and microwave chemistry to the processes of oxidation and oxidative modification of coal, activation of the processes of immobilization of humic acids and their derivatives on the surface of burnt rocks, as well as the effect of carbon nanotubes on the processes of obtaining humic-mineral compositions were studied. The properties of new activated forms of humic sorbents were studied and tested as sorbents for wastewater treatment. Composite catalysts based on compounds of VIII (Fe, Ni, Co, Mo) group metals were obtained and their activity was studied in the process of hydrogenation of anthracene and phenanthrene. The optimal parameters of cavitation treatment of fuel oil fractions in the presence of synthesized composite catalysts based on water-soluble metal salts deposited on zeolites and carbon sorbents were determined. Based on aniline-formaldehyde polymer and its mixed compositions with melamine-formaldehyde polymer and polyaniline, new metal-polymer composites with electrocatalytic properties were obtained. Their structure and morphological features were studied by IR spectroscopy, X-ray phase analysis, atomic emission spectroscopy and electron microscopy. Electrocatalytic activity was investigated in the processes of electrohydrogenation of organic compounds. New derivatives of 4-amino-1,2,4-triazole, thiosemicarbazides N-morpholinyl acetic and N-anabasinyl acetic acids were synthesized, their structure, biological activity, reaction mechanisms were studied and optimal conditions for their synthesis were proposed.

*Keywords:* humic acid, burnt rock, multi-walled carbon nanotubes, humic-mineral composites, composite catalysts, anthracene, phenanthrene, fuel oil, hydrogenation, polymer-metal composites, aniline and melamine-formaldehyde polymers, polyaniline, electrocatalytic properties, 4-amino-1,2,4-triazole derivatives, fulleropyrrolidines, bioactivity.

In 2018, the Institute of Organic Synthesis and Coal Chemistry celebrated its 35th anniversary, the creation of which was associated with the need to expand and deepen basic and applied research in Central Kazakhstan, since the billions reserves of low-energy coals from Shubarkul, Maikubensky and other deposits that are here, also the industrial enterprises of the Karagandaugol and Carbid factories, the coke-chemical production of the Karaganda Metallurgical Plant represented a unique basis for the development of industrial organic synthesis and chemistry of coal. The Institute has carried out a large amount of research, the results of which are published in numerous monographs and rating journals. This article presents the most important results of the last time.

*In the field of modification of low-energy coals*, the processes of oxidation, oxidative amination, nitration and sulfonation of selected black and brown coals of Kazakhstan were carried out under conditions of ultrasonic and microwave activation. Oxidized coals of the Shubarkol deposit and brown coals of the Kuznetsky and Oi-Karagaysky (Almaty region) deposits were used.

Physical methods using ultrasonic processing (USP) and microwave radiation (MWR), which were first used to intensify the reactions of obtaining a number of coal-chemical products and carrying out chemical modification of coal, are among the poorly studied and promising methods for the intensification of technological processes for the production of humic substances and their compositions. Elucidation of the types of reactions under the influence of ultrasound and microwaves, as well as the prospects for their use, is an important task.

Studies have shown that ultrasound contributes to the accumulation of new acid groups in the coal composition and to an increase in the yield of humic acids from the products of sonolysis. Oxidation processes in coals under the action of ultrasound occur at moderate temperatures for a short time (5–30 minutes) and depend on the nature of the coals. According to the susceptibility of the energy of ultrasound, the coals are arranged in the following row: Oi-Karagai ≥ Shubarkol > Kuznetsky. The effect of various oxidative additives (hydrogen peroxide, nitric acid and sulfuric acid) with modifying ability on the oxidation of coal has been studied. The possibility of introducing nitrogen, sulfur in the form of amino-, amido-, nitro- and sulfo-groups, which increase the sorption characteristics of the oxidation products obtained, was proved by the methods of functional analysis and data of the elemental composition [1].

According to the study of sorption and other characteristics of sorbents and comparison with conventional methods for their preparation, the high efficiency of using physical methods of exposure to obtain new humic compositions was noted, including by introducing them into a nonorganic matrix based on burnt rocks that are waste coal mining.

Studies on the activating effect of ultrasound and microwaves on the immobilization of humic acids and their derivatives on the surface of the burnt rock showed that immobilization in USP and MVR conditions showed the promise of using porous aluminosilicate rocks as available and effective sorption-filtration materials. However, to solve the problem of chemical resistance and mechanical strength of humic mineral sorbents, the use of «Taunit» multi-walled carbon nanotubes (MWCNTs) (produced by LLC Nanotechtsentr, Tambov, Russia) allowed.

According to the electron microscopic analysis, the MWCNTs are filamentous formations of polycrystalline graphite, which are predominantly cylindrical. The outer diameter is 20–70 nm, the inner diameter is 5–10 nm. The length is several orders of magnitude greater than the diameter and is 3–10 microns. Modification of the side and end sections of the MWCNTs is often a necessary manipulation when creating materials with improved surface and bulk properties.

Oxidation is the most common method of chemical modification of carbon nanotubes. A mixture of concentrated nitric and sulfuric acids, potassium permanganate, a mixture of ammonia and hydrogen peroxide solutions was used as oxidizing agents. The yield of products using a mixture of concentrated acids was 50–60 %. The highest yield of products (92–95 %) was obtained when potassium permanganate was used as an oxidizing agent. For the first time, the processes of immobilization of humic acid and multi-walled carbon nanotubes on the surface of burned rocks (BR) have been carried out by ultrasonic and microwave activation.

Ultrasonic dispersion and microwave irradiation of components were also used to create humino-mineral compositions modified with carbon nanotubes [2]. For the immobilization processes being developed, an ultrasonic disperser of the IL-100-6/2 brand with an operating frequency of 22 kHz was used. Modification of humic acid with MWCNTs was performed by ultrasonic homogenization of humic acid with MWCNTs. During the study, the influence of various factors (the ratio of initial reagents, the duration of the USP) was investigated. The largest amount of acid groups (4.26 mmol-eq/g) is contained in the sample, which was irradiated with ultrasound for 10 minutes. The product yield was 60–68 %. It was established that the most homogeneous structure, according to microscopic analysis, was achieved with the ratio BR:HA:MWCNT = 50:20:1 and 50:10:1. The yield of products was 94–97 %. The number of acidic groups in the samples is in the range of 2.07–2.38 mmol-eq/g, the largest number of them is contained in humic-mineral composites with activated forms of carbon nanotubes obtained by USP for 10 minutes [3].

The effect of microwave radiation on the immobilization process was carried out in aqueous suspensions at a ratio of the initial components of the BR:HA:MWCNT = 50:20:1 and 50:10:1. The influence of the ratio of the initial components, the duration of MWR-effects and the nature of the modifier on the processes of obtaining humic-mineral nanocomposites has been studied. The number of acidic groups in the samples is in the range of 1.97–2.19 mmol-eq/g [4].

The laboratory tests of humic-mineral nanocomposites during the purification of industrial wastewater from the processing plant Priozersk indicate that humic-mineral sorbents (including those obtained under UZO and MVI conditions) containing nanotubes are highly competitive on the sorption activity with nanohumic composites. In particular, BR + GA + MWCNT composites purify sewage from the main components: aluminum (by 99.93 %), iron (by 98.02 %), manganese (by 60.58 %), lead (by 97.35 %), strontium (by 67.37 %) and zinc (by 97.98 %). The efficiency of using humic-mineral sorbents containing multi-walled carbon nanotubes as sorbents for wastewater treatment at enterprises has been proven [5, 6].

Thus, for the first time, the high efficiency of ultrasonic treatment on the process of obtaining humic-mineral compositions has been established, and the use of microwave radiation reduces the time of the synthesis process. The composition and structure of humic-mineral samples activated by MWCNTs under conditions of ultrasonic and microwave radiation has been proved by modern physicochemical methods. It has been shown that humic-mineral composites modified by multi-walled carbon nanotubes can be used as sorbents for wastewater purification.

As a result of the research work, a pilot setup was manufactured for testing the developed technologies of humic-mineral sorbents under experimental conditions and the optimization of the technological mode of their production. A draft technical specification for the design of the plant has been drawn up. The calculation of the equipment was done. Two chemical reactors have been manufactured for carrying out processes for the preparation of sorbents [7].

Products of modification of coal and coal waste with various chemical compounds and their applications as sorbents for wastewater treatment, restoration of fertility of depleted and man-made soils, and improving the soil structure are new and have no domestic and foreign analogues. The novelty is confirmed by the patent of the Republic of Kazakhstan [8].

*In the field of hydrogenation of heavy hydrocarbon raw materials*, studies were carried out to obtain composite catalysts based on compounds of VIII Group metals (Fe, Ni, Co, Mo), and their activity was studied in the process of hydrogenation of polyaromatic compounds. The optimal parameters of cavitation treatment of heavy hydrocarbon feedstock (fuel oil) in the presence of these composite catalysts based on water-soluble salts of iron, nickel, cobalt, and molybdenum deposited on zeolites and coal sorbent were determined.

It has been established that the highly dispersed distribution of the compounds of these metals by the impregnation of active carbon with solutions of their salts and their complex compounds leads to the conversion of metal compounds deposited on the surface of the coal into an oxide form. So it was shown that the impregnation of iron, nickel and cobalt sulfates on a carbon sorbent results in highly dispersed metal-sulfate catalysts on a carbon carrier ($FeSO_4 \cdot 7H_2O/C$, $NiSO_4 \cdot 7H_2O/C$, binary $FeSO_4 \cdot 7H_2O$ — $CoSO_4 \cdot 7H_2O/C$) with a content of active ingredient of 5 % (for metal). High-dispersion catalysts based on iron, nickel and cobalt oxides on a carbon substrate $Fe_2O_3/C$, $NiO/C$, binary catalyst $Fe_2O_3$–$CoO/C$ were synthesized by a thermal modification of the corresponding metal sulfates [9].

The catalytic properties of the synthesized catalysts in the hydrogenation reactions of model polycyclic hydrocarbons — anthracene and phenanthrene — have been studied [10].

In a comparative analysis of the catalytic activity of the obtained composite catalysts with a known iron-chromium catalyst (STK-1), it was found that under the same conditions, $Fe_2O_3$ and $Fe_2O_3/C$ catalysts give the composition of the reaction products with different ratio of components. It should be noted that, in terms of the active component of the catalysts, iron, the content of the latter in $Fe_2O_3/C$ is 14 times lower than in $Fe_2O_3$. It was revealed that the replacement of nickel-sulfate by nickel-oxide catalyst leads to a more noticeable increase in the products of hydrogenolysis than on iron-containing analogues, while the content of hydrogenated components in the process of hydrogenation decreases. The composition of gaseous products of anthracene hydrogenation on the catalyst, including methane, ethane and propane, was established by gas-liquid chromatography (GLC). The product of isomerization of anthracene (phenanthrene) on nickel catalysts is formed in larger quantities than on iron ones.

It was established that as a result of the anthracene hydrogenation reaction, two groups of compounds are formed: hydrogenated and hydrogenolysis products. In this case, the transition of the linear form of anthracene to angular phenanthrene and its transformation products is observed [11].

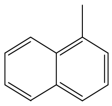
The reaction proceeds according to the scheme:

I anthracene

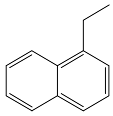
II dihydroanthracene

III tetrahydroanthracene

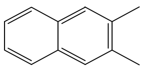
IV octahydroanthracene



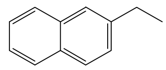
V
1-methyl-naphthalene



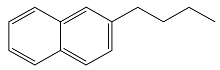
VI
1-ethyl-naphthalene



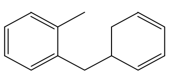
VII
2,3-dimethyl-naphthalene



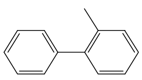
VIII
2-ethyl-naphthalene



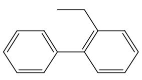
IX
2-buthyl-naphthalene



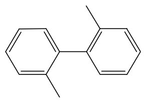
X
1-methyl-2-phenylmethyl-benzene



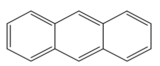
XI
2- methyl-1,1'-diphenyl



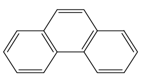
XII
2-ethyl-1,1'-diphenyl



XIII
2,2'-dimethyl-1,1'-diphenyl

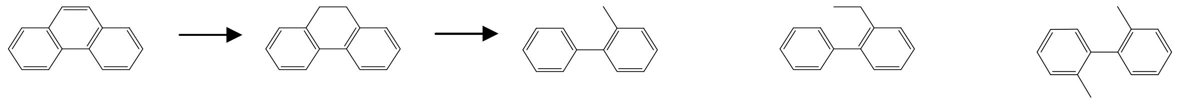


XIV
anthracene

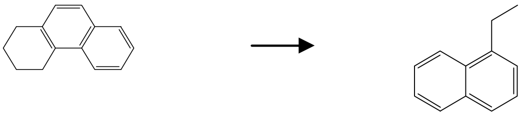


XV
phenanthrene

As a result, two groups of compounds were obtained: hydrogenated II–IV, which include 9,10-dihydroanthracene, 1,2,3,4-tetrahydroanthracene and 1,2,3,4,5,6,7,8-octahydroanthracene, and V–XV hydrogenolysis products: 1-methyl-naphthalene, 1-ethyl naphthalene, 2,3-dimethylnaphthalene, 2-ethylnaphthalene, 2-butylnaphthalene, 1-methyl-2-phenylmethylbenzene, 2-methyl-1,1'-diphenyl, 2,2'-dimethyl-1,1'-diphenyl and 2-ethyl-1,1'-diphenyl. Compounds V, VI, XI–XIII do not belong to the products of destruction of anthracene or its hydro-derivatives. The presence in the reaction mixture of 1-methyl-naphthalene V, 1-ethylnaphthalene VI, 2-methyl-1,1'-diphenyl XI, 2-ethyl-1,1'-diphenyl XII and 2,2'-dimethyl-1,1'-diphenyl XIII can be explained by the result of the destruction of phenanthrene or its hydrogenated derivatives — di- and tetrahydrophenanthrene. In this case, there is a transition of the linear form of anthracene to angular phenanthrene and the products of its transformation:



phenanthrene
9,10-dihydro-phenanthrene
2-methyl-1,1'-diphenyl
2-ethyl-1,1'-diphenyl
2,2'-dimethyl-1,1'-diphenyl



1,2,3,4-tetrahydrophenanthrene
1-ethyl-naphthalene

The use of zeolite as a carrier was associated with their geometry, porous structure, frame chemistry, and the nature of extra-frame structures. The presence of a large group of microporous crystalline aluminosilicates, the three-dimensional framework of which is permeated with cavities and channels of nanometric dimensions, creates a unique opportunity to modify catalysts. Impregnation of zeolites with aqueous solutions of metal salts, the cations of which are required to be introduced into the zeolite, is the most common method of modifying zeolites.

In order to study the activity of the synthesized iron-containing composite catalysts supported on zeolite, hydrogenation of polyaromatic compounds was carried out.

During the research the following results were obtained:

– by an impregnation of iron, nickel and cobalt sulfate on zeolite, the highly dispersed metal-sulfate catalysts based on synthetic zeolites CaA and ZSM were prepared: $FeSO_4 \cdot 7H_2O$/CaA ($FeSO_4 \cdot 7H_2O$/ZSM), $NiSO_4 \cdot 7H_2O$/CaA ($NiSO_4 \cdot 7H_2O$/ZSM), binary $FeSO_4 \cdot 7H_2O$ – $CoSO_4 \cdot 7H_2O$/CaA ($FeSO_4 \cdot 7H_2O$ – $CoSO_4 \cdot 7H_2O$/ZSM) with the content of the active component 5 % (by metal). By a thermal modification of iron, cobalt and nickel sulfates supported on a carrier (zeolite), the composite catalysts based on iron, nickel and cobalt oxides on a CaA and ZSM zeolite substrate were synthesized: $Fe_2O_3$/CaA ($Fe_2O_3$/ZSM), NiO/CaA (NiO/ZSM), binary catalyst $Fe_2O_3$ – CoO/CaA ($Fe_2O_3$ – CoO/ZSM) [12].

– the catalytic activity of synthesized catalysts was investigated in the reactions of hydrogenation of anthracene. The chromatographic mass-spectroscopy (CMS) and GLC analysis established the component composition of the hydrogenation products. A method for analyzing the products of anthracene hydrogenation was developed for GLC. The method used a database of component composition, created on the basis of the results of the analysis of standard samples and CMS analysis of reaction products [13].

– it was established that under the same conditions, the synthesis of catalysts $Fe_2O_3$/CaA and CoO/CaA give the composition of the reaction products of different component ratios. So, with a slight difference in the degree of conversion of anthracene — 95.02 % for $Fe_2O_3$/CaA and 97.38 % for CoO/CaA, the difference in the content of the products of hydrogenolysis and hydrogenation is more noticeable. In the process of hydrogenation in the presence of Fe-Co/CaA catalyst, hydrogenation products amounted to > 80 %, cleavage products < 10 % [11].

– it was found that the replacement of a cobalt sulfate by a cobalt oxide catalyst leads to a more noticeable increase in the products of hydrogenolysis, in comparison with nickel and iron based analogues (14.12–23.62 % for Ni and 9.01–12.96 % for Fe). At the same time, the content of hydrogenated components decreases (77.67–63.81 % for Ni and 84.95–77.49 % for Fe) [14].

Thus, the synthesized binary catalysts based on compounds of VIII group metals deposited on a coal sorbent and zeolite demonstrate high activity in the process of hydrogenation of model compounds.

In the process of fuel oil hydrogenation, it was established that the conversion and the quantitative composition of the products formed are different and depend on the activity and selectivity of the catalysts, which, in turn, are associated with the surface, dimensionality and porous structure. The use of iron-containing composite catalysts makes it possible not only to increase the conversion of hydrocarbon derivatives, but also to improve the quality of the products obtained, in particular, alkanes of iso-construction with a lower molecular weight (2-methylpentane, 2-methylpentene, etc.) [15].

It was noted a rather significant increase in the content of paraffinic hydrocarbons and a decrease in aromatic, polyaromatic, oxygen-containing hydrocarbons. In the cavitation treatment of the fuel oil fraction in the presence of the composite catalysts $Fe_2O_3$/C, $Fe_2O_3$/ZSM and $Fe_2O_3$/CaA, the content of paraffins with a longer $C_{15}$-$C_{19}$ chain increases. This is due to the fact that during cavitation treatment in the presence of $Fe_2O_3$/ZSM, $Fe_2O_3$/CaA, $Fe_2O_3$/C catalysts, two coupled processes occur in the mixture — destruction and condensation, however, the destruction of paraffins prevails over condensation processes [16].

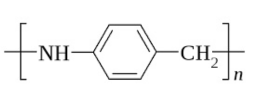
Optimal conditions and a number of factors influencing the cavitation treatment of the fuel oil fraction in the presence of the $Fe_2O_3$/C catalyst are determined. In accordance with the regression equation obtained, the optimal conditions for cavitation treatment are as follows: $\tau$ = 90–120 s, the amount of added catalyst is 0.7–1 g and the amount of added water is 1.5–2 ml [17].

Thus, by quantifying the individual composition of the fuel oil fraction, the positive effect of the catalytic-cavitation treatment in the presence of the studied catalysts was established. According to the hydrocarbon conversion, the catalytic systems are arranged in the following order: $Fe_2O_3$/C > $Fe_2O_3$/CaA > $Fe_2O_3$/ZSM.

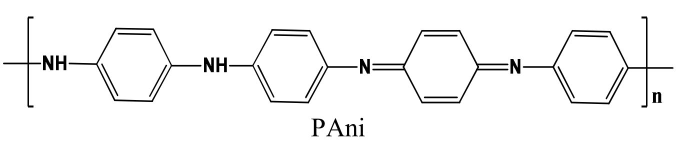
*In the field of electrocatalysis of organic compounds,* by a combined chemical and electrochemical method, new polymer-metal catalytic systems were created with the study of their activity in the electrohydrogenation of organic compounds [18–26].

The synthesis of metal-polymer composites based on conductive polyaniline (PAni) polymer with immobilized metal salts (Ni, Co, Cu, Pd, Zn, Ag, Fe), metal oxides (CuO, FeO) without and with further chemical and electrochemical reduction of their cations were carried out [18–23]. The possibility of electrochemical reduction of cations of a number of metals in the composition of the PAni polymer matrix was established when powder composites were deposited on the surface of the Cu cathode (without fixing them), and PAni + $M^0$ composites possessing electrocatalytic activity were created.

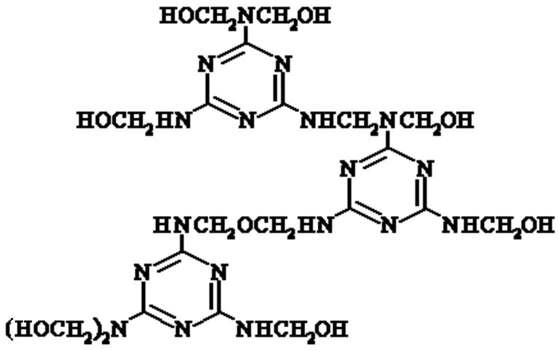
Preparation of polymer-metal composites according to the developed direction was continued with the participation of aniline-formaldehyde polymer (AFP) and its mixed compositions with melamine-formaldehyde polymer (MFP) and PAni with the following monomeric structures:



AFP



PAni



MFP

It should be noted that, unlike polyaniline, AF- and MF-polymers do not have conductive properties and even, on the contrary, are good insulators. The introduction of salt or metal nanoparticles allows to create new materials with semiconductor properties on the basis of individual polymers or their mixed compositions.

Metal-polymer composites with the participation of AF-polymer were obtained by introducing a metal salt ($CuCl_2$, $NiCl_2$, $FeCl_3$, $FeSO_4$) *in situ* polycondensation of aniline and formaldehyde with further thermal treatment (TT), as well as the «impregnation» method by sorbing metal salts with polymer from their aqueous solutions. X-ray diffraction (XRD) analyzes revealed the influence of the synthesis conditions and the nature of the introduced metal (in the form of its salt) on the phase constitution of the synthesized AFP composites. Metal oxides ($Cu_2O$, CuO, NiO, $Fe_3O_4$) are formed in composites synthesized *in situ*; $2CuCl_2 \cdot 5Cu(OH)_2 \cdot H_2O$ complex salt, hydroxides and oxyhydroxide ($Ni(OH)_2$, FeOOOH) are present in the composites prepared according to the second variant of the synthesis.

The electrocatalytic activity of the synthesized composites was studied in the electrohydrogenation of *o*-nitroaniline (*o*-NA) in a diaphragm cell when they are deposited on the surface of the Cu cathode (current 1.5 A, 30 °C, catholyte — 2 % NaOH solution with the addition of ethanol, anolyte — 20 % NaOH solution). The electrochemical reduction of *o*-NA under the same conditions is carried out at a rate (W) of 3.3 mL $H_2$/min, and a degree of transformation of *o*-NA to *o*-phenylene-diamine (α) is equal to 84 %.

Experiments have shown that Ni- and Fe-containing AFP composites (AFP + $NiCl_2$, AFP + $Ni^0$, AFP + $FeCl_3$ and AFP + $FeSO_4$) exhibit a weak electrocatalytic activity in *o*-NA electrohydrogenation, which is caused by the inability of the cations of these metals to electrochemical reduction under given conditions. According to the XRD analysis, copper cations are reduced from copper oxides and its complex salt formed during the synthesis and TT, giving copper particles in the zero-valence state in the polymer matrix, which catalyze the electrohydrogenation of *o*-NA [24]. At the same time, AFP + $CuCl_2$ composites obtained by the «impregnation» method showed a higher electrocatalytic activity: *o*-NA hydrogenation rate increases to 5.6–6.1 mL/min, its conversion — to 91–94 % with the formation of one product — *o*-phenylene-diamine having a wide range of practical applications. Preliminary ultrasonic treatment (UST) of these composites contributes to a more complete extraction of copper cations from its aqueous solutions and to a greater amount of their electrochemical reduction.

For the synthesized new polymer-metal composites based on an AF-polymer and salts of metals $CuCl_2$, $NiCl_2$, $FeCl_3$, $FeSO_4$, their electrical conductivity was determined to be about $10^{-6}$–$10^{-4}$ $Ohm^{-1} \cdot m^{-1}$, which allows us to classify them as organic semiconductors with promising applications in microelectronics, for the manufacture of various kinds of sensors, etc.

Mixed aniline-melamine-formaldehyde polymers (AMFP) were obtained mainly according to the developed method of synthesis, which consists in carrying out the polycondensation of aniline and melamine with formaldehyde separately for each monomer (with a 1:1 ratio), followed by their combination.

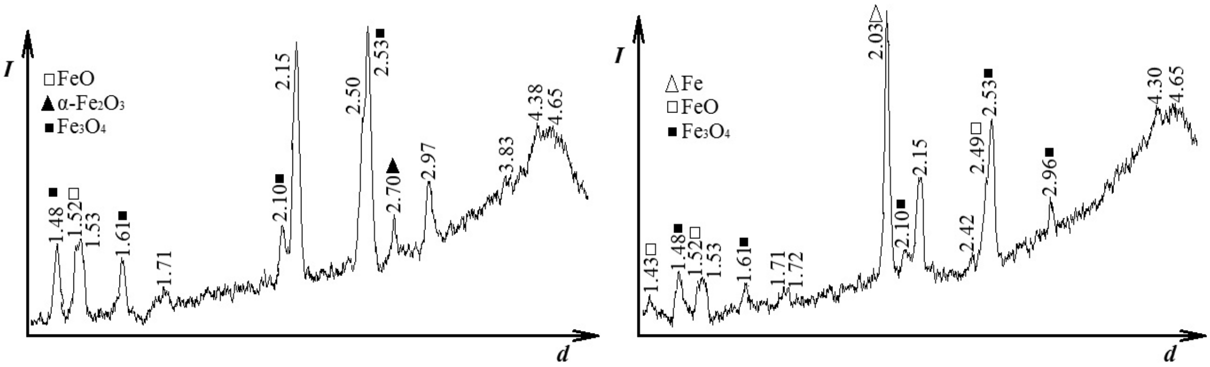
Metal-polymer AMFP-composites were prepared by two methods: *1* — *in situ* by immobilizing metal chlorides ($Cu^{2+}$, $Ni^{2+}$, $Co^{2+}$), their oxides and metal nanoparticles (synthesized by chemical reduction of their cations from aqueous solutions of salts with sodium borohydride and hydrazine hydrate and sonicated) into the polymer matrix, and *2* — the «impregnation» method. By the XRD analyzes of AMFP composites before and after their application in electrohydrogenation of *o*-NA, the electrochemical reduction of copper cations from AMFP powder composites doped with $CuCl_2$, CuO and $Cu_2O$ and the highest electrocatalytic activity of composites synthesized *in situ* were established (Table 1) [25]. As follows from the data presented, the rate of *o*-NA hydrogenation and its conversion increase with an increase in the copper content in 1 g of AMFP + $CuCl_2$ composites.

Table 1

**Electrocatalytic hydrogenation of *o*-NA on the copper-containing AMFP composites**

| Composites | The copper content in 1 g of composite | *W*, mL $H_2$/min ($\alpha = 0.25$) | $\eta$, % ($\alpha = 0.25$) | $\alpha$, % |
|---|---|---|---|---|
| Cu cathode | – | 3.3 | 27.7 | 84.0 |
| AMFP (1:1) + $CuCl_2$ (1:0.5) | 0.150 | 2.4 | 20.7 | 80.5 |
| AMFP (1:1) + $CuCl_2$ (1:1) | 0.253 | 4.8 | 46.7 | 84.8 |
| AMFP (1:1) + $CuCl_2$ (1:1.5) | 0.324 | 6.1 | 62.7 | 98.0 |
| AMFP (1:1) + $CuCl_2$ (1:2) | 0.559 | 8.5 | 80.3 | 100 |
| AMFP (1:1) + $CuCl_2$ (1:1) + $NaBH_4$ | 0.252 | 4.1 | 37.2 | 100 |
| AMFP (1:1) + CuO (1:1) | 0.369 | 4.7 | 41.7 | 89.1 |
| AMFP (1:1) + $Cu_2O$ (1:1) | 0.209 | 3.2 | 30.6 | 73.7 |

Mixed AFP + PAni and PAni + AFP polymers were prepared according to the synthesis procedures of AF-polymer and PAni, respectively. Metal-polymer composites PAni + AFP (2:1) with introduced metals ($Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$) chlorides and their oxides sonicated were produced according to several synthesis options. Their structure, phase composition and morphological features were studied by IR spectroscopy, X-ray powder diffraction, and electron microscopy. The structural-phase changes in the composites under the action of the reaction medium of the oxidative polymerization of aniline and current cathodic polarization are analyzed. It was found that the metal cations in copper (II) and zinc (II) chlorides, as well as in FeO (wustite) (Fig. 1), CuO and ZnO oxides introduced into the polymer matrix undergo electrochemical reduction (on the stage of hydrogen saturation) to form copper, zinc and iron particles in the zero-valent state, which catalyze the electrohydrogenation of *o*-NA.



*a*) *b*)

Figure 1. X-ray patterns of the PAni(2) + AFP(1) + FeO(1:0.6) composite before (*a*) and after (*b*) electrohydrogenation of *o*-NA

Comparison of the electrocatalytic activity of the synthesized composites based on the mixed polymer PAni(2) + AFP(1), doped with metal salt, gives the following series of their activity: $CuCl_2 > ZnCl_2 > FeCl_3$ (not active). The electrocatalytic activity of the PAni(2) + AFP(1) + MeO composites decreases in the following sequence of oxides introduced: CuO > FeO > ZnO.

Table 2 shows the results of experiments on the electrohydrogenation of *o*-NA using Zn-containing composites PAni + AFP, performed under the above described conditions with a current of 2.0 A [26].

Table 2

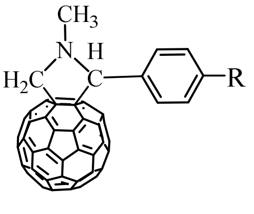
**Electrocatalytic hydrogenation of *o*-NA on the PAni(2) + AFP(1) + $ZnCl_2$ (ZnO) composites**

| Composites | The zinc content in 1 g of composite | *W*, mL $H_2$/min ($\alpha$= 0.25) | $\eta$, % ($\alpha$= 0.25) | $\alpha$, % |
|---|---|---|---|---|
| Cu cathode | – | 3.5 | 25.0 | 71.0 |
| PAni(2) + AFP(1) + $ZnCl_2$ composites | | | | |
| PAni + AFP + $ZnCl_2$ (1:2) | 0.138 | 3.7 | 26.7 | 78.1 |
| PAni + AFP + $ZnCl_2$ (1:2) + NaOH | 0.243 | 4.9 | 34.4 | 85.0 |
| PAni + AFP + $ZnCl_2$ (1:2) + $NH_4OH$ | 0.270 | 5.4 | 39.4 | 97.7 |
| PAni + AFP + $ZnCl_2$ (1:1) + evaporation | 0.085 | 6.6 | 47.7 | 87.6 |
| PAni + AFP + $ZnCl_2$(1:1) + evaporation + TT | 0.089 | 7.0 | 50.8 | 92.1 |
| PAni(2) + AFP(1) + ZnO (Zn) composites | | | | |
| PAni + AFP + ZnO (1:1) + NaOH | 0.285 | 5.1 | 33.8 | 99.9 |
| PAni + AFP + ZnO (1:1) + $NH_4OH$ | 0.275 | 4.0 | 26.7 | 92.0 |
| PAni + AFP + Zn (1:1) + NaOH | 0.384 | 7.1 | 52.3 | 86.4 |
| PAni + AFP + Zn (1:1) + $NH_4OH$ | 0.370 | 7.1 | 51.6 | 81.2 |

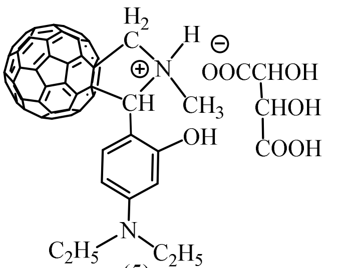
It follows from the above data that all synthesized Zn-containing composites based on the mixed PAni(2) + AFP(1) polymer possess electrocatalytic activity in electrohydrogenation of *o*-NA; in their presence electrocatalytic hydrogenation of *o*-NA is carried out at higher rates and more complete *o*-NA conversion than electrochemical reduction at the Cu cathode.

Thus, on the basis of the AF-polymer and its mixed compositions with MFP and PAni, metal salts and oxides, new metal-polymer composites have been created, relating mainly to organic semiconductors and exhibiting electrocatalytic properties depended on the nature of the introduced metal, its content, conditions of synthesis and the influence of ultrasonic treatment. The resulting metal-polymer composites are multifunctional materials and can be used not only as catalysts or electrocatalysts in the synthesis of chemical compounds, but also in other areas of technics, including nanotechnology.

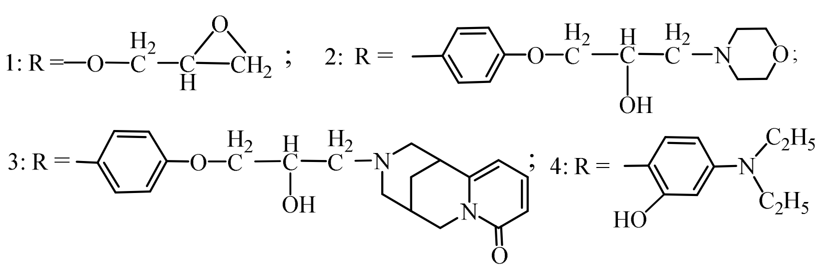
*In the field of synthesis of biologically active substances,* in continuation of previous studies [27–30] on the basis of heterocyclic compounds, new approaches were proposed to the reactions of interaction of acetoacetic acid anilide with 5-aminotetrazole and substituted aromatic aldehydes, which led to the development of methods for obtaining new series of 7-aryl-5-methyl-N-phenyl-4,7-dihydrotetrazolo-[1,5-α]-pyrimidine-6-carboxamides [31]. Studies are being carried out on the chemical transformation of the structure of fullerene C60 with modified derivatives of alkaloids with obtaining interesting in terms of studying the biological properties of fulleropyrrolidines [32, 33].



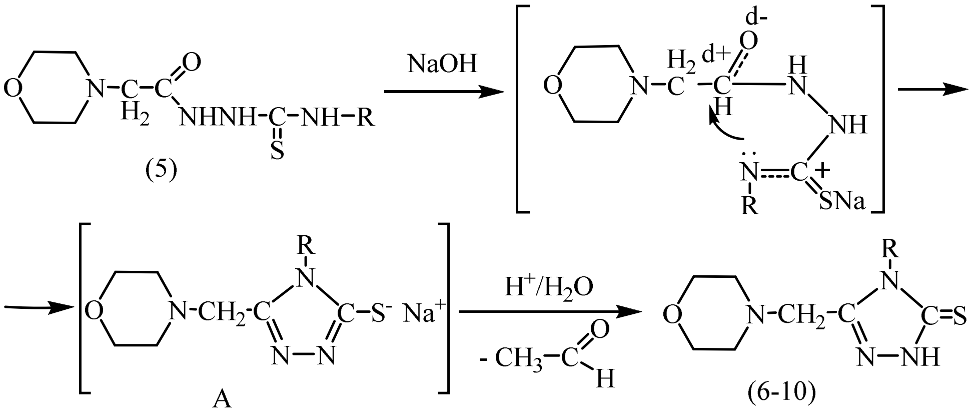
(I - 4)



(5)



In order to expand a number of polyfunctional 1,2,4-triazoles bearing valuable biologically active groups [34, 35] based on N-morpholinyl acetic acid hydrazide, were synthesized and intramolecular heterocyclization of thiosemicarbazide derivatives (5) was carried out. These compounds can be widely used in organic chemistry as starting synthons in the synthesis of many nitrogen-containing heterocyclic compounds.



R = $CH_2$=CH-$CH_2$- (6); $CH_3$-$CH_2$- (7); $C_6H_5$- (8);
$C_6H_5$-C(O)- (9); 4-Br-$C_6H_4$-C(O)- (10)

The cyclization of thiosemicarbazide derivatives (5) was carried out in an aqueous-alkaline medium by heating the reaction medium to 80–85 °C. The starting N-morpholinyl acetic acid thiosemicarbazides were obtained by the interaction of N-morpholinyl acetic acid hydrazide with alkyl and aryl isothiocyanates. In the presence of alkali, N-alkyl(aryl)thiosemicarbazides of N-morpholinyl acetic acid (5) are converted to thiolate, and upon further acidification, 5-(morpholinomethyl)-4-alkyl(aryl)-1,2,4-triazole-3-thions are formed (6–10) [35–37].

In order to establish the spatial structure of 5-(morpholinomethyl)-4-allyl-1,2,4-triazol-3-thione (6), its X-ray structural examination was carried out, the general view of which is shown in Figure 2. From the obtained data it follows that the bond lengths and valent angles are close to normal [37].

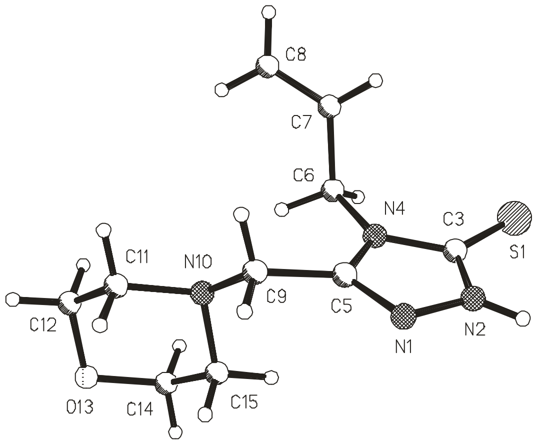
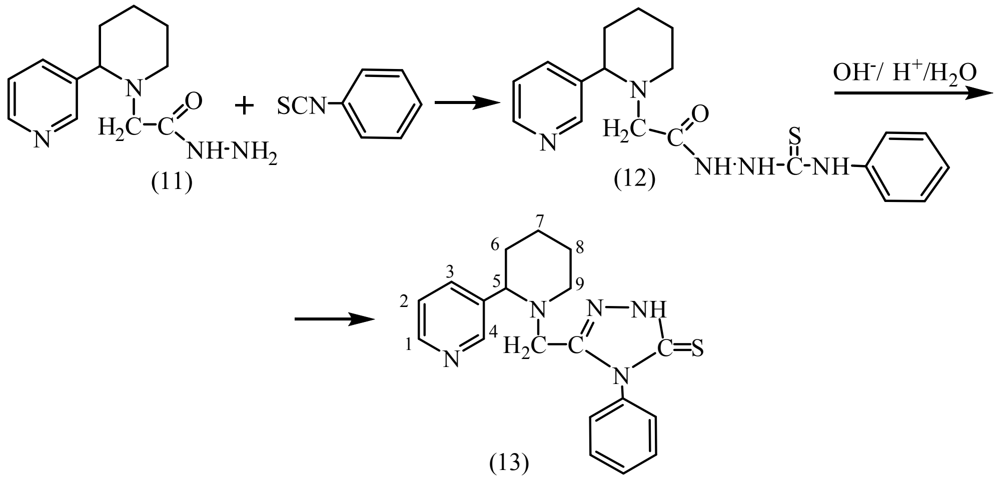


Figure 2. The structure of the molecule 5-(morpholinomethyl)-4-allyl-1,2,4-triazole-3-thione (6)

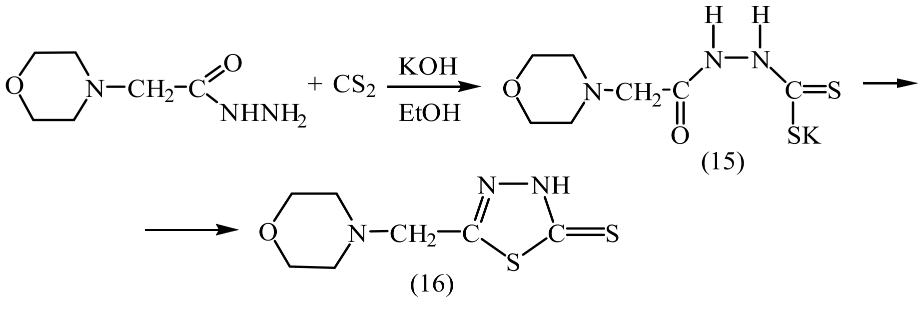
In continuation of these studies, N-phenyl thiosemicarbazide N-anabasinyl acetic acid (12) was synthesized by reacting N-anabasinyl acetic acid hydroxide (11) with phenyl isothiocyanate in ethanol with a yield of 74 %. It is established that upon acidification of a water-alkaline solution of the obtained phenylthiocarbazide derivative (8), the latter one is subjected to intramolecular hetero-cyclization with the formation of 4-phenyl-5-anabazinomethyl-1,2,4-triazole-3-thione (13) [38].



The synthesis of N-allylthiosemicarbazide N-anabasinyl-acetic acid was carried out in a similar way, and further its acidification leads to intramolecular hetero-cyclization with the formation of 4-allyl-5-anabasine-nomethyl-1,2,4-triazole-3-thione.

Among the extensive class of sulfur-containing compounds, an important role belongs to derivatives of dithiocarbamic acids [39, 40]. Derivatives of hydrazides and thiosemicarbazides are known to be important syntons in the synthesis of azaheterocycles [41]. It was established that using various reagents and changing the conditions of the reaction, it is possible to direct cyclization towards the formation of 1,3,4-oxadiazoles, 1,3,4-thiadiazoles or 1,2,4-triazoles.

In order to study the influence of the nature of substituents in the hydrazine component on the structure of condensation products, the interaction of N-morpholinyl acetic acid hydrazide (14) with carbon disulfide in an alkaline medium was studied. It was established that as a result of the reaction, the potassium salt of hydrazinodithiomorpholinyl acetic acid (15) is formed, which was used for further syntheses. The potassium salt of hydrazino-dithiomorpholinyl acetic acid (15) under the action of sulfuric acid (concentrated) at a low temperature easily undergoes cyclization to 5-(morpholinomethyl)-1,3,4-thiadiazol-2(3H)-thione (16) [38, 39]. In order to optimize this reaction, we studied the conversion of N-morpholinyl acetic acid hydrazide to a 1,3,4-thiadiazole derivative in the interaction of hydrazide with carbon disulfide in an alkaline medium under the conditions of «one pot» microwave activation in an aqueous medium [39–42].



The structure of the substance (16) is confirmed by X-ray structural analysis (Fig. 3).

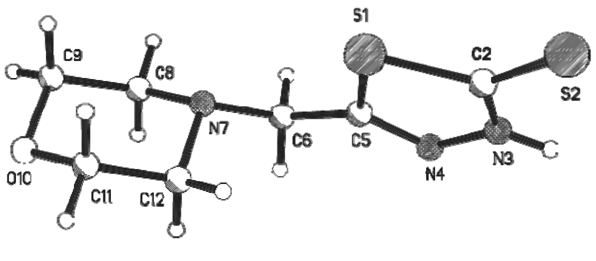
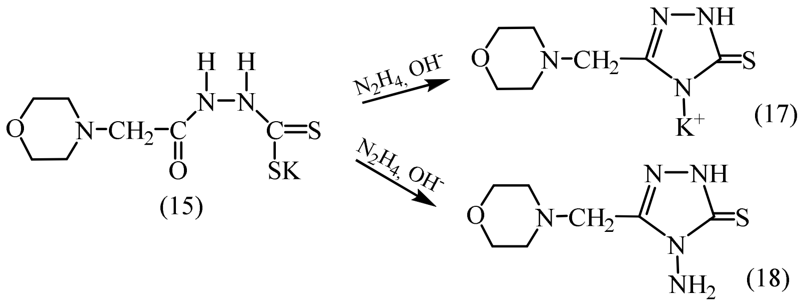


Figure 3. The spatial structure of the molecule 5-(morpholinomethyl)-1,3,4-thiadiazol-2(3H)-thione (16)

In continuation of the ongoing research on dithiocarbamine derivatives, a series of preparatively convenient chemical transformations with the potassium salt of hydrazinodithiomorpholinyl acetic acid (15) was carried out. A study of the hetero-cyclization of the potassium salt of hydrazinodiomorpholinyl acetic acid (15) showed that the nature of the forming substances depended on the conditions of the process [41–43].



So, by reacting the potassium salt of hydrazinodithiomorpholine-acetic acid (15) with hydrazine hydrate in the presence of potassium hydroxide in absolute ethanol, followed by acidification with hydrochloric acid to a neutral medium (pH = 7), 4-amino-3-(morpholinomethyl)-(1H)-1,2,4-thiazolo-5e(4H)-thione (18) was synthesized [44]. It should be noted that a change in the nature of the reaction medium from absolute ethanol to water-ethanol (1:2) leads to the formation of the potassium salt of 3-(morpholinomethyl) -1,2,4-thiazole-4-thione (17). The structure of the substance (17) was also confirmed by X-ray diffraction [40–43].

As a result of research and experimental works, optimal methods of synthesis were developed and the physico-chemical properties of new potentially biologically active compounds of dithiocarbamate, thiourea, thiazole, and thioamide structures based on N-morpholylacetic acid hydrazides, as well as the known anabasine alkaloid, were studied. The synthesized new substances are of interest as potential objects for studying the biological properties and establishing the regularities of the «structure-bioactivity» relationship.

It should be noted that Institute of Organic Synthesis and Coal Chemistry of RK throughout all the years of its activity takes an active part in the implementation of the most important tasks in the framework of the priority directions of the development of science of the RK. The Institute staff at a high modern level conducts the scientific researches on the development of high technologies for the production of industrially important coal products, including modern approaches based on the use of microwave and ultrasound activation technology in chemical processes for the creation of new natural-synthetic polymers nanostructured catalysts, nanocomposites of various purposes and biologically active substances with the participation of C60 fullerene and nanofibers and other new products.

At the same time, the Institute should pay attention to the issues of commercialization of scientific results, taking into account the experience of promoting a number of developments, namely, the electrocatalytic production of 2,4,5,6-tetraaminopyrimidine and 2,4,5-triamino-6-oxypyrimidine used in the production of the antitumor drug «Methotrexate» and folic acid, introduced at the Shchyolkovo Vitamin Plant (Russia), the creation of the production of the highly effective flotation reagent dimethyl(isopropenyl ethynyl)carbinol (DMIPEK) in Moscow, the release of coal-alkaline reagent from off-balance coals Central Kazakhstan on SJSA «Ekibastuzugol» and LLP «Uglesintez» with capacity up to 1000 tons of products per year.

At this stage, it is necessary to increase the efficiency of implementation works on the basis of the created mini-workshops for obtaining sodium humate and coal-fuel briquettes based on coal screenings from the Shubarkol coal deposit.

It is necessary to ensure further improvement of the created innovative developments of the Institute:

- on the creation of new domestic polymer-humic soil builders and organic-mineral humic fertilizers, coal-alkaline reagent, coagulants and corrosion inhibitors based on coal products;
- on obtaining magnetically controlled nanosorbents for collecting oil spills from the water surface;
- on obtaining valuable chemical compounds (*p*-aminobenzoic acid in the electrocatalytic system, piperidine by electrocatalytic reduction of pyridine, methylphenylcarbonyl by electrocatalytic reduction of acetophenone and etc.), which are the basis of medicinal and fragrant substances.

The results of the implementation of these developments will contribute to the advanced development of high-tech and knowledge-intensive industries that save mineral resources, diversify the economy from raw materials to processing, and also contribute to solving environmental problems in the region.

## References

1 Василец Е.П. Продукты химической переработки окисленных углей / Е.П. Василец, Г.К. Кудайберген, О.В. Арнт // Проблемы геологии и освоения недр: материалы XXI Междунар. науч. симпозиума студентов и молодых ученых им. акад. М.А. Усова (3–7 апреля 2017 г.). — Томск, 2017. — С. 379–380.

2 Akkulova Z.G. Surface morphology and sorption characteristics of humates and sulphohumate nanocomposites with natural and synthetic polymers and carbon nanotubes / Z.G. Akkulova, A.K. Amirkhanova, A.Kh. Zhakina, G.K. Kudaibergen, E.P. Vassilets, O.V. Sadykova // Chemical Journal of Kazakhstan. — 2015. — No. 4. — P. 184–188.

3 Аккулова З.Г. Получение и сорбционные свойства гуминоминеральных сорбентов на основе вмещающих пород угольных шахт / З.Г. Аккулова, А.К. Амирханова, А.Х. Жакина, З.М. Мулдахметов, Е.П. Василец, Г.К. Кудайберген, О.В. Арнт // Известия НАН РК. Сер. химии и технологии. — 2016. — № 6. — С. 14–22.

4 Василец Е.П. Исследование влияния ультразвуковой обработки и перекиси водорода на процесс окисления шубаркольских углей / Е.П. Василец, А.Х. Жакина, А.К. Амирханова, Г.К. Кудайберген // Тезисы докл. XXVI Рос. молодежной науч. конф., посвящ. 120-летию со дня рожд. акад. Н.Н. Семенова (27–29 апреля 2016). — Екатеринбург, 2016. — С. 20–21.

5 Жакина А.Х. Влияние ультразвукового метода иммобилизации гуминовой кислоты на горелую породу / А.Х. Жакина, Е.П. Василец, А.Р. Рапиков // Тезисы докл. XX Всерос. конф. молодых ученых-химиков (18–20 апреля 2017). — Нижний Новгород, 2017. — С. 477.

6 Василец Е.П. Влияние термохимических и микроволновых методов воздействия на сорбционные свойства гуминоминеральных композитов / Е.П. Василец, А.Х. Жакина, З.Г. Аккулова, З.М. Мулдахметов, А.К. Амирханова, Г.К. Кудайберген, О.В. Арнт, А.Р. Рапиков // Тенденции развития науки и образования в области естественно-научных дисциплин: материалы Междунар. науч.-практ. конф., посвящ. 70-летию со дня рожд. д-ра хим. наук Б.М. Бутина (7–8 октября 2016). — Алматы, 2016. — С. 87–89.

7 Жакина А.Х. Сорбенты многофункционального назначения на основе углеотходов / А.Х. Жакина, Е.П. Василец, А.К. Амирханова, О.В. Арнт, А.Р. Рапиков, З.М. Мулдахметов. — Караганда: Гласир, 2017. — 104 с.

8 Патент на полезную модель 3157 РК. Способ получения гуминоминерального сорбента для извлечения тяжелых металлов / Жакина А.Х., Мулдахметов З.М., Амирханова А.К., Василец Е.П., Рапиков А.Р., Кудайберген Г.К., Арнт О.В. Опубл. 2018.

9 Baikenov M.I. Effect of new catalytic systems on the process of anthracene hydrogenation / M.I. Baikenov, G.G. Baikenova, A.S. Isabaev, A.B. Tateeva, Zh.S. Akhmetkarimova, A. Tussipkhan, A.Zh. Mataeva, K.K. Esenbaeva // Solid Fuel Chemistry. — 2015. — Vol. 49, No. 3. — P. 150–155. DOI 10.3103/S0361521915030039.

10 Ахметкаримова Ж.С. Гидрогенизация смеси полиароматических углеводородов / Ж.С. Ахметкаримова, М.З. Мулдахметов, М.Г. Мейрамов, А.Т. Ордабаева, Ж.Х. Мулдахметов, А.М. Дюсекенов // Успехи в химии и химической технологии: сб. науч. тр. — М., 2016. — С. 89–91.

11 Мейрамов М.Г. Ангулярно-линеарная изомеризация при гидрировании фенантрена в присутствии железосодержащих катализаторов / М.Г. Мейрамов // Химия твердого топлива. — 2017. — № 2. — С. 42–45. DOI 10.7868/S0023117717020074.

12 Ордабаева А.Т. Изучение процесса гидрогенизации антрацена в присутствии композитного катализатора / А.Т. Ордабаева, М.Г. Мейрамов, В.А. Хрупов, Р.К. Бакирова // Хим. журн. Казахстана. — 2015. — № 3. — С. 338–344.

13 Meiramov M.G. Hydrogenation of model compounds in the presence of iron-containing catalysts / M.G. Meiramov // Solid Fuel Chemistry. — 2014. — No. 2. — P. 50–55. DOI 10.3103/S0361521914020104.

14 Ахметкаримова Ж.С. Влияние нанокатализаторов на процесс гидрогенизации модельного соединения — антрацена / Ж.С. Ахметкаримова, М.И. Байкенов, М.Г. Мейрамов, А.Т. Ордабаева, В.А. Хрупов, Ж.Х. Мулдахметов // Хим. журн. Казахстана. — 2015. — № 4. — С. 219–225.

15 Ахметкаримова Ж.С. Синтез бинарных композитных катализаторов на основе солей металлов VIII группы на цеолитном носителе / Ж.С. Ахметкаримова, З.М. Мулдахметов, Ж.Х. Мулдахметов, А.Т. Ордабаева, М.И. Байкенов, А.М. Дюсекенов // Хим. журн. Казахстана. — 2017. — № 2. — С. 251–259.

16 Ахметкаримова Ж.С. Гидрирование антрацена в присутствии композитных катализаторов / Ж.С. Ахметкаримова, З.М. Мулдахметов, М.Г. Мейрамов, А.Т. Ордабаева, Ж.Х. Мулдахметов, М.И. Байкенов, А.М. Дюсекенов // Известия НАН РК. Сер. химии и технологии. — 2017. — № 1. — С. 33–40.

17 Ахметкаримова Ж.С. Применение катализаторов в процессах гидрогенизации твердого и тяжелого углеводородного сырья / Ж.С. Ахметкаримова, М.Г. Мейрамов, М.И. Байкенов, М.З. Мулдахметов, А.Н. Жакупова, Р.А. Таженова, З.С. Даутова // Известия НАН РК. Сер. химии и технологии. — 2015. — № 3. — С. 116–124.

18 Ivanova N.M. Electrocatalytic activity of polyaniline-copper composites in electrohydrogenation of *p*-nitroaniline / N.M. Ivanova, E.A. Soboleva, Ya.A. Visurkhanova, I.V. Kirilyus // Russian J. Electrochem. — 2015. — Vol. 51, No. 2. — P. 166–173. DOI 10.7868/S042485701502005X.

19 Инновационный патент 29408 РК. Применение композитов на основе полианилина и солей металлов для активации катода в процессах электрогидрирования органических соединений / Иванова Н.М., Соболева Е.А., Избастенова Д.С., Висурханова Я.А., Тусупбекова Г.К. Опубл. 2014.

20 Ivanova N.M. Bimetallic Co-Cu polyaniline composites: Structure and electrocatalytic activity / N.M. Ivanova, E.A. Soboleva, Ya.A. Visurkhanova // Russian J. Appl. Chem. — 2016. — Vol. 89, No. 7. — P. 1072–1081. DOI 10.1134/S1070427216070053.

21 Соболева Е.А. Биметаллические Pd-Cu-композиты полианилина в электрокаталитическом гидрировании фенилацетилена / Е.А. Соболева, Я.А. Висурханова, Н.М. Иванова // Вестн. КазНУ. Сер. хим. — 2017. — № 1. — С. 5–14. DOI 10.15328/cb773.

22 Ivanova N.M. Two-step fabrication of iron-containing polyaniline composites for electrocatalytic hydrogenation of nitroarenes / N.M. Ivanova, Ya.A. Visurkhanova, E.A. Soboleva, S.O. Kenzhetaeva // Electrochem. Comm. — 2018. — Vol. 96. — P. 66–70. DOI 10.1016/j.elecom.2018.09.016.

23 Ivanova N.M. Structure-phase changes in polymer composites doped with silver nitrate and their electrocatalytic activity / N.M. Ivanova, E.A. Soboleva, Ya.A. Visurkhanova, E.S. Lazareva // Russian J. Electrochem. — 2018. — Vol. 54, No. 11. — P. 999–1005. DOI 10.1134/S1023193518130207.

24 Ivanova N.M. Structure and electrocatalytic activity of aniline-formaldehyde polymer doped with copper (II) chloride / N.M. Ivanova, Ya.A. Visurkhanova, E.A. Soboleva, N.A. Pavlenko, Z.M. Muldakhmetov // Chemistry Select. — 2016. — No. 1. — P. 5304–5309. DOI 10.1002/slct.201601101.

25 Ivanova N.M. Structure and Electrocatalytic Properties of Copper-Containing Aniline-Melamine-Formaldehyde Polymer Composite / N.M. Ivanova, Ya.A. Visurkhanova, E.A. Soboleva // Russian J. Appl. Chem. — 2018. — Vol. 91, No. 3. — P. 396–403. DOI 10.1134/S1070427218030084.

26 Ivanova N.M. Structure and electrocatalytic activity of zinc-containing composites of polyaniline with aniline-formaldehyde polymer / N.M. Ivanova, Ye.S. Lazareva, Ya.A. Visurkhanova, E.A. Soboleva // Chemical Journal of Kazakhstan. — 2018. — No. 2. — P. 120–129.

27 Журинов М.Ж. Синтез тиомочевинных и тиазолиновых производных пиразола / М.Ж. Журинов, А.М. Газалиев, М.Б. Исабеков, О.В. Бакбардина, М.К. Ибраев // Доклады НАН РК. — 2010. — № 5. — С. 27–28.

28 Журинов М.Ж. Реакция взаимодействия монотиооксамидов с α-галогенкетонами с образованием тиазолов / М.Ж. Журинов, А.М. Газалиев, О.В. Бакбардина, М.К. Ибраев // Доклады НАН РК. — 2010. — № 3. — С. 44–46.

29 Газалиев А.М. Синтез тиомочевинных производных алкалоидов анабазина, цитизина и *d*-псевдоэфедрина. Кристаллическая структура N-этил-N-анабазинокарботиоамида / А.М. Газалиев, О.А. Нуркенов, Ж.Б. Сатпаева, С.Д. Фазылов, К.М. Турдыбеков, Д.М. Турдыбеков, С.Б. Ахметова, А.С. Махмутова // Хим. природ. соед. — 2016. — № 2. — С. 243–245.

30 Gazaliev A.M. Synthesis and molecular structure of 2-(4-pyridyl)-3,4-dimethyl-5-phenyl-1,3-oxazolidine / A.M. Gazaliev, O.A. Nurkenov, Zh.B. Satpaeva, S.D. Fazylov, T.M. Turdybekov, D.M. Turdybekov, S.B. Akhmetova, A.S. Makhmutova // Chem. Natural Comp. — 2016. — Vol. 52, No. 2. — P. 370–372. DOI 10.1007/s10600–016–1649–9.

31 Нуркенов О.А. Синтез и модификация 5-этокси-6-метил-4-(4-диэтиламинофенил)-2-тиоксо-1,2,3,4-тетрагидропиримидин-5-карбоксилата / О.А. Нуркенов, С.Д. Фазылов, Т.М. Сейлханов, Т.С. Животова, А.Е. Аринова, Ж.Б. Сатпаева, А.Ж. Исаева, Г.Ж. Карипова, А.Б. Мукашев, З.М. Мулдахметов // Изв. НАН РК. Сер. химии и технологии. — 2016. — № 2. — С. 77–84.

32 Фазылов С.Д. Синтез и спектральное исследование строения N-метил-1-[(4-бром-3,5-диметил-1н-пиразол-1)-фенил]-фуллерен-$C_{60}$-[1,9C]-пирролидина / С.Д. Фазылов, О.А. Нуркенов, А.Е. Аринова, Т.М. Сейлханов, А.Р. Туктаров, А.А. Хузин, Р.Е. Бакирова, Л.Е. Муравлева // Журн. общ. химии. — 2015. — № 5. — С. 751–754.

33 Fazylov S.D. Synthesis and spectral study of the structure of N-methyl-1-[(4-bromo-3,5-dimethyl-1n-pyrazole-1)-phenyl] fullerene-C60-[1,9C]-pyrrolidine / S.D. Fazylov, O.A. Nurkenov, A.E. Arinova, T.M. Seilkhanov, A.R. Tuktarov, A.A. Khuzin, R.E. Bakirova, L.E. Muravleva // Russian J. General Chem. — 2015. — Vol. 85, No. 5. — P. 751–754. DOI 10.1134/S1070363215050072.

34 Nurkenov O.A. Synthesis and structure of condensed biheterocycles on the basis of 3-amino-1,2,4-triazole / O.A. Nurkenov, S.D. Fazylov, T.M. Seilkhanov, A.E. Arinova, A.Zh. Issayeva, Zh.B. Satpaeva, M.Z. Muldahmetov // Bulletin of the Karaganda University. Chemistry series. — 2017. — No. 3. — P. 9–17.

35 Nurkenov O.A. Synthesis and structure of new 1,2,4-triazoles based on *p*-hydroxybenzoic acid hydrazide / O.A. Nurkenov, S.D. Fazylov, Zh.B. Satpaeva, K.M. Turdybekov, G.Zh. Karipova, A.Zh. Isaeva, S.A. Talipov, B.T. Ibragimov // Russian J. of General Chem. — 2015. — Vol. 85, No. 1. — P. 62–66. DOI 10.1134/S1070363215010107.

36 Нуркенов О.А. Синтез, химические превращения и антимикробная активность некоторых тиосемикарбазидов *о*- и *п*-гидроксибензойной кислоты / О.А. Нуркенов, С.Д. Фазылов, Т.С. Животова, Ж.Б. Сатпаева, С.Б. Ахметова, Ж.Ж. Курманбаева, Г.К. Карипова, А.Ж. Исаева // Изв. НАН РК. Сер. химии и технологии. — 2015. — No. 1. — С. 9–14.

37 Nurkenov O.A. Intramolecular heterocyclization of N-allyl-(phenyl)thiosemicarbazide N-morpholinyl acetic acid / O.A. Nurkenov, S.D. Fazylov, Zh.B. Satpaeva, K.M. Turdybekov, D.M. Turdybekov, S.A. Talipov, B.T. Ibragimov // Russian Journal of General Chem. — 2013. — Vol. 83, No. 11. — P. 1879–1881. DOI 10.1134/S1070363213110194.

38 Nurkenov O.A. Synthesis and intramolecular heterocyclization of N-phenylthiosemicarbazide N-anabasinyl acetic acid / O.A. Nurkenov, S.D. Fazylov, Zh.B. Satpaeva, L.A. Smakova // Russian Journal of General Chem. — 2013. — Vol. 83, No. 9. — P. 1581–1582. DOI 10.1134/S1070363213090302.

39 Fazylov S.D. The interaction of thiazolidin-2,4-dione with aromatic aldehydes under microwave irradiation / S.D. Fazylov, O.A. Nurkenov, Sch.K. Amerkhanova, & I.S. Tolepbek // Russian Journal of General Chem. — 2013. — Vol. 83, No. 9. — P. 1577–1578. DOI 10.1134/S1070363213090284.

40 Fazylov S.D. Obtaining 5-(morpholinomethyl)-3,4-thiadiazole-2-thione under microwave irradiation / S.D. Fazylov, O.A. Nurkenov, S.O. Kenzhetaeva, Zh.B. Satpaeva, G.Zh. Karipova // Russian Journal of General Chem. — 2013. — Vol. 83, No. 9. — P. 1579–1580. DOI 10.1134/S1070363213090296.

41 Фазылов С.Д. Внутримолекулярная гетероциклизация гидразидных производных N-анабазинилуксусной кислоты / С.Д. Фазылов, О.А. Нуркенов, Ж.Б. Сатпаева, А.К. Свидерский, А.Н. Жакупова, А.Е. Аринова, Д.К. Макенов, М.З. Мулдахметов // Известия НАН РК. Сер. химии и технологии. — 2015. — № 1. — С. 5–8.

42 Нуркенов О.А. Синтез и свойства производных гидразида изоникотиновой кислоты / О.А. Нуркенов, С.Д. Фазылов, А.М. Газалиев, Ж.Б. Сатпаева, Ш.К. Амерханова, Г.Ж. Карипова // Доклады НАН РК. — 2017. — Т. 311. — С. 68–78.

43 Fazylov S.D. The study of the anti-inflammatory activity of thiosemicarbazide N-morpholinyl acetic acid / S.D. Fazylov, R.E. Bakirova, O.A. Nurkenov, L.E. Muravleva, A.N. Zhakupova // Georgian Medical News. — 2015. — No. 3. — P. 88–102.

44 Нуркенов О.А. Конденсация N-морфолинил-уксусной кислоты с дикарбонильными соединениями / О.А. Нуркенов, С.Д. Фазылов, Ж.Б. Сатпаева, К.М. Турдыбеков, М.З. Мулдахметов, З.Т. Шульгау, Л.К. Салькеева, С.А. Талипов // Известия НАН РК. Сер. химии и технологии. — 2014. — № 2. — С. 3–7.

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## Органикалық синтез және көмірхимия институты: қазіргі жетістіктері мен даму бағдарламалары

Мақалада «ҚР Органикалық синтез және көмірхимия институты» ЖШС-де соңғы жылдары орындалған зерттеулер негізінде шолу жасалған. Ультрадыбыстық және микротолқынды химия әдістерін көмірді тотықтыру және тотығу түрлендіру үрдістеріне қолдану, жанған жыныстың бетіне гумин қышқылдарын және олардың туындыларын иммобилизациялау үрдістерін белсендіру, сондай-ақ гуминминералды композицияларды алу процестеріне көміртекті нанотүтіктердің әсері зерттелді. Гуминді сорбенттердің жаңа белсенді формаларының қасиеттері анықталып ағынды суларды тазарту үшін сорбенттер ретінде сынаулар жүргізілді. VIII-ші топтағы (Fe, Ni, Co, Mo) металдардың қосылыстары негізінде композиттік катализаторлар алынды және антрацен мен фенантренді гидрирлеу процесінде олардың белсенділігі зерттелді. Цеолиттер мен көмір сорбенттеріне қондырылған металдардың суда еритін тұздары негізінде синтезделген композитті катализаторлардың қатысуымен мазут фракцияларын кавитациялық өңдеудің оңтайлы параметрлері анықталды. Анилиноформальдегид полимері және оның меламиноформальдегид полимерімен және полианилинмен аралас композициялары негізінде электркаталитикалық қасиеттері бар жаңа полимер-металды композиттер алынды. Олардың құрылысы мен морфологиялық ерекшеліктері ИҚ-спектроскопия, рентгенофазалық талдау, атомды-эмиссиялық спектроскопия және электрондық микроскопия әдістерімен зерттелген. Электркаталитикалық белсенділік органикалық қосылыстарды электргидрациялауда зерттелді. 4-Амино-1,2,4-триазолдың, N-морфолинилсірке және N-анабазинилсірке қышқылдарының тиосемикарбазидтерінің жаңа туындылары синтезделген, олардың құрылысы мен биологиялық белсенділігі, реакция механизмдері зерттелген және де оларды синтездеу әдістемелерінің оңтайлы шарттары ұсынылған.

*Кілт сөздер:* гумин қышқылы, жанған жыныс, көпқабатты көміртекті нанотүтіктер, гуминоминералды композиттер, композитті катализаторлар, антрацен, фенантрен, мазут, гидрогенизация, полимер-металды композиттер, анилинді және меламиноформальдегидті полимерлер, полианилин, электркаталитикалық қасиеттер, 4-амино-1,2,4-триазол туындылары, фуллеропирролиндер, биобелсенділік.

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## Институт органического синтеза и углехимии: состояние и перспективы развития

Статья носит обзорный характер по исследованиям, выполненным в ТОО «Институт органического синтеза и углехимии РК» за последние годы. Изучено применение методов ультразвуковой и микроволновой химии к процессам окисления и окислительного модифицирования углей, активации процессов иммобилизации гуминовых кислот и их производных на поверхность горелых пород, а также влияние углеродных нанотрубок на процессы получения гуминоминеральных композиций. Изучены свойства новых активированных форм гуминовых сорбентов и проведены испытания их в качестве сорбентов для очистки сточных вод. Получены композитные катализаторы на основе соединений металлов VIII группы (Fe, Ni, Co, Mo), и изучена их активность в процессе гидрирования антрацена и фенантрена. Определены оптимальные параметры кавитационной обработки фракций мазута в присутствии синтезированных композитных катализаторов на основе водорастворимых солей металлов, нанесённых на цеолиты и угольные сорбенты. На основе анилиноформальдегидного полимера и его смешанных композиций с меламиноформальдегидным полимером и полианилином получены новые металлополимерные композиты, обладающие электрокаталитическими свойствами. Их строение и морфологические особенности изучены методами ИК-спектроскопии, рентгенофазового анализа, атомно-эмиссионной спектроскопии и электронной микроскопии. Электрокаталитическая активность исследована в процессах электрогидрирования органических соединений. Синтезированы новые производные 4-амино-1,2,4-триазола, тиосемикарбазидов N-морфолинилуксусной и N-анабазинилуксусной кислот, изучены их строение, биологическая активность, механизмы реакций и предложены оптимальные условия их синтеза.

*Ключевые слова:* гуминовая кислота, горелая порода, многостенные углеродные нанотрубки, гуминоминеральные композиты, композитные катализаторы, антрацен, фенантрен, мазут, гидрогенизация, полимер-металлические композиты, анилино- и меламиноформальдегидные полимеры, полианилин, электрокаталитические свойства, производные 4-амино-1,2,4-триазола, фуллеропирролидины, биоактивность.

## References

1 Vassilets, E.P., Kudaibergen, G.K., & Arnt, O.V. (2017). Produkty khimicheskoi pererabotki okislennykh uhlei [Products of chemical processing of oxidized coal]. Proceedings from The Problems of geology and exploration of mineral resources: *XXI Mezhdunarodnyi nauchnyi simpozium studentov i molodykh uchenykh imeni akademika Usova M.A. (3–7 aprelia 2017 hoda) — The XXI Int. scientific symposium of students and young scientists named after academician M.A. Usov (pp. 379–380).* Tomsk, Russian Federation [in Russian].

2 Akkulova, Z.G., Amirkhanova, A.K., Zhakina, A.Kh., Kudaibergen, G.K., Vassilets, E.P., & Sadykova, O.V. (2015). Surface morphology and sorption characteristics of humates and sulphohumate nanocomposites with natural and synthetic polymers and carbon nanotubes. *Chemical Journal of Kazakhstan*, *4*, 184–188.

3 Akkulova, Z.G., Amirkhanova, A.K., Zhakina, A.Kh., Muldakhmetov, Z.M., Vassilets, E.P., Kudaibergen, G.K., & Arnt, O.V. (2016). Poluchenie i sorbtsionnye svoistva huminomineralnykh sorbentov na osnove vmeshchaiushchikh porod uholnykh shakht [Preparation and sorption properties of humic-mineral sorbents based on the enclosing rocks of coal mines]. *Izvestiia NAN RK. Ser. khimii i tekhnolohii. — News NAS RK. Ser. chemistry and technology*, *6*, 14–22 [in Russian].

4 Vassilets, E.P., Zhakina, A.Kh., Amirkhanova, A.K., & Kudaibergen, G.K. (2016). Issledovanie vliianiia ultrazvukovoi obrabotki i perekisi vodoroda na protsess okisleniia shubarkulskikh uhlei [Investigation of the effect of ultrasonic treatment and hydrogen peroxide on the oxidation process of the Shubarkol coals]. Abstracts of conference: *XXVI Ros. molodezhnaia nauchnaia konferentsiia, posviashchennaia 120-letiiu so dnia rozhdeniia akademika N.N. Semenova (27–29 aprelia) — XXVI Russian Youth Scientific Conference dedicated to 120th anniversary of the birth of Academician N.N. Semenov* (pp. 20–21). Yekaterinburg, Russian Federation [in Russian].

5 Zhakina, A.Kh., Vassilets, E.P., & Rapikov, A.R. (2017*).* Vliianie ultrazvukovoho metoda immobilizatsii huminovoi kisloty na horeluiu porodu [The effect of ultrasonic method of immobilization of humic acid on the burnt rocks]. Abstracts of conference: *XX Vseros. konferentsiia molodykh uchenykh-khimikov (18–20 aprelia) — All-Russian Conference of young chemists.* (p. 477). Nizhnii Novgorod, Russian Federation [in Russian].

6 Vassilets, E.P., Zhakina, A.Kh., Akkulova, Z.G., Muldakhmetov, Z.M., Amirkhanova, A.K., Kudaibergen, G.K., Arnt, O.V., & Rapikov, A.R. (2016). Vliianie termokhimicheskikh i mikrovolnovykh metodov vozdeistviia na sorbtsionnye svoistva huminomineralnykh kompozitov [Influence of thermochemical and microwave methods of influence on the sorption properties of humic mineral composites]. Proceedings from Trends in the development of science and education in the field of natural sciences, dedicated to the 70th anniversary of the birth of Doctor of Chem. Sciences B.M. Butin: *Mezhdunarodnaia nauchnaia i prakticheskaia konferentsiia (7–8 oktiabria) — Int. scientific and practical conference* (p. 87–89). Almaty, Republic of Kazakhstan [in Russian].

7 Zhakina, A.Kh, Vassilets, E.P, Amirkhanova, A.K., Arnt, O.V., Rapikov, A.R., & Muldakhmetov, Z.M. (2017). *Sorbenty mnohofunktsionalnoho naznacheniia na osnove uhleotkhodov [Coal waste based multi-purpose sorbents]*. Karaganda: Glasir [in Russian].

8 Zhakina, A.Kh., Muldakhmetov, Z.M., Amirkhanova, A.K., Vassilets, E.P., Rapikov, A.R., Kudaibergen, G.K., & Arnt, O.V. (2018). Patent for utility model RK No. 3157. *Sposob polucheniia huminomineralnoho sorbenta dlia izvlecheniia tiazhelykh metallov [The method of obtaining humic mineral sorbent for the extraction of heavy metals]* [in Russian].

9 Baikenov, M.I., Baikenova, G.G., Isabaev, A.S., Tateeva, A.B., Akhmetkarimova, Zh.S., Tussipkhan, A., Mataeva, A.Zh., & Esenbaeva, K.K. (2015). Effect of new catalytic systems on the process of anthracene hydrogenation. *Solid Fuel Chemistry*, *49*(3), 150–155. DOI 10.3103/S0361521915030039.

10 Akhmetkarimova, Zh.S., Muldakhmetov, M.Z, Meiramov, M.G., Ordabaeva, A.T., Muldakhmetov, Zh.Kh., & Dusekenov, A.M. (2016). Hidrohenizatsiia smesi poliaromaticheskikh uhlevodorodov [Hydrogenation of a mixture of polyaromatic hydrocarbons]. *Uspekhi v khimii i khimicheskoi tekhnolihii — Advances in chemistry and chemical technology, XXX(9)*, 89–91 [in Russian].

11 Meiramov, M.G. (2017). Anhuliarno-linearnaia izomerizatsiia pri hidrirovanii fenantrena v prisutstvii zhelezosoderzhahchikh katalizatorov [Angular-linear isomerization in the hydrogenation of phenanthrene in the presence of iron-containing catalysts]. *Khimiia tverdoho topliva*. *— Solid Fuel Chemistry, 2,* 42–45 DOI 10.7868/S0023117717020074 [in Russian].

12 Ordabaeva, A.T., Meiramov, M.G., Khrupov, V.A., & Bakirova, R.K. (2015). Izuchenie protsessa hidrohenizatsii antratsena v prisutstvii kompozitnoho katalizatora [The study of the hydrogenation of anthracene in the presence of a composite catalyst]. *Khimicheskii zhurnal Kazakhstana — Chemical Journal of Kazakhstan*, *3*, 338–344 [in Russian].

13 Meiramov, M.G. (2014). Hydrogenation of model compounds in the presence of iron-containing catalysts. *Solid Fuel Chemistry*, *2*, 50–55. DOI 10.3103/S0361521914020104.

14 Akhmetkarimova, Zh.S., Baikenov, M.I., Meiramov, M.G., Ordabaeva, A.T., Khrupov, V.A., & Muldakhmetov, Zh.H. (2015). Vliianie nanokatalizatorov na protsess hidrogenizatsii modelnoho soedineniia — antratsena [Effect of nanocatalysts on the process of hydrogenation of the model compound — anthracene]. *Khimicheskii zhurnal Kazahstana. — Chemical Journal of Kazakhstan*, *4*, 219–225 [in Russian].

15 Akhmetkarimova, Zh.S., Muldakhmetov, Z.M., Muldahmetov, Zh.Kh., Ordabaeva, A.T., Baikenov, M.I., & Dyusekenov, A.M. (2017.) Sintez binarnykh kompozitnykh katalizatorov na osnove solei metallov VIII gruppy na tseolitnom nositele [Synthesis of binary composite catalysts based on VIII Group metal salts on a zeolite carrier]. *Khimicheskii zhurnal Kazakhstana. — Chemical Journal of Kazakhstan*, *2*, 251–259 [in Russian].

16 Akhmetkarimova, Zh.S., Muldakhmetov, Z.M., Meiramov, M.G., Ordabaeva, A.T., Muldakhmetov, Zh.K., Baikenov, M.I., & Dyusekenov, A.M. (2017) Hidrirovanie antratsena v prisutstvii kompozitnykh katalizatorov [Hydrogenation of anthracene in the presence of composite catalysts]. *Izvestiia NAN RK. Seriia khimii i tekhnolohii. — News of NAS RK. Chemistry and technology series*, *1*, 33–40 [in Russian].

17 Akhmetkarimova, Zh.S., Meiramov, M.G., Baikenov, M.I., Muldakhmetov, M.Z., Zhakupova, A.N., Tazhenova R.A., & Dautova, Zh.S. (2015). Primenenie katalizatorov v protsessakh hidrohenizatsii tverdoho i tiazheloho uhlevodorodnoho syria [Application of catalysts in the processes of hydrogenation of solid and heavy hydrocarbon of raw materials]. *Izvestiia NAN RK. Seriia khimii i tekhnolohii. — News of NAS RK. Chemistry and technology series*, *3*, 116–124 [in Russian].

18 Ivanova, N.M., Soboleva, E.A., Visurkhanova, Ya.A., Kirilyus, I.V. (2015). Electrocatalytic activity of polyaniline-copper composites in electrohydrogenation of *p*-nitroaniline. *Russian J. Electrochem., 51*, 166–173. DOI 10.7868/S042485701502005X.

19 Ivanova, N.M., Soboleva, E.A., Izbastenova, D.S., Visurkhanova, Ya.A., & Tusupbekova, G.K. (2014). Innovative patent of RK No. 29408. *Primenenie kompozitov na osnove polianilina i solei metallov dlia aktivatsii katoda v protsessakh electrohidrirovaniia orhanicheskikh soedinenii [The use of composites based on polyaniline and metal salts for the activation of a cathode in the electrohydrogenation processes of organic compounds]* [in Russian].

20 Ivanova, N.M., Soboleva, E.A., & Visurkhanova, Ya.A. (2016.) Bimetallic Co-Cu polyaniline composites: Structure and electrocatalytic activity. *Russian J. Appl. Chem., 89*(7), 1072–1081. DOI: 10.1134/S1070427216070053.

21 Soboleva, E.A., Visurkhanova, Ya.A., & Ivanova, N.M. (2017). Bimetallicheskie Pd-Cu-kompozity polianilina v electrokatalitiCheskom hidrirovanii phenilatsetilena [Bimetallic Pd-Cu-composites of polyaniline in electrocatalytic hydrogenation of phenylacetylene]. *Vestnik KazNU. Seriia khimicheskaia. — Chemical Bulletin of Kazakh National University*, *1*, 5–14. DOI 10.15328/cb773 [in Russian].

22 Ivanova, N.M., Visurkhanova, Ya.A., Soboleva, E.A., & Kenzhetaeva, S.O. (2018). Two-step fabrication of iron-containing polyaniline composites for electrocatalytic hydrogenation of nitroarenes. *Electrochem. Comm.*, *96*, 66–70. DOI 10.1016/j.elecom.2018.09.016.

23 Ivanova, N.M., Soboleva, E.A., Visurkhanova, Ya.A., & Lazareva, E.S. (2018). Structure-phase changes in polymer composites doped with silver nitrate and their electrocatalytic activity. *Russian J. Electrochem., 54*(11), 999–1005. DOI 10.1134/S1023193518130207.

24 Ivanova, N.M., Visurkhanova, Ya.A., Soboleva, E.A., Pavlenko, N.A., & Muldakhmetov, Z.M. (2016). Structure and electrocatalytic activity of aniline-formaldehyde polymer doped with copper (II) chloride. *Chemistry Select., 1*, 5304–5309. DOI 10.1002/slct.201601101.

25 Ivanova, N.M., Visurkhanova, Ya.A., & Soboleva, E.A. (2018). Structure and Electrocatalytic Properties of Copper-Containing Aniline-Melamine-Formaldehyde Polymer Composite. *Russian J. Appl. Chem., 91*(3), 396–403. DOI 10.1134/S1070427218030084.

26 Ivanova, N.M., Lazareva, Ye.S., Visurkhanova, Ya.A., & Soboleva, E.A. (2018). Structure and electrocatalytic activity of zinc-containing composites of polyaniline with aniline-formaldehyde polymer. *Chemical Journal of Kazakhstan*, *2*, 120–129.

27 Zhurinov, M.Zh., Gazaliev, A.M., Isabekov, M.B., Bakbardina, O.V., & Ibraev, M.K. (2010). Sintez tiomochevinnykh i tiazolinovykh proizvodnykh pirazola [Synthesis of thiourea and thiazoline pyrazole derivatives]. *Doklady Natsionalnoi akademii nauk Respubliki Kazakhstan. — Reports of NAS RK*, *5*, 27–28 [in Russian].

28 Zhurinov, M.Zh., Gazaliev, A.M., Bakbardina, O.V., & Ibraev, M.K. (2010). Reaktsiia vzaimodeistviia monotiooksamidov s α-halohenketonami s obrazovaniem tiazolov [Interaction reaction of monothioxamides with α-halogen ketones to produce thiazoles]. *Doklady Natsionalnoi akademii nauk Respubliki Kazakhstan. — Reports of NAS RK, 3*, 44–46 [in Russian].

29 Gazaliev, A.M., Nurkenov, O.A., Satpaeva, Zh.B., Fazylov, S.D., Turdybekov, K.M., Turdybekov, D.M., Akhmetova, S.B., & Makhmutova, A.S. (2016). Sintez tiomochevinnykh proizvodnykh alkaloidov anabazina, tsitizina i d-psevdoefedrina. Kristallicheskaia structura N-etil-N-anabazinokarbotioamida [Synthesis of thiourea derivatives of the anabasine, cytisine and d-pseudoephedrine alkaloids. Crystal structure of N-ethyl-N-anabazinocarbothioamide]. *Khimiia prirodnykh soedinenii. — Chemistry of Natural compounds, 2*, 243–245 [in Russian].

30 Gazaliev, A.M., Nurkenov, O.A., Satpaeva, Zh.B., Fazylov, S.D., Turdybekov, T.M., Turdybekov, D.M., Akhmetova, S.B., & Makhmutova, A.S. (2016). Synthesis and molecular structure of 2-(4-pyridyl)-3,4-dimethyl-5-phenyl-1,3-oxazolidine. *Chemistry of Natural compounds, 52*(2), 370–372. DOI 10.1007/s10600–016–1649–9.

31 Nurkenov, O.A., Fazylov, S.D., Seilkhanov, T.M., Zhivotova, T.S., Arinova, A.E., Satpaeva, Zh.B., Issyaeva, A.Zh., Karipova, G.Zh., Mukashev, A.B., & Muldahmetov, Z.M. (2016). Sintez i modifikatsiia 5-etoksi-6-metil-4-(4-dietilaminofenil)-2-tiokso-1,2,3,4-tetrahidropirimidin-5-karboksilata [Synthesis and modification of 5-ethoxy-6-methyl-4-(4-diethylaminophenyl)-2-thioxo-1,2,3,4-tetrahydropyrimidine-5-carboxylate]. *Izvestiia NAN RK. Seriia khimii i tekhnolohii. — News of NAS RK*, *2*, 77–84. DOI 10.32014/2018.2518–1491 [in Russian].

32 Fazylov, S.D., Nurkenov, O.A., Arinova, A.E., Seilkhanov, T.M., Tuktarov, A.R., Khuzin, A.A., Bakirova, R.E., & Muravleva, L.E. (2015). Synthesis and spectral study of the structure of N-methyl-1-[(4-bromo-3,5-dimethyl-1n-pyrazole-1)-phenyl] fullerene-C60-[1,9C]-pyrrolidine. *Russian J. Gen. Chem., 85*(5), 751–754. DOI 10.1134/S1070363215050072.

33 Nurkenov, O.A., Fazylov, S.D., Seilkhanov, T.M., Arinova, A.E., Issayeva, A.Zh., Satpaeva, Zh.B., & Muldahmetov, M.Z. (2017). Synthesis and structure of condensed biheterocycles on the basis of 3-amino-1,2,4-triazole. *Vestnik Karahandinskoho Universiteta. Seriia khimiia. — Bulletin of the Karaganda University. Chemistry series*, *3*, 9–17. DOI 10.31489/2017Ch3/9–17.

34 Nurkenov, O.A., Fazylov, S.D., Satpaeva, Zh.B., Turdybekov, K.M., Karipova, G.Zh., Isaeva, A.Zh., Talipov, S.A., & Ibragimov, B.T. (2015). Synthesis and structure of new 1,2,4-triazoles based on p-hydroxybenzoic acid hydrazide, *Russian J. of General Chem., 85*(1), 62–66. DOI 10.1134/S1070363215010107.

35 Nurkenov, O.A., Fazylov, S.D., Zhivotova, T.S., Satpayeva, Zh.B., Akhmetova, S.B., Kurmanbayeva, Zh.Zh., Karipova, G.K., & Issayeva, A.Zh. (2015). Sintez, khimicheskie transformatsii i antimikrobnaia aktivnost nekotorykh tiosemikarbazidov *o*- i *p*-hidrobenzoinoi kisloty [Synthesis, chemical transformations and antimicrobial activity of some thiosemicarbazides of *o*- and *p*-hydrobenzoic acid]. *Izvestiia NAN RK. Seriia khimii i tekhnolohii. — News of NAS RK. Chemistry and technology series, 1*, 9–14 [in Russian].

36 Nurkenov, O.A., Fazylov, S.D., Satpaeva, Zh.B., Turdybekov, K.M., Turdybekov, D.M., Talipov, S.A., Ibragimov, B.T. (2013). Intramolecular heterocyclization of N-allyl-(phenyl) thiosemicarbazide N-morpholinyl acetic acid. *Russian J. General Chem., 83*(11), 1879–1881. DOI 10.1134/S1070363213110194.

37 Nurkenov, O.A., Fazylov, S.D., Satpaeva, Zh.B., & Smakova, L.A. (2013). Synthesis and intramolecular heterocyclization of N-phenylthiosemicarbazide N-anabasinyl acetic acid. *Russian J. of General Chem., 83*(9), 1581–1582. DOI 10.1134/S1070363213090302.

38 Fazylov, S.D., Nurkenov, O.A., Amerkhanova, Sh.K., & Tolepbek, I.S. (2013). The interaction of thiazolidin-2,4-dione with aromatic aldehydes under microwave irradiation, *Russian J. General Chem., 83*(9), 1577–1578. DOI 10.1134/S1070363213090284.

39 Fazylov, S.D., Nurkenov, O.A., Kenzhetaeva, S.O., Satpaeva, Zh.B., & Karipova, G.Zh. (2013). Obtaining 5-(morpholinomethyl)-3,4-thiadiazole-2-thione under microwave irradiation. *Russian J. General Chem., 83*(9), 1579–1580. DOI 10.1134/S1070363213090296.

40 Fazylov, S.D., Nurkenov, O.A., Satpayeva, Zh. B., Sviderskiy, A.K., Zhakupova, A.N., Arinova, A.E., Makenov, D.K., Muldakhmetov, M.Z. (2015). Vnutrimolekuliarnaia heterotsiklizatsiia proizvodnykh hidrazida N-anabazinil uksusnoi kisloty [Intramolecular heterocyclization of hydrazide N-anabasinil acetic acid derivatives]. *Izvestiia NAN RK. Seriia khimii i tekhnolohii. — News of NAS RK*, *1*, 5–8 [in Russian].

41 Nurkenov, O.A., Fazylov, S.D., Gazaliev, A.M., Satpaeva, Zh.B., Amerhanova, Sh.K., & Karipova, G.Zh. (2017). Sintez i svoistva proizvodnykh hidrazida izonikotinovoi kisloty [Synthesis and properties of derivatives of isonicotinic acid hydrazide]. *Doklady Natsionalnoi akademii nauk Respubliki Kazakhstan. — Reports of NAS RK, 1*, 68–78 [in Russian].

42 Fazylov, S.D., Bakirova, R.E., Nurkenov, O.A., Muravleva, L.E., & Zhakupova, A.N. (2015). The study of the anti-inflammatory activity of thiosemicarbazide N-morpholinyl acetic acid. *Georgian Medical News, 3*, 88–102.

43 Nurkenov, O.A., Fazylov, S.D., Satpaeva, Zh.B., Turdybekov, K.M., Muldahmetov, M.Z., Shulgau, Z.T., Salkeeva, L.K., Talipov, S.A. (2014). Kondensatsiia N-morfolinil-uksusnoi kisloty s dikarbonilnymi soedineniiami [Condensation of N-morpholinyl acetic acid with dicarbonyl compounds]. *Izvestiia NAN RK. Seriia khimii i tekhnolohii. — News of NAS RK*, *2*, 3–7 [in Russian].