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ЯНВАРЬ – МАРТ 2018 г.

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Валентина Константиновна

Қазақстан халқы Ассамблеясы Сізге ел бірлігі мен қоғамдық келісімді нығайтуға, гуманистік мұраттарға дәйекті қызмет етіп, қоғамның рухани дамуына қосқан елеулі үлесіңіз үшін алғыс білдіреді.

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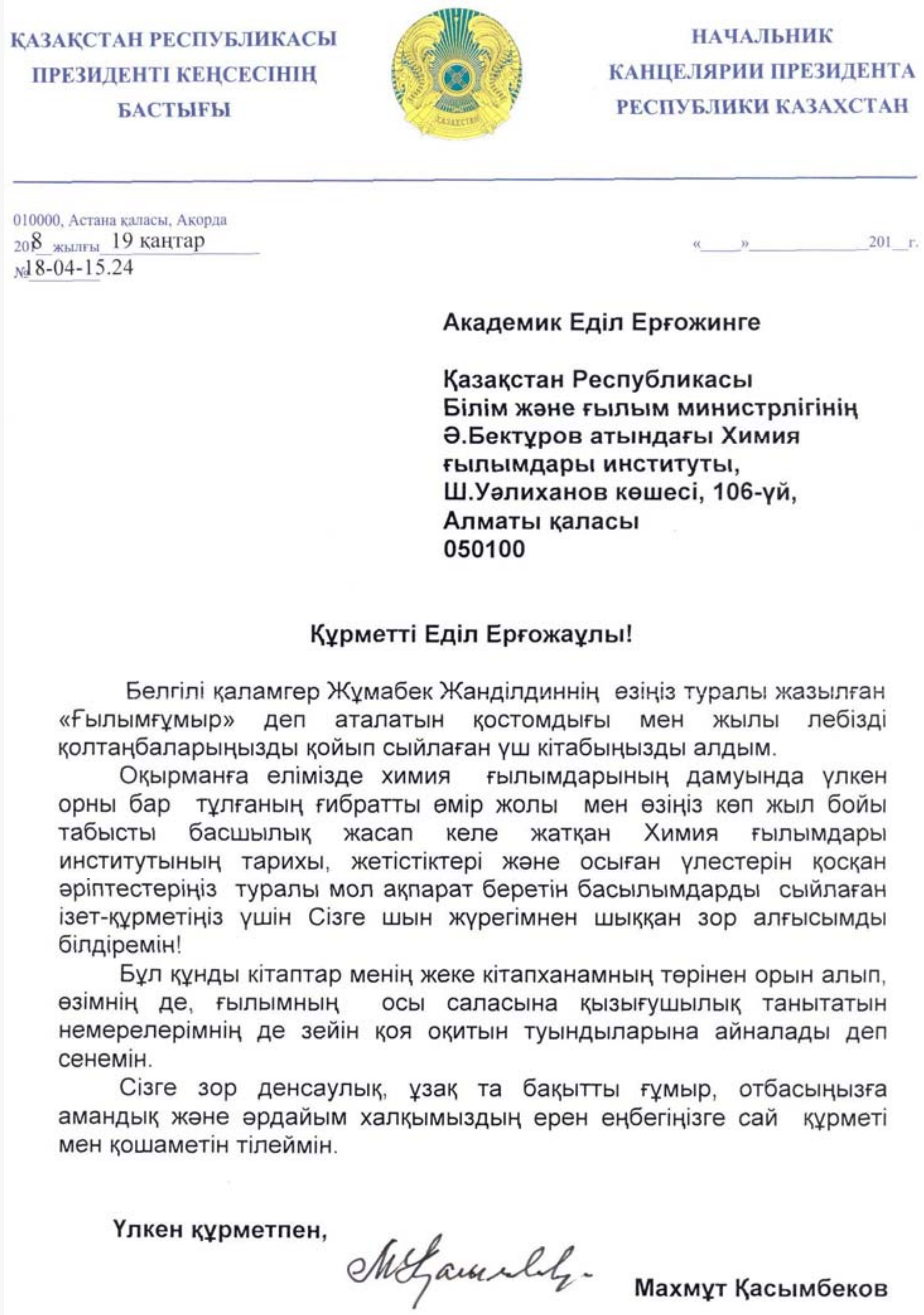

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Белгілі қаламгер Жұмабек Жанділдиннің өзіңіз туралы жазылған «Ғылымғұмыр» деп аталатын қостомдығы мен жылы лебізді қолтаңбаларыңызды қойып сыйлаған үш кітабыңызды алдым.

Оқырманға елімізде химия ғылымдарының дамуында үлкен орны бар тұлғаның ғибратты өмір жолы мен өзіңіз көп жыл бойы табысты басшылық жасап келе жатқан Химия ғылымдары институтының тарихы, жетістіктері және осыған үлестерін қосқан әріптестеріңіз туралы мол ақпарат беретін басылымдарды сыйлаған ізет-құрметіңіз үшін Сізге шын жүрегімнен шыққан зор алғысымды білдіремін!

Бұл құнды кітаптар менің жеке кітапханамның төрінен орын алып, өзімнің де, ғылымның осы саласына қызығушылық танытатын немерелерімнің де зейін қоя оқитын туындыларына айналады деп сенемін.

Сізге зор денсаулық, ұзақ та бақытты ғұмыр, отбасыңызға амандық және әрдайым халқымыздың ерен еңбегіңізге сай құрметі мен қошаметін тілеймін.

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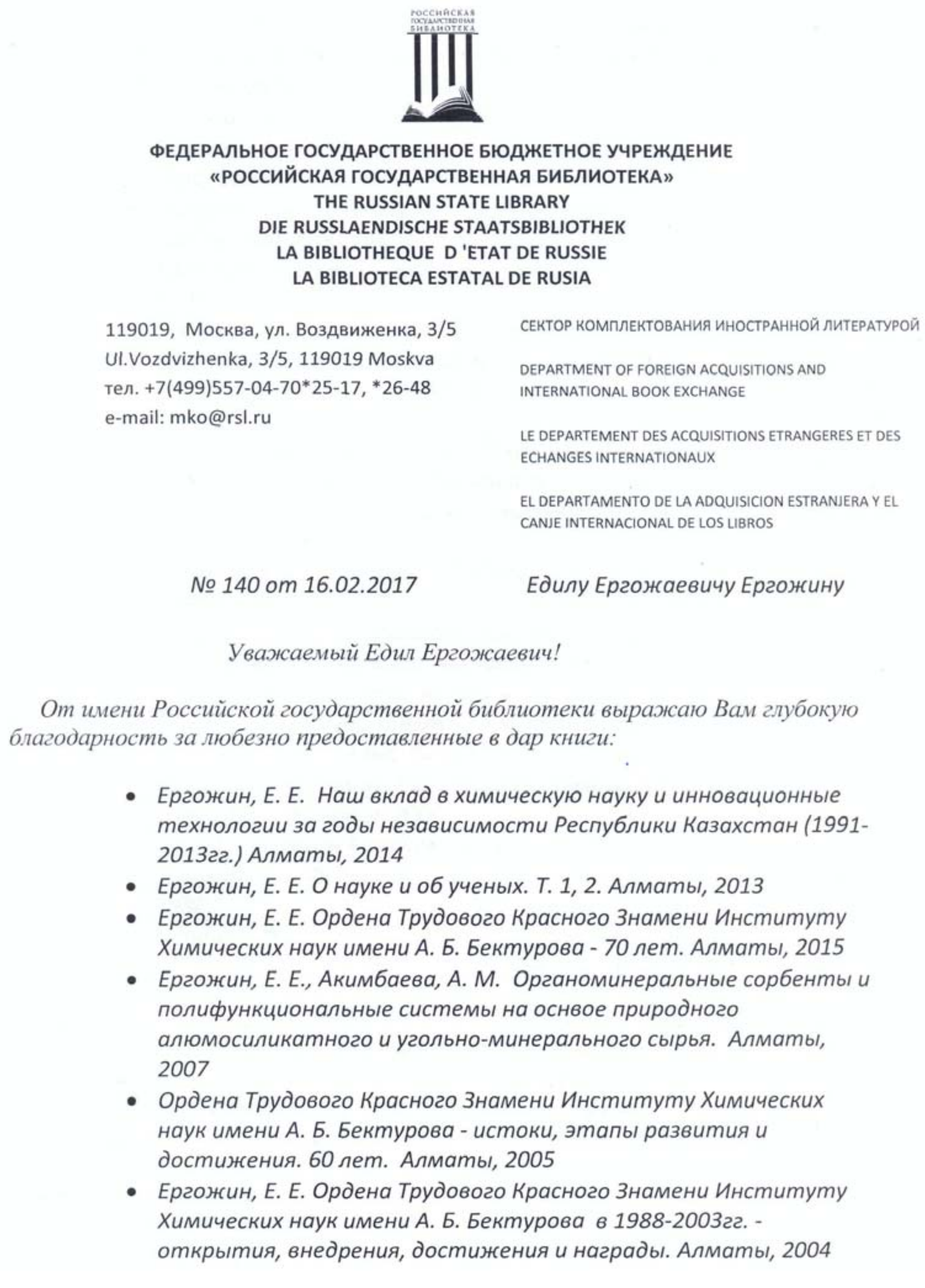

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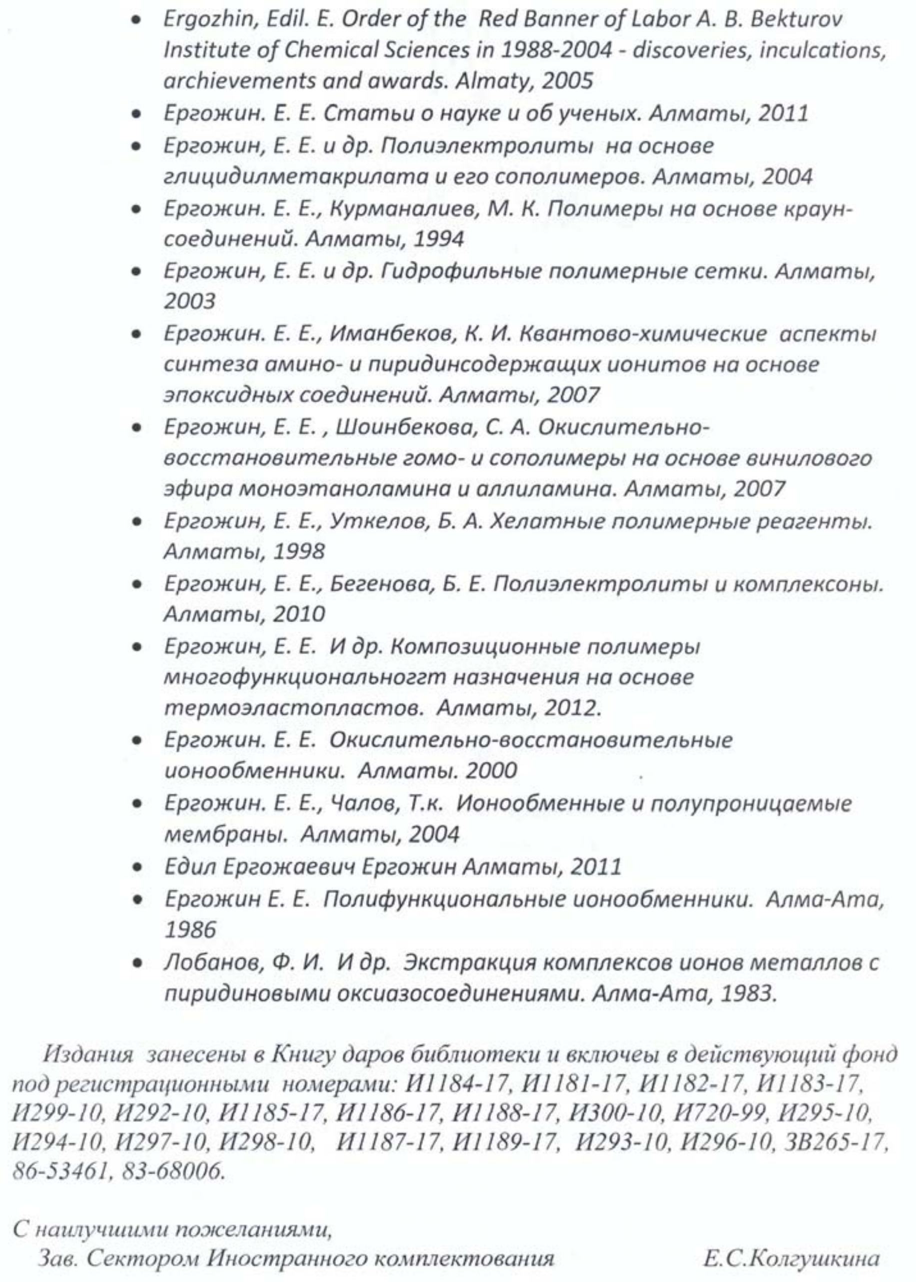

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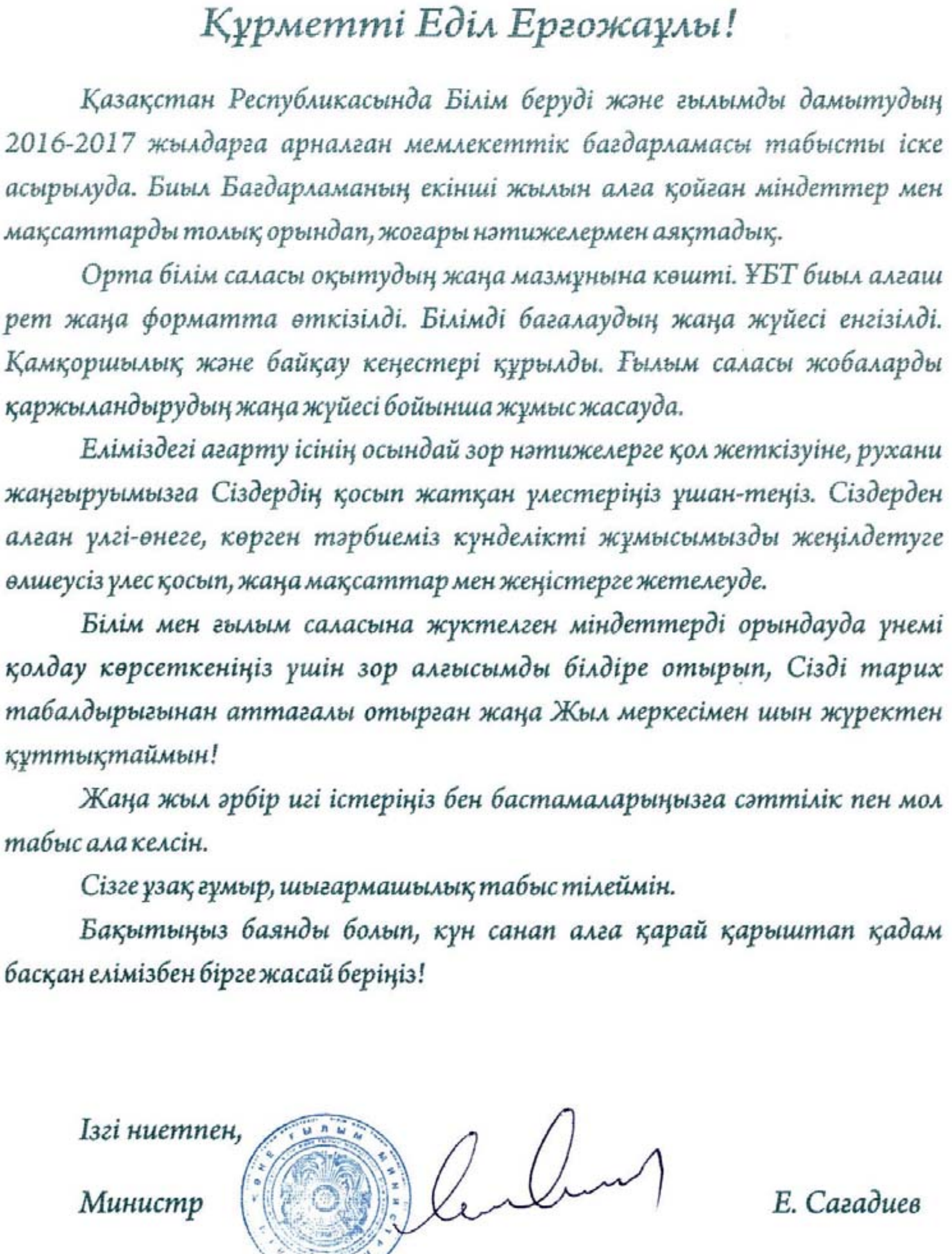

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Қазақстан Республикасында Білім беруді және ғылымды дамытудың 2016-2017 жылдарға арналған мемлекеттік бағдарламасы табысты іске асырылуда. Биыл Бағдарламаның екінші жылын алға қойған міндеттер мен мақсаттарды толық орындап, жоғары нәтижелермен аяқтадық.

Орта білім саласы оқытудың жаңа мазмұнына көшті. ҰБТ биыл алғаш рет жаңа форматта өткізілді. Білімді бағалаудың жаңа жүйесі енгізілді. Қамқоршылық және байқау кеңестері құрылды. Ғылым саласы жобаларды қаржыландырудың жаңа жүйесі бойынша жұмыс жасауда.

Еліміздегі ағарту ісінің осындай зор нәтижелерге қол жеткізуіне, рухани жаңғыруымызға Сіздердің қосып жатқан үлестеріңіз ұшан-теңіз. Сіздерден алған үлгі-өнеге, көрген тәрбиеміз күнделікті жұмысымызды жеңілдетуге өлшеусіз үлес қосып, жаңа мақсаттар мен жеңістерге жетелеуде.

Білім мен ғылым саласына жүктелген міндеттерді орындауда үнемі қолдау көрсеткеніңіз үшін зор алғысымды білдіре отырып, Сізді тарих табалдырығынан аттағалы отырған жаңа Жыл мерекесімен шын жүректен құттықтаймын!

Жаңа жыл әрбір игі істеріңіз бен бастамаларыңызға сәттілік пен мол табыс ала келсін.

Сізге ұзақ ғұмыр, шығармашылық табыс тілеймін.

Бақытыңыз баянды болып, күн санап алға қарай қарыштап қадам басқан елімізбен бірге жасай беріңіз!

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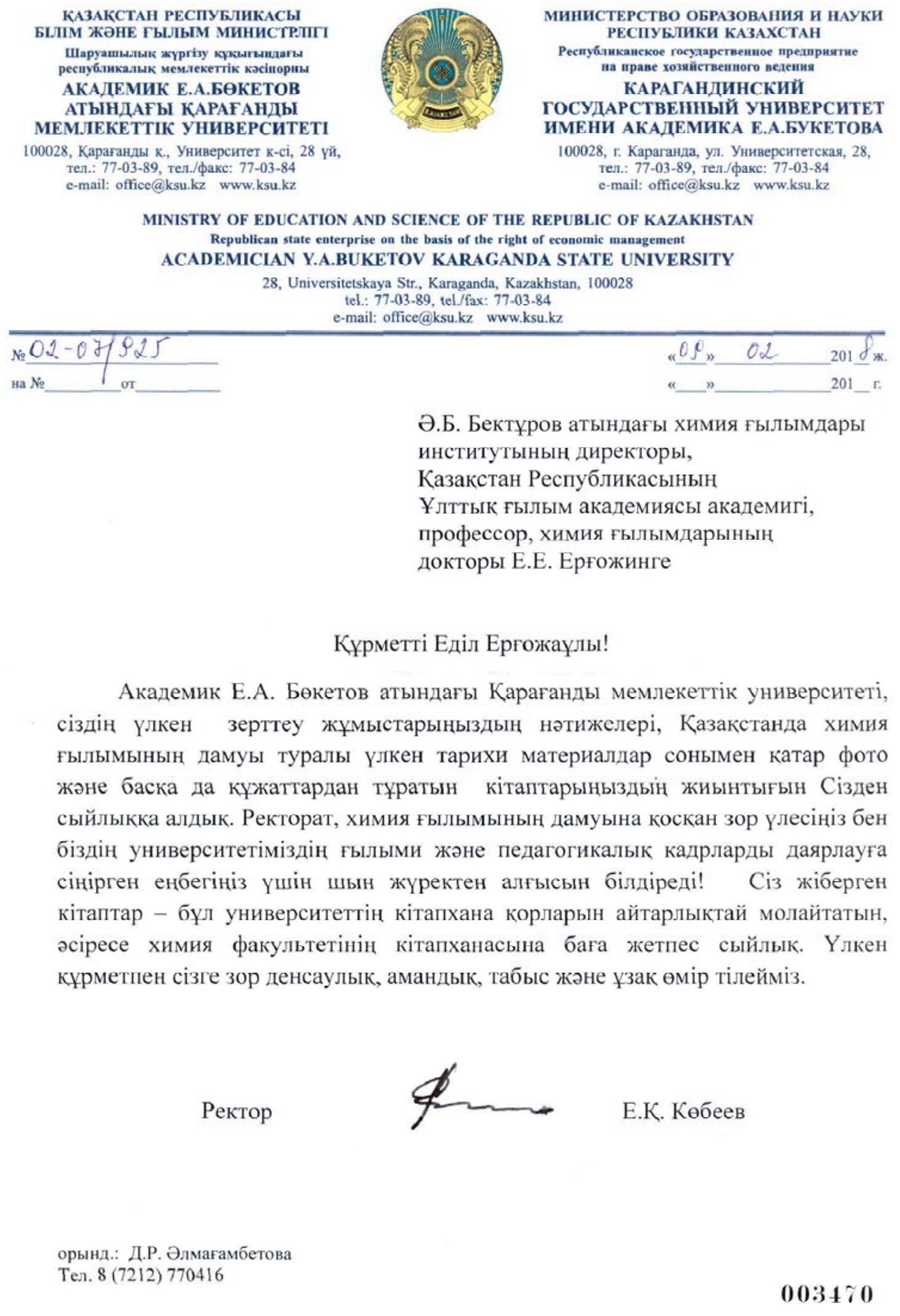

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Ә.Б. Бектұров атындағы химия ғылымдары
институтының директоры,
Қазақстан Республикасының
Ұлттық ғылым академиясы академигі,
профессор, химия ғылымдарының
докторы Е.Е. Ерғожинге

Құрметті Еділ Ерғожаұлы!

Академик Е.А. Бөкетов атындағы Қарағанды мемлекеттік университеті, сіздің үлкен зерттеу жұмыстарыңыздың нәтижелері, Қазақстанда химия ғылымының дамуы туралы үлкен тарихи материалдар сонымен қатар фото және басқа да құжаттардан тұратын кітаптарыңыздың жиынтығын Сізден сыйлыққа алдық. Ректорат, химия ғылымының дамуына қосқан зор үлесіңіз бен біздің университетіміздің ғылыми және педагогикалық кадрларды даярлауға сіңірген еңбегіңіз үшін шын жүректен алғысын білдіреді! Сіз жіберген кітаптар – бұл университеттің кітапхана қорларын айтарлықтай молайтатын, әсіресе химия факультетінің кітапханасына баға жетпес сыйлық. Үлкен құрметпен сізге зор денсаулық, амандық, табыс және ұзақ өмір тілейміз.

Ректор Е.Қ. Көбеев

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003470

Қазақстан Республикасы Мәдениет және спорт министрлігінің
«Қазақстан Республикасының Ұлттық кітапханасы» РММ

ҰЛТТЫҚ КІТАПХАНА
ҚАЗАҚСТАН РЕСПУБЛИКАСЫ

АЛҒЫС ХАТ

Құрметті Еділ Ерғожаұлы!

Қазақстан Республикасының Ұлттық кітапханасы Сіздің ғылыми басылымыңызды кітапхана қорына ізгі ниетпен сыйға тартқаныңыз үшін зор алғысын білдіреді.

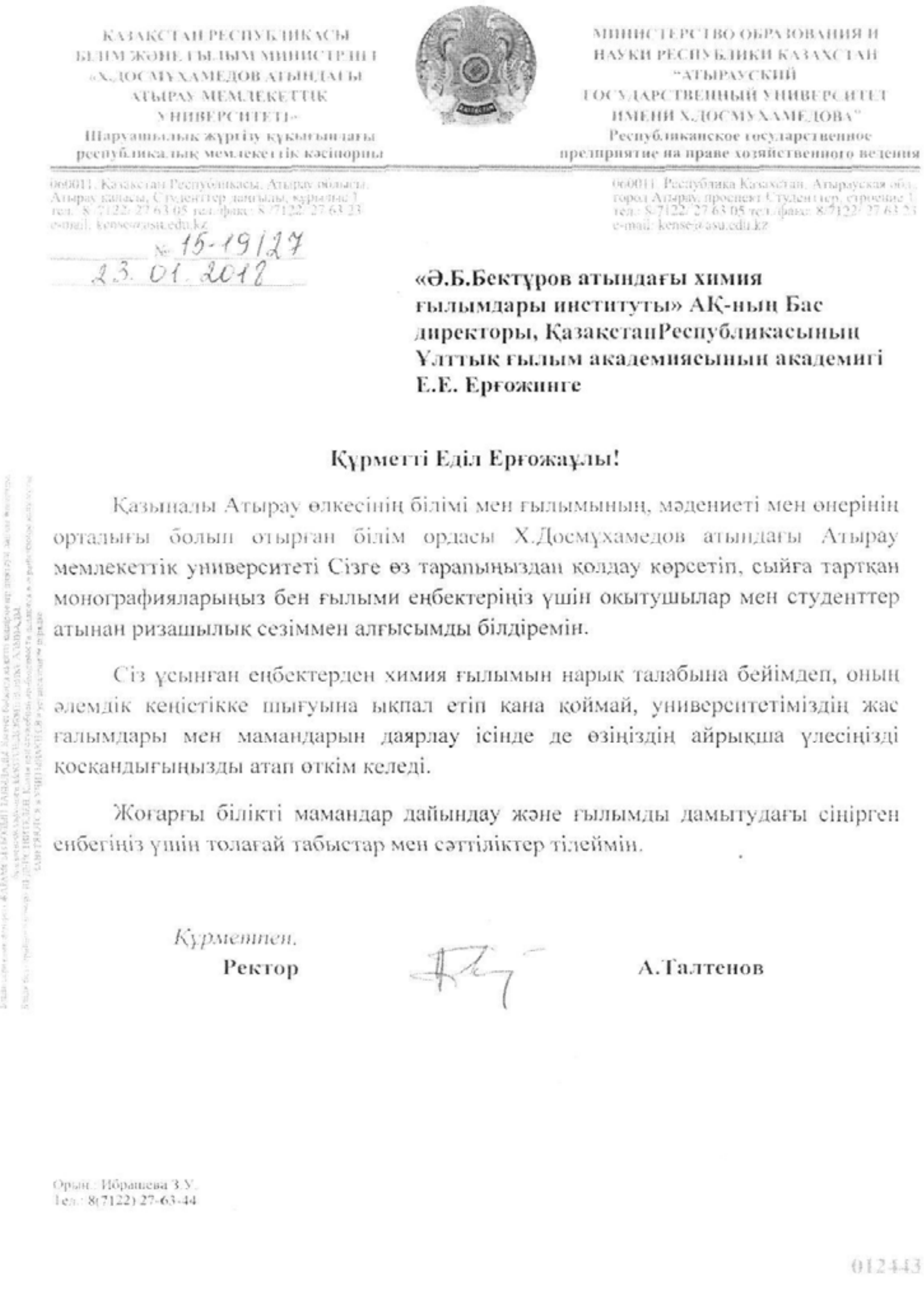
Бұл сыйға берген кітаптарыңыз кітапхана оқырмандарына, әсіресе ғылыми қызметкерлерге, студенттерге және техникалық-инженерлік мамандарға еркін пайдалануға мол мүмкіндік береді.

Сыйға тартылған кітаптар Қазақстандағы бас кітапхана қорын қалыптастыру мен толықтыруда және ұлттық жазба мұрамызды ұрпаққа аманат етіп жүйелі түрде жинақтауда, сондай-ақ Ұлттық кітапхананың сан мыңдаған оқырмандары үшін баға жетпес рухани құндылық болып табылады.

Сізге зор денсаулық, отбасыңызға амандық мен бақ-береке тілейміз.

Құрметпен,
Директор ***Ж. Сейдуманов***

Алматы, 2017



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АТЫРАУ МЕМЛЕКЕТТІК
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МИНИСТЕРСТВО ОБРАЗОВАНИЯ И
НАУКИ РЕСПУБЛИКИ КАЗАХСТАН
"АТЫРАУСКИЙ
ГОСУДАРСТВЕННЫЙ УНИВЕРСИТЕТ
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№ 15-19/27
23. 01. 2018

**«Ә.Б.Бектұров атындағы химия
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директоры, ҚазақстанРеспубликасының
Ұлттық ғылым академиясының академигі
Е.Е. Ерғожинге**

Құрметті Еділ Ерғожаұлы!

Қазыналы Атырау өлкесінің білімі мен ғылымының, мәдениеті мен өнерінің орталығы болып отырған білім ордасы Х.Досмұхамедов атындағы Атырау мемлекеттік университеті Сізге өз тарапыңыздан қолдау көрсетіп, сыйға тартқан монографияларыңыз бен ғылыми еңбектеріңіз үшін оқытушылар мен студенттер атынан ризашылық сезіммен алғысымды білдіремін.

Сіз ұсынған еңбектерден химия ғылымын нарық талабына бейімдеп, оның әлемдік кеңістікке шығуына ықпал етіп қана қоймай, университетіміздің жас ғалымдары мен мамандарын даярлау ісінде де өзіңіздің айрықша үлесіңізді қосқандығыңызды атап өткім келеді.

Жоғары білікті мамандар дайындау және ғылымды дамытудағы сіңірген еңбегіңіз үшін толағай табыстар мен сәттіліктер тілеймін.

Құрметпен,
Ректор **А.Таптенов**

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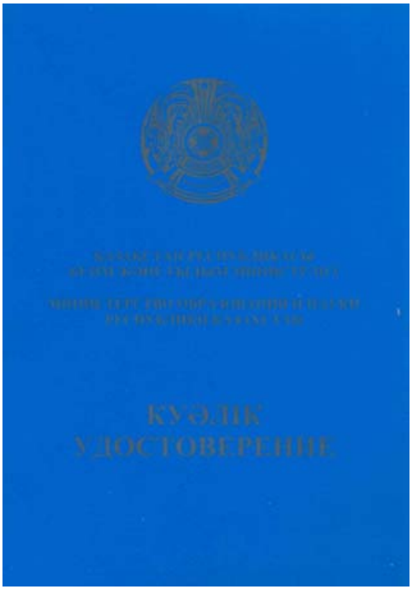
« 06 » сәуір 200 18 жыл
год

КУӘЛІК
УДОСТОВЕРЕНИЕ
№ 176

Осы куәлік ғылым беру саласындағы ерекше еңбегі үшін "ҚАЗАҚСТАН РЕСПУБЛИКАСЫНЫҢ ҒЫЛЫМЫН ДАМЫТУҒА СІҢІРГЕН ЕҢБЕГІ ҮШІН" белгісімен марапатталғандығы туралы берілді.

Настоящее удостоверение выдано в том, что он(а) за достигнутые успехи в области науки Республики Казахстан награжден(а) нагрудным знаком "ЗА ЗАСЛУГИ В РАЗВИТИИ НАУКИ РЕСПУБЛИКИ КАЗАХСТАН".

Министр Е. Сагадиев



Коллектив, профсоюзный комитет, совет молодых ученых Ордена Трудового Красного Знамени АО «Институт химических наук имени А.Б.Бектурова» поздравляют Генерального директора Института, главного редактора «Химического Журнала Казахстана», академика НАН РК **Ергожина Едила Ергожаевича** с очередной наградой. Желаем здоровья, новых научных свершений, открытий и плодотворной неиссякаемой энергии!

КАЗАХСТАН

Ергожина Рабия Даулетқызы, 2017
Ученица 11 класса, Международная школа «Мирас»,
г.Астана, Республика Казахстан

О великий Казахстан!
Мой отец Родной.
Опоясан твой гордый стан
Светлою луной.

На твоей большой груди
Спит моя земля.
Тихо дремлют у реки
Ветви камыша.

Горделивые холмы,
Ваш прекрасен лик.
И моё полно любви
Сердце в этот миг.

Простирается вдали
Колыбель степей.
Тихо музыка души
Раздается в ней.

На фото: Ергожина Рабия Даулетқызы с мамой Ергожиной Асель Нурланқызы на школьном выпускном вечере в день вручения «Алтын белгі», г. Астана, 2017. Рабия ныне студентка – отличница учебы университа Глион в Швейцарии.

27 марта 2018 года в Информационно-библиотечном Центре НБ КБТУ при АО «Институт химических наук имени А.Б.Бектурова» состоялся семинар на темы "Использование платформы Springerlink для проведения научных исследований" и "Как подготовить качественную статью и опубликовать в рейтинговых зарубежных журналах", который провела лицензионный менеджер Springer Nature по Казахстану, Кыргызстану, Таджикистану, Узбекистану и Туркменистану Ирина Александрова. Семинар открыл генеральный директор АО ИХН, академик НАН РК Е.Е.Ергожин. Ниже представлен фотоотчет семинара.

До конца 2018 года в Информационно-библиотечном Центре НБ КБТУ при ИХН по IP-адресам открыт полный доступ к журнальной коллекции Springer Complete Collection на платформе Springerlink на основе национальной подписки Министерства образования и науки Республики Казахстан.

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УНИВЕРСИТЕТ ИМ. К.И. САТПАЕВА

СЕРТИФИКАТ

Выдан участнику(ам) Сатпаевских чтений - 2018:

«ИННОВАЦИОННЫЕ РЕШЕНИЯ ТРАДИЦИОННЫХ ПРОБЛЕМ: ИНЖЕНЕРИЯ И ТЕХНОЛОГИИ»

Бектенов Н.А., Садыков К.А., Ергожин Е.Е., Рыспаева С.Б.

Директор ИХБТ **З.К. Туйебахова**

12.04.2018

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За лучший доклад

Награждается Рыспаева С., Бектенов Н.А.

III место

за лучший доклад на Сатпаевских чтениях - 2018: «ИННОВАЦИОННЫЕ РЕШЕНИЯ ТРАДИЦИОННЫХ ПРОБЛЕМ: ИНЖЕНЕРИЯ И ТЕХНОЛОГИИ»

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12.04.2018

Московский государственный университет
имени М.В.Ломоносова

ЛОМОНОСОВ
МЕЖДУНАРОДНЫЙ МОЛОДЕЖНЫЙ НАУЧНЫЙ ФОРУМ

СЕРТИФИКАТ

НАСТОЯЩИМ ПОДТВЕРЖДАЕТСЯ, ЧТО

Ермекова
Кымбат
Ермековна

принял(а) участие
в XXV Международной научной
конференции студентов, аспирантов
и молодых ученых «Ломоносов»

И.А. Алешковский

Ответственный секретарь Международной
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кандидат экономических наук

9 - 13 апреля 2018 года

Московский государственный университет
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ЛОМОНОСОВ
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ГРАМОТА

За III место
Секция
„Инновационное
природопользование"

Ермекова
Кымбат
Ермековна

UDC 541.183/49+544.726

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S. B. RYSPAEVA, K. M. KALMURATOVA, A. K. BAIDULLAEVA

A. B. Bekturov Institute of Chemical Sciences JSC, Almaty, Kazakhstan

SORPTION OF COPPER (II) AND LEAD (II) IONS BY A NEW CHELATE-FORMING IONITE BASED ON SOME COPOLYMERS OF EPOXYACRYLATES

Abstract. Sorption properties of a new chelating ion-exchange resins based on copolymers of glycidylmethacrylate (GMA) and the chelating agent 1-hydroxy ethylidene-1,1-diphosphonic acid(HEDP) are studied. The optimal sorption conditions with respect to copper (II) and lead (II) metals ions have been determined.

Key words: chelate-forming ion exchangers, chelating agents, chelates, sorption, heavy metals, ion exchange.

The main problem with the development of science and technology is pollution of the environment with ions of heavy metals, for example, water pollution is one of the most urgent. Because, the shortage of drinking water on the planet is becoming a global problem. The removal of heavy metal ions from industrial wastewater and their reuse in the production process will result in the conservation of natural water resources.

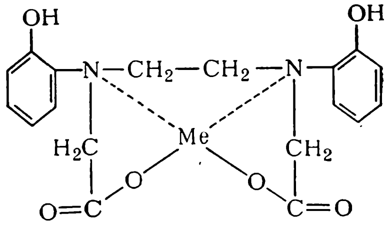
In this case, it would be useful to use ion exchangers to separate various metal ions from water. That is why the requirements for ion exchangers have been increasing lately. They should have improved ion-exchange and wide spectra of physico-chemical properties, which are insoluble in various solutions. An effective method for this purpose is the synthesis of new chelating-forming polyelectrolytes obtained from glycidyl methacrylate (GMA). In the structure of GMA, the polymer double bonds are well defined and are able to identify the reaction epoxide group and the possibility of radical ionic polymerization by the addition of various polymers [1, 2].

The greatest advantage of using ion-exchange sorption for wastewater treatment from galvanic production is the high regeneration of Cu (II), Pb (II), etc. ions in accordance with modern requirements and return of purified water to the production of these metals. Lead ions are included in the group of the most dangerous ecotoxicants that accumulate in the environment due to emissions from coal combustion in power plants, sewage from industrial enterprises (concentrating mills, metallurgical and chemical plants, mines). In this regard, there is a need to use new sorbents to remove metal ions from the solution.

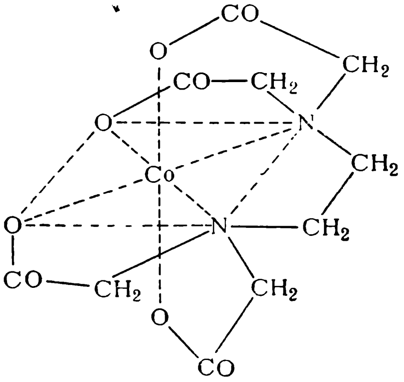
For the practical use of ion exchangers, it is necessary to study the dependence of the sorption of metal ions on the process conditions. The removal of metal ions from the solution largely depends on the concentration and pH of the solution, as well as on the kinetic activity of the ion exchangers.

We have studied and studied the processes of extraction of copper (II) and lead (II) ions from model aqueous solutions with new synthesized ion exchangers based on glycidyl methacrylate and complexonHEDP.

In the studies of Dyatlov NM. Complexes of EDTA and HED Phaving the structure of tick-shaped compounds analogous to chelating groups that contain ethylenediamine-N, N'-di (o-hydroxyphenyl) -N, N-diacetic acid (EDOFA) are shown:



EDOFA



EDTA

The resulting compounds of metal ions with complexons - complexates - have in their structure several so-called chelate cycles. The term chelate (English chelate from the Greek cilh - claw) is used to refer to the cyclic structures that result from the addition of a cation to two or more donor atoms belonging to the same molecule of the complexon. In accordance with the term chelated chelator should be presented in the form of a crab, which with its polydentate claws firmly grasps the metal ion, and the more claws, the stronger the grip [3-5].

The experimental part

Sorption properties of chelating ion exchangers were studied with respect to lead (II) and copper (II) ions from model solutions of the corresponding "hp" nitrate, sulfate salts. Samples of polymers before each series of experiments were dried in a vacuum drying oven to constant weight.

To determine the sorption capacity of the ion exchangers, a polymer weighing 0.05 g, weighted to an accuracy of 0.0002 g, was placed in a Erlenmeyer flask, then 20 ml of a solution of the corresponding metal salt were added. The method of atomic absorption spectroscopy was used to determine the concentration of metal cations [6].

Results and its discussion

It is known that when chelated ion exchangers interact with metal ions by ionic, coordination bonds, they form strong complexes. This ability of chelating-forming ion exchangers to complex formation with metal ions is due to the presence in the polymer matrix of chemical active groups containing electron-donating oxygen and nitrogen atoms.

With increasing concentration (from 18.5 to 105.5 mg/l) of metal ions in the initial solution, the sorption capacity of GMA-St-AKN-HEDP ion exchanger for lead ion (II) increases from 10, 60 to 41 mg/g , the ion of copper (II) from 6.5 to 37 mg/g, the recovery rate reaches up to 99 and 90%, respectively (figure 1).

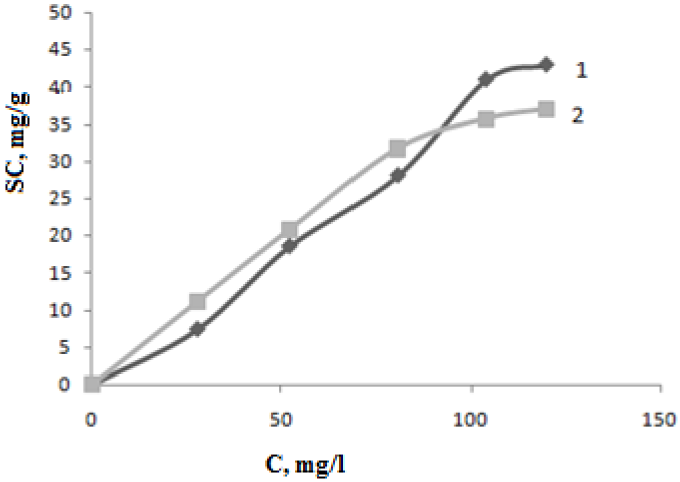


Figure 1 – Influence of the initial concentration of lead (II) 1 and copper (II) 2 ions on the sorption capacity of ion exchangers based on GMA-St-AKN-HEDP(duration of contact 7 days)

An important role in the sorption of metal ions is played by the pH medium, since a change in its value contributes to an improvement in the dissociation of the functional groups of the ion exchanger. For the ionization of GMA-ST-AKN-HEDP,

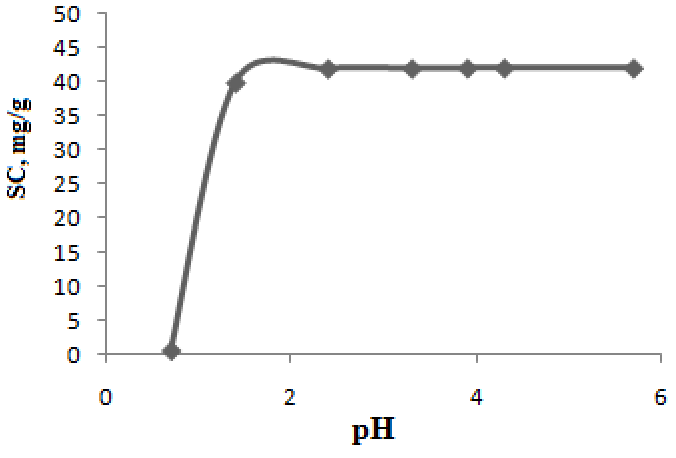


Figure 2 – Dependence of sorption capacity of ion exchanger on the basis of GMA-ST-AKN-HEDP for lead ions (II) from the pH of the solution ($C_{Pb}{}^{2+}$=102 mg /l, 7 days)

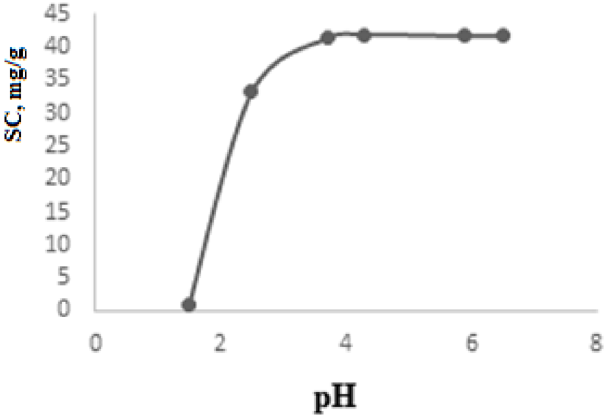


Figure 3 – Dependence of sorption capacity of ion exchanger on the basis
Of GMA-St-AKN- HEDP for copper ions (II) from the pH of the solution
($C_{Cu}{}^{2+}$ = 101 mg/l, 7 days)

the acidity of the solution does not particularly affect the sorption process (figure 2), since the sorption of lead ions (II) passes almost in all pH regions. The sorption capacity of the ion exchanger is 41.22 mg/g, the recovery rate reaches 95%.

The sorption capacity of the cation exchange resin GMA-St-AKN-OEDF with respect to copper (II) ions decreases somewhat with decreasing acidity of the solution. The equilibrium between a solution of $CuSO_4$ containing 101 mg/l of copper ions and cation exchanger GMA-ST-AKN-HEDP is set at pH 3.5; the sorption capacity of the ion exchanger is 41.1 mg/g (figure 3).

The tasks of creating high-performance ion-exchange processes and high-quality materials can be solved only by a detailed study of both the equilibrium and kinetic properties of ion exchangers. It can be seen from Fig. 4 that for lead ions the equilibrium state between the solution of $Pb(NO_3)_2$ containing 100 mg/l, having a pH = 3.1 and the cation exchanger GMA-St-AKN- HEDP is set for 3 hours.

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Резюме

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СОРБЦИЯ ИОНОВ МЕДИ (II) И СВИНЦА (II) НОВЫМ ХЕЛАТООБРАЗУЮЩИМ ИОНИТОМ НА ОСНОВЕ НЕКОТОРЫХ СОПОЛИМЕРОВ ЭПОКСИАКРИЛАТОВ

Изучены сорбционные свойства новых хелатообразующих ионитов на основе сополимеров глицидилметакрилата (ГМА) и комплексона ОЭДФ. Определены оптимальные условия сорбции по отношению к ионам металлов меди (II) и свинца (II).

Ключевые слова: хелатообразующие иониты, комплексоны, хелат, сорбция, тяжелые металлы, ионный обмен.

Резюме

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КЕЙБІР ЭПОКСИАКРИЛАТТАР СОПОЛИМЕРЛЕРІ НЕГІЗІНДЕГІ ЖАҢА ХЕЛАТТҮЗГІШ ИОНИТПЕН МЫС (II) ЖӘНЕ ҚОРҒАСЫН (II) ИОНДАРЫН СОРЫП АЛУ

Глицидилметакрилат және комплексон (ОЭДФ) негізіндегі жаңа хелаттүзгішиониттің сорбциялық қасиеттері зерттелді. Мыс (II) және қорғасын (II) иондары үшін сорбцияның оңтайлы жағдайлары анықталды.

Түйін сөздер: хелаттүзушiиониттер, комплексондар, хелат, ауыр металдар, ион алмасу.

UDC 541.6 + 678.021.16

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SOME PECULIARITIES OF OBTAINING COMPOSITIONS ON THE BASIS OF ALICYCLIC POLYIMIDE AND NATURAL MINERAL MONTMORILLONITE

Abstract. In this work, an analysis was conducted of research on the production of materials on the basis of alicyclic polyimide with plasticizing additives in the presence of the inorganic filler is montmorillonite by the method of IR-spectroscopy. Installed some of the features of their production, namely, compositions based on alicyclic polyimide with additives alkylated montmorillonite and polyacrylic acid formed intercalated structure. In the ternary compositions of alicyclic polyimide with polyethylene glycol and alkylated montmorillonite, a natural mineral, apparently, forms a complex with terminal groups of polyethylene glycol. The presence of a complex in the ternary composition based on polyimide, polyethylene glycol and montmorillonite, is reflected in the DSC diagram, which manifests itself 2 the specific heat jump corresponding to the polymer-polimer interactions and polymer-low-molecular substance.

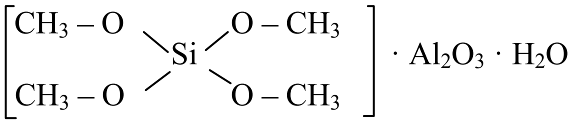
Key words: polyimide, montmorillonite, composition, intercalation, complex.

Obtaining composite materials based on polyimides with additives of natural mineral montmorillonite are currently, is a promising direction [1]. As such materials, due to the large surface of the filler particles of nanoscale range, enhanced interaction of polymer matrix with the inorganic component, thereby increasing the thermal and mechanical properties of the composition as a whole [2].

In the literature there are publications on the development of composite material based on various polyimides, for example, in [3] use particles of Na-montmorillonite (exfoliating filler) to activate the process of imidization of polymetakrilate aromatic structure. Known composite materials based on polyimide derived from dianhydride 3,3',4,4'-oxydiphthalic and 1,3-bis-(4- aminophenoxy)-2-propanol silica [4,5], it is shown that the synthesized nanocomposites covalently bound silica is distributed in the PI of the active amino groups. The obtained thermoplastics based on poly[4,4'-bis(4"-N-phenoxy)-diphenylsulfone]imide 1,3-bis(3',4 dicarbofenoxy)benzene with modified montmorillonite [6].

It is known that composite materials based on layered silicates are classified into three main types, depending on the nature of initial components, conditions and the production method [1]. This is a traditional microcomposite, in which the particles retain their original size, which is formed under the condition that the polymer does not penetrate into the interlayer space of the silicate. Another type of the composite when the material is formed intercalated structure, i.e., the polymer penetrates between the layers of silicate. In this case, there is an increase in the interlayer distance, but while maintaining an orderly layered structure of the mineral. The third type is the so-called exfoliating nanocomposite in which the silicate delamination of the individual layers dispersed in the polymer matrix. The latest nanocomposite is formed in the harsh conditions of the modified clay an organic compound with the chemical reactions of polymerization of monomers (in the processes of mixing of the reaction) [7] or in the melt of polymers.

In this work, we used the alkylated montmorillonite (AMM), for which earlier [8] based on methods of IR spectroscopy, x-ray diffraction and differential scanning calorimetry were installed structure :



It was determined that AMM is a compound where the methyl group with silicon oxide are linked directly by a covalent bond. And thus, AMM is a holistic layered silicate.

Upon receipt of the ternary compositions based on PI, AMM and various polyfunctional polymers, such as PEG, and PAK, the formation of different types of nanocomposites. It was found that the formation of compositions from AMM+PAK for these investigated systems in the spectra (figure 1, curve 3, 4) observed deformation of the main characteristic bands of stretching vibrations of PAK (ν_{1683}^{-1}) [9].

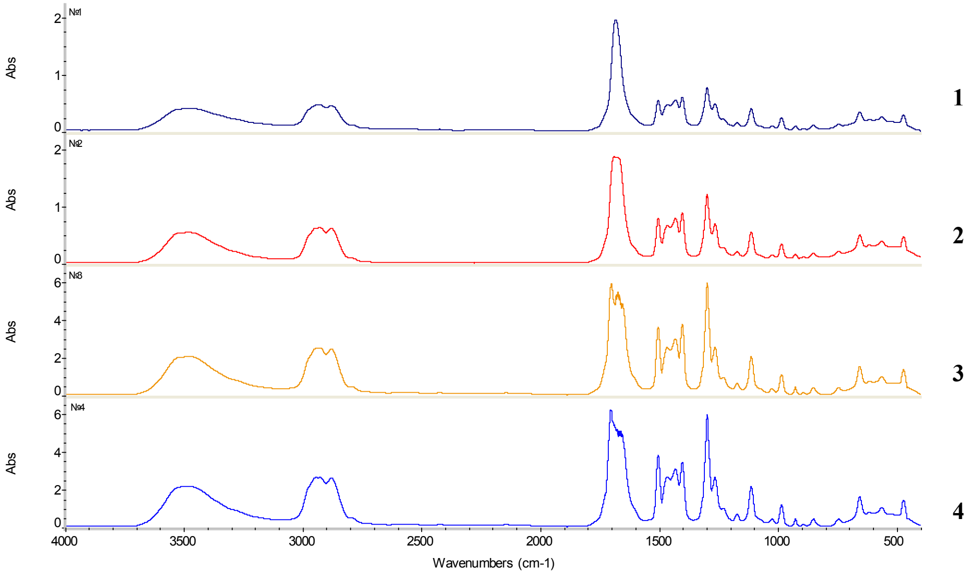


Figure 1 – IR spectra PAK (1) and compositions based on it with AMM
when the ratio (wt.%) PAK: AMM = 1:0,25 (2); 0,5 (3); 1(4)
in the solution of MP in glasses (KBr)

Whereas in the ternary composition PI+AMM+PEG these deformities stretching vibrations characteristic bands (figure 2, curve 1, 2; $\nu_{1638-1680\ см}^{-1}$, $\nu_{1645-1706\ см}^{-1}$) related to aminoacide and C-O groups [9] PI and PEG, respectively, does not occur. This implies that in the composite AMM+PAK intercalation occurs the entry of PAK into the interlayer space of a layered silicate.

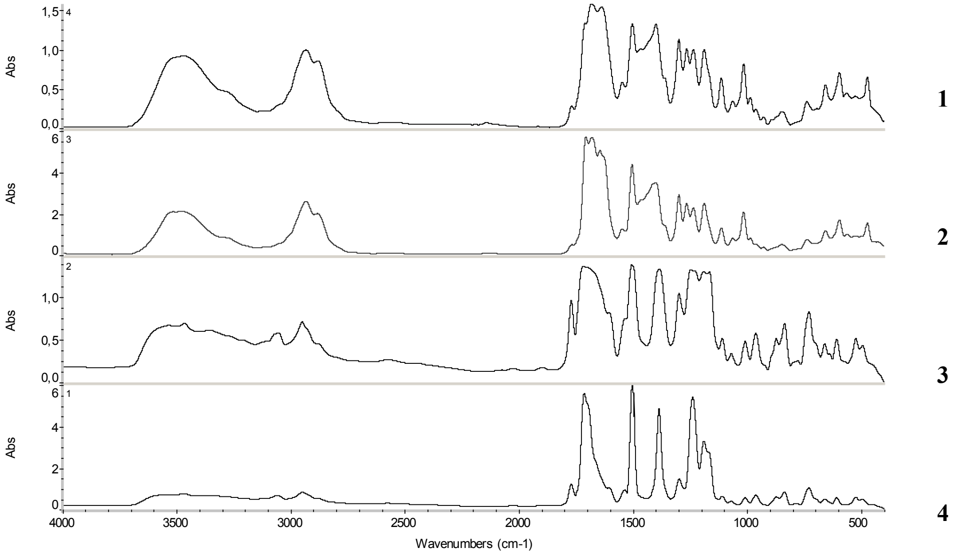


Figure 2 – IR spectra compositions based on PI+1.5 wt.%AMM+6 wt..%PEG(4)(2);
PI+3 wt.%AMM+6 wt.%PEG(3)(1) 3.4 film,
dried at 90^{o}C; 1.2 the solutions of the ternary mixture in the glass (KBr)

This does not contradict the literary data [10], where in the polymerization of polyacrylice acid used layered silicate montmorillonite (MM). The study gives the following interpretation of the process of intercalation between layers MM there is a weak link at the level of Van der Waals, whereby a polar molecule PAK can be introduced between the layers of the mineral. X-ray diffraction analysis, it was shown that in this case, the structure of two-dimensional layers of MM is not changed, and only increases the distance between the layers.

Apparently, in this material system AMM+PAK, the penetration of PAK molecules in the interlayer space of a natural mineral of the montmorillonite leads to deformation of the stretching vibrations of the functional groups PAK on compositional spectra mixture. This pattern is observed for ternary compositions based on PI, MM and PAK (figure 3).

In the formation of a triple composition based on PI, PEG and AMM intercalation does not occur – deformation of stretching vibrations of functional groups of the components of the mixture have not been identified (figure 4). It can be assumed that the destruction of the layers of the AMM does not occur, because getting a double (PI+PEG) and the triple composite (PI+PEG+AMM) were not in hard conditions – mechanical method of mixing [11] at 40^{o}C.

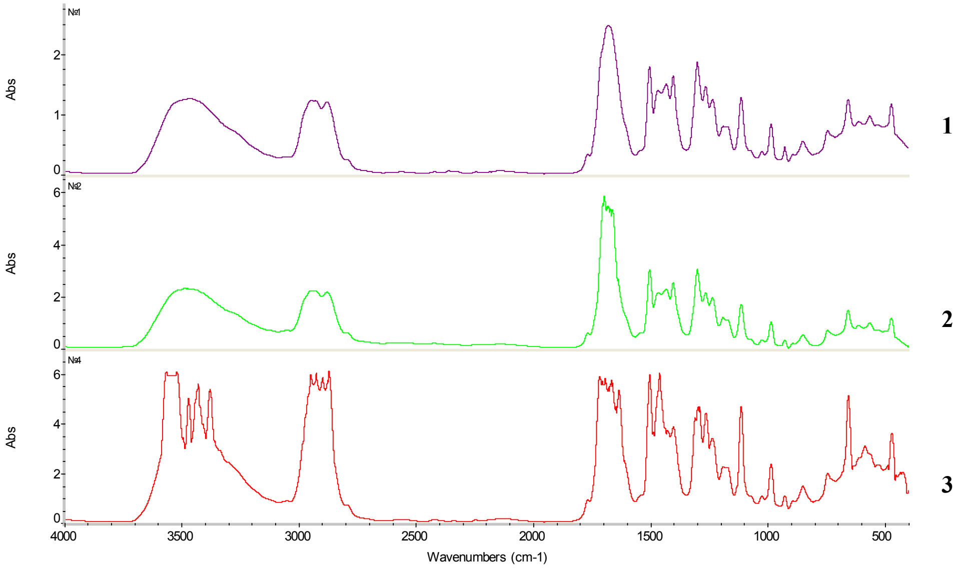


Figure 3 – IR spectra PI and PAC (1) and ternary compositions based on PI, PAK and AMM at a ratio of PAK:AMM=2,7:0,7(2); 1,4; 2,7(3) wt.% in relation to PI (100 wt.%); in the solution of MP in glasses (KBr)

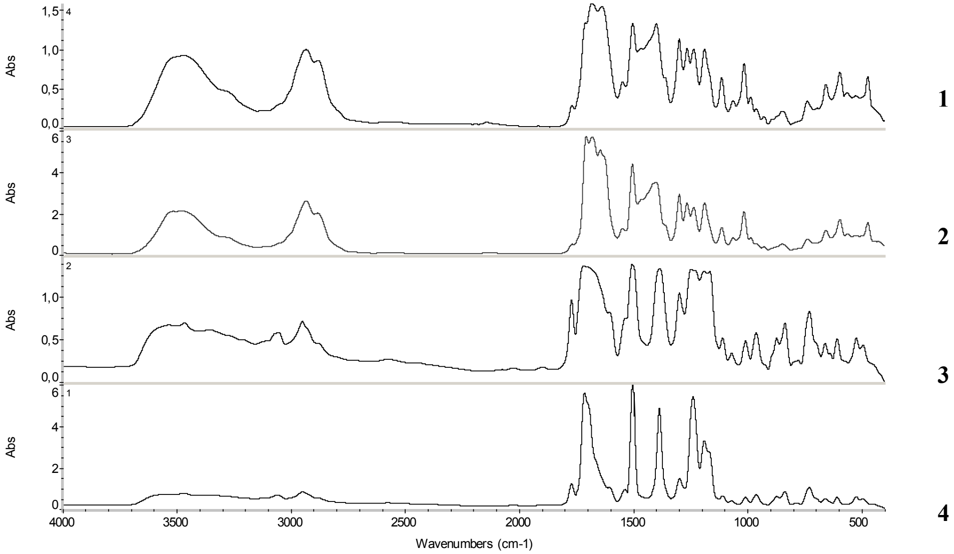


Figure 4 – IR spectra of the compositions on the basis of PI+1.5 wt.%AMM+6 wt.%PEG(4)(2); PI+3 wt.%AMM+6 wt.%PEG(3)(1) 3.4 film, dried at 90°C; 1.2 the solutions of the ternary mixture in glasses (KBr)

Perhaps the particles of AMM, form a complex with PEG via the terminal hydroxyl groups. It is known that the oxides of silicon (in the silicon exhibits four valence) with oxygen-containing substances, silicon can exhibit a coordination number 5 and forming in this direction the complex [12]. The diagrams DSK ternary composition PI, AMM and PEG 2 is observed in the specific heat jump, the lower sheets stitched T_{g1}=343°C, apparently, refers to the PI associated with the PEG partial cross-linking [13]. The second glass transition temperature T_{g2}=511°C corresponds to the manifestation of the energy relations ternary mixtures of PI+PEG+AMM and the complex of PEG with AMM in particular, because the pure PI does not react with the particles of AMM [14].

It should be clarified that in polymer composite materials the criterion for the compatibility of components in the mixture is the glass transition temperature (T_g), namely, if the compatibility of components in polymer blends manifested a single glass transition temperature. For low molecular weight substances, this assessment is somewhat different. In this case, when the formation of complexes on the figures, changes in the heat capacity manifests the individual jumps corresponding to the different means of communication, as it was shown in [8]. Therefore, the chart of change in internal energy in the composition of PI+PEG+AMM were two of a specific heat jump corresponding relations of polymer-polymer and polymer-low-molecular substance. But while maintaining the compatibility of all components in the material, as evidenced by the transparency of the material, and it persists for a long time (2 years). Because, in the absence of the compatibility of components in the composite material, the particles of montmorillonite vipotest on the film surface for six months.

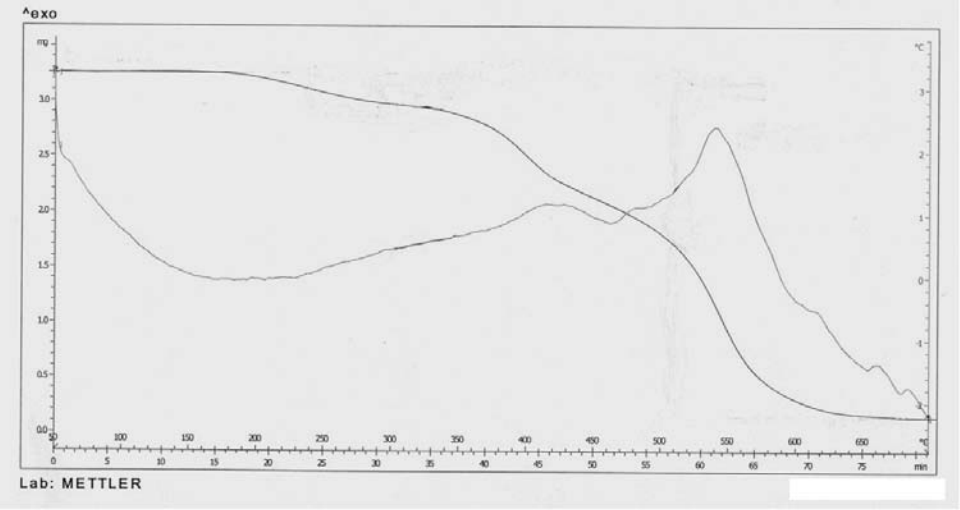


Figure 5 – Is a Thermogravimetric and calorimetric chart films triple compositions based on songs from the PI+3 wt.%AMM+6 wt.%PEG

On the basis of conducted research we can say that in the ternary compositions based on PI+PEG+AMM and PI+PAK+AMM form different types of nanocomposites, namely in the first case is the formation of a complex of a layered silicate with end groups of PEG, in the second case is formed intercalated structure of the mineral PAK. In both cases, the resulting nanocomposite in certain proportions are well aligned with PI.

Thus, to obtain thermodynamically compatible composites based on alicyclic polyimide particles of natural mineral montmorillonite, can be successfully used small additions of polyfunctional polymers, such as PEG, and PAK.

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Резюме

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АЛИЦИКЛДЫ ПОЛИИМИДТІ ЖӘНЕ ТАБИҒИ МИНЕРАЛ МОНТМОРИЛЛОНИТ НЕГІЗІНДЕГІ АЛЫНҒАН КОМПАЗИЦИЯНЫҢ КЕЙБІР ЕРЕКШЕЛІКТЕРІ

Жұмыста пластмассамен қаныққан алициклды полиимид негізінде алынған материалдарды монтмориллонитті бейорганикалық қоспасының қатысуымен ИҚ-спектроскопия әдісімен анализ жасалынды. Оларды алудың кейбір ерекшеліктері анықталды, атап айтсақ, алициклды полиимид негізіндегі композицияға алкилделінген монтмориллонитті және полиакрил қышқылды қоспалардың қатысында интеркалирленген құрылысы түзіледі. Алициклды полиимидті, полиэтиленгликольмен және алкилденген табиғи минерал монтмориллонитті үштік композиция композиция полиэтиленгликольдің тобымен аяқталады деген тұжырым бар. Монтмориллонит және полиэтиленгликоль, полиимид негізіндегі үштік композиция полимер-полимерлік өзара әрекеттесу және полимер-төменгі молекулалы заттарға сәйкес ДСК диаграммада 2 секірісті жылусиымдылығы бар.

Түйін сөздер: полиимид, монтмориллонит, композициялар, интеркаляция, комплекс.

Резюме

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НЕКОТРЫЕ ОСОБЕННОСТИ ПОЛУЧЕНИЯ КОМПОЗИЦИЙ НА ОСНОВЕ АЛИЦИКЛИЧЕСКОГО ПОЛИИМИДА И ПРИРОДНОГО МИНЕРАЛА МОНТМОРИЛЛОНИТА

Проведен анализ исследований по получению материалов на основе алициклического полиимида с пластифицирующими добавками в присутствии неорганического наполнителя монтмориллонита методом ИК-спектроскопии. Установлены некоторые особенности их получения, а именно в композиции на основе алициклического полиимида с добавками алкилированного монтмориллонита и полиакриловой кислоты образуются интеркалированные структуры. В тройной композиции из алициклического полиимида с полиэтиленгликолем и алкилированным монтмориллонитом природный минерал, по-видимому, образует комплекс с концевыми группами полиэтиленгликоля. Наличие комплекса в тройной композиции на основе полиимида, полиэтиленгликоля и монтмориллонита отражается на диаграмме ДСК, на которой проявляется 2 скачка теплоемкости, соответствующие взаимодействиям полимер-полимер и полимер-низкомолекулярное вещество.

Ключевые слова: полиимид, монтмориллонит, композиция, интеркаляция, комплекс.

UDC 547.992 +661.875

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INTERACTION OF Cr (III) IONS WITH SODIUM HUMATE IN ACQUEOUS MEDIUM

Abstract. The regularities of the influence of chromium ions concentration and sodium humate rate on the process of complex formation upon the interaction of chromium (III) chloride with sodium humate have been studied. In the course of the performed works it has been established that an increase in the concentration of the chromium ions rate from 0,005 up to 0,5% and the sodium humate rate from 0,1 up to 1,0 g contributes to increasing of the yield of humic substances up to 36,49% and chromium mass content up to 4,31%. Shifting of pH to the acidic field and the IRS data, have shown the formation of humate complex compounds with chromium ions. IR-spectra of the studied samples of complex humic compounds show complexity of their composition. It follows from the data of thermal analysis of the obtained complex compounds that the introduction of chromium ions into the structure of humic compounds in the form of Me-O bond contributes to the acceleration of the processes of oxidation of humic compounds (the organic part) until complete burning-out of humates at the temperature up to 550°C. At the temperatures above 940°C the processes of destruction of the mineral part of humates start. The results of the functional analysis testify to the interaction of sodium humate with chromium ions, though no complete substitution of carboxylic and phenolic groups for chromium ions occurs. It has been established that other functional groups of humic compounds participate in the reactions of complex formation.

Keywords: sodium humate, chromium chloride, complex formation, functional groups.

Introduction. Due to a specific combination of different functional groups and paramagnetic centers humic compounds enter into the ionic and donor-acceptor interactions, participate in oxidation-reduction and sorption processes [1-4]. An ability of humic compounds to ion exchange and complex formation provides for the possibilities of their usage for water purification from heavy metals. The formation of complexes with humic substances results in lowering of their free form concentration and decreasing of toxicity. That is why humic compounds are applied as natural detoxicants, and a chemical modification of humates increases their sorption properties. Herewith, humic compounds are complex polyfunctional ligands, requiring a special approach upon the study of their complex-forming properties. In this connection, a study of complex-forming properties of the modified humic compounds with chromium ions is rather topical.

The goal of the study is an investigation of the regularities of the interaction process of sodium humate with chromium ions, a study of the dependence of the composition and properties of the new complex compounds upon different factors.

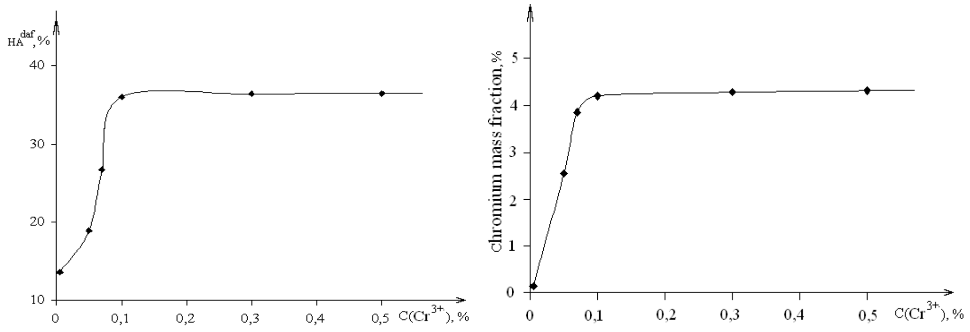
EXPERIMENT

Chemicals and instrumentation. Sodium humate of the following composition, mass %, was used in this work: yield of free humic acids (HA^{daf}) – 41,02; ash content (A^a) – 21,40; humidity (W^a) – 12,97, and chromium chloride (III). The experiments were carried out at 60°C and the process duration was 60 min with constant stirring of the reaction mixture.

Infra-red spectra of the studied samples were registered in tablets with KBr on IR-Furier spectrometer Nicolet 5700, "Thermo Electron" (USA) in the field of 200-4000 cm^{-1}. Assignment of the absorption bands in IR-spectra was carried out in accordance with the literature data [5, 6]. Thermal gravitational analyses were carried out on derivatograph Q-1000/D of the F.Paulik, J.Paulik and L.Erdey system, manufactured by "MOM" company (Budapest). Shooting was carried out in the air medium in the temperature range of 20 - 1000°C. Heating regime was linear (dT/dt = 10 degree/min), a reference substance was incinerated Al_2O_3, sample weight was 300 mg. Sensitivity of the measuring systems of the device was set up to be equal for the samples: TG = 100 mg = 500 μV, DTA = 250 μV, DTG = 500 μV, T = 500 μV. The analysis results were compared with the data, provided in the atlases of thermal curves [7, 8] and with the description of the destruction of monomineral samples, provided in reference sources and in the database. The microstructure of the samples was studied on electron probe microanalyzer "JXA-8230", produced by "JEOL" company (Japan) with accelerating voltage of 25 kV and electron stream current up to 100 nA. A spot energy-dispersion spectroscopic (EMF) analysis, EMF-mapping of the site by elements, EMF-microanalysis of the chosen site and semi-quantitative wave-dispersion spectroscopic analyses were made. For each analysis an adjustment by carbon was carried out, the signal of which was registered due to the applied two-sided carbonic conducting tape, on which the samples were mounted [9, 10]. The content of chromium was determined by an atomic-absorption method with the use of atomic-absorption spectrometer AA240, manufactured by "Varian Optical Spectroscopy Instruments" (Australia). The yield of free humic acids was determined according to [11], the content of the functional groups – following the methods [5].

Results and discussion

The present paper has studied the influence of the concentrations of chromium ions and the sodium humate rate upon the composition and properties of the obtained compounds. The experimental data have shown that increasing of the concentrations of chromium ions from 0,005 up to 0,5% leads to an increase in the yield of humic substances and chromium mass fraction (figure 1). Thus, with chromium chloride concentration of 0,005%, the yield of humic substances makes up 13,60%, chromium mass fraction – 0,14%, and with the concentration of 0,5% it increases correspondingly up to 36,49% and 4,31%. Probably, upon the



a b

Figure 1 – An isotherm of the dependence of the yield of humic acids (a) and chromium mass fraction (б) upon the concentration of chromium ions

interaction of sodium humate with chromium ions an ion exchange reaction proceeds due to hydrogen of carboxylic groups and phenolic hydroxyls, with which insoluble chromium humates are formed, as well as the reactions, leading to the formation of complex compounds.

It is known that pH shifting to the acidic field is characteristic for the complex formation process. As it is seen from table 1, with an increase of the concentrations of chromium ions a decrease of pH from 9,17 down to 4,65 is observed. The presence of a large number of functional groups in humic compounds, as well as pH shifting to the acidic field upon the formation of precipitates, allows one to assume a formation of complex compounds of chromium ions with sodium humate.

Table 1 – Change of pH in dependence of the concentrations of chromium ions

Concentration of chromium ions, %					
0,005	0,05	0,07	0,1	0,3	0,5
9,17	8,25	7,59	6,45	4,90	4,65

In the obtained samples the contents of carboxylic and phenolic hydroxylic groups are determined (table 2). As it is seen from table 2, the studied samples differ considerably by the content of acidic functional groups. It has been established that with an increase of the concentrations of chromium ions from 0,005 up to 0,5% the number of chromium-substituted carboxylic groups increases, and the content of phenolic groups, bound with chromium, decreases. For example, upon the interaction of sodium humate with chromium chloride a number of carboxylic groups, bound with chromium, increases from 0,35 to 0,45 mg-equ per 100 g of the organic mass. An increase in the concentrations of chromium ions results in a decrease of the content of phenolic groups, substituted for chromium, from 1,65 up down to 1,50 mg-equ/g. A decrease of pH confirms the obtained results. This testifies to the fact that in the reactions of complex formation with chromium ions

Table 2 – Influence of the concentration of chromium ions upon the content of the functional groups in the obtained samples

$C(Cr^{3+})$, %	Content of acidic groups, mg-equ/g		
	COOH	$OH_{phen.}$	COOH+ $OH_{phen.}$
0,005	0,35	1,65	2,00
0,05	0,37	1,62	1,99
0,07	0,38	1,61	1,99
0,1	0,39	1,60	1,99
0,3	0,43	1,53	1,96
0,5	0,45	1,50	1,95

mainly carboxylic groups take part. However, no complete substitution of carboxylic groups by chromium ions has been observed under conditions of the conducted experiments.

It follows from the analysis of the IRS results (figure2), that a poly-component structure and complexity of the composition of the studied samples produce an effect upon the character of the spectra, a mutual influence of some absorption bands is observed to the extent of their merging, broadening and shifting, etc. It is noteworthy that in case of appearance of a new phase in the composition of the obtained products the values of the absorption band of this compound in the spectrum of the studied samples should not obligatory coincide with the value of the same band in the spectrum of the same individual compound, in view of the presence of other substances, making the general picture of the spectrum more complex. For example, the IR-spectra of the studied samples contain a large number of absorption bands, characteristic for different functional groups of humic compounds [5, 6]. In the spectra of the obtained products intensive absorption bands of valence vibrations of hydroxylic groups, forming intermolecular hydrogen bonds, are observed in the fields of 3550-3545, 3480-3475 and 3415-3410 cm^{-1}, the weak bands at 3290-3285 cm^{-1} belong to valence vibrations of OH-groups in the complex compounds, the intensity of this band increases with an increase of the concentration of chromium ions. Strong absorption bands in the field of 1640-1635 cm^{-1} and 1390-1385 $cm^{-1}$are assigned to symmetric and asymmetric valence vibrations of carboxylate-ions, which testifies to the formation of chromium humates. The absorption bands in the field of 1620-1615 cm^{-1} are characteristic for vibrations of conjugated double bonds C=C of the aromatic fragments. It is noteworthy that overlapping of this band and the absorption band of carboxylate-ions takes place. In the field of 1275-1270 cm^{-1} absorptions of phenolic OH-groups at 1050-1045 cm^{-1}, deformation vibrations of alcohol hydroxylic groups, are observed. Most remarkable differences are observed in the field of 960-950, 925-920, 825-820, 780-775, 620-615, 550-545, 480-475 and 425-420 cm^{-1}, characterizing the vibrations of coordination bonds of oxygen atoms of carboxylic, phenolic and quinoid groups in the complex compounds.

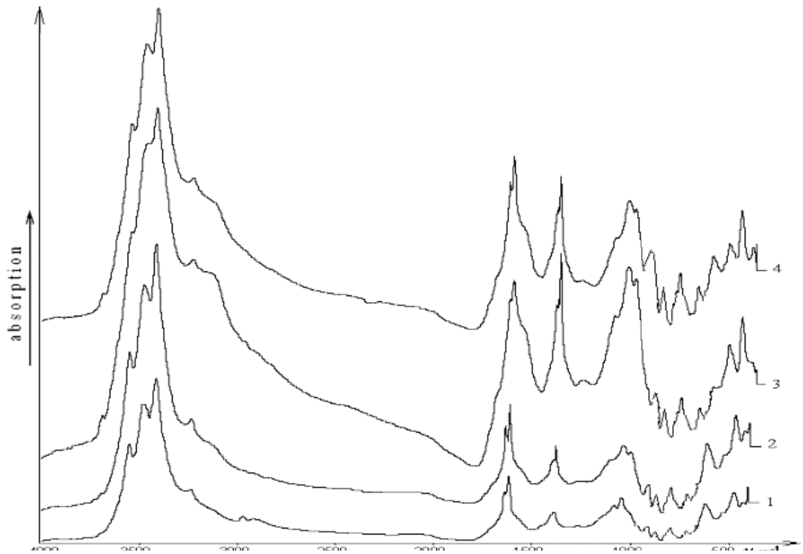
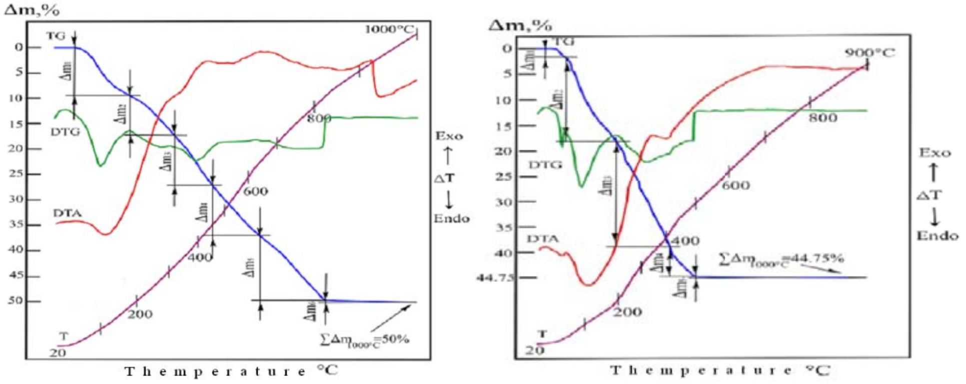


Figure 2– The IR-spectra of the studied samples,
obtained with the concentration of chromium ions, %: 1 – 0,005; 2 – 0,07; 3 – 0,1; 4 – 0,5

The influence of the concentration of chromium ions upon the structure of the obtained products has been studied by the method of thermal analysis (figure 3). On DTA curves the following effects are marked: a small endothermic decay at 60^{o}C is connected with the start of the process of extraneous moisture evaporation and removal of occluded gasses; a considerable endo-effect at 120^{o}C is stipulated by dehydration processes; exothermic effects in the field of310, 345 and 410^{o}C are caused by breaking of a macromolecule of humates and oxidation of the aliphatic part, i.e. removal of hydrocarbon and acid-containing groups from the structure proceeds; heat effects at 430 and 550^{o}C are connected with the breaking

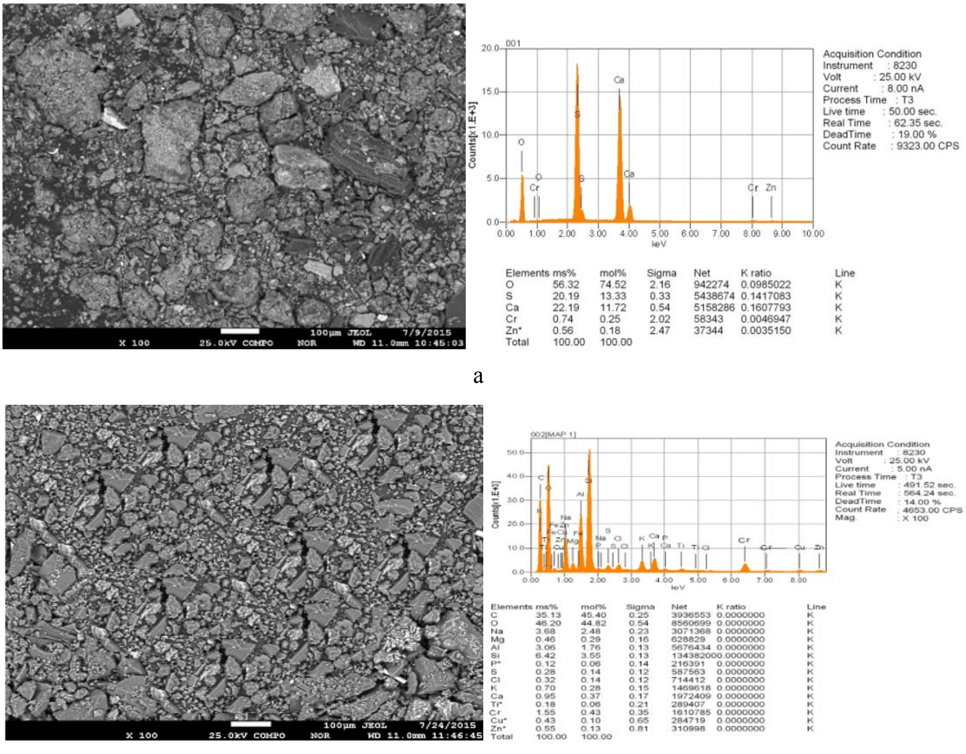


a b

Figure 3 – Thermograms of the studied samples,
obtained with different concentration of chromium chloride, %: a – 0,005; b – 0,1

of the side chains, the start of breaking of the aromatic structures [12, 13]. Heat effects in the field of 940°Care caused by the destruction of the mineral part and formation of metal oxide. On the basis of an analysis of thermal destruction of the new complex compounds it has been established that in different temperature fields Me-O bond produces a different effect upon the dynamics of isolation of volatile substances upon the thermal destruction of chromium humates. Herewith, a number of temperature fields have been found, in which a preferable proceeding of a certain type of reactions, connected with the breaking of this or that bond type, is observed. It has been established that an intensive decomposition of chromium humates starts at 310°C and a complete burning-out occurs at 550°C.

Figure 4 provides electronic microscopic shots of the studied samples, which are represented by grains of different sizes. At electronic microphotos (figure 4a) small and large particles of different sizes (3-270 mkm) are seen. Most of them represent agglomerates of still smaller particles. The form of the particles is mainly irregular. It follows from the results of EMF-mapping that the content of chromium makes up 0,74 weight %. The sample, obtained upon the interaction of sodium humate with 0,1% of chromium chloride solution (figure 4б), is represented by the aggregates, consisting of small particles of different sizes (3-102 mkm).



Acquisition Condition
Instrument : 8230
Volt : 25.00 kV
Current : 8.00 nA
Process Time : T3
Live time : 50.00 sec.
Real Time : 62.35 sec.
DeadTime : 19.00 %
Count Rate : 9323.00 CPS

Elements	ms%	mol%	Sigma	Net	K ratio	Line
O	56.32	74.52	2.16	942274	0.0985022	K
S	20.19	13.33	0.33	5438674	0.1417083	K
Ca	22.19	11.72	0.54	5158286	0.1607793	K
Cr	0.74	0.25	2.02	58343	0.0046947	K
Zn*	0.56	0.18	2.47	37344	0.0035150	K
Total	100.00	100.00				

a

Acquisition Condition
Instrument : 8230
Volt : 25.00 kV
Current : 5.00 nA
Process Time : T3
Live time : 491.52 sec.
Real Time : 564.24 sec.
DeadTime : 14.00 %
Count Rate : 4653.00 CPS
Mag. : X 100

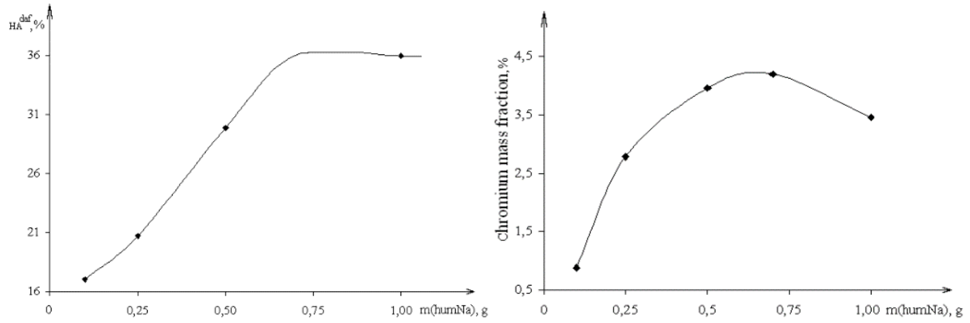
Elements	ms%	mol%	Sigma	Net	K ratio	Line
C	35.13	45.40	0.25	3936553	0.0000000	K
O	46.20	44.82	0.54	8560699	0.0000000	K
Na	3.68	2.48	0.23	3071368	0.0000000	K
Mg	0.46	0.29	0.16	628829	0.0000000	K
Al	3.06	1.76	0.13	5676434	0.0000000	K
Si	6.42	3.55	0.13	13438200	0.0000000	K
P*	0.12	0.06	0.14	216391	0.0000000	K
S	0.28	0.14	0.12	587563	0.0000000	K
Cl	0.32	0.14	0.12	714412	0.0000000	K
K	0.70	0.28	0.15	1469618	0.0000000	K
Ca	0.95	0.37	0.17	1972409	0.0000000	K
Ti*	0.18	0.06	0.21	289407	0.0000000	K
Cr	1.55	0.43	0.35	1610785	0.0000000	K
Cu*	0.43	0.10	0.65	284719	0.0000000	K
Zn*	0.55	0.13	0.81	310998	0.0000000	K
Total	100.00	100.00				

b

Figure 4 – Electronic microscopic shot of the obtained samples, obtained with different concentration of chromium chloride, %: a – 0,005; b – 0,1

Rare large particles of heavy fraction are observed. A crystalline particle of heavy fraction has been identified by the EDS method. The results of elemental analysis have shown that the content of chromium makes up 1,55 weight %.

In the course of the conducted works it has been established that with increasing of the humate rate from 0,1 up to 1,0 g the yield of humic substances increases (figure 5a). For example, upon the interaction of 0,1% of chromium chloride solution with 0,1 g of humate the yield of humic acids makes up 17,02%, and upon the use of 1,0 g it attains 35,95%. It follows from the analysis of the obtained data (figure 5б), that with increasing of the humate rate from 0,1 up to 0,70 g the mass fraction of chromium increases from 0,88 up to 4,20%, and the further increasing of the humate rate up to 1,0 g results in a decrease of the content of chromium down to 3,46%. Probably, herewith, a desorption of chromium ions occurs.



a b

Figure 5 – An isotherm of the dependence of the yield of humic acids (a) and chromium mass fraction (б) upon the sodium humate rate

It has been revealed that with increasing of the humate rate an increase of pH is observed (table 3). Thus, upon the interaction of chromium chloride with 0,1 g of humate pH makes up 4,51, and with 1,0 it attains 7,44. It seems that with increasing of pH of the medium the viscosity of the humate solution decreases, herewith, the extent of their aggregative character decreases, i.e. the colloid aggregates of humic compounds become smaller in sizes and due to this fact they become more movable. As a result the velocity of the interaction of the initial components increases, which leads to an increase in the velocity of the formation of the complex humic compounds of chromium.

Table 3 – Changing of pH in dependence of the concentration of chromium ions

Humate rate, g				
0,10	0,25	0,50	0,70	1,00
4,51	4,69	5,78	6,45	7,44

It is seen from the functional analysis data, provided in Table 4, that in the interaction reactions of sodium humate with chromium ions, different functional groups take part. It has been established that in all studied samples with increasing of the humate rate the content of chromium, bound with the carboxylic and phenolic groups, increases. Thus, the number of carboxylic groups, bound with chromium, increases from 0,38 up to 0,47 mg-equ/g, and the content of the phenolic groups, bound with chromium, increases from 1,50 up to 1,60 mg-equ per 100 g of organic mass. It is noteworthy that under conditions of the conducted studies both the carboxylic and phenolic groups interact partially with chromium ions. Probably, other functional groups of the humic compounds also participate in the reactions.

Table 4 – The influence of sodium humate upon the content of the functional groups in the obtained samples

m (HumNa), g	Content of acidic groups, mg-equ/g		
	COOH	$OH_{phen.}$	COOH+ OH_{phen}
0,10	0,38	1,50	1,88
0,25	0,39	1,52	1,91
0,50	0,43	1,55	1,98
0,70	0,46	1,59	2,05
1,00	0,47	1,60	2,07

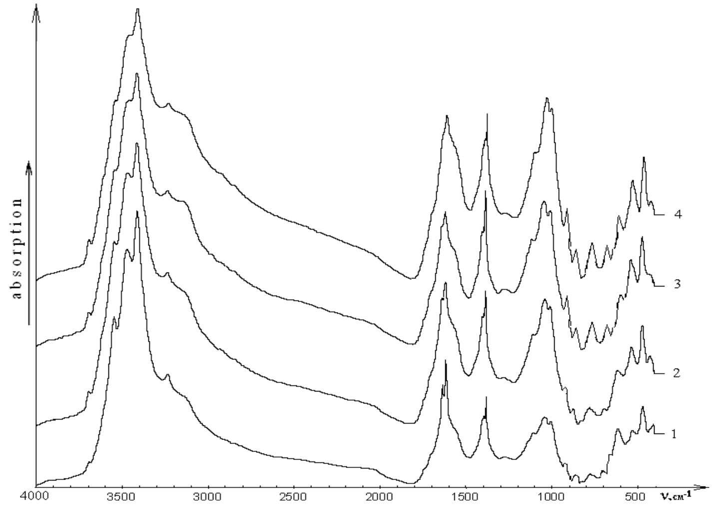


Figure 6 – The IR-spectra of the studied samples, obtained with the humate rate of: 1 – 0,1; 2 – 0,5; 3 – 0,7; 4 – 1,0 g.

The IR-spectra of the studied samples, provided in figure 6, show the complexity of their composition: strong and intensive absorption bands at 3550-3545, 3475-3470, 3420-3415 and 3290-3280 cm^{-1} correspond to valence vibrations of

OH- and NH-groups, bound by intermolecular hydrogen bonds, and those at 1620-1615 and 1390-1380 cm^{-1} correspond to asymmetric and symmetric vibrations of the ionic form of carboxylic groups. An increase of their intensity is connected with the overlapping of surface vibrations of C=C-bonds of the aromatic structures at 1620-1610 cm^{-1}. The absorption bands in the field of 1275-1270 cm^{-1} are characteristic for the deformation vibrations of OH-groups of phenols, -C-O-groups of aromatic carboxylic acids and complex esters, the absorption bands in the field of 1050-1045 cm^{-1} are characteristic for the deformation vibrations of OH-groups of alcohols. The absorption bands of average intensity in the field of 960-955, 925-920, 830-825, 780-770, 620-615, 545-540, 475-470 and 425-420 cm^{-1} confirm the formation of Me-O bond in the complex humic compounds with chromium. It has been established that an intensity of the indicated absorption bands increases with increasing of the humate rate.

Conclusions. The regularities of the influence of the concentrations of chromium ions and the humate rate upon the interaction process of humate and chromium have been revealed. It has been shown that increasing of the specified parameters contribute to an increase in the yield of humic substances up to 36,49% and chromium mass fraction up to 4,31%. The formation of complex compounds of humates with chromium ions has been established by the chemical-physical and chemical methods. Shifting of pH to the acidic field and the absorption bands in the field of 960-955, 925-920, 830-825, 780-770, 620-615, 545-540, 475-470 and 425-420 cm^{-1} confirm the formation of Me-O bond in the complex humic compounds with chromium ions. It has been established that the introduction of chromium ions into the structure of humic compounds is accompanied by more intensive processes of oxidation of organic molecule of humates to the extent of their complete burning-out.

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Резюме

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Cr (III) ИОНДАРЫНЫҢ НАТРИЙ ГУМАТЫМЕН СУЛЫ ОРТАДА ӘРЕКЕТТЕСУІ

Натрий гуматының хром (III) хлоридімен әртүрлі жағдайларда әрекеттесу заңдылықтары зерттелді. Химиялық талдау және физика-химиялық (ИҚС, ДТТ, РЭМ) әдістермен гуматтардың хром иондарымен кешенді қосылыстар түзетіндігі айқындалып, алынған үлгілердің құрамы мен қасиеттері анықталды.

Түйін сөздер: натрий гуматы, хром хлориді, кешен түзу, функциональды топтар.

Резюме

У. Ж. Джусипбеков, Х. Темел, Г. О. Нургалиева,
З. К. Баяхметова, А. К. Шакирова, Д. Дуйсенбай

ВЗАИМОДЕЙСТВИЕ ИОНОВ Cr (III) С ГУМАТОМ НАТРИЯ В ВОДНЫХ РАСТВОРАХ

Исследованы закономерности процесса взаимодействия гуматанатрия с хлоридом хрома (III) при различных условиях. Химическим анализом и физико-химическими методами (ИКС, ДТА, РЭМ) установлено образование комплексных соединений гуматов с ионами хрома, определены состав и свойства полученных образцов.

Ключевые слова: гумат натрия, хлорид хрома, комплексообразование, функциональные группы.

UDC 54.06

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CHEMICAL COMPOSITION AND GROWTH REGULATING ACTIVITY OF *Tamarix hispida* SUBSTANCE

Abstract. This article considers the growth of regulating activity of 50 and 70% of the extract obtained from the aerial weight of the Tamarixhispida plant of the Tamaricaceae family harvested in Almaty in September 2016.

While testing the obtained extracts on the Lenma minor strain of the Araceae family found that 70% shows much greater activity when the concentration of the extract in the test medium is lower by 2 times. The obtained data prompted us to study in more detail the chemical composition of 70% alcohol extract by the method of high-performance liquid chromatography with a mass-selective detector. As a result, 70% of the extract identified a significant number of compounds structurally similar and potentially possessing a growth regulating ability. Namely chlorine azoorganic compounds of the type 7-chloro-4- (dimethylamino) 1,4,4a, 5,5a, 6,11,12a- 3,6,10,12,12a-pentahydroxy-1,11-dioxo-2-naphthacenecarboxamide, 3,5-dichloro-6-nitrocholestane, Phenol, 4,4 '- (3H-2,1-benzoxathiol-3- ylidene) bis-2-bromo-3-methyl-6- (1-methylethyl) -, S, S-dioxide, and their share in the extract reaches more than 40% of all the identified substances.

Key words: Tamarixhispida, Tamaricaceae, growth-regulating activity, Lenma minor, HPLC-MS

Introduction. Among the many classes of biologically active substances isolated from the plant and obtained by the method of synthesis, substances with a growing regulation ability, that is capable of exerting a certain influence on the development of individual organs or plants as a whole, or stimulating a set of biomass [1].

Regulators of development are physiologically active substances that show their effect in extremely small amounts (usually the dosage is measured in microliters), they allow to influence the intensity and direction of physiological processes in agricultural crops, increasing their yield, speeding up the collection of green mass or vice versa suppressing the growth of weeds [2].

Growth regulators primarily include phytohormones are divided into 5 main groups, auxins, gibberlins, cytokinins, abscisins, and ethylene. The first 3 classes have the ability to induce growth, an example of such compounds is indole acetic acid and 2,4-dichloro-phenoxyacetic acid [3].

Abscisins and ethylene are natural inhibitors, that is, substances that inhibit growth. Natural inhibitors often accumulate in resting organs, in particular in the kidneys, seeds and tubers.

In our article, as an object, we chose the aboveground mass of the plant *Tamarixhispida* of the family *Tamaricaceae* harvested in September 2016 in the Almaty region.

Plants of this genus are basically perennial evergreen plants distributed in the arid zones of southern Europe, Iran, Pakistan, India, the South Caucasus, North America and Central Asia [4, 5].

Extracts obtained from representatives of the *tamarix* family were previously considered as medicinal phytocomplexes and capable of metabolites isolated from *tamarix* to regulate plant growth have not previously been studied.

Antioxidant, anti-bacterial, anti-cancer activity of various *tamarix* species, including hyspids, was previously considered in the study of alcohol extracts of the aerial part, many compounds of various classes were isolated, such as ursolic acid -1,2 methyl 3β-al-D-firdoolean- 14-ene-28-one acid, 3-α- [3", 4"-dihydroxy-transcamolamoxy] -D-firdoolean-14-ene-28-tartaric acid (isotamarixene) -3,3-α-hydroxy -D-Fredoolean-14-ene-28-tartaric acid-4, 3-α- [4"-hydroxy-transcamolamoxy] -D-firdoolean-14-ene-28-ol Lota-5 isoramnetin, 3,5-dihydroxy-4 ', 7-dimethoxyflavone, rhamnocetri, afzelin, 5,3'-dihydroxy-7,4'-dimethoxyflavone 3-O-β-D-glucopyranoside, 4-hydroxy- 3,5-O-dimethylbenzoic acid, 7,3 ', 4'-trigoroxy-5-methoxyflavone, 3,7,4'-trihydroxy-5-methoxyflavone, 3,5,7-trihydroxy-3', 4 ' dimethoxy flavone, Kampferid-3-O-β-glucopyranoside [4-6].

We studied the growth-regulating activity of extracts obtained from the above-ground mass of *Tamarixhispida* family *Tamaricaceae* using a standard test sample in the form of the *Lenma minor* family of *Araceae*, as well as the chemical composition of 70% alcohol-water extract by high-performance liquid chromatography with a mass-selective detector [7,8].

Methods

Preparation of 70% ethanol extract from the above-ground part of *Tamarixhispida* family *Tamaricaceae.* To determine the optimum from the point of view of the grow regulating ability of *Tamarix* extract, we prepared and sample, 50% and 70% alcohol extracts from the aerial part of the studied plant.

Extracts were obtained according to the following procedure:

The aerial part of a plant of the species *Tamarixhispida* harvested and dried in accordance with the requirements of the state Pharmacopoeia of the Republic of Kazakhstan [3-4] was crushed and the extractant in a ratio of 1 to 10. After them plant was insisted for 72 hours, then the extract was separated from the grass by filtration and concentrated extraction on a rotary evaporator until the solvent is completely removed at a temperature of 40-50 °C

Determination of grow regulation activity. Then, the determination of the growth regulating activity is carried out according to the following procedure:

The E-medium for plant development is obtained by mixing various components in 1000 ml of distilled water and adjusting the pH from 6.0 to 7.0 by adding KOH in the mother liquor.

Then the stock solution is dissolved to the working concentration by mixing 100 ml of the stock solution and 900 ml of water is distilled. Then prepare the test sample where 30 mg for the crude extract / compound is dissolved in 1.5 ml of solvent (methanol / ethanol, etc.) serving as the starting solution. Subsequently, 10, 100 and 1000 μl of the solution were inoculated from the mother liquor in 10, 100 and 1000 μg / ml in three flasks. Then let the solvent evaporate overnight. After add 20 ml of working E. medium, and then plant *Lenma minor*, each of which contains a rosette of two or three leaves, in each flask. (a total of 20).

Other flasks prepare control experiments using plant growth inhibitors and promoters acting as a negative and positive control, respectively.

After all the cooking, place the flasks in the incubator cabinet for seven days. Plants should be inspected daily during incubation. The results are analyzed both in the regulation of growth of% age, calculated with reference to negative control.

The standard preparation was 1,1'-dimethyl-4,4'-bipyridinium hydrate hydrate

The results are shown in table 1.

Table 1 – Grow regulating ability of 50 and 70% ethanol extract
from aboveground masses *Tamarixhispida* Wild

70% Ethanol extract					
Control plant	Concentration of sample	Types of standards		Degree of Growth	Concentration of standard drug
		Organisms that have not changed after the drug is administered	Control		
Lemna minor	10 μL	20	40	50 %	0,015
	100 μL	18		55 %	
	1000 μL	16		69 %	
50% Ethanol extract					
Lemna minor	10 μL	51	51	0 %	0,015
	100 μL	51		0 %	
	1000 μL	29		43.13 %	

Further, the extract exhibiting the highest activity values is analyzed by high performance liquid chromatography with a mass selective detector of Aligent Technologies 6400 Series Triple Quadrupole LC/MS. For analyze we use Poroshell 120 EC-C18 column (50 mm long, 3 mm in diameter, sorbent particle size 4, 0, 2.7 and 1.9 μm) with 10% methanol with an aqueous solution of methanol as the starting solvent and 90% methanol as the final solvent at a pressure of 11.5 mPa and a temperature of 40 °C.

The components were identified by mass spectra and retention times, using the NIST library and Wiley LC/MS.

The results are shown in table 2.

Results and discussion

From the data presented in table 1, we see that 70% ethanol extract from the aerial part of *Tamarixhispida* exhibits significantly greater growth regulating activity at a much lower concentration, that is, 50% extract exhibits significant activity (43.13%). Only at a maximum concentration of 100 µl, then time as 70% shows activity of 50% already at 10 µl.But when the concentration is increased, the changes are not so large and make up 55% at 100 µl and 69 at 1000 µl, which implies that a change in concentration of 10 does not lead to a significant increase in of activity, which confirms the statement of the feasibility of using growth regulating substances. Only in low concentrations, as the increase in concentration only leads to senseless consumption of the drug.

The data obtained clearly demonstrate that the growth regulating effect achieved in 50% extract at a concentration of 1000 µl per 1000 ml is 43.13% significantly less than in 70% at a concentration of 10 µl (50%) that is 70% extract shows more than 100 times greater efficiency in laboratory tests. This fact convinced us to consider 70% extract as the main one in determining grow regulating activity and further study its chemical composition in more detail.

From the data presented in table 2, we can say that the dominant compound in the 70% extract is 7-chloro-4-(dimethylamino) 1,4,4a, 5,5a, 6,11,12a-3,6,10, 12 , 12a-pentahydroxy-1,11-dioxo-2-naphthacenecarboxamide (12.78%), 7-Azadabenz [a, e] azulen-12-one, 5,6,7,7a, 12,12a-hexahydro-7-methyl -8,9-bis (methoxy) -12a-hydroxy-2,3-methylenedioxy (13.46%), 5a, 7-dihydroxy-9a, 11a-dimethyl-1-(2-oxo-2H-pyran-5-yl (14.88%), Phenol, 4.4 '- (3H-2,1-benzoxathiol-3-ylidene)) bis-2-bromo-3-methyl-6- (1-methylethyl) -, S, S-dioxide (20.42%) and 4- (2-methyl-1-cyclohexenyl) -trans-3-butene ene-2-one 2,4-dinitrophenylhydrazone (10.74%). The proportion of beta carotene derivatives of 3,3'-dihydroxy-beta, beta-carotene-4,4'-dione is also significant 2.5%, the total number of organohalogen compounds is estimated at 35.9%, the quantity of nitrogen-organic substances in 48.89%, sulfur compounds in 24.88% and oxygen-containing organic substances 98.14%, ie the bulk. Of particular interest are natural halogen-organic compounds exhibiting, as a rule, high growth stimulating and potentially anti-cancer activity [9-18].

Conclusion. Thus, we studied the growth-regulating activity of 50 and 70 percent extracts of the aerial masses of the *Tamarixhispida* family *Tamaricaceae*.

On the test plant of the *Lenma minor* family *Araceae* with the comparative preparation being 1,1'-dimethyl-4,4'-bipyridinium hydrate hydrate, we found that 70 % the extract shows 100 times more activity. That is, it shows a 50% result at 10 µl, but with an increase in the concentration of 70% the extract of multiple growth does not occur, but only 5% increase at 10 concentration increase and a result of 69%. The further study of the chemical composition revealed a large amount of chlorine and organo-organic compounds in a 70% extract of 35.9% and 48.89%, respectively, with some of the identified compounds. For example, 7-chloro-4- (dimethylamino) 1,4,4a, 5, 5a, 6,11,12a-3,6,10,12,12a - pentahydroxy-

Table 2 – Results of determination of the chemical composition of 70% alcohol-water extract obtained from the aerial part of the plant *Tamarixhispida* Wild

№	Name of compound	Formula	Molecular weight	Retention time	Content, %
1	7-chloro-4- (dimethylamino) 1,4,4a, 5,5a, 6,11,12a-3,6,10,12,12a-pentahydroxy-1,11-dioxo-2-naphthacenecarboxamide	$C_{21}H_{21}ClN_2O_8$	464	0,44	12,78
2	7-Azadabenz [a, e] azulen-12-one, 5,6,7,7a, 12,12a-hexahydro-7-methyl-8,9-bis (methoxy) -12a-hydroxy-2,3-methylenedioxy	$C_{21}H_{21}NO_6$	383	0,56	13,46
3	5a, 7-dihydroxy-9a, 11a-dimethyl-1- (2-oxo-2H-pyran-5-yl) -hexadecahydronaphtho [1 ', 2': 6,7] indeno [1,7a-b] oxirene-2 -acetate	$C_{26}H_{34}O_7$	458	1,401	14,88
4	3,3'-dihydroxy-beta, beta-carotene-4,4'-dione	$C_{40}H_{52}O_4$	596	2,31	2,5
5	3,5-dichloro-6-nitro cholestane	$C_{27}H_{45}Cl_2NO_2$	485	3,46	2,7
6	Carda-4.20 (22) -dienolide, 3 - [(6-deoxy-3-O-methyl-α-D-allopyranosyl) oxy] -1,14-dihydroxy-, (1β, 3β) -	$C_{30}H_{44}O_9$	548	3,82	8,15
7	6-oxo-1-phenyl-1,6-dihydropyridazin-3-yloxy) acetic acid, ethyl ester	$C_{14}H_{14}N_2O_4$	274	4,96	4,91
8	Phenol, 4,4 '- (3H-2,1-benzoxathiol-3-ylidene) bis-2-bromo-3-methyl-6- (1-methylethyl) -, S, S-dioxide	$C_{27}H_{28}Br_2O_5S$	622	5,20	20,42
9	4,4 ', 4' '- methylidentris (N, N-dimethylaniline)	$C_{25}H_{31}N_3$	373	5,37	1,61
10	4- (2-methyl-1-cyclohexenyl) -trans-3-buten-2-one 2,4-dinitrophenylhydrazone	$C_{17}H_{20}N_4O_4$	344	5,66	10,74
11	Benzo (g) indolo (2,3-a) quinolizine-1-carboxylic acid, 1,2,3,4,4a, 5,7,8,13,13b, 14,14a-dodecahydro-3-hydroxy-2 methoxy, methyl ester, 3,4,5-trimethoxybenzoate	$C_{32}H_{38}N_2O_8$	578	6,01	3,14
12	2-thiophenecarboxaldehyde, 5-ethynyl-, (2,4-dinitrophenyl) hydrazone	$C_{13}H_8N_4O_4S$	316	6,55	4,46

1,11-dioxo-2-naphthacenecarboxamide, 3,5-dichloro-6-nitrocholestane, are halogenated steroids exhibiting growth stimulating activity.

It should be noted that the growth-stimulating activity of the aboveground part of the Kazakhstan tamarix species was studied for the first time. As well as 7-chloro-4- (dimethylamino) 1,4,4a, 5,5a, 6,11,12a-3,6,10,12,12a- pentahydroxy-1,11-dioxo-2-naphthacenecarboxamide, Phenol, 4,4 '- (3H-2,1-benzoxathiol-3-ylidene) bis-2-bromo-3-methyl-6- (1-methylethyl) - , S, S-dioxide, 2-thiophenecarboxaldehyde, 5-ethynyl-, (2,4-dinitrophenyl) hydrazone were first found in the plant *Tamarixhispida*.

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Резюме

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TAMARIX HISPIDA ХИМИЯЛЫҚ ҚҰРАМ ЖӘНЕ ӨСУ НОРМАТИВІН РЕТТЕУ СУБСТАНЦИЯЛАРЫ

Мақалада 2016 жылы қыркүйекте Алматыда жиналған Tamarix отбасының Tamarix hispida зауытында жер үстінен алынған 50-70% өсімдік сығындыларының өсуін реттеуші қызметі қарастырылған, Araceae отбасының кішігірім ленма өсімдігінің 70% экстракт кезінде аздаған активтілік екінші қатарда, тәжірибелік ортада концентрациясы төмен. Алынған деретер бізді масс-селективті детектормен жоғары сапалы сұйық хромотаграфия әдісімен 70% спирт сығындысының химиялық құрамын егжей-текжейлі зерделеуге мәжбүр етті.

Нәтижесінде 70% сығындыда құрылымдық, ұқсас және ықтимал өсу нормативін реттеу қабілеті бар атап айтқанда, 7-хлор-4-(диметиламин) 1,4,4а,5,5а,6,11,12а-3,6,10,12,12а-пентагидрокси-1,11-диоксо-2-нафтаценкарбоксамид,3,5-дихлор-6-нитрохолестан, Фенол,4,4- (3H-2,1-бензоксатиол-3-илиден) бис-2-бром-3-метил-6-(1-метилэтил)-S,S-диоксид, сияқты хлордың қосылыстары анықталды,олардың сығындылары 40%-дан асады.

Түйін сөздер: *Tamarix hispida, Tamaricaceae, регрегулярлық қызмет, Lenta minor,* HPLC-MS.

Резюме

Е. С. Ихсанов, Н. А. Султанова, Ж. А. Абилов, М. И. Чоудхари

ХИМИЧЕСКИЙ СОСТАВ И РОСТРЕГУЛИРУЮЩАЯ АКТИВНОСТЬ СУБСТАНЦИИ *TAMARIXHISPIDA*

В статье рассматривается рострегулирующая активность 50 и 70% экстракта, полученного из надземной массы растения Tamarixhispida семейства Tamaricaceae, заготовленного в сентябре 2016 г в Алматинской области. В ходе испытаний полученных экстрактов на тестовом растении Lenmaminor семейства Araceae было выяснено, что при более низкой концентрации экстракта в испытательной среде (на 2 порядка), 70%-ный экстракт проявляет намного большую активность. Полученные данные побудили нас более подробно изучить химический состав 70%-ного спиртового экстракта с помощью метода высокоэффективной жидкостной хроматографии с масс-селективным детектором. В итоге в 70%-ном экстракте было идентифицировано значительное количество соединений, структурно схожих и потенциально обладающих рострегулирующей способностью, а именно, хлор- и азоорганические соединения типа 7-хлор-4- (диметиламино) 1,4,4a, 5,5a, 6,11,12a-3,6,10,12,12a-пентагидрокси-1,11-диоксо-2-нафтаценкарбоксамид, 3,5-дихлор-6-нитрохолестан, Фенол, 4,4 '- (3H-2,1-бензоксатиол-3-илиден) бис-2-бром-3-метил-6- (1-метилэтил) -, S, S-диоксид, при этом их доля в экстракте достигает более 40% из всех идентифицированных веществ.

Ключевые слова: Tamarixhispida, Tamaricaceae, рострегулирующая активность, Lenmaminor, HPLC-MS.

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INFLUENCE OF INITIAL STATE OF HYDROGELS ON SELF-ORGANIZATION OF POLYMER NETWORKS OF POLYMETHACRYLIC ACID AND POLY-4-VINYLPYRIDINE AT THEIR REMOTE INTERACTION IN AN AQUEOUS MEDIUM

Abstract. Process of mutual activation of hydrogels of polymethacrylic acid (PMAA) and poly-4-vinylpyridine (P4VP) in intergel system on their basis is studied. Effect of dry initial state of hydrogels on their remote interaction, mutual activation and self-organization is studied by methods of conductometry, pH-metry, gravimetry. It is found that self-organization of macromolecules provides transfer of hydrogel of PMAA into highly ionized state in intergel system at gPMAA:gP4VP=1:5 ratio, and hydrogel of P4VP – at gPMAA:gP4VP=5:1 ratio of polymer hydrogels. Low values of swelling degree of gP4VP at gPMAA:gP4VP=1:5 ratio are due to formation of intermolecular cross-links leading to folding of macromolecular globe.

Keywords: intergel system, mutual activation, self-organization, initial state, hydrogels, polymethacrylic acid, poly-4-vinyl-pyridine.

In previous studies [1-6] it was found that remote interaction of rare-cross-linked polymer hydrogels has significant impact on their electrochemical and volume-gravimetric properties. Overwhelming majority of hydrogels are polyelectrolytes [7]. Conformational behavior of polyelectrolytes is influenced mainly by ionization degree of macromolecular globes [8-11]. In intergel systems ionization degree and conformational state of each hydrogel is significantly determined by concentration of another hydrogel. High sorption degree of polymers in intergel systems is due to absence of counter ions at ionized groups. This is consequence of intergel interactions, result of which is mutual activation of hydrogels and formation of uncompensated charges along polymer chain. Uncompensated charge is formed due to cleavage of proton from carboxyl groups during dissociation of acid hydrogel and binding of this ion with heteroatom of polybasis in an aqueous medium. Wherein charge density of basic hydrogels in limited by dissociation degree of acid hydrogel. Subsequently both hydrogels are ionized and do not have counter ions at major part of functional groups. Formation of ionized groups is caused by conformational changes of internode links of polymer chains due to what unfolding of macromolecular globe takes place. In this regard, the goal of the work is to study impact of dry initial state of polymer hydrogels of PMAA and P4VP on electrochemical and volume-gravimetric properties of intergel system gPMAA-gP4VP.

Experimental part

Equipment. For measurement of specific electric conductivity conductometer MARK 603 (Russia) was used, pH of solutions was measured on pH-meter Metrohm 827 pH-Lab (Switzerland). Mass of swollen samples of hydrogels for further calculation of swelling degree (α) was measured by weighing on electronic analytical scales SHIMADZU AY220 (Japan).

Materials. Investigations was carried out in distillated water. Hydrogels of polymethacrylic acid were synthesized in presence of cross-linking agent N,N-methylene-bis-acrylamide and red-ox system $K_2S_2O_8$–$Na_2S_2O_3$. Hydrogel of poly-4-vinylpyridine (hP4VP) (2% of cross-linking agent) was synthesized by «Sigma Aldrich» company. Synthesized hydrogels in an aqueous medium were put to create intergel system polymethacrylic acid hydrogel – poly-4-vinylpyridine hydrogel (hPMAA-hP4VP). Swelling degrees of hydrogels are: $\alpha_{(hPMAA)}$=20,65 g/g; $\alpha_{(hP4VP)}$=2,65 g/g.

Experiment. Experiments were made at room temperature. Study of the intergel system was made as follows: calculated amount of each hydrogel in dry state was put in special glass filters, pores of which permeable for low-molecular ions and molecules, but non-permeable for hydrogels dispersion. After that, parameters (electric conductivity, pH and mass of samples) were measured. Measurement of electric conductivity and pH was made in absence of hydrogels in an aqueous medium. Swelling degree was calculated by the equation

$$\alpha = \frac{m_2 - m_1}{m_1}$$

where m_1 – mass of dry hydrogel, g, m_2 – mass of swollen hydrogel, g.

Results and discussion

In process of hydrogels remote interaction in intergel system hPMAA-hP4VP there are chages in specific electric conductivity of water solutions. Dependence of electric conductivity from time is presented on figure 1. As seen from data, increase of electric conductivity occur at hPMAA:hP4VP=3:3 ratio during all time of remote interaction. Maximum values of electric conductivity are observed at 48 hours. Minimum values of conductivity are reached in presence of only polybasis (ratio hPMAA:hP4VP=0:6), what is due to it’s ionization in result of proton association, which were formed at water molecules dissociation.

For more clear description of low and high values of electric conductivity, it is necessary to consider processes of ionization and dissociation of hydrogels. In process of carboxyl group dissociation there is a formation of proton, further binding of which is occurred by nitrogen atom of vinylpyridine. This is the main cause of low values of conductivity. It should be noted, that high values of electric conductivity (ex. Ratio hPMAA:hP4VP=3:3) point to the fact that in result of

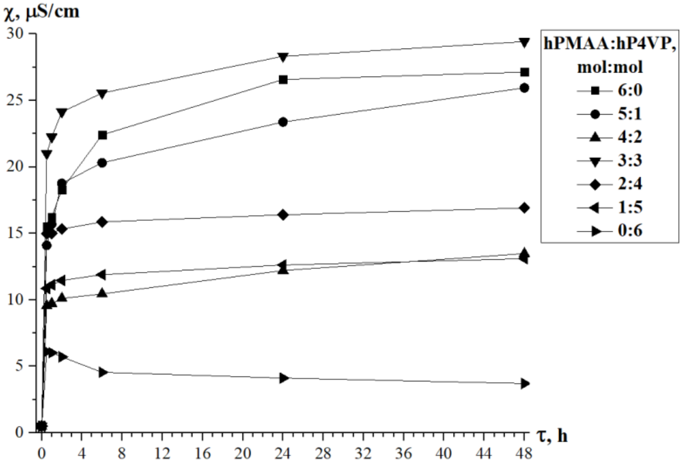

Figure 1 – Dependence of electric conductivity of aqueous solutions from time in presence of intergel system hPMAA-hP4VP

self-organization carboxyl groups dissociation process prevails over protons association by polybasis heteroatom. High conductivity values cannot point to high degree of mutual activation.

Dependence of hydrogen ions concentration from time is shown on figure 2. As seen from figure, increase of hydrogen ions concentration occur at ratio hPMAA:hP4VP=3:3. Comparison of this data with values of electric conductivity allows to conclude that carboxyl groups dissociation process prevails over protons association by vinylpyridine at this ratio.

As seen from figure 2, significant decrease of H^+ ions concentration occurs at hPMAA:hP4VP=1:5 during 6 hours of hydrogels remote interaction. In case with specific electric conductivity at this ratio it is seen, that values of electric

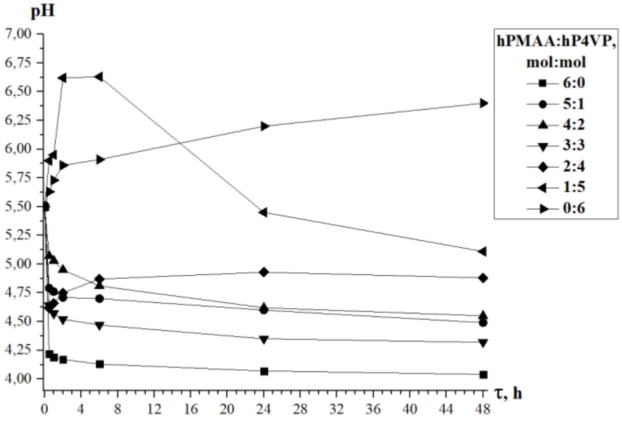

Figure 2 – Dependence of pH of aqueous solutions from time in presence of intergel system hPMAA-hP4VP

conductivity is not very high. Result of such interactions is formation of similarly charged groups without counter ions. And as consequence – transfer of acid and basic hydrogels into high ionized state. Maximum amount of protons is released in presence of polyacid (ratio hPMAA:hP4VP=6:0), what is directly connected with COOH-groups dissociation.

Appearance of H^+ ions excess is due to high swelling rate and COOH-groups dissociation, and not sufficient swelling rate of basic groups and their low concentration. Increase of OH^- concentration in an aqueous medium is due to low swelling rate and low concentration of COOH-groups, and high swelling rate and interaction of basic functional groups with H^+ ions.

Dependence of swelling degree of acid hydrogel of polymethacrylic acid in intergel system hPMAA-hP4VP from time is presented on figure 3. Increase of polyacid swelling degree occurs gradually with time. Wherein it should be noted that increase of α occurs with increase of polybasis concentration in solution. Minimum swelling occurs in presence of only polyacid in solution (ratio hPMAA:hP4VP=6:0), what is due to absence of phenomenon of mutual activation of polymer structures. As seen from obtained data, maximum swelling of polymethacrylic acid hydrogel occurs at hPMAA:hP4VP=1:5 ratio at 48 hours of hydrogels remote interaction. Also there is strong increase at hydrogels ratio equal 2:4. Such swelling increase is due to predominance of proton association process over carboxyl groups dissociation. Result of this phenomenon is transfer of acid hydrogel into highly ionized state. Not sufficiently full ionization of the hydrogels occurs at ratios of hPMAA:hP4VP=5:1, 4:2 and 3:3 what is indicated by not significant increase of swelling degree values.

Figure 4 shows dependence of swelling degree of basic hydrogel of poly-4-vinylpyridine in intergel system hPMAA-hP4VP from time. Low values of α are

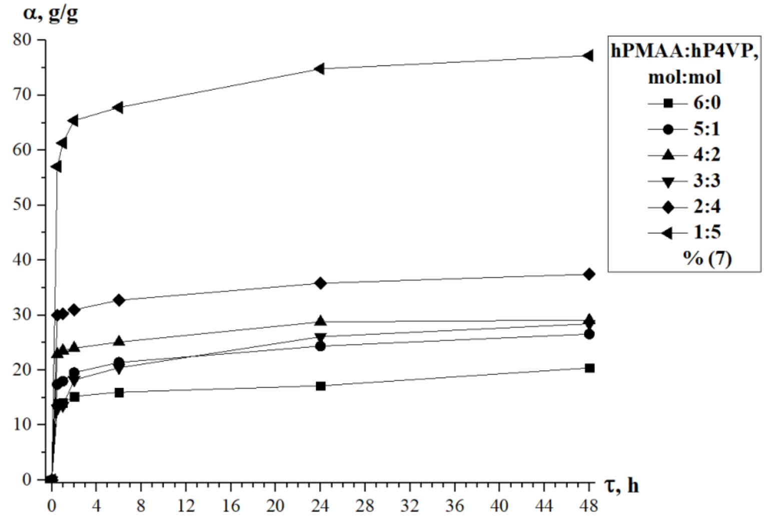

Figure 3 – Dependence of hPMAA swelling degree from time in presence of hP4VP

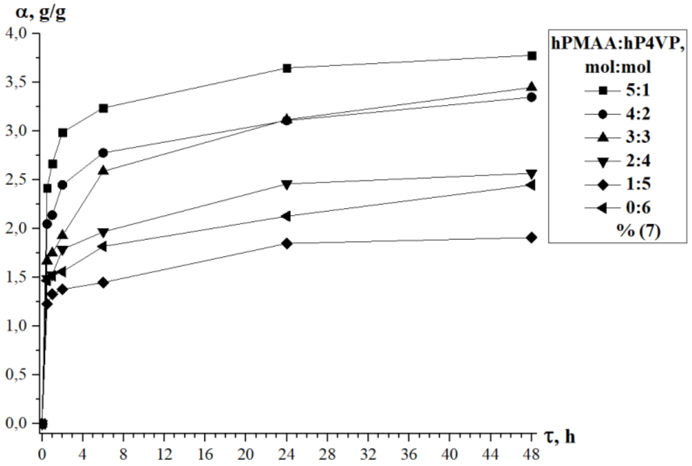

Figure 4 – Dependence of hP4VP swelling degree from time in presence of hPMAA

observed at hPMAA:hP4VP=0:6 ratio (individual hP4VP), what is caused by not very high ionization rate of individual basic hydrogel.

It should be noted that low swelling of polybasis occurs at hPMAA:hP4VP=1:5 ratio. This is due to formation of ≥N...H$^+$…N≡ intermolecular cross-links, result of what is folding of polymer globe and swelling decrease. With increase of polyacid share swelling degree of polybasis increases in result of high ionization rate at mutual activation of both macromolecules. Area of maximum swelling is hPMAA:hP4VP=5:1 ratio, wherein maximum values of α are observed at 48 hours.

As seen from obtained data, self-organization of polymer networks of PMAA and P4VP mainly depends from ionization degree of macromolecules.

Conclusion.

1. Obtained experimental data on specific electric conductivity and pH of solutions and swelling degree of PMAA and P4VP hydrogels allow to conclude that mutual activation of polymer structures of acid and basic nature has significant influence on their electrochemical and conformational properties.

2. Significant increase of values of specific electric conductivity, concentration of hydrogen ions and swelling degree is directly connected with self-organization of polymer hydrogels of acid and basic nature at their mutual activation in intergel pairs.

3. Obtained results on specific electric conductivity, pH and swelling degree point to the fact, that high ionized state of hPMAA is observed at hPMAA:hP4VP=1:5 ratio, and hP4VP – at hPMAA:hP4VP=5:1 ratio.

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Резюме

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СПОРТТЫҢ САҚТАНДЫРУ ШАРУАШЫЛЫҒЫНДА ҚОЛДАНЫЛАТЫН ПОЛИМЕТАКЛИКАЛЫҚ ЖӘНЕ ПОЛИ-4-ВИНИЛ ПИРИДИНІ ПОЛИМЕР ЖЕЛІСІНІҢ ӨЗІ-ҰЙЫМДАСТЫРУҒА АРНАЛҒАН ГИДРОГЕЛЬДІҢ НЕГІЗГІ МЕМЛЕКЕТТІЛІГІН ҚАТЫСУЫ

Полиметакрил қышқылы (гПМАҚ) және поли-4-винилпиридин (гП4ВП) гидрогелдерінің интергелді жүйедегі өзара активтену процесі зерттелді. Кондуктометрия, рН-метрия және гравиметрия әдістерімен гидрогелдердің бастапқы құрғақ күйінің олардың қашықтан өзара әрекеттесуіне, өзара активтенуіне және су ортасында өзін-өзі ұйымдастыруына әсері зерттелді. Макромолекулалардың өзін-өзі ұйымдастыруына байланысты интергелді жүйеде ПМАҚ гидрогелі ПМАҚг: П4ВПг=1:5 қатынасында, ал П4ВП гидрогелі полимерлік гидрогелдердің 5:1 қатынасында жоғары ионизацияланған күйге өтетіні анықталды. Макромолекулярлы шумақтардың жиналуына әкелетін молекулаішілік тігілу өзгерісіне байланысты ПМАҚг: П4ВПг=1:5 қатынасында П4ВП гидрогелінің ісіну дәрежесі төмен болатыны белгілі блды.

Түйін сөздер: интергелді жүйе, өзара активтену, өзін-өзі ұйымдастыру, бастақы күй, гидрогелдер, полиметакрил қышқылы, поли-4-винилпиридин.

Резюме

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ВЛИЯНИЕ НАЧАЛЬНОГО СОСТОЯНИЯ ГИДРОГЕЛЕЙ НА САМООРГАНИЗАЦИЮ ПОЛИМЕРНЫХ СЕТЕЙ ПОЛИМЕТАКРИЛОВЫХ КИСЛОТ И ПОЛИ-4-ВИНИЛПИРИДИНА ПРИ ИХ ДИСТАНЦИОННОМ ВЗАИМОДЕЙСТВИИ В ВОДНОЙ СРЕДЕ

Исследован процесс взаимной активации гидрогелей полиметакриловой кислоты (гПМАК) и поли-4-винилпиридина (гП4ВП) в интергелевой системе на их основе. Методами кондуктометрии, рН-метрии, гравиметрии исследовано влияние сухого исходного состояния гидрогелей на их дистанционное взаимодействие, взаимную активацию, самоорганизацию в водной среде. Установлено, что гидрогель ПМАК переходит в высокоионизованное состояние в интергелевой системе при соотношении гПМАК:гП4ВП=1:5, а гидрогель П4ВП – при соотношении полимерных гидрогелей, равном 5:1, вследствие самоорганизации макромолекул. Низкие значения степени набухания гП4ВП при соотношении гПМАК:гП4ВП=1:5 связаны с образованием внутримолекулярных сшивок, приводящих к сворачиванию макромолекулярного клубка.

Ключевые слова: интергелевая система, взаимная активация, самоорганизация, исходное состояние, гидрогели, полиметакриловая кислота, поли-4-винилпиридин.

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HIGH-TEMPERATURE HYDROGENATION (HYDRODEALKYLATION) OF THE MIXTURE OF COAL TAR PITCH DISTILLATE FRACTIONS AND RAW COKE-CHEMICAL BENZENE

Abstract. New basic process parameters for carrying out the high-temperature hydrogenation (hydrodealkylation) of the mixture of coal tar pitch distillate fractions and raw coke-chemical benzene were developed. Optimal conditions of the process of hydrogenation of preliminarily hydrotreated mixture of tar fractions with boiling temperature 180-230^{0}C and raw coke-chemical benzene in the presence of water vapor were defined. By high-temperature hydrogenation of hydrotreated mixture in the presence of catalyzer 5 % MoO_3 + zeolite HNaY high-purity benzene with crystallization temperature +5.35-5.45°C, sulfur content 0.002%, was obtained.

Key words: coke chemical resin, catalysts, benzene, naphthalene, hydrogenation.

Introduction. The main source of benzene yield increase are raw material alkylaromatic hydrocarbons (toluene). This circumstance is proven by the production practice of raw benzene treatment abroad, and the results of research, design and construction and development work carried out in CIS. Nowadays, with the purpose of transforming toluene or gasoline pyrolysis liquid products into benzene on an industrial scale, imported hydrodealkylation catalysts are used. At hydrodealkylation of aromatic carbohydrates and hydrocracking of saturated carbohydrates into gas, which is required for subsequent obtaining of high-purity benzene with precise fractionation, decontaminating coke settles on the catalyst surface which reduces the catalyst activity and requires its frequent regeneration because the process is carried out at high temperature – to 650°C.

Nowadays, in connection with the toughening of requirements to the quality of raw material for organic syntheses, increase of need for benzene and naphthalene, studies and development work on the improvement of coke-chemical raw material hydrotreatment processes are carried out actively. The experimental and theoretical data obtained formed the basis for the development of technology and new technical solutions of the process of high-temperature hydrogenation (hydrodealkylation) of preliminarily hydrotreated mixture of tar fractions with boiling temperature 180-230^{0}C and raw coke-chemical benzene for production of benzene and naphthalene high-purity sorts at treatment of 95 ths. t of raw material annually.

The goal of this paper is to define basic production parameters of the conduct of high-temperature hydrogenation (hydrodealkylation) of the mixture of coal tar pitch distillate fractions and raw coke-chemical benzene.

Experiment. With the purpose of producing high-quality benzene and naphthalene, experimental studies on high-temperature hydrogenation mixture (4:1) of raw coke-chemical benzene and tar fractions with boiling temperature 180-230°C, obtained at devolatilization of coal from Shubarkolskii deposit at the enterprise Sary-ArkaSpetskoks JSC, were carried out.

Raw material hydroforming was carried out on the high-pressure laboratory installation under hydrogen pressure of 4.0 MPa in the system of two reaction areasoperating in series. In the first zone, hydrogenation of non-saturated high-reactive compounds (styrolene, indene, etc.) was carried out in the presence of the production catalyst 0.5 % PdS + Al_2O_3 (MA-15) in order to provide the possibility to heat raw material to higher temperature (280-300°C) without polymerization. Deep removal of S, N, O heteroatoms and methylnaphthalenes to the corresponding tetrahydro derivatives – H-donor source for hydrodealkylation stage occurred in the second zone in the presence of Mo/Ni-Raney catalyst.

Results and discussion. Characteristic of raw coke-chemical benzene by Sary-Arka Spetskoks JSC is given in table 1.

Table 1 – Material composition of raw coke-chemical benzene
by Sary-Arka Spetskoks JSC

Compound	Content, % wt.
benzene	58,00
toluene	8,30
naphthalene	0,40
methylnaphthalene	2,85
xylenes	2,45
styrene	2,03
indene	2,14
hydrindene	0,30
thiophen and methylthiophens	0,18
ethylbenzene	0,15
pseudocumene	0,25

As it is seen from table 1, the content of benzene in raw coke-chemical benzene by Sary-ArkaSpetskoks JSC is 58 % wt., toluene - 8.3 % wt., naphthalene - 0.4 % wt.

The results of hydrotreatment of the mixture of raw benzene and coke-chemical tar fraction with boiling temperature 180-230°C are given in table 2.

It is seen from table 2 that in comparison with starting material, benzene concentration in the hydrotreated product increased from 40.5 to 49.0 % wt., and naphthalene concentration decreased from 24.2 to 10.0 % wt.

Table 2 – The results of hydrotreatment of the mixture of raw benzene and coke-chemical tar fraction with boiling temperature 180-230°C (conditions: 4.0 MPa, 150°C, 0.5 % PdS + Al_2O_3 catalyst in the first zone; 380°C, Mo/Ni-Raney catalyst in the second zone, weight hour space velocity 2.0 kg/l·h)

Parameter	Initial mixture of raw benzene and tar fraction with boiling temperature of 180-230°C	Hydrotreated Product
Liquid products yield, % wt.	–	97,5
Gas (C_1-C_4, H_2S, NH_3) yield, % wt.	–	2,5
Water yield, % wt.	–	0,8
Hydrogen flow, % wt.	–	1,0
Characteristic of liquid products:		
Density, ρ^{20}_4	0,9356	0,9296
Chemical composition, % wt.:		
saturated hydrocarbons	0,6	3,2
Benzene	40,5	49,0
thiophen and methylthiophens	0,7	No
Toluene	13,1	13,5
Xylenes	4,0	4,9
Ethylbenzene	0,7	0,9
C_9 aromatic hydrocarbons	3,5	4,0
tetralin + methyltetralins	–	17,2
naphthalene	24,2	10,0
2-methylnaphthalene	2,2	1,0
1-methylnaphthalene	2,0	0,5
Tionaphthen	0,35	No
Phenols	0,9	No
basic nitrogens	0,7	No
Elemental composition, % wt.:		
C	92,06	92,15
H	6,65	7,85
S	0,15	<0,001
N	0,58	<0,003
O	0,56	No

With the purpose of increasing the high-purity benzene and naphthalene yield, and for destruction of saturated carbohydrates that prevent their complete isolation at fractionation, the obtained hydrotreated mixture was exposed to high-temperature hydrogenation (Table 3). 5 % MoO_3 + zeolite HNaY was used as a catalyst, in the presence of which the process proceeds at temperature 475-500°C, instead of 600-650°C for known production catalysts containing chrome compounds. Temperature decrease prevents the formation of carbonaceous deposits on the catalyst surface. The results of high-temperature hydrogenation of hydrotreated raw material are given in table 3.

Table 3 – The results of high-temperature hydrogenation of hydrotreated raw material (conditions: 4.0 MPa, 500°C, weight hour space velocity 1.0-1.2 kg/l·h, catalyst 5 % MoO_3+HNaY)

Parameter	Tetralin concentration in raw material, %	
	17,2	6,5
Liquid products yield, % wt.	95,7	96,6
Gas (C_1-C_4) yield, % wt.	6,3	4,2
Hydrogen flow, % wt.	1,0	0,8
Coke content on the catalyst, % wt.	2,4	3,6
Pure product yield at precise fractionation, % wt.		
Benzene	56,1	51,2
Naphthalene	22,1	23,7
Note. Benzene concentration in raw material 40,5-49,0 %.		

It is seen from table 3 that the yield of hydrogenates for both raw material types is rather close (95.7 and 96.6 %, respectively) but coke settling in the raw material catalyst containing the reduced amount of tetralin (6.5 %) is 1.5 times higher in comparison with raw material containing 17.2 %.

At hydrogenation of raw material with higher tetralin content, slight H-donor destruction is observed and naphthalene yield is decreases by 1.6 %. Although, it is not so significant when taking into account the effect of coke formation reduction on the catalyst. Benzene, isolated from hydrogenate by precise fractionation, has crystallization temperature 5.4°C, density $\rho^{20}{}_4$ = 0.8878, refractive index $n^{20}{}_D$ = 1.5011, sulfur content – less than 0.002 % which conforms to the requirements of standard for high-purity benzene for organic synthesis; naphthalene has crystallization temperature 80°C, sulfur content – less than 0.001 %. For the reason that no full transformation of raw material into benzene, naphthalene and gas per one raw material run occurs, aromatic carbohydrates C_7-C_9 and C_{11} should return to the process into the amount from 30% as recycle benzene and naphthalene after benzene and naphthalene isolation. At this, benzene and naphthalene yield increases by 1.4 and 1.9% for both raw material types, respectively, due to hydrodealkylation and hydrocracking of aromatic carbohydrates.

Thus, it can be said on the basis of the completed studies on studying high-temperature hydrogenation (hydrodealkylation) of the mixture of coal tar pitch distillate fractions and raw coke-chemical benzene that adding the catalyst (0.5 % PdS + Al_2O_3 in the first zone; 380°C, Mo/Ni-Raney catalyst in the second zone) has a positive impact on benzene formation but does not contribute to naphthalene yield.

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Резюме

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ТАС КӨМІР ШАЙЫРЫНЫҢ ДИСТИЛЛЯТТЫ ФРАКЦИЯЛАРЫ МЕН ШИКІ КОКСОХИМИЯЛЫҚ БЕНЗОЛ ҚОСПАСЫН ЖОҒАРЫ ТЕМПЕРАТУРАДА ГИДРОГЕНИЗАЦИЯЛАУ (ГИДРОДЕАЛКИЛДЕУ)

Тас көмір шайырының дистиляты және шикі коксохимиялық бензол қоспасының жоғары температуралық гидрогенизациясын жүргізудің негізгі технологиялық параметрлері жасалды. Су буы қатысында алдын ала тазаланған шайырдың қ.т. 180-230 °С фракциясы мен шикі коксохимиялық бензол қоспасының гидрогенизациялық процесінің қолайлы жағдайлары анықталды. 5 % MoO_3 + цеолит HNaY катализаторы қатысында гидротазаланған қоспасын жоғары температуралық гидрогенизациялап кристаллдану температурасы +5,35-5,45^{0}С, күкірт мөлшері 0,002% болатын тазалығы жоғары бензол алынды.

Түйін сөздер: коксохимиялық шайыр, катализаторлар, бензол, нафталин, гидрогенизация.

Резюме

Ж. К. Каирбеков, А. С. Малолетнев, Н. Т. Смагулова, А. Н. Сабитова, Н. Сатжанов

ВЫСОКОТЕМПЕРАТУРНАЯ ГИДРОГЕНИЗАЦИЯ (ГИДРОДЕАЛКИЛИРОВАНИЕ) СМЕСИ ДИСТИЛЛЯТНЫХ ФРАКЦИЙ КАМЕННОУГОЛЬНОЙ СМОЛЫ И СЫРОГО КОКСОХИМИЧЕСКОГО БЕНЗОЛА

Разработаны основные технологические параметры проведения высокотемпературной гидрогенизации (гидродеалкилирования) смеси дистиллятных фракций каменноугольной смолы и сырого коксохимического бензола. Определены оптимальные условия процесса гидрогенизации предварительно гидроочищенной смеси фракций каменноугольной смолы и сырого коксохимического бензола с т. кип. 180-230 °С в присутствии водяного пара. Путем высокотемпературной гидрогенизации гидроочищенной смеси в присутствии катализатора 5 % MoO_3 + цеолит HNaY получен высокочистый бензол с температурой кристаллизации +5,35-5,45^{0}С, содержанием серы 0,002%.

Ключевые слова: коксохимическая смола, катализаторы, бензол, нафталин, гидрогенизация.

UDK 547.541.3, 547.542.7

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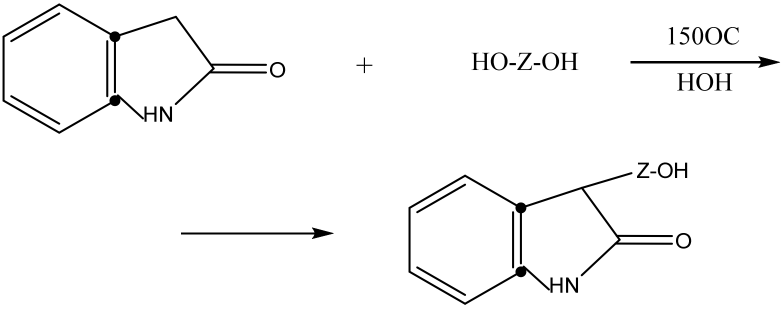
SYNTHESIS OF DIHYDROXYALKYLCYCLOPENTADIENES

Abstract. Alkylation of cyclopentadiene with dihydric alcohols of the C_2-C_4 series in the presence of an alkaline catalyst in a molar ratio of 1 : 2 in good yield have been carried out. The physico-chemical parameters of the synthesized products are determined. The structure of adducts is confirmed by modern physico-chemical methods of analysis.

Key words: alkylation, dihydric alcohols, cyclopentadiene.

It is known that dihydric alcohols can be used as alkylation agents of various classes of organic compounds and the results of similar studies are described in a number of scientific publications [1-14]. These studies describe the use and study of the mechanism of reactions involving alkylating agents used to convert carboxylic acids to esters, phenols to arylphenols, enols to enol esters and thiols to thioethers.

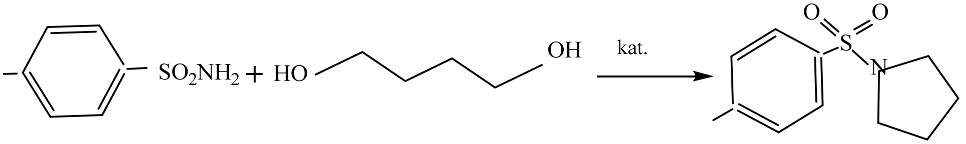
In work [1] a new synthetically convenient method of obtaining compounds interesting from the pharmaceutical point of view, based on alkylation of oxindole with diols, proceeds according to the scheme:

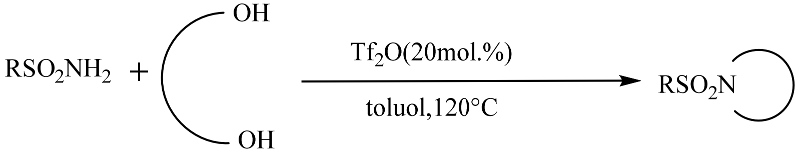


Z = $(CH_2)_7$ (yield 66 %)
Z = $(CH_2)_8$ (yield 72 %)

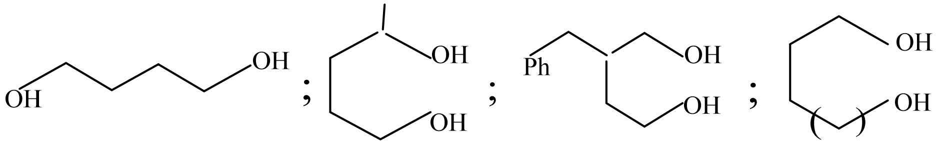
The monoalkylation of aniline and benzylamine with diols has been studied, leading to the formation of important 5-, 6- and 7-membered nitrogen-containing heterocycles used in pharmaceutics [2].

In work [3] it is reported that sulfonamides are mainly used as antibacterial, diuretic, anticolvus and hypoglycemic drugs. In the alkylation of sulfonamides with 1,4-diols in the presence of trifluoromethanesulfonic anhydride, the reaction proceeds in moderate conditions in high yields to form N-sulfonylpyrrolidine derivatives, which are the structural basis of a number of biologically active compounds.





Toluene, xylene, DMF, DMSO for 23-57 hours were used as a solvent. The yield of products was 68-96%. The following diols were used:

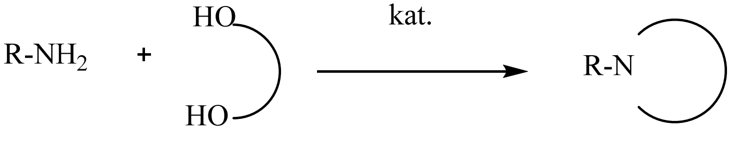


Patent [4] describes a process for the alkylation of ortho-disubstituted phenols with α, ω-alkanediols containing 3 to 8 carbon atoms in the presence of an alkali metal hydroxide or alkoxide at a temperature of 200 to 300°C with the continuous removal of the by-product of water upon its formation.

The selective N-alkylation of primary amines by diols, promoted by an iridium catalyst supported on a metal oxide [5], was carried out.

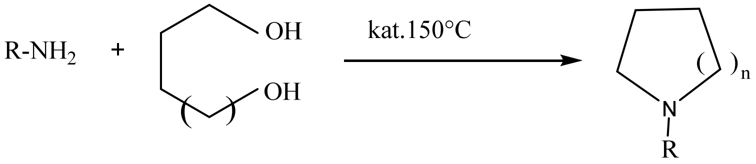
An effective method of N-alkylation of tryptamine and phenethylamine using alcohols and diols as an alkylating agent was proposed [6]. The reaction proceeds through catalytic electron activation involving an iridium catalyst that activates the alcohol by borrowing the hydrogen atom from the substate, returning it later in the catalytic cycle.

N-alkylation of amines and ammonia with monohydric alcohols and diols has been studied with the aim of obtaining new biologically active compounds in the presence of transition metal complexes (Ir, Ru, Cu, Fe, Pd), in the complex part 2.5 mol. % $[Ru\ (p\text{-cymene})\ Cl_2]_2$ [7].



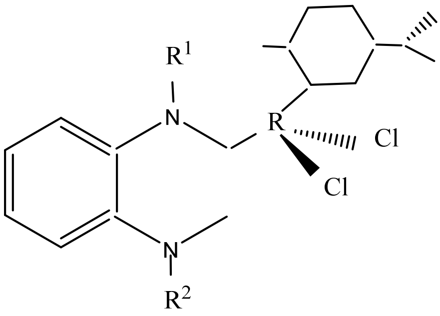
The review [8] presents the reactions of hydrogenation, addition, N-heterocyclization, and also alkylation involving alcohols and diols in the presence of an iridium catalyst that acts as a hydrogen acceptor from the alcohols forming iridium hydride, which is the key intermediate.

The simple ruthenium complexes stable to air and moisture, which are effective catalysts for alkylation of amines with the use of alcohols and diols [9], are synthesized according to the scheme:



n = 1-3 yield= 99 %

catalyst -



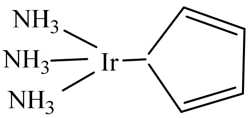
R^1, R^2 – isopropyl, benzyl

The reaction proceeds at a temperature of 130^{0}C for 18 hours in the absence of a solvent. This environmentally friendly method can serve for the synthesis of pharmaceutically important amines.

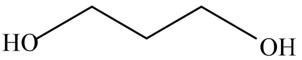
Friedel-Crafts alkylation of simple aromatics (toluene, benzene, o-, m- and p-xylenes) by various diols in the presence of very strong trifluoromethanesulfonic acid was studied [10]. It has been found that 1,2- and 1,3-diols lead to the formation of unexpected products of predominantly monoalkylation. Thus, bis (1-methyl-2-phenyl) propyl ester forms in the reaction with 2,3-butanediol, and 2,4-dimethyl-2,4-pentanediol results in the formation of mono- and di-tert-butyl substituted benzenes. Higher homologues of diols, in turn, undergo electrophilic cycloalkylation with the formation of tetralin derivatives with high selectivity and good yields. By-side primary alkylation processes are monoalkylation to form alkylbenzenes and diphenylalkanes.

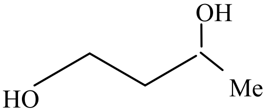
Direct amination of amines by mono- and dihydric alcohols in the presence of complexes of transition metals, in particular Ru, Pd, Ir [11]. However, recently, iron complexes have been used as a catalyst for this purpose. In this paper, monoalkylation of anilines and benzylamines with diols is carried out, leading to the formation of 5-, 6- and 7-membered heterocycles of nitrogen, which are the structural units of a number of pharmaceutical preparations.

New water-soluble iridium complexes were synthesized and used as a catalyst in the multi-alkylation reaction of aqueous solutions of ammonia with alcohols [12]. It was shown that the catalyst exhibits a high activity in this reaction. When 1,5,9-nonantriol was used, quinolizidine was synthesized.



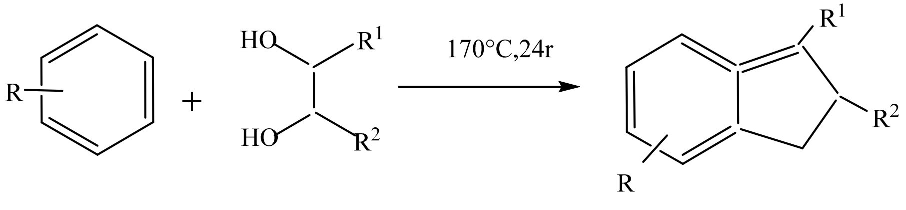
In the work [13] describes the catalytic alkylation of heteroarenes using mono- and dihydric alcohols as soft alkylating agents. The following diols were used:





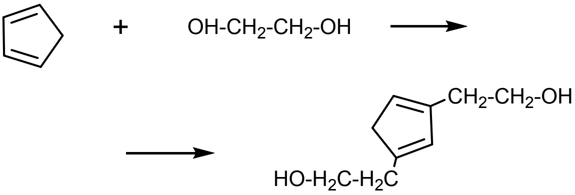
These reactions are the key stages in the synthesis of such drugs as fasudil and mildrinone.

Alkylation of aniline with vicinal diols was carried out in the presence of a catalytic ruthenium complex $RuCl_3$ (PPh_3 or xanthos) [14].



Thus, a review of literary reports shows that dihydric alcohols, as well as their monoatomic representatives, are often used in organic chemistry in alkylation reactions as an alkylating agent.

In this connection, in the continuation of our previous reports [13-16], we carried out the alkylation of cyclopentadiene with dihydric alcohols of the C_2-C_4 series in a molar ratio of 1: 2 according to the scheme:



Experimental part

Physic-chemical parameters of the starting compounds are presented in table 1.

Table 1 – Physicochemical properties of the starting compounds

Compounds	T. melt., ^{0}C	T. boil, ^{0}C	M_r	n_D^{20}	d_4^{20}
Dicyclopentadiene	32,5	172 (destr.)	132	1.5005	0.8280
Cyclopentadiene	- 97	42	66	1.4450	0.8050
Ethanediol-1,2	- 13.2	197.2	62	1.4319	1.1140
Propandiol-1,2	- 60	187.4	76	1.4326	1.0363
Butandiol-1,4	20	235	90	1.4463	1.0170

The IR spectra of the starting and synthesized compounds were taken on a UR-20 spectrophotometer in the 700-4000 cm^{-1} region. NMR^{1}H spectra were recorded on a Bruker WP-400 instrument (400 MHz). Chemical shifts are determined with respect to TMS, solvent C_6D_6.

The synthesis of the desired products was carried out according to the following procedure. A reaction flask equipped with a mechanical stirrer, a dropping funnel, a Dean-Stark nozzle with a condenser and a thermometer was charged with the calculated amount of the corresponding diol and 87% KOH solution. Before heating, a portion of DCPD was added to the reaction mixture. Then, the heating was adjusted to 200°C. After the water starts to collect in the Din-Stark nozzle, the remaining portion of the calculated amount of DCPD is added dropwise within 1.5 hours. After the end of the addition of the DCPD, the reaction mixture was heated for 4 hours. After cooling, the mixture was washed with water, hexane, dried over $MgSO_4$ and distilled under vacuum (p = 25 mm Hg). The corresponding di-n-hydroxyalkylcyclopentadiene was obtained.

Physic-chemical parameters of synthesized di-n-hydroxyalkylcyclopentadienes are presented in table 2.

Table 2 – Physicochemical properties of synthesized dihydroxyalkylcyclopentadienes

Compounds	$T_{boil.}$, °C / mm Hg	M_r	n_D^{20}	d_4^{20}
Di-hydroxyethylcyclopentadiene	148-50/50	154	1,4250	0, 9850
Di-hydroxypropylcyclopentadiene	153-55/50	182	1,4435	0,9875
Di-hydroxybutylcyclopentadiene	165-68/50	210	1,4750	0, 9820

Figures 1–3 show IR-spectra of synthesized di-n-hydroxyalkylcyclopentadienes.

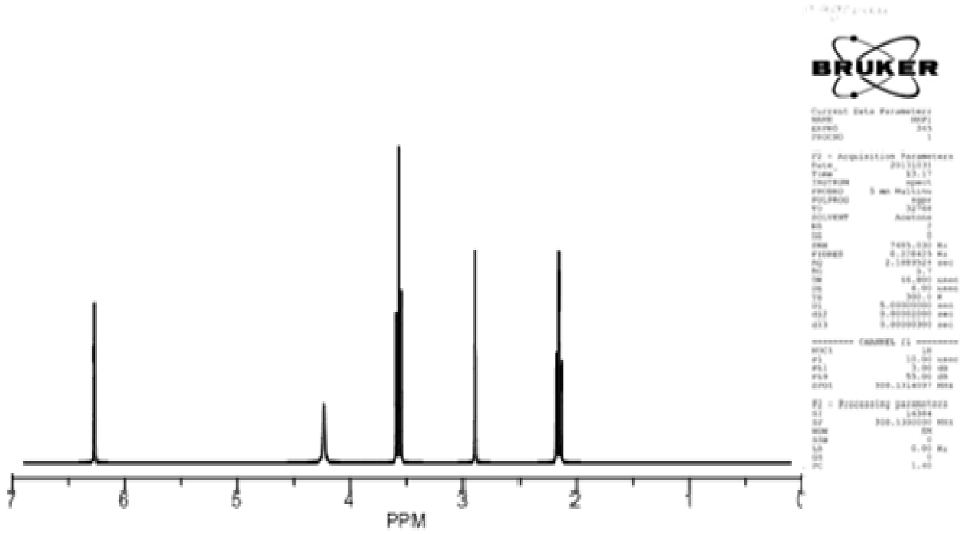


Figure 1 – NMR spectrum of dihydroxyethylcyclopentadiene

In the spectrum, absorption bands characteristic of the CH_2 group in the radical 2.15 (α), 3.55 (β) are observed; CH_2 groups in the 2.90 ppm cycle, as well as for the CH (in the ring) groups, 6.20 ppm. and OH groups 4.20 ppm.

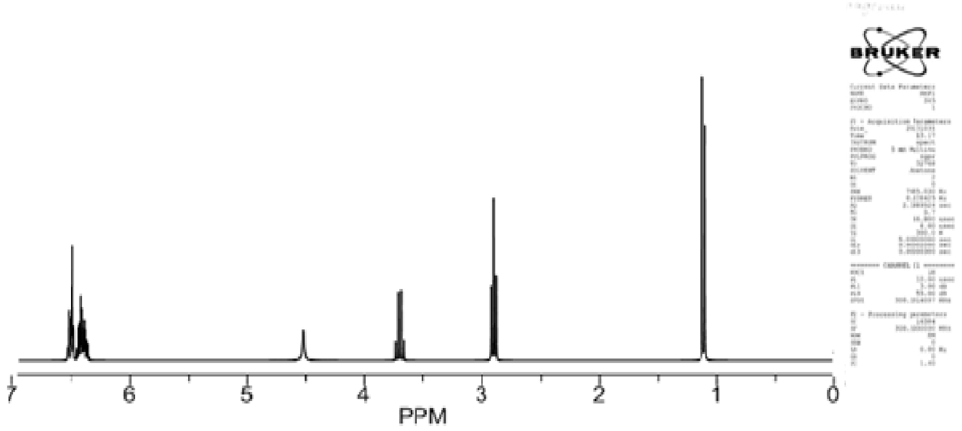
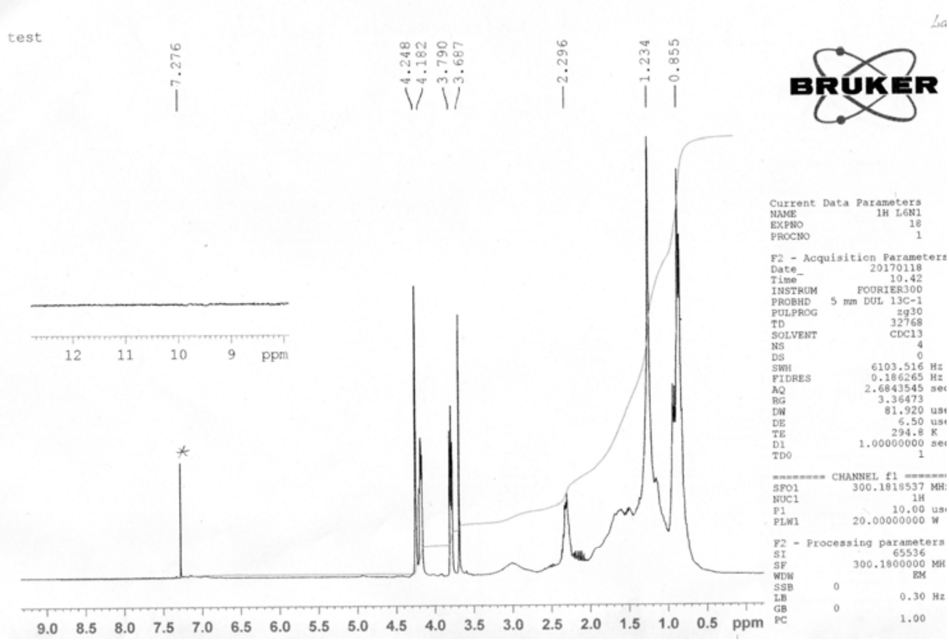


Figure 2 – NMR spectrum of dihydroxypropylcyclopentadiene

In the spectrum, absorption bands characteristic of the CH_2 group in the 2.20 radical are observed, and also for the CH groups (in the cycle), 6.40 ppm, 6.50 ppm. and OH groups of 4.30 ppm.



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PULPROG             zg30
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DS                     0
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FIDRES          0.186265 Hz
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RG               3.36473
DW                81.920 us
DE                  6.50 us
TE                 294.8 K
D1            1.00000000 se
TD0                    1

======== CHANNEL f1 ======
SFO1         300.1818537 MH
NUC1                  1H
P1                 10.00 us
PLW1         20.00000000 W

F2 - Processing parameters
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SF           300.1800000 MH
WDW                   EM
SSB       0
LB                  0.30 Hz
GB        0
PC                  1.00
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Figure 3 – NMR spectrum of dihydroxybutylcyclopentadiene

In the spectrum, absorption bands characteristic of the CH_2 group in the radical 2,15 (α) are observed; 1,30(β); 1,52(γ); 3,45(δ); 1,85(α); 1, 39(β); 1,56(γ); 3,60(δ), and also for the CH_2 groups (in the cycle) 2.90 ppm, the CH groups (in the cycle) 6.25 ppm, and the OH groups 4.20 and 4.70 ppm.

The compounds obtained are synthones for the synthesis of the corresponding di-n-hydroxyalkylcyclopentanes, which can be obtained by hydrogenating the di-n-hydroxyalkylcyclopentadienes synthesized in this paper and used as additives to synthetic oils.

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Резюме

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ДИГИДРОКСИАЛКИЛЦИКЛОПЕНТАДИЕНДЕРДІ СИНТЕЗДЕУ

1:2 мольдік қатынасында сілтілік катализатордың қатысуымен C_2-C_4 қатарының екіатомды спиртімен циклопентадиенді алкилдеу жүзеге асырылды. Синтезделген өнімдердің физика-химиялық көрсеткіштері анықталды. Аддуктердің құрылымы заманауи физика-химиялық талдау әдістерімен анықталған.

Түйін сөздер: алкилдеу, екіатомды спирттер, циклопентадиен.

Резюме

А. Г. Гасанов, А. М. Мамедова, И. Г. Аюбов, С. Т. Алиева, И. М. Мамедова

СИНТЕЗ ДИГИДРОКСИАЛКИЛЦИКЛОПЕНТАДИЕНОВ

Осуществлено алкилирование циклопентадиена двухатомными спиртами ряда C_2-C_4 в присутствии щелочного катализатора в мольном соотношении 1:2 с хорошим выходом. Определены физико-химические показатели синтезированных продуктов. Строение аддуктов подтверждено современными физико-химическими методами анализа.

Ключевые слова: алкилирование, двухатомные спирты, циклопентадиен.

UDC 628.165

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SEMIPERMEABLE MEMBRANES FOR MEMBRANE TECHNOLOGIES

Abstract. The review shows membrane technologies based on the principle of baromembrane processes (microfiltration, ultrafiltration, nanofiltration, reverse osmosis are considered and are increasingly used in industrial use and household purposes). Their main feature is the presence of a semipermeable membrane based on ceramics, polymers or nanocarbon materials with selective permeability for certain components of the separated mixture (charged metal cations, molecules of organic substances, bacteria, viruses).

Keywords: membrane technology, microfiltration, ultrafiltration, nanofiltration, reverse osmosis.

Ion exchange membranes play a leading part in an electrodialyzer, and the performance of an electrodialyzer strongly depend on the characteristics of ion exchange membranes. In order to operate an electrodialyzer effectively, it is necessary to understand the membrane characteristics definitely [1].

The separation of substances by membranes is essential in industry and human life. Of the various separation membranes, the ion exchange membrane is one of the most advanced and is widely used in various industrial fields: electrodialysis, diffusion dialysis, separator and solid polymer electrolyte in electrolysis, separator and solid polymer electrolyte of various batteries, sensing materials, medical use, a part of analytical chemistry, etc. The ion exchange membrane originated from two different sources: the finding of ion exchange phenomena in soil and in explaining biological phenomena in cell membranes. The ion exchange phenomenon was found by the English agriculturist, H.P. Thompson and the chemist J.T. Way in 1850, who noted the adsorption of ammonium sulfate on soil as follows,

$$\text{Ca-Soil} + (NH_4)_2SO_4 = 2NH_4\text{-Soil} + CaS0_4$$

Their finding led to the synthesis of inorganic ion exchangers (aluminosilicate corn pounds). Subsequently, the English chemists, B.A. Adams and E.L. Holmes synthesized organic cation and anion exchange resins by the condensation reaction of phenolic compounds having ionic groups and formaldehyde. D’Alelio developed polymerization type ion exchange resins and laid the basis of today's ion exchange resins [2].

Membrane systems excel because they are precisely tailored to the specific requirements of the finished product. To date, we have developed four primary membrane technologies spanning a range of pore sizes that suit numerous applications, from removing salt to filtering large particulates in viscous fluids. Reverse osmosis offers the finest degree of separation, followed by nanofiltration, ultrafiltration, and microfiltration, which has the largest pore size. Membrane technologies can also be used in combination, such as ultrafiltration followed by reverse osmosis for seawater desalination processes. Food, beverage, and general industrial processes utilize membrane pore size and charge to selectively reject macromolecules and ionic species [3].

Figure 1 shows membrane technologies that operate on the principle of baromembrane processes: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RS).

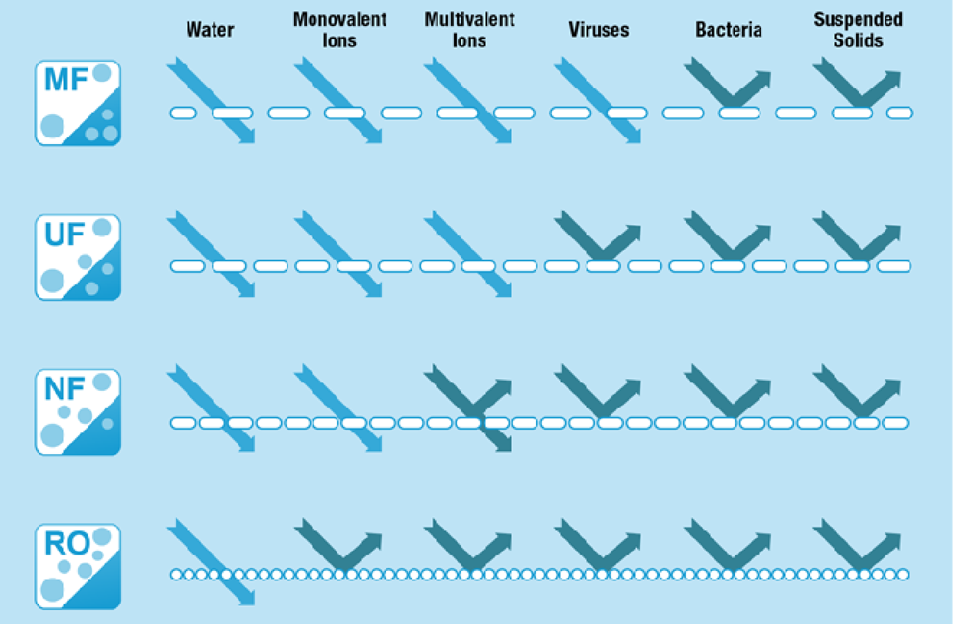

Figure 1 – Comparison of Membrane Technologies

Microfiltration membranes. MF has significant applications in simple dead-end filtration for water, sterile fruit juices and wine, and aseptic pharmaceuticals. However, not all applications that benefit from MF operate successfully in the dead-end mode, and a large portion of the MF market has been captured by crossflow.

The most common of these is the clarification of whole cell broths and purification processes in which macromolecules must be separated from other large molecules, proteins, or cell debris. Clarification of dextrose and highly-colored fruit juices employ MF extremely well. There are also large markets for MF crossflow filtration in wine production, milk and whey de-fatting, and brewing. As with ultrafiltration, MF systems operate at relatively low pressures and come in a variety of configurations [3].

MF membranes with pore sizes of 0.1–10 μm are used extensively for removing contaminants from mixed feed solutions and can isolate a targeted product from such solutions [3, 4]. Commercial MF membranes made from various thermoplastic polymers such as polysulfone, polyethersulfone, poly(vinylidene difluoride) (PVDF), and polyacrylonitrile are used extensively for aqueous feed streams. However, because of membrane solubility in organic solvents, their application for solvent-phase separation is somewhat limited. Postcrosslinking these membranes with suitable chemical agents might prevent the membranes from dissolving in organic solvents [5]. Another concern is that the postcrosslinked membranes can become highly swollen in solvents, and this can result in them losing their separation function and performance. Therefore, organic solvent–resistant MF membranes are desired for specific applications such as solvent-phase filtration, oil–water separation, and porous support of composite membranes [6]; however, recent studies have focused on organic solvent nanofiltration.

For harsh separation conditions such as high polar solvents and high temperatures, filtration membranes made of polytetrafluoroethylene (PTFE) and polyimide (PI) fabric woven are commercially available. Because of their mechanical strength and thermal stability, organosoluble PIs may be the most studied polymers for organic solvent nanofiltration [7]. Organosoluble PI–based membranes are generally prepared through phase inversion processes. However, these membranes remain unsuitable for filtration with feed solution of high polar aprotic solvents. In one study, PI-based membranes were postcrosslinked to enhance their stability in filtration operations. By contrast, conventional aromatic PI-based dense films, which are insoluble in organic solvents, are obtained by casting a poly(amic acid) (PAAc) solution into PAAc films and subsequently converting the films into corresponding PI films through thermal imidization. However, fabricating PI-based porous membranes through a nonsolvent phase separation process is impossible with a PAAc precursor because of the strong interaction between PAAc and water (the nonsolvent). To address this problem, Kang et al. [3, 8] attempted to reduce the interaction between PAAc and water through partial imidization of the PAAc precursor, and successfully prepared asymmetric PI membranes. In another such attempt, Chun et al. [8] added PAAc solvent (N,N-dimethylacetamide [DMAc]) into a coagulation solution to delay the demixing phase inversion. As not many successive works have been reported on preparation of solvent-resistant PI-based porous membranes, porous membranes made of thermosetting resins have been reported [9]. However, applying these membranes to filtration is rare because of the inconvenience of fabrication and unsatisfactory membrane properties.

As an alternative to postcrosslinking thermoplastic polymer–based membranes during fabrication processes, crosslinked membranes made of organosoluble self-crosslinkable polymers are relatively attractive because they can be fabricated through the conventional process. In the present study, a linear polybenzoxazine (PBz; figure 2) [10] was utilized because of its self-crosslinking ability, low cost, and processing property. Moreover, crosslinked PBz exhibits some attractive properties for membrane separation, including low-surface free energy [11], excellent solvent resistance, and high thermal stability. Crosslinked PBz–based dense membranes for pervaporation and electrospun nanofiber mats for oil–water separation and separators for lithium-ion batteries have been reported. In the present study, porous membranes of linear PBz were obtained through a conventional vapor-induced phase separation (VIPS) process and subsequently in situ thermally crosslinked through a simple thermal process (Fig. 2). Additionally, applications of the crosslinked PBz–based membranes for size-selective particle separation in organic solvents and for separating surfactant-stabilized oil–water emulsion were examined [12].

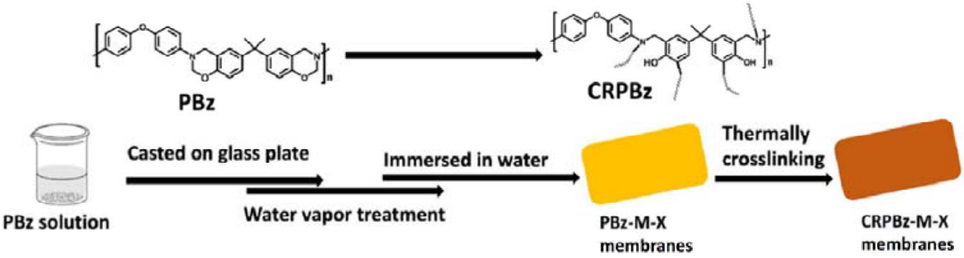

Figure 2 – Fabrication of cross-linked PBz based membranes

Ultrafiltration membranes. UF is a pressure-driven process that removes emulsified oils, metal hydroxides, colloids, emulsions, dispersed material, suspended solids, and other large molecular weight materials from water and other solutions. UF membranes are characterized by their molecular weight cut-off.

UF excels at the clarification of solutions containing suspended solids, bacteria, and high concentrations of macromolecules, including oil and water, fruit juice, milk and whey, electrocoat paints, pharmaceuticals, poly-vinyl alcohol and indigo, potable water, and tertiary wastewater [13].

In recent decades, UF has been extensively used in drinking water treatment. Compared to conventional treatment, UF provides treated water with better quality. Complete removal of pathogens and particulate impurities can be achieved with an UF membrane, which significantly improves the biological security of drinking water. However, although the UF process is recognized as an advanced technology for producing high-quality drinking water, membrane fouling, which leads to reduced membrane productivity and increased energy consumption, remains as an obstacle in the long-term operation of UF, particularly in full-scale waterworks [14].

Natural organic matter (NOM) in surface water, mainly composed of humic acids (HA), polysaccharides, proteins and lipids, has been identified as the most problematic membrane foulant and causes severe membrane fouling, particularly irreversible fouling. Therefore, a variety of pretreatments are adopted prior to membrane filtration to retard membrane fouling. Organic foulants can be removed or transformed to a certain extent with pretreatment, and UF membrane fouling is alleviated to some degree. Widely investigated pretreatments include coagulation, adsorption, bio-filtration and peroxidation. Coagulation is generally considered one of the most successful pretreatments for fouling control, because it can effectively remove the high molecular weight (MW) fraction in NOM, which is primarily responsible for irreversible membrane fouling. However, coagulation is ineffective in the removal of low-MW and hydrophilic fractions in NOM, which may also contribute to membrane pore blocking [15].

Adsorption pretreatment with powdered activated carbon (PAC) or ion exchange resins can eliminate low-MW organics and improve feed water quality, but the high demand for adsorbents 66 may offset the limited benefits associated with fouling mitigation obtained by adsorption. Moreover, the presence of absorbents sometimes aggravates rather than mitigates membrane fouling. For example, investigated a hybrid PAC-UF process for surface water treatment and found that PAC and HA formed a combined fouling layer on the membrane surface, resulting in a significant synergistic fouling effect [16]. In general, both coagulation and adsorption pretreatment only succeed in transferring NOM fractions from feed water to the solid phase, and further treatment/disposal of the solid waste is still required. Although coagulation remains the most popular method for minimizing membrane fouling, pre-oxidation attracts greater interests in recent years due to its capacity in removing NOM, particularly in the occurrence of emerging organic contaminants. Among the investigated oxidation methods, ozonation has been most intensively investigated. However, residual ozone in feed water may be detrimental to the membrane material, resulting in accelerated membrane aging [17].

In recent years, an advanced oxidation process (AOP) using activated peroxymonosulfate (PMS) or persulfate (PS) has attracted much attention for the degradation of micro pollutants such as pharmaceutical organic compounds, algal toxins and odor compounds [18, 19]. Sulfate radicals (SO_4^-), produced via activating PMS or PS with UV and reducing ions, have very high oxidation capacity (E_0=2.65-3.1 V) and can degrade both NOM and micro pollutants [20]. Hence, it is reasonable to assume that oxidation pretreatment with activated PMS or PS would contribute to NOM fouling control during surface water treatment using low-pressure membrane filtration. To our knowledge, there are only two reports involving the control of membrane fouling by model foulants and NOM with PMS pre-oxidation activated by ferrous ions (Fe (II)). Fe (II)/PMS pretreatment (15μM) was demonstrated to effectively alleviate fouling caused by humic acids and alginate, but fouling caused by bovine serum albumin was aggravated except when applied at an increased PMS dose (50 μM) was applied [21]. For surface water, NOM was effectively removed via dual mechanisms, i.e., pre-oxidation with sulfate radicals and coagulation with in situ formed Fe (III), resulting in substantial reductions in organic compounds, particularly for macromolecular fractions, and thus increased membrane permeability and fouling reversibility [13, 21]. Despite great performance in fouling control, the Fe (II)/PMS pretreatment may increase sludge due to precipitation of ferric flocs, particularly for practical applications. To address this issue, an ultraviolet-activated persulfate (UV/PS) process is alternatively put forward for UF membrane fouling control in this work. UV irradiation, which is widely applied in disinfection for both drinking water and wastewater effluent, is a relatively cleaner activation method for the generation of sulfate radicals compared to Fe (II). In addition, the UV/PS process proves to be effective in degrading a variety of emerging organic compounds such as sulfamethoxazole, methyl paraben, haloacetonitriles. In terms of fouling control performance and the mechanisms involved, the UV/PS pretreatment has not yet been systematically investigated [22].

The objective of study [13] was to evaluate the performance of a combined process of UV/PS and UF for surface water treatment. To gain insight into the effects of UV/PS pretreatment on membrane fouling, the amounts and characteristics of NOM before and after pretreatment were systematically compared using fluorescence spectra, MW distribution and hydrophobicity/hydrophilicity. Moreover, filtration tests were performed using a continuous-flow immersed UF system, which could better simulate practical applications. The fouled membranes were further analyzed with scanning electron microscopy (SEM) and attenuated total reflection-Fourier transform infrared spectroscopy (FTIR) to gain more insight into mechanisms for NOM fouling control via UV/PS pretreatment.

In this study, the effects of UV/PS oxidation on UF membrane fouling by NOM in surface water were investigated. The following conclusions can be drawn:

1. NOM in surface water was substantially degraded by UV/PS pretreatment with UV254 and DOC decreases of 97% and 58%, respectively, within 120 min at a PS dose of 0.6 mM. UV-adsorbing fractions in NOM were preferentially degraded.
2. A four-component model described the fluorescent EEM spectra of NOM well and the dominance of C3 over other components was verified in terms of fluorescent intensity. UV/PS pretreatment was most effective in removing tryptophan-like proteins, followed by microbially derived humic-like substances.
3. UV/PS pretreatment significantly retarded irreversible UF membrane fouling (~75%) caused by NOM. The performance of fouling control considerably improved at increased PS doses and extended UV irradiation times.
4. Mechanisms for NOM fouling control using UV/PS pretreatment include the preferential removal of hydrophobic fractions and degradation of medium-MW and high-MW compounds into hydrophilic small molecules, which were significantly smaller than the membrane pores.

A combined UV/PS system, in which PS was activated by UV irradiation to generate reactive radicals such as $SO_4\cdot^-$ and $HO\cdot$ via Eq. (1) – Eq. (3), was employed to pretreat the river water [22, 23]. Figure 3 (a) shows a schematic diagram of the oxidation reactor. The oxidation reactor consisted of a cylindrical reactor coated with silver paper, a low pressure mercury UV lamp with a quartz tube pro-viding principal light emission at 254 nm, a peristaltic pump to maintain solution circulation, and a thermostatic water-bath to stabilize water temperature at 20 ± 1 ºC. The height and inner diameter of the reactor were 28 and 9 cm, respectively. The UV lamp, which was placed in the centerline of the cylindrical reactor axially along the length of the reactor, was immersed into feed water to

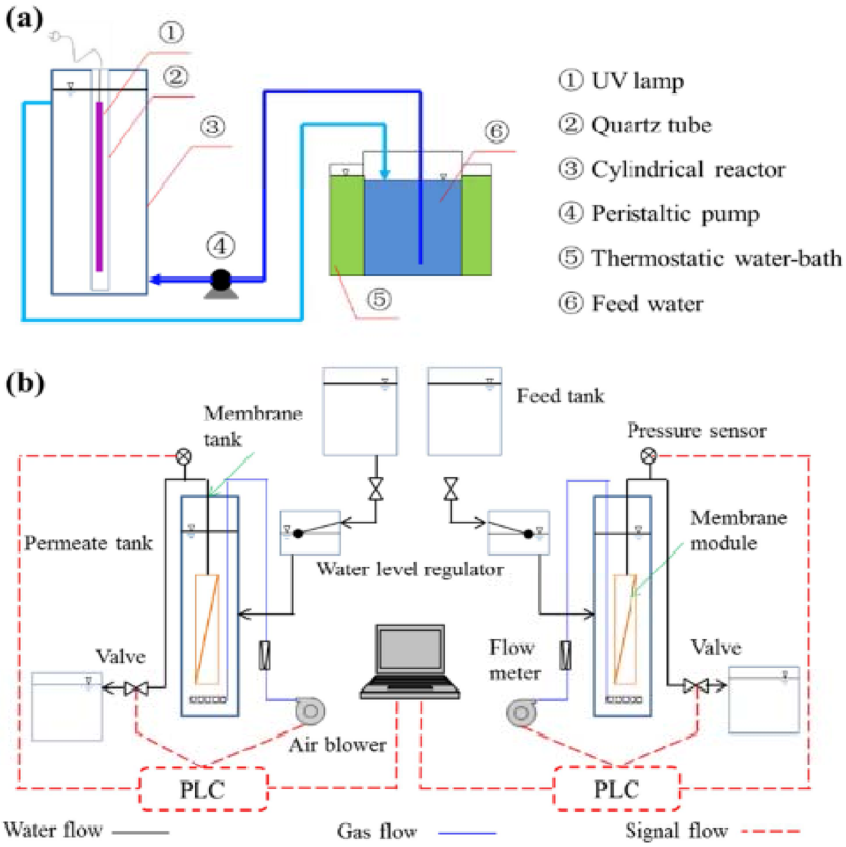

Figure 3 – Schematic diagrams of the oxidation reactor and immersed UF system

enhance penetration of UV light. The incident light intensity of the UV lamp was determined 0.44 μE L^{-1} s^{-1} as by iodide-iodate chemical actinometry. The average fluency rate was estimated to be 1.54 $mWcm^{-2}$ using an integrated form of the Beer-Lambert law. The lamps were warmed up for 15 min prior to reaction to ensure a stable output. In this work, PS was applied at the doses of 0, 0.05, 0.1, 0.2, 0.4, and 0.6 mM. The UV irradiation time was investigated within a range of 0–120 min, corresponding to a UV fluency range of 0-1.1×105 mJ cm^{-2}. To quench the residual oxidants, $Na_2S_2O_3$ were added into samples immediately after sampling at the stoichiometric doses of PS applied. The terminator dose was equivalent to the concentration of added PS according to the stoichiometric criteria.

$$S_2O_8{}^{2-} \xrightarrow{UV} 2SO_4^{\cdot-} \quad \emptyset = 1.4 \tag{1}$$

$$SO_4^{\cdot-} + \mathrm{OH}^- \rightarrow \mathrm{SO}_4^{2-} + \mathrm{HO}^{\cdot} \quad k = 6.5 \times 10^7\ M^{-1}s^{-1} \tag{2}$$

$$SO_4^{\cdot-} + H_2O \rightarrow \mathrm{HSO}_4^{2-} + \mathrm{HO}^{\cdot} \quad k = 8.3\ M^{-1}s^{-1} \tag{3}$$

An immersed UF experimental system was described in detail in our previous work. The system was comprised of a membrane tank, a high-level tank, a peristaltic pump, a pressure transducer, a programmable logic controller and a personal computer (figure 1 (b)). Tiny membrane modules with an effective membrane area of 21.7 cm^2 were fabricated in the lab. Before use, the membrane module was thoroughly cleaned with deionized water to remove organic residue on the membrane surface. The multi-cycle UF experiments were performed under a constant permeate flux 35 Lm^{-2} h^{-1}. Each UF cycle consisted of min filtration and 1 min backwashing at 70 Lm^{-2} h^{-1} with the permeate water. The trans-membrane pressure (TMP) was automatically logged by an online pressure transducer. Fouling resistances were calculated by equation. The raw water and pretreated water were stored in feed tanks and continuously fed into the UF systems. Filtration tests were performed in triplicate.

Nanofiltration membranes. NF functions similarly to reverse osmosis, but is generally targeted to remove only divalent and larger ions. Monovalent ions such as sodium and chloride will pass through a nanofiltration membrane, therefore many of its uses involve de-salting of the process stream (figure 4).

In the production of lactose from cheese whey, for example, NF concentrates lactose molecules while passing salts, a procedure that purifies and concentrates the lactose stream. In water treatment, NF membranes are used for hardness removal (in place of water softeners), pesticide elimination, and color reduction. It can also be used to reclaim spent NaOH solutions, in which case the permeate stream is purified NaOH, allowing reuse many times over.

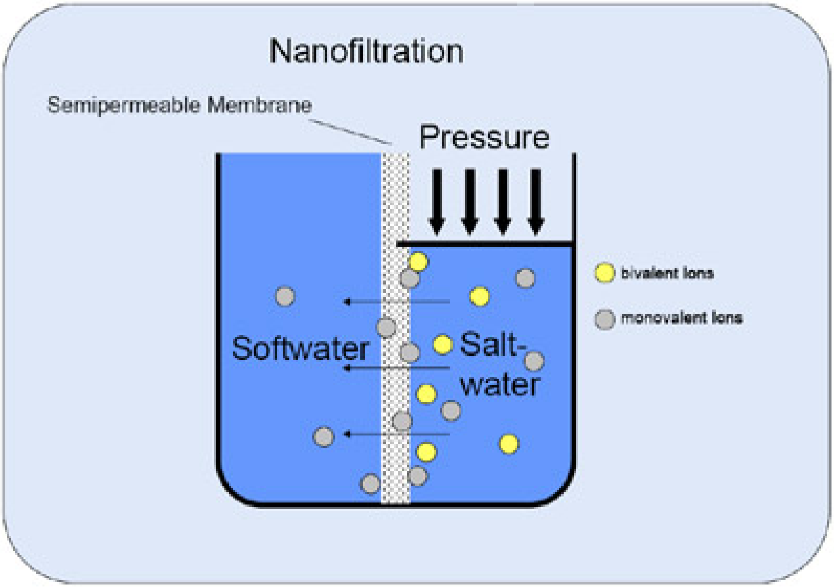

Figure 4 – NF system

High water permeability and rejection of solutes are features which make NF membranes economically viable in water softening applications, attractive for water purification and removal of harmful organic solutes from water [24]. However, theirs in general hydrophobic selective layer facilitates adsorption and the transport of organic solutes [25], which often results with inadequate removal of, for example pesticides, pharmaceuticals and endocrine disrupting compounds, and limits their practical use [26]. Rejections of non-hydrophobic or ionized organics are generally higher than those of non-ionized hydrophobic solutes due to much lesser solute affinity toward membrane, or charge repulsion through NF membranes. The latter was confirmed in a recent study of authors [27] on the RO (SWC1) membrane, where it was shown that non-ionized phenolic solutes enter the selective layer, and freely partition inside by an order of ten, even if solute radius is close to the radius of the pore. Moreover, it was shown that sorption of organics in the selective layer is unfavourable because it changes membrane characteristics in terms of both salts and water permeability.

Authors [28] correlated membrane surface hydrophilicity with membrane fouling and it can be assumed that rejection of at least some of organics could be improved by rendering the membrane surface more hydrophilic. Furthermore, authors [29] found that RO membranes, declared as low fouling, are resistant to fouling in terms of specific flux decrease over time. It is widely accepted today that commercial brackish water RO membranes declared as low fouling, such as BW30 and LFC, have increased oxygen content and are probably coated [30]. Our past study also found [31] that LFC membrane was more resistant to fouling in terms of irreversible pesticide adsorption and flux decrease compared to other membranes.

Many studies focused on surface modification of membranes [32, 33] while the general benefits of modifications are permanently reduced membrane fouling [34] and increased rejection of proteins or organic solutes and salts. But, according to authors' knowledge very few were focused on a mechanism which could explain why membranes became better rejecting to some organic solutes while rejections of some solutes remain the same or even decrease. This study aimed at proposing a plausible way to study such mechanism. Commercial thin film NF membrane, NF270, was coated with a thick layer of polyvinyl alcohol (PVA) and the rejections of various organic solutes of different sizes and physicochemical properties were studied before and after the addition of PVA layer. Pesticides, bentazone and tebuconazole, were used in this study as model compounds which represent an entire class of high affinity, non-ionized and hydrophobic compounds such as bisphenol A and hormones.

NF performance as a function of feed temperature is relevant to several industrial settings including pretreatment for scale control in thermal desalination. Understanding of solute transport as a function of temperature is critical for effective membrane and system design. In wotk study, nanofiltration is modeled at 22, 40 and 50 °C using the Donnan Steric Pore Model with dielectric exclusion (DSPM-DE). This modeling includes the temperature dependence of the three modes of solute transport, namely the convective, electromigrative, and diffusive modes, and the three mechanisms of solute exclusion, namely Donnan, steric, and dielectric exclusion. The effect of temperature is captured through the variation of membrane parameters and solvent and ionic mobilities with temperature. Authors compare the most abundant ionic compound in natural water, sodium-chloride with magnesium-chloride to portray how the salt passage and rejection change for a 1:1 salt compared to a 2:1 salt, and analyze Arabian Gulf seawater to understand how rejection of scale-forming ions, such as Mg^{2+} and Ca^{2+}, is affected by feed temperature. In all cases, solute transport increases with temperature, attributed predominantly to the cumulative effect of membrane parameters and only to a small extent (up to 5%) to the solvent viscosity and ion diffusivity together [35].

In work [36], polysulfone (PSf) substrates with different properties were made by varying the polymer concentration in the dope solution in the range 12–20 wt.%. Polyamide (PA) thin layers were then formed via interfacial polymerization between piperazine and trimethylchloride over the PSf substrates. Both top PA thin layers and bottom PSf substrates were characterized with respect to physicochemical properties, structural morphology, and water flux/salt rejection to investigate the influence of substrate properties on the characteristics of PA thin layers. Physical properties of the PA layers were reported to be altered using different PSf substrate properties and were in good agreement with the change in water flux. From the FESEM pictures, it is found that the thickness of PA layer increased as the surface pore size of support membrane decreased. The change in the membrane structural properties in particular pore size is found to portray significant contribution to the changes of formed PA layer. Interestingly, only slight changes on Na_2SO_4 and $MgSO_4$ salt rejection were reported on any TFC membranes. Considering both water permeability and salt rejection rate, the best performing TFC membrane produced in this work was the membrane made over substrate of 15 wt.% PSf concentration.

Reverse osmosis membranes. RO membranes feature the smallest pores and involve, appropriately enough, the reversal of osmotic pressure in order to drive water away from dissolved molecules. Strictly speaking, RO is not a size exclusion process based on pore size; it depends on ionic diffusion to affect separation. One of its common applications is seawater desalination, in which pure water is produced from a highly saline feed stream, similar to evaporation with far better economy (figure 5).

RO is also used in cheese whey concentration, fruit juice concentration, ice making, car wash reclamation, wastewater volume reduction, and other industrial processes, with the goal of producing a pure filtrate (typically water) or retaining the components. Because the osmotic pressure of many process streams is quite high, RO membranes must operate at pressures of 400-1,200 psi (29-83 bars), which restricts available membrane geometries.

Desalination, especially the RO membrane technology, has been recognized as an effective purification technology to supply potable water from seawater and wastewater. Compared with the thermal technology desalination, the RO techno-

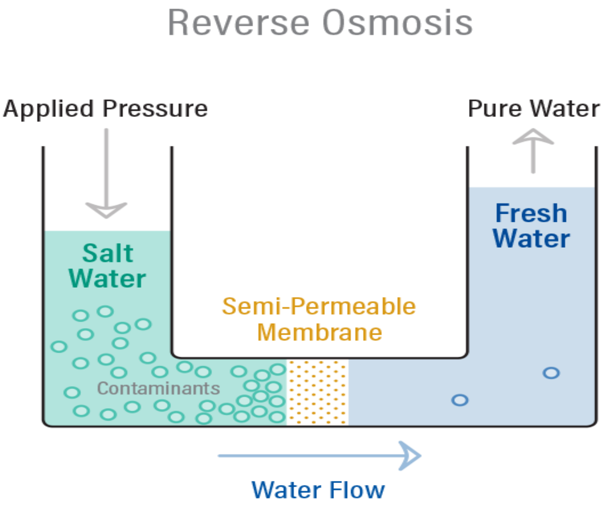

Figure 5 – Schematic diagram of a typical RO system

logy requires less energy input. However, the RO technology is still a high-energy consumption industry. High-pressure pumps are applied to feed the seawater through the RO membrane module at a high pressure, ranging from 6 to 8 MPa. This causes a large amount of consumption in electricity cost, 40% in the overall operating cost [37]. Thus, the energy recovery device (ERD) has been proposed to recover the high-pressure energy from the brine reject stream and deliver the high-pressure energy back to the seawater stream. These devices can significantly decrease the electricity consumption and improve the RO system efficiency. Based on their working principle, ERDs can be categorized as the turbine-type device and the isobaric device [38, 39]. Due to applying positive displacement principle [40], the isobaric ERD can achieve higher energy recovery efficiency than the turbine-type ERD [41–43]. The rotary-type ERD (RERD) and the piston-type ERD are two types of isobaric ERDs nowadays [44, 45]. Figure 6 shows a typical RO system equipped with a RERD [46].

During the energy recovery process of the ERED, the seawater stream is pressurized directly by the brine reject stream in a rotor duct [40]. Because there is no physical piston between the seawater stream and the brine reject stream in the rotor duct, the RERD can achieve a highest energy recovery efficiency. The PX Pressure Exchanger device is one of the typical commercial product of the RERD, which can achieve an energy recovery efficiency of up to 98% [47]. However, for lack of the physical piston, the seawater stream will directly contact with the brine reject stream, resulting in a formation of a mixing zone between the two streams. The mixing zone increases the salinity of the seawater stream which would be supplied into the RO membrane module, leading to higher electricity consumption of high-pressure pumps in the RO system [46]. Therefore, much research has been carried out on the effect of flow dynamics on the mixing

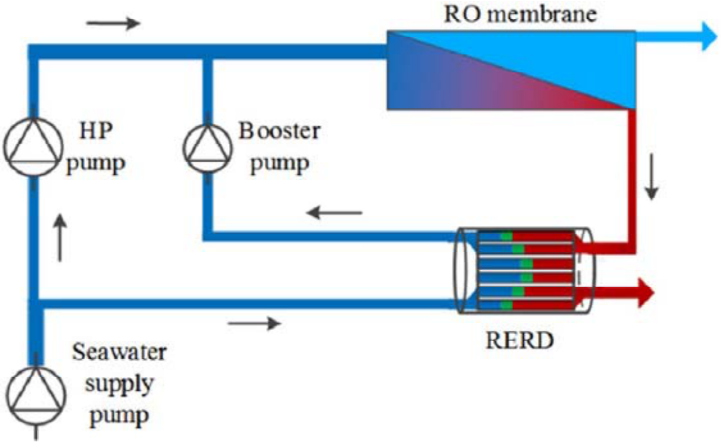

Figure 6 – Schematic of RO system with RERD

process. Mei et al. [48] performed a theoretical research on the efficiency of a RERD. They found that the longitudinal diffusivity affected the mixing rate in the duct under the laminar flow condition. Cao et al. [49] numerically explored the mixing performance and the flow pattern. They pointed out that the mixing rate could be controlled at a low value when the flow pattern in the duct was closed to a plug flow. In work [50] authors performed a 2D simulation to investigate the flow characteristic in the duct. The simulation results showed that the rotor speed and the working condition could affect the formation and movement of the mixing zone. They suggested that the characteristic of the mixing zone should regard as a key factor on the performance of a RERD to guarantee the salinity of the seawater stream. Xu et al. [51] researched the mixing process in the duct with a 3D simulation. The flow structure showed a liquid piston formed between the seawater stream and the brine reject stream. The liquid piston prevented these two streams over mixing with each other. From the aforementioned discussion, it is reasonable to conclude that the flow structure and the formation of the mixing zone have a direct influence on the mixing process. However, due to the high-speed rotation of the duct, none of the foregoing literature has investigated the flow structure or the formation of mixing zone with experimental methods, such as the particle image velocimetry (PIV) measurement.

The purpose of the experiment reported here was to research the detailed flow characteristics in the duct. A visualization apparatus of a RERD (hereinafter abbreviated as V-RERD) was proposed to measure flow structures in the duct by a two-dimensional (2-D) PIV measurement. For easy measurements, this visualization apparatus was set with a single stationary duct and two rotary endcovers in this experiment. The experiment results may be beneficial to better understanding flow dynamics and the mixing zone formation during the working process.

In work [52], a visualization apparatus of a RERD with a stationary duct and two rotary endcovers, employing the same working principle as the typical rotary-type ERD, was proposed to visualize the flow structure in the duct. A 2-D PIV measurement was performed to directly measure flow characteristics.

According to experiment results, an "entrance effect" can be observed in the duct, resulted from the relative rotation of the endcover and the duct. It caused the formation of unstable flows with three-dimensional structures at the duct entrance. In addition, it led to a higher turbulence intensity level in the vertical plane than that in the horizontal plane. The liquid piston, a stable flow region with almost uniform velocity magnitude and low turbulence intensity, can be clearly identified in the middle section of the duct, effectively preventing the mass transfer between the seawater stream and the brine stream. From instantaneous flow fields, the vortex evolution was captured at the duct entrance and the duct exit. Due to the repeating sequence of the vortex formation, expansion and motion in the working cycle, the turbulence intensity increased significantly, which may result in an increase in the mixing degree between the two streams and eventually degrade the RERD performance. These experimental results can be used to validate numerical predictions as well as for designing purposes. In the future, more experimental research needs to be carried out to clarify the fundamental mechanism of the pressure recovery and mass transfer.

Ion exchange membranes emerging as renewable materials play prominent roles in promoting the development of traditional industry and innovative energy technologies. To date, most of the attention has been focused on exploring promising materials, developing diverse preparation methods, and expanding a wide variety of applications related to ion exchange membranes. Over the past ten years, such field has significantly bloomed and a large number of achievements have been gained. To date, there are a tremendous number of ionic polymer candidates available for the preparation of various kinds of ion exchange membranes, including cation exchange membranes, anion exchange membranes, monovalent ion perm-selective membranes, mixed matrix membranes, and bipolar membranes. Although progresses in exploring new ion exchange membranes are prominent, there are still a few challenges, which need to be urgently addressed. For example, the chemical stability of the membranes should be promoted furthermore to ensure the longevity of their lifetime in various applications.

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Резюме

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МЕМБРАНАЛЫҚ ТЕХНОЛОГИЯЛАРҒА АРНАЛҒАН ЖАРТЫЛАЙ ӨТКІЗГІШТІ МЕМБРАНАЛАР

Шолу мақаласында баромембраналық үдерістер (микрофильтрация, ультрафильтрация, нанофильтрация, кері осмос) қағидаттарына негізделген және өнеркәсіптік пайдалануда және тұрмыстық мақсаттарда жиі пайдаланылатын мембраналық технологиялар қарастырылған. Полимерлер, керамика немесе нанокөміртекті материалдар негізінде бөлінетін қоспаның белгілі компоненттері бойынша (металдардың зарядталған катиондары, органикалық заттардың молекулалары, бактериялар, вирустар) талғамды өткізгіштігі бар жартылай өткізгіш мембрананың болуы олардың басты ерекшелігі болып табылады.

Түйін сөздер: мембраналық технологиялар, микрофильтрация, ультрафильтрация, нанофильтрация, кері осмос.

Резюме

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ПОЛУПРОНИЦАЕМЫЕ МЕМБРАНЫ ДЛЯ МЕМБРАННЫХ ТЕХНОЛОГИИ

В обзорной статье рассмотрены мембранные технологии, работающие по принципу баромембранных процессов (микрофильтрация, ультрафильтрация, нанофильтрация, обратный осмос) и получающие все большее применение в промышленности и бытовых целях. Главной их особенностью является наличие полупроницаемой мембраны на основе полимеров, керамики или наноуглеродных материалов с селективной проницаемостью по определенным компонентам разделяемой смеси (заряженные катионы металлов, молекулы органических веществ, бактерии, вирусы).

Ключевые слова: мембранные технологии, микрофильтрация, ультрафильтрация, нанофильтрация, обратный осмос.

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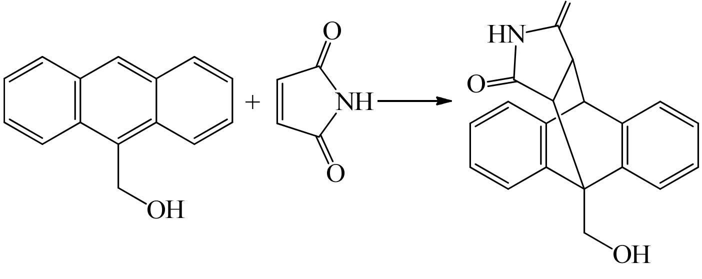
STUDY OF INFLUENCE THE TEMPERATURE ON THE REACTION OF DIENESYNTHESIS OF MONOESTERS OF NORBORNENDICARBONIC ACID ON THE TOTAL AND OPTICAL YIELD OF THE ADDUCT

Abstract. The influence of temperature of Diels-Alder reaction between cyclopentadiene and monoesters of maleic acid to the yield of obtained adducts has been studied. The optimum conditions of reaction have been founded. It is showed that at low temperatures the total yield of adduct has been decreased, but its optically yield increased. The increasing of temperature lead to increasing of total yield. But optically yield is decrase.

Key words: cyclopentadiene, diene synthesis, monoesters of maleic acid, norbornenedicarboxylic acid.

It is known that maleic derivatives are one of the classical dienophiles in the reaction of diene synthesis and a huge amount of work has been done in this direction. However, research in this field continues to develop intensively and the search for new applications of the adducts obtained remains relevant to this day. Thus, the kinetic regularities of a second-order reaction between cyclopentadiene and a series of dienophiles, including maleic anhydride and N-phenylmaleimide, were studied in [1]. It is shown that in the dioxane medium, the reaction rate constant for maleic anhydride is $1.22 \cdot 10^{-1}$ 1 / mole c, and for N-phenylmaleimide $1.22 \cdot 10^{-1}$ 1 / mole c, respectively, while the optimal rate for maleic anhydride is $2, 45 \cdot 10^{3}$ 1 / mole c, and for N-phenylmaleimide $2{,}30 \cdot 10^{3}$ 1 / mole s. The authors note that the yield of the adduct in the case of maleic anhydride is 99.5%, and for N-phenylmaleimide, respectively, exceeds 99.8%.

The reaction of anthracene-9-methanol and maleimide in an aqueous medium under the conditions of "green chemistry" was studied in [2]. It is shown that in this reaction water serves not only as a solvent but also as an active catalyst. The reaction proceeds according to the scheme:



The authors studied in detail the effect of solvents and the duration of the reaction on the yield of the adduct.

Solvent	Duration, h	Yield of adduct, %
Heptane	4	42
n-Propanediol	4	47
Dioxane	4	51
H_2O	1	78
H_2O / LiCl	0,5	87
H_2O /NaCl	1	76

In [3], the rate constants of the reaction of diene synthesis between cyclopentadiene (CPD) and various dienophiles, including those of maleic series, were calculated. The authors give the results of the studies in table 1.

Table 1 – The values of the rate constants of Diels-Alder reactions
between cyclopentadiene and certain dienophiles

Diene	Dienophile	Configuration of adduct	Rate constant, 1/mol c
CPD	Maleic anhydride	endo	0,008
CPD	Maleic anhydride	exo	0,002
CPD	N-maleimide	endo	0,001
CPD	N-maleimide	exo	0,024
CPD	Di-n-propylmaleat	endo	0,005

Diene condensation of maleic anhydride with isoprene in various media (ethyl ether, butanol, isopropanol, diphenyl ether, dichloromethane, dioxane, ace-tone, benzene, nitrobenzene, nitromethane, chloroform, THF) has been studied [4].

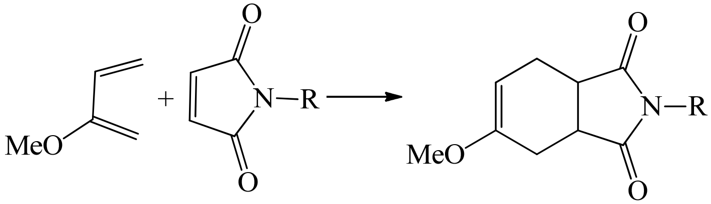
In continuation of these studies, diene condensation of CPD with various dienophiles of the maleic series has been studied [5]. The reaction was carried out at a temperature of 800°C. The authors give the results of the studies in table 2.

Table 2 – The yields of diene condensation adducts of the CPD with various maleic dienophiles

Diene	Dienophile	Yield of adduct, %
CPD	Maleic anhydride	67
CPD	Maleimide	70
CPD	N-phenylmaleimide	80
CPD	Diethylmaleat	43

In [6], the Diels-Alder reaction of CPD with maleic anhydride was studied at room temperature in the absence of a solvent with the formation of an endo-adduct in quantitative yield.

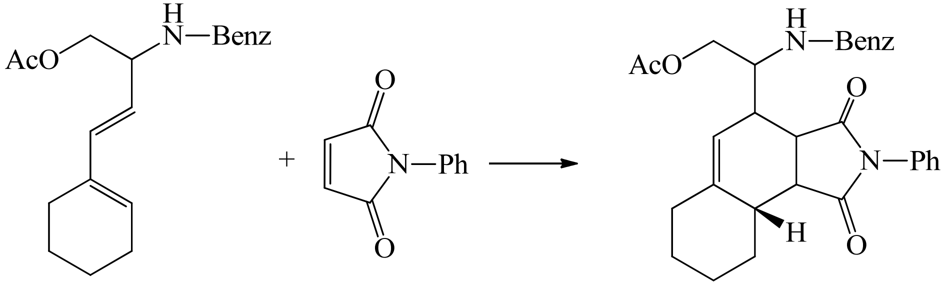
The Diels-Alder reaction of 2-methoxybutadiene with maleic anhydride in the presence of chiral Lewis acids (Al, B, Ti, Cu, La, Mg, etc. complexes), proceeding according to the scheme [7]:



The yield of the adduct was 98%, e.e. 93%.

In [8], diene condensation of 2,4-hexadiene-1-ol with maleic anhydride was studied. The structure of the obtained isomeric adducts was confirmed by IR and NMR spectroscopy.

The Diels-Alder reaction of a chiral cyclohexene derivative with N-phenylmaleimide was studied according to the scheme



The authors note [9] that the ratio of endo: exo isomers is 4.4: 1, and the yield of the adduct is 53%. The reaction was carried out in a 1M solution of $CDCl_3$ at a temperature of 250°C for 7 days.

The reaction of diene furo [3.4-b]-benzodioxin synthesis with various dienophiles, including maleic anhydride, is described in [10] and the formation of stable bis-adducts is shown.

Diene condensation of allocymene with maleic and citraconic anhydride has been studied, leading to the formation of preferentially endo-adducts [11]. As a result of these reactions, new synthetic sesquiterpenoids were synthesized. The structure of the adducts obtained is confirmed by X-ray spectroscopy.

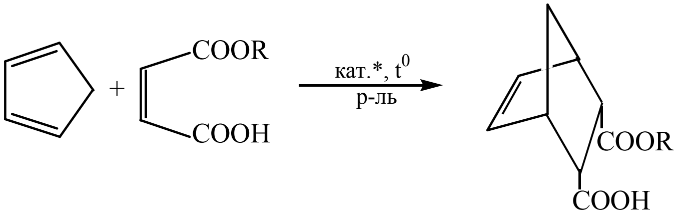
In [12], the [4+2]-cycloaddition of substituted Al- and Mg-cyclopenta-2,4-diones with dienophiles such as maleic anhydride, N-methylmaleimide and 1,4-benzoquinone was investigated.

Thus, a review of these reports shows that studies in the field of studying diene condensation based on maleic dienophiles continue to develop intensively and are of great scientific and practical interest. In connection with this, our studies have synthesized monoesters of norbornenedicarboxylic acid by the reaction of diene synthesis of cyclopentadiene and maleic acid monoesters, and optimization of this process has been carried out.

Results and discussions

The aim of this work is to develop a regression mathematical model with the subsequent solution of the optimization problem, as well as to study the process of obtaining racemic and optically active forms of mono-esters of norbornene dicarboxylic acid on this model.

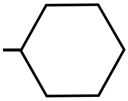
The synthesis of the optically active forms of the corresponding compounds was carried out in the presence of a catalyst, a chiral menthol complex with aluminum chloride in a benzene solvent medium according to:



2 S, 3S (+)

I II - VI VII - XI

R = н - C_3H_7 (II; VII); i - C_3H_7 (III, VIII); н - C_4H_9 (IV; IX); i - C_4H_9 (V; X);



(VI; XI)

cat.* – $AlCl_2OMent$
temperature – -40 : +20^{0}C
solvent – C_6H_6;

Physic-chemical parameters and yields of synthesized adducts are presented in table 3 [14].

Table 3 – Physico-chemical parameters of synthesized monoesters of norbornene dicarboxylic acid

Compound	Configuration	Brutto-formule	T, ^{0}C		d_4^{20}, g/ml	n_D^{20}
			melt.	boil. (mm.Hg)		
VII	2S, 3S (+)	$C_{12}H_{16}O_4$	140-142	–	–	–
VIII	“–”	$C_{12}H_{16}O_4$	138-139	–	–	–
IX	“–”	$C_{13}H_{18}O_4$	135-137	–	–	–
X	“–”	$C_{13}H_{18}O_4$	138-139	–	–	–
XI	“–”	$C_{15}H_{20}O_4$	115	–	–	–

To find the optimal conditions that ensure the maximum total and optical yields of the compounds was obtained, the influence of temperature and the ratio of the catalyst: dienophile was studied. The molar ratio of the catalyst: dienophile was varied from 0.25: 1 to 0.5: 1, the reaction temperature was changed in the range (-) 50: (+) 40^{0}C.

The results of studies using isopropyl monoester of norbornenedicarboxylic acid (III) are presented in table 2, 3.

Table 2 – Effect of temperature on the total yield of the isopropyl monoester of norbornenedicarboxylic acid

Temperature, ^{0}C	Molar ratio catalyst : dienophile	Total yield of adduct, %
-50	0.5 : 1	77
-40	0.5 : 1	79,8
-30	0.5 : 1	82
-20	0.5 : 1	84,5
-10	0.5 : 1	87
0	0.5 : 1	89
10	0.5 : 1	93
20	0.5 : 1	96
30	0.5 : 1	99
40	0.5 : 1	99
-50	0.3 : 1	79
-40	0.3 : 1	81
-30	0.3 : 1	83
-20	0.3 : 1	85
-10	0.3 : 1	87
0	0.3 : 1	89
10	0.3 : 1	91
20	0.3 : 1	92,5
30	0.3 : 1	94
40	0.3 : 1	99
-50	0.25 : 1	78,5
-40	0.25 : 1	80
-30	0.25 : 1	82
-20	0.25 : 1	84,2
-10	0.25 : 1	86
0	0.25 : 1	88,6
10	0.25 : 1	91
20	0.25 : 1	93,5
30	0.25 : 1	96,5
40	0.25 : 1	99
-50	0.2 : 1	77,5
-40	0.2 : 1	79
-30	0.2 : 1	81
-20	0.2 : 1	83
-10	0.2 : 1	85
0	0.2 : 1	87
10	0.2 : 1	89
20	0.2 : 1	92
30	0.2 : 1	94,5
40	0.2 : 1	97,4

As can be seen from table 2, the greatest yield of the adduct is observed in the region of positive temperatures o f 30-40 C, whereas at low temperatures the total yield of the adduct decreases.

Table 3 – Effect of temperature on the optical yield of the isopropyl mono ester of norbornenedicarboxylic acid

Temperature, ^{0}C	Molar ratio catalyst : dienophile	Optically l yield of adduct, %
-50	0.5 : 1	65
-40	0.5 : 1	60,5
-30	0.5 : 1	57
-20	0.5 : 1	55,1
-10	0.5 : 1	54,6
0	0.5 : 1	55,6
10	0.5 : 1	58
20	0.5 : 1	62
30	0.5 : 1	67
40	0.5 : 1	74
-50	0.3 : 1	95
-40	0.3 : 1	86
-30	0.3 : 1	78
-20	0.3 : 1	72
-10	0.3 : 1	68
0	0.3 : 1	63,5
10	0.3 : 1	61,5
20	0.3 : 1	61
30	0.3 : 1	62
40	0.3 : 1	64,5
-50	0.25 : 1	97,2
-40	0.25 : 1	87
-30	0.25 : 1	78
-20	0.25 : 1	70
-10	0.25 : 1	64,5
0	0.25 : 1	60
10	0.25 : 1	57
20	0.25 : 1	55
30	0.25 : 1	54,8
40	0.25 : 1	56
-50	0.2 : 1	97
-40	0.2 : 1	85,5
-30	0.2 : 1	75,4
-20	0.2 : 1	67
-10	0.2 : 1	60
0	0.2 : 1	54
10	0.2 : 1	50
20	0.2 : 1	47
30	0.2 : 1	45,8
40	0.2 : 1	45

From figure 2 it follows that the optimal optical yield of the adduct is observed in the region of negative temperatures (-) 50^0C at a molar ratio of 0.3: 1 to 0.2: 1. Under these conditions, the optical yield of the isopropyl monoester of norbornene dicarboxylic acid is 95-97%.

With the help of the developed mathematical model in the form of a regression polynomial adequately describing the experimental data, optimal values of the reaction input variables were found: catalyst: dienophile ratio equal to 0.3: 1, temperature equal to (+) 40^0C at which the maximum yield of the isopropyl monoester of norbornene dicarboxylic acid was 99 %. However, under these conditions, the optical yield of adduct was 64.3%. The maximum optical yield of adduct (97.2%) is observed at a temperature of (-) 50^0C and a catalyst: dienophile ratio of 0.25: 1, but the total yield of adduct is 78.5%.

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Резюме

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НОРБОРНЕНДИКАРБОН ҚЫШҚЫЛЫНЫҢ МОНОЭФИРЛЕРІН ДИЕНДІ СИНТЕЗДЕУ РЕАКЦИЯСЫ ТЕМПЕРАТУРАСЫНЫҢ АДДУКТІҢ ЖАЛПЫ ЖӘНЕ ОПТИКАЛЫҚ ШЫҒЫМЫНА ӘСЕРІН ЗЕРТТЕУ

Циклопентадиен мен малеин қышқылының моноэфирлері арасындағы Дильса-Альдер реакциясы температурасының алынған аддуктердің шығымына әсері зерттелді. Реакция күйінің оңтайлы жағдайлары анықталды. төмен температураларда аддуктің жалпы шығымы азаятыны, ал оның оптикалық шығымы артатыны көрсетілді. Температура артқан сайын аддуктің жалпы шығымы артады, ал оптикалық шығымы төмендейді.

Түйін сөздер: циклопентадиен, диенді синтез, малеин қышқылының моноэфирлері, норборнендикарбон қышқылы.

Резюме

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ИЗУЧЕНИЕ ВЛИЯНИЯ ТЕМПЕРАТУРЫ РЕАКЦИИ ДИЕНОВОГО СИНТЕЗА МОНОЭФИРОВ НОРБОРНЕНДИКАРБОНОВОЙ КИСЛОТЫ НА ОБЩИЙ И ОПТИЧЕСКИЙ ВЫХОД АДДУКТА

Изучено влияние температуры реакции Дильса-Альдера между циклопентадиеном и моноэфирами малеиновой кислоты на выход полученных аддуктов. Определены оптимальные условия проведения реакции. Показано, что при низких температурах общий выход аддукта уменьшается, тогда как его оптический выход возрастает. С увеличением температуры общий выход аддукта закономерно возрастает, а оптический выход снижается.

Ключевые слова: циклопентадиен, диеновый синтез, моноэфиры малеиновой кислоты, норборнендикарбоновая кислота.

UDC 547(1+435+6+822)+541.341

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FLUOROPHENYL-CONTAINING A-AMINOPHOSPHONATES: SYNTHESIS AND STRUCTURE

Abstract. Novel α-aminophosphonates ***1-3*** were synthesized by the one-pot three component reaction of equimolar quantities of dimethylphosphite, diphenylmethylpiperazine and a carbonyl component (4, 3 or 2-fluorobenzaldehyde) in benzene at reflux conditionsfor 30 h viaKabachnik-Fields reaction in high yields (82.9-90.3%). The progress of the reaction was monitored by thin layer chromatography analysis. The chemical structures were established by the physico-chemical methods as IR, ^{1}H, ^{13}C NMR and elemental analyses.

Key words: α-aminophosphonates, fluorophenyl, Kabachnik-Fields reaction, synthesis, structure.

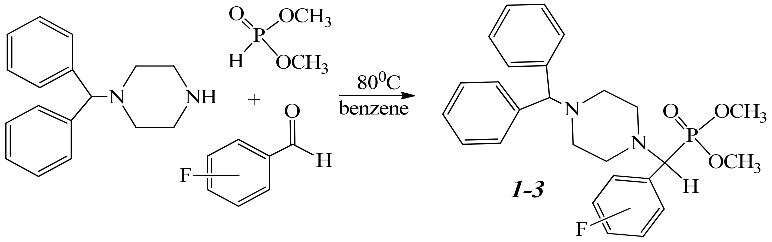
The α-aminophosphonate fragment is a universal pharmacophoredue to the spectrum of biological activity exhibited by the compounds having this structural unit. Studies are underway to develop new synthetic methods for the preparation of α-aminophosphonates [1-3]. The attractiveness of the chemistry of this family of compounds is explained by the fact that a significant number of derivatives of α-aminophosphonates are used in medicine as antiviral [4] antifungal, antibacterial [5] and antitumor drugs [6-8] inhibitors of enzymes [9], antibiotics and pharmacological agents [10]. It addition theaminophosphonates are valuable intermediates for the preparation of medicinal and agriculture compounds, reagents for the recovery of metal ions, etc.

In the present workthe problem of introducing a fluorophenyl group into a molecule having an aminophosphonate fragment is solving.

Interest tofluorophenyl derivatives is dictated by their pharmacological potential – in particular, fluorophenyl is a part of the known neuroleptics haloperidol [11], droperidol [12], melperone [13], some antiseptic and antipsychotic agents. Although organofluorine compounds are practically not found among natural products, it is interesting to note that about 25% of pharmaceutical drugs contain at least one fluorine atom. Thus, there are nine new synthetic preparations out of thirty-one approved in 2002 for pharmaceutical production, contain fluorine [14-16].

Synthesis of aminophosphonic acids derivatives is an active research field, and many methods are currently available. Among the synthetic approaches to aminophosphonates, one of the most important methods is the Kabachnik-Fields reaction [17, 18]. This reliable method for the synthesis of aminophosphonates is a three-component reaction ofa carbonyl compound, primary or secondary amine and dialkyl or trialkylphosphites.

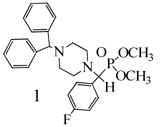
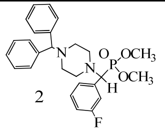
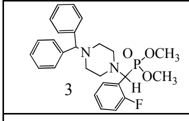
To continue Research related to the synthetic design of potential bioactive nitrogen heterocycles carried out in the laboratory of the Synthetic and Natural Medicinal Compounds Chemistry, pharmacophorediphenylmethylpiperazine [19] was used as the initial amine component, which is a synthetic analogue of natural alkaloids. The interaction of diphenylmethylpiperazine with *p-, m-* or *o*-fluorobenzaldehydes and dimethylphosphite under the conditionsof the one-pot reactor three-component classical Kabachnik-Fields reaction in benzene at 80°C, using a Dean-Stark trap to divert the obtained water from the reaction zone by distilling its azeotrope– water+benzene, leads to the target α-aminophosphonates ***1-3***:



1-3

The yields and physico-chemical characteristics of α-aminophosphonates ***1-3*** are presented in table 1. α-Aminophosphonates 1-3 were prepared with the yields of 82.9-90.3% after long time boiling (for 30 hours).

Table 1 – The yields and physico-chemical characteristics of dimethyl[(4-benzhydrylpiperazin-1-yl)(*p*-, *m*- and *o*-fluorophenyl)methyl]phosphonate

Compound	Yield, %	R_f*	$T_{melting,}$, ^0C	Calculated for $C_{26}H_{30}FN_2O_3P$ / Found, %				
				C	H	N	P	F
 1	82,9	0,56	72	66,65 66,83	6,45 6,62	5,98 6,03	6,61 6,92	4,06 3,83
 2	85,7	0,53	58	66,65 66,74	6,45 6,69	5,98 6,11	6,61 6,59	4,06 4,10
 3	90,3	0,48	98	66,65 66,56	6,45 6,51	5,98 5,83	6,61 6,77	4,06 3,99
Note: * –Al_2O_3, eluent hexane: chloroform1:3.								

The structure of synthesizedcompounds ***1-3*** were established by IR,^{1}H and ^{13}C NMR. In the IR spectra (figure 1), the peaks at 1507-1588 cm^{-1}were attributed to the absorption of C = C of the aromatic ring, 1227-1287 cm^{-1} to C-N, 1035 to 1022 cm^{-1} to P = O and 754 to 769 cm $^{-1}$ to -P-C.

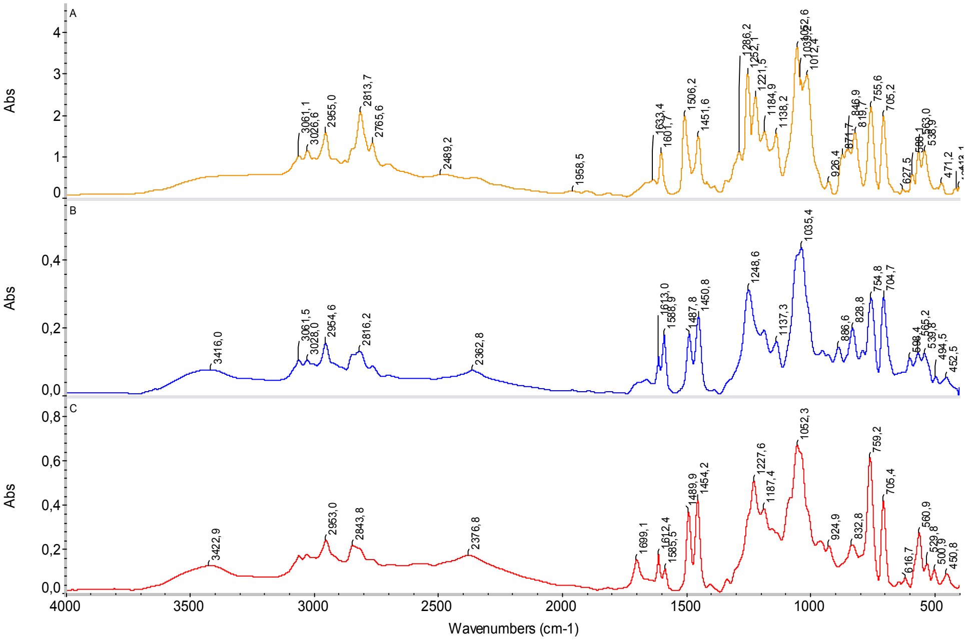


Figure 1 – The IR spectra
of dimethyl[(4-benzhydrylpiperazin-1-yl)(*p*-, *m*- and *o*-fluorophenyl)methyl]phosphonate

The proton (figure 2) and the carbon spectra of fluorophenyl-containing benzhydrylpiperazineaminophosphonates***1-3*** differed by signals of protons and carbons in the "aromatic" region, associated with the position of the fluorine atom in the benzene ring. Signals in the area of 0.75-1.25 ppmwere in the axial protons of the piperazine cycle, the equatorial ones were 2.25-2.75 ppm.

The methoxy protons resonated at 3.75 ppm. The methine proton adjacent to the phosphorus atom resonated in the region of 4.25 ppm, analogous to the benzhydryl group - 5.0 ppm (for *n*- and *m*-F), in the *o*-F signal the signal was shifted to a weaker field (5.8 ppm). All aromatic protons resonated in the region of 7.1-8.0 ppm, but they differed greatly in signalsform.

A similar character,as similar carbon signals of the piperazine fragment, methine and methoxy groups, only the difference in the signals of aromatic carbons, was observed in the ^{13}C NMR spectra.

The most informative proof of the structure of the synthesized systems werethe carbon ^{13}C NMR spectra of 4-benzhydrylpiperazine aminophosphonates (table 2).

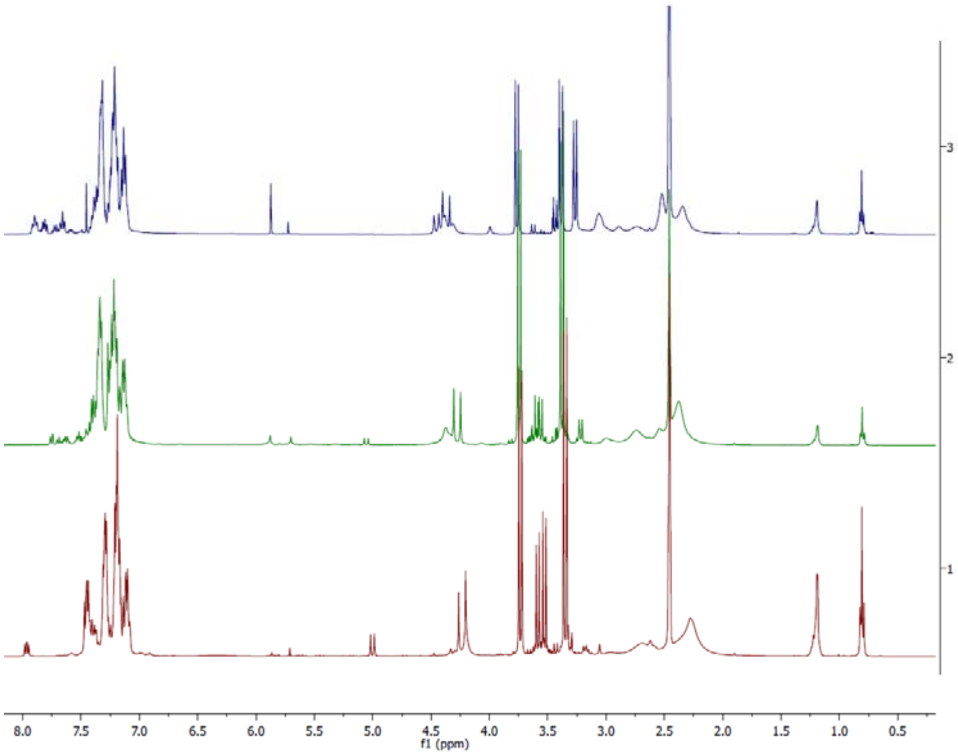


Figure 2 – ^{1}H NMR spectra
of fluorine-containing 4-benzhydrylpiperazine aminophosphonates ***1-3***

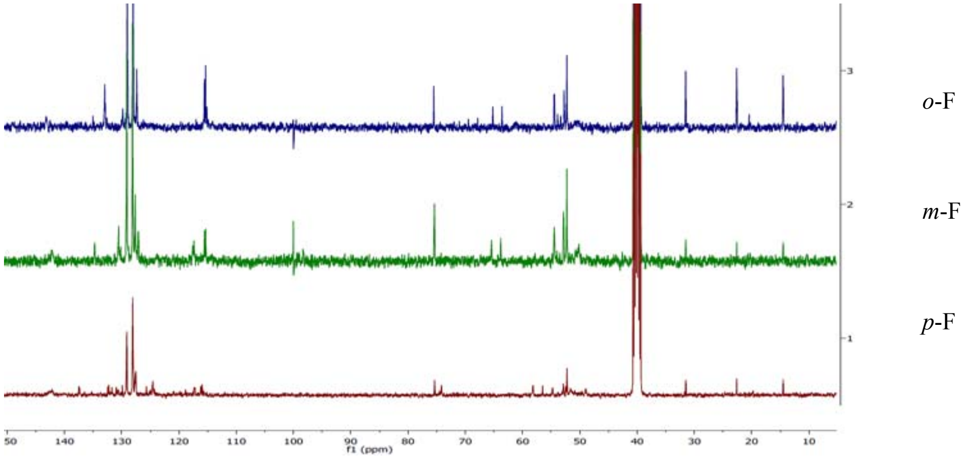
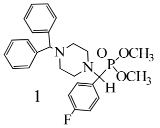
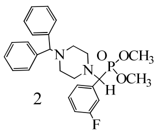
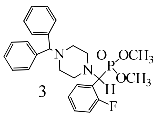


Figure 3 – ^{13}C NMR spectra
of fluorine-containing 4-benzhydrylpiperazine aminophosphonates **(*1-3*)**

Table 2 – ^{13}CNMRspectra of 4-benzhydrylpiperazineaminophosphonates ***1-3***

Compound	Chemical shifts ($CDCl_3$), δ, ppm					
	C-2, C-6	C-3, C-5	CH(P) (CH)	(P)OCH_3	C_6H_4F	$(C_6H_5)_2$ (CHN)
 1	51.1	53.8	67.5 (75.4)	53.0-53.9	115.8-166.1	127.8-142.1
 2	51.7	53.3	68.0 (76.1)	52.9-54.5	116.7-164.8	126.1-146.9
 3	52.1	53.7	67.6 (77.5)	52.6-53.8	117.2-163.8	116,2-162,2

The carbon composition completely corresponded to the expected composition of the synthesized dimethyl[(4-benzhydrylpiperazin-1-yl)(*p-, m-* and *o*-fluorophenyl)methyl]phosphonates ***1-3***. Strong-field signals of double intensity at 51.1-52.1 and 53.3-53.8 ppm belong to the carbon atoms of the piperazine (C-2, C-6 and C-3 and C-5) cycle. In the same area at 52.6-54.9 ppm the signals of the carbon atom of the dimethylphosphoryl fragment of $P(O)(OCH_3)_2$were observed. The low-field region is "populated" with aromatic carbon atoms. The methine carbon CH(P) resonated at 67.5-68.0 ppm. A similar signal of the benzhydryl group appeared in the region of 116.2-162.2 ppm.

Experimental

The reaction and the individuality of the compounds were monitored by TLC on alumina oxide of III activity (eluent hexane: chloroform 1:3) with the appearance of spots by iodine vapor. The IR spectra were recorded on a Nicolet 5700 spectrometer in a thin layer between the KBr plates. NMR spectra in $CDCl_3$ are recorded on a JNM-ECA400 spectrometer, Jeol (Japan), an operating frequency of 400 MHz (^1H) and 100 MHz ($C^{13}C$).

Synthesis of dimethyl[(4-benzhydrylpiperazin-1-yl)(p-fluorophenyl)methyl]-phosphonate (1). 3 g (0.0185mol) 1-Benzhydrylpiperazine, 3.46 g (0.018 mol) of *p*-fluorobenzaldehyde and 1.7 ml of dimethyl phosphate in 185 ml of benzene were placed in a flask equipped with a Dean-Stark trap and a reflux condenser. The mixture was stirred for 20 min at room temperature. With constant stirring, the reaction mixture is heated at the boiling point of benzene. After distillation of the solvent, the residue was repeatedly washed with hot hexane. 4.62 g (82.9% of theory) of dimethyl[(4-benzhydrylpiperazin-1-yl)(*p*-fluorophenyl)methyl]phosphonate was isolated from the hexane fraction, m.p. 72°C (transparent needle-like crystals).

*Synthesis of dimethyl[(4-benzhydrylpiperazin-1-yl)(m-fluorophenyl)methyl]-phosphonate (2).*3 g (0.0185 mol) 1-Benzhydrylpiperazine, 3.4 ml (0.018 mol) of *m*-fluorobenzaldehyde and 1.7 ml of dimethyl phosphate in 185 ml ofbenzene were placed in a flask equipped with a Dean-Stark trap and a reflux condenser. The mixture was stirred for 20 minutes at room temperature. With constant stirring, the reaction mixture is heated at the boiling point of benzene. After distillation of the solvent, the residue was repeatedly washed with hot hexane. 3.96 g (85.7% of theory) of dimethyl [(4-benzhydrylpiperazin-1-yl)(*m*-fluorophenyl)methyl]phosphonatewas isolated from the hexane fraction, m.p. 58°C (transparent needle-like crystals).

*Synthesis of dimethyl [(4-benzhydrylpiperazin-1-yl) (o-fluorophenyl)methyl] phosphonate (3).*3 g (0.0185 mol) 1-Benzhydrylpiperazine, 3.4 ml (0.018 mol) of of*o*-fluorobenzaldehydeand 1.7 ml of dimethyl phosphite in 185 ml of benzene were placed in a flask equipped with a Dean-Stark trap and a reflux condenser. The mixture was stirred for 20 minutes at room temperature. With constant stirring, the reaction mixture is heated at the boiling point of benzene. After distillation of the solvent, the residue was repeatedly washed with hot hexane.5.03 g (90.3% of theory) of dimethyl[(4-benzhydrylpiperazin-1-yl)(*o*-fluorophenyl)methyl]phosphonate was isolatedfrom the hexane fraction, m.p. 98°C (transparent needle-like crystals).

Conclusion. Novel α-aminophosphonates with fluorophenyl moiety by the reaction of aldehyde, 1-benzhydrylpiperazine and dimethyl phosphatehave been synthesized. These fluorinated aminophosphonates could be very interesting for their biological activity, because α-aminophosphonate derivatives are important building blocks in organic synthesis of biologically active compounds.

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Резюме

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ФТОРФЕНИЛДІ α-АМИНОФОСФОНАТТАР: СИНТЕЗІ ЖӘНЕ ҚҰРЫЛЫСЫ

Жаңа α-аминофосфонаттар ***1-3*** үш компонентті «*one-pot*» реакциясы бойынша эквимолярлы мөлшердегі диметилфосфиттің, дифенилметилпиперазиннің және карбонильді компоненттің (4, 3 немесе 2-фторбензальдегид) бензолда 30 сағ. Кабачник-Филдс реакциясы жағдайында қайнату арқылы жоғары шығымммен (82,9-90,3%) синтезделді. Реакция бағытыжұқа қабатты хроматография әдісімен бақыланды. Химиялыққұрылым ИҚ, ^{1}H, ^{13}C ЯМР және элементтісараптама сияқты физика-химиялық әдістермен анықталды.

Түйін сөздер: α-аминофосфонаттар, фторфенил, Кабачник-Филдс реакциясы, синтез, құрылым.

Резюме

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Т. М. Сейлханов, К. Д. Пралиев, К. Д. Берлин, В. К. Ю

ФТОРФЕНИЛСОДЕРЖАЩИЕ α-АМИНОФОСФОНАТЫ: СИНТЕЗ И СТРОЕНИЕ

Новые α-аминофосфонаты ***1-3*** были синтезированы с высокими выходами (82,9-90,3%) из эквимолярных количеств диметилфосфита, дифенилметилпиперазина и карбонильного компонента (4, 3 или 2-фторбензальдегида) в условиях однореакторной трехкомпонентной классической реакции Кабачника-Филдса, кипячением в бензоле в течение 30 ч. Ход реакции контролировали методом ТСХ. Химическая структура была установлена физико-химическими методами – ИК, ^{1}H, ^{13}C ЯМР и элементный анализ.

Ключевые слова: α-аминофосфонаты, фторфенил, реакция Кабачника-Филдса, синтез, строение.

UDK 547.541.3, 547.542.7

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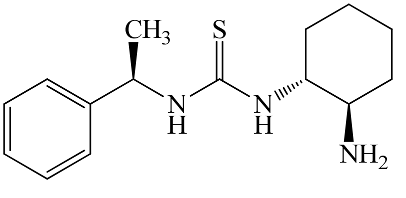
CHIRAL ORGANIC CATALYSTS IN THE DIELS-ALDER REACTION

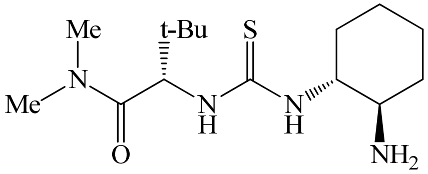
Abstract. The analysis of scientific investigations in the field of application of chiral organic catalysts in the reaction of diene synthesis has been carried out. The directions of using of synthesized adducts in the different part of industry have been described. The effect of used catalysts to stereo- and enantioselectivity of reactions have been studied.

Key words: diene synthesis, chiral organocatalysts, optically active compounds.

It is known that chiral organic catalysts find wide application in the reaction of diene synthesis and a huge amount of work has been done in this direction. However, research in this field continues to develop intensively and the search for new chiral organocatalytic systems remains relevant to this day [1-18].

Thus, in [19] new highly enantioselective bifunctional organocatalysts for enantioselective addition reactions, including [4+2] -cycloaddition reactions, were developed. These catalysts contain fragments of thiourea and a primary amino group or amine-sqvaramid groups:





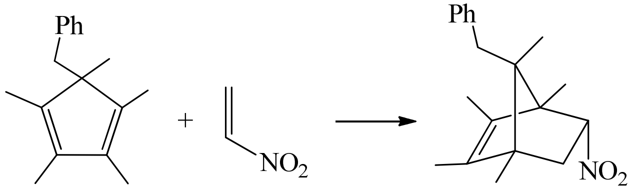
Synthesized catalysts are widely used in the Diels-Alder reaction (DA) for the synthesis of structured complex spirocyclic skeletons and indolo- and benzo-quinolizidine derivatives, which belong to pharmaceutical compounds.

An unusual reaction of cycloaddition of 2-pyrones with aliphatic nitroalkenes, catalyzed by new bifunctional catalysts based on cinchon alkaloid derivatives, is associated with a cumbersome ethereal group at position 9 [20]. Bicyclic [2.2.2] -adducts with good yield and high diastereo- and enantioselectivity were obtained. The isotope effects of the C atom were studied by the C13-NMR spectroscopy method and the reaction mechanism was proposed. At the end, the areas of application of synthesized adducts are shown.

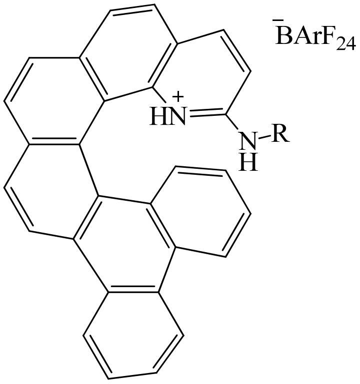
In [21], the Sc (OTf) 3 / bis (oxazoline) complex was proposed as a catalyst for the asymmetric reaction of DA 2-arylidene-1,3-indanediones with 2-vinyl-indoles. It was shown that the reaction is a convenient and important practical approach to biologically valuable and synthetically advantageous spiro-tetrahydrocarbazoles in good yield (92%) and high enantioselectivity (ee 94%).

A bimetallic heme-DNA cofactor containing Fe and Cu centers was synthesized as new hybrid catalysts for stereoselective synthesis, in particular for DA reactions [22].

Enantiomeric and periselective D-A reactions were performed with the participation of nitroalkenes in the presence of catalysts that are donors of a helico- chiral double hydrogen bond [23]. As a diene, 5-substituted pentamethylcyclopentadiene was used:



The reaction was carried out in a CH_2Cl_2 medium at a temperature of (-78^0) C for 20 hours and in the presence of 10 mol% % of catalyst



where -BArF24 is tetrakis [3,5-bis(trifluoromethyl) phenyl] borate.

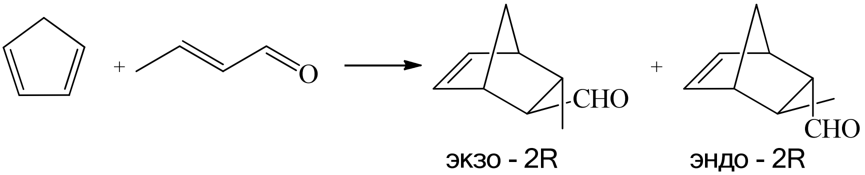
The authors note that the yield of the adduct in this reaction was 70-84%, and e.e. 67-70%.

In [24], chiral supramolecular B-containing Lewis acids were obtained from chiral 3-phosphoryl-1, 11-bis-2-naphthol, (2-cyanophenyl) boronic acid and tri (pentafluorophenyl) borane containing CN … B coordination bonds and PO ... B. It is shown that these catalysts increase the acidity of the active site in the Lewis acid. They were tested in the DA reaction between acrolein and cyclic (acyclic) dienes, proceeding in good yield and high enantioselectivity.

It was noted in [25] that the asymmetric D-A reaction is one of the convenient and effective methods for obtaining optically active compounds, for the production of which various kinds of catalysts are widely used. Most often, complexes based on Schiff bases and transition metal ions, in particular the Salen complex, are used. Chiral salen ligands can easily be synthesized from enantiomerically pure diamines and two moles of salicylic aldehyde or its derivatives. Mn, Cr, Co, V, Cu, Ti, Ru, Pd, Au, Zn and Al are used as the transition metals.

Chiral sulphinamide urea together with the cochlear-an a chiral strong Bronsted acid (o-nitrobenzenesulfonic acid) was used as a catalyst system in the (4 + 2) -cycloaddition of N-arylimines with electron-enriched olefins, such as vinyllactams and dihydropyrroles [26]. These catalysts have been successfully applied for the synthesis of tetrahydroisoquinolines, which form the basis of a number of natural and synthetic biologically active compounds, such as martinellin, skueryrin and tubocurarine.

Chiral polyoxometallate-imidazolidinones were used as catalysts for the D-A reaction between cyclopentadiene and crotonaldehyde in [27]. The reaction was carried out in the presence of 5 mol. % catalyst in a medium of 0.5 M CH2Cl2 for 3 days according to the scheme:



The yield of adducts ranged from 45-95%, e.e. 46-54%, the ratio of exo-endo isomers was 2: 1 to 1: 3.

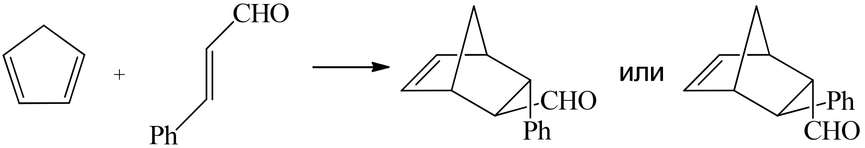
In [28], phosphorylated imidazolidinones were used in the asymmetric D-A reaction involving 1,2-unsaturated aldehydes with good yield and high enantioselectivity.

(S) - (-) - 2- (α-hydroxyethyl) benzimidazole and (S) - (-) - 2- (α-hydroxybenzyl) benzimidazole were used as chiral Bronsted bases in the DA reaction between anthrone t maleimide in moderate conditions [29].

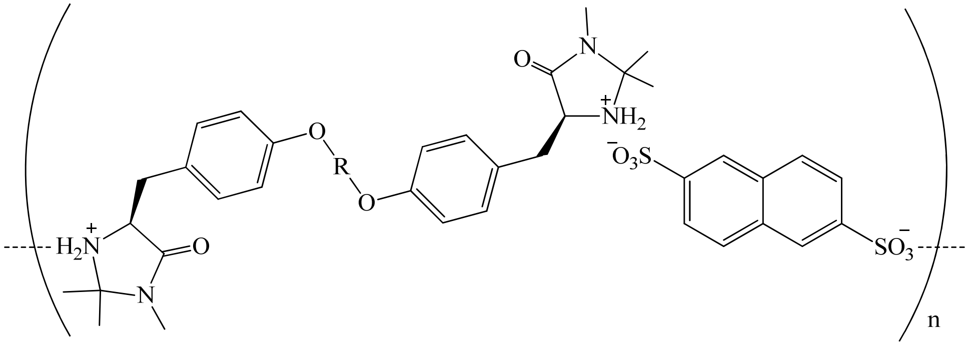
It is shown that chiral C-H acids during the silylation reaction generate silicon carbanion, which is an extremely active acidic Lewis catalyst for the enantioselective D-A reaction between cinnamate and cyclopentadiene. The ratio of enantiomers in the reaction was 97: 3, and the ratio of the diastereomers is 20: 1, respectively [30].

In [31], new main chain polyesters, functionalized with chiral imidazolidine salts, were synthesized. These polyesters were used as heterogeneous organocatalysts in the asymmetric D-A reaction between cyclopentadiene and trans-cinnamaldehyde. The authors note that the enantioselectivity of the reaction reaches up to 97%.

In another paper by the same authors [32], the main chain polymers of chiral imidazolidinones were successfully synthesized by the reaction of dimers of chiral imidazolidinone with disulfonic acid. The fatty imidazolidinones were introduced into the main polymer chain through ionic bonding. These compounds can be used as polymer chiral organocatalysts for asymmetric D-A reaction according to the scheme:



The yield of the adduct was 99%, e.e. up to 99%, the endo: exo ratio is 45: 55. The catalyst has the following structure:



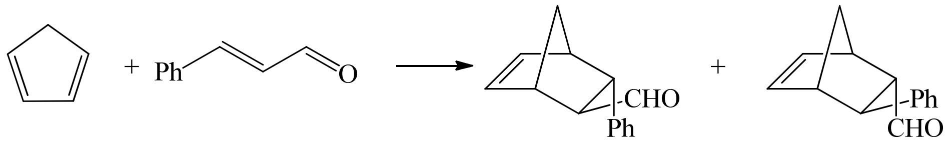
Ionic liquids were used to regenerate the McMillan catalyst in the D-A reaction [33]. The catalyst is an imidazolidinone derivative.

In work [34], benzopyrans were used as starting compounds for the organocatalytic reaction DA, leading to the formation of tricyclic systems. As catalysts, imidazolidinones were used. At the same time, the asymmetric induction was 96%. Synthesized tricyclic scaffold-tetrahydrocannabinol systems form the basis of many natural compounds.

It was noted that in the first successfully implemented catalytic asymmetric reaction of D-A in 1979, Koga and co-workers. The chiral aluminum complex was used as the Lewis acid, and after that the researchers developed a huge number of catalytic systems for these reactions [35]. In particular, chiral organic compounds, such as imidazolidinone or TADDOL salts, have been used as catalysts in the asymmetric reaction of DA. In this paper, chiral amines were proposed as catalysts for these reactions on the basis of the theory of frontal molecular orbitals. It is shown that they exhibit high chemo-, regio- and stereoselectivity.

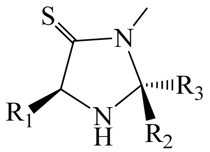
In [36, 37], derivatives of chiral phosphoric acids derived from linear chiral biaryls, as well as analogous chiral Bronsted acids, were used as effective and widely used compounds - enantioselective organocatalysts for various organic transformations, including DA reactions.

Endo- and S-selective retro-D-A reactions catalyzed by chiral imidazolethioles were studied [38]. The process between cyclopentadiene and cinnamaldehyde was carried out in a methanol-water or methyl cyanide-water solvent system with a high yield of adduct and good enantioselectivity according to the scheme:



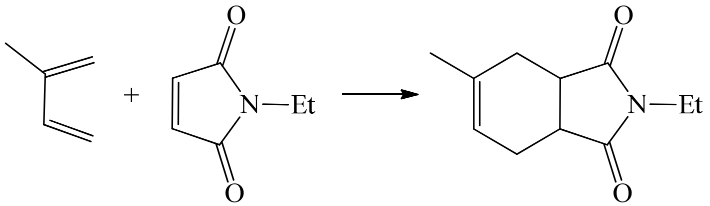
The yield of the adduct is 85-96%, e.e. 56-95%.

The ratio of exo: endo = 1.1: 1 - 1.3: 1. The catalyst used was

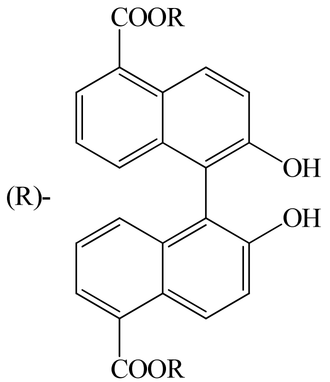


R_1 = Benz, indolyl
R_2 = H, CH_3, Cyclohexyl
R_3 = CH_3, t-Butyl, Cyclohexyl

A new homochiral porous metal-organic complex (MOF) was synthesized on the basis of (R) -2,21-dihydroxy-1,11-binaphthyl-4,41-dibenzoic acid as a chiral ligand [39]. It was shown that this complex is an effective heterogeneous catalyst for the enantioselective D-A reaction between isoprene and N-ethylmaleimide according to the scheme:



The catalyst used was a complex of the type:



The reaction was carried out at a temperature of 200°C for 24 hours in the presence of various solvents. The authors give the results of the studies in the form of table 1.

The authors also studied the effect of the catalyst in this reaction in the presence of the solvent AcOEt at 0^0C for 48 hours. The results of these studies are given in table 2.

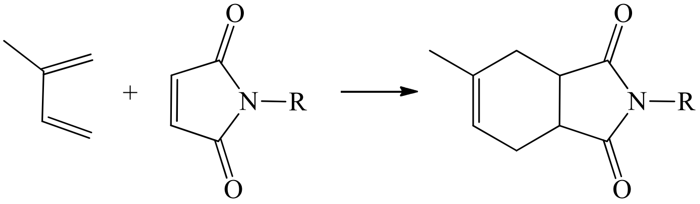
Table 1 – Effect of solvents on the yield and enantiomeric composition of the adduct in the reaction of isoprene with N-ethylmaleimide

Solvents	Yield of adduct, %	E.e., %
Methanol	48	0
Ethanol	66	21
Isopropanol	87	33
AcOEt	49	71
$CHCl_3$	85	13
Toluene	77	21
Cyclohexane	59	63
n-Hexane	80	31

Table 2 – Effect of catalyst on the yield and enantiomeric composition of the adduct in the reaction of isoprene with N-ethylmaleimide

Catalyst	Yield of adduct, %	E.e., %
–	10	0
$Cu(OAc)_2$	25	0
(R)- BINOL	21	0
$Cu(OAc)_2$ + (R)- BINOL	10	0
(R)-MOF	81	75

In conclusion, the authors also studied the effect of the substituent R in N-alkylmaleimide in the same reaction in the presence of an AcOEt solvent at 0^0C for 48 hours.



The results of these studies are presented in table 3.

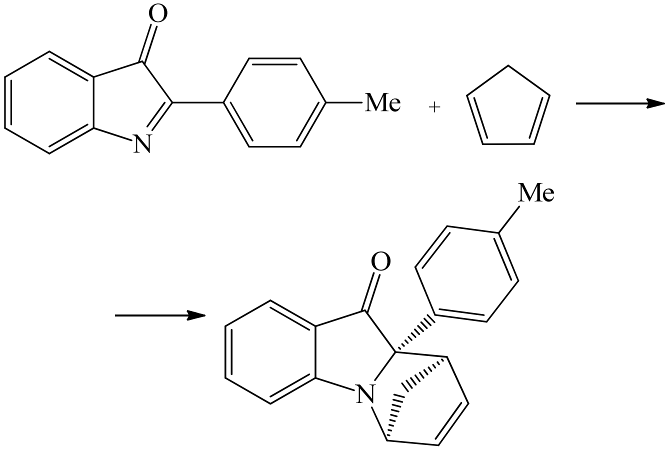
Table 3 – Effect of substituent R on the yield and enantiomeric composition of the adduct in the reaction of isoprene with N-alkylmaleimide

Substituent R	Yield of adduct, %	E.e., %
Me	37	87
Et	31	75
n-Pr	11	5
Ph	17	7
Cyclohexyl	18	0

It was shown in [40] that imino reactions of DA are an effective method for the synthesis of aza-heterocycles Zn / BINOL complex was used as catalysts.

The hetero-D-A reaction between o-quinone methides and azlactones has been studied, leading to the formation of important pharmacophore dihydrocoumarins catalyzed by the Sc (III) N, N1-Sci-III chiral complex [41]. It was shown that the reaction proceeds with a high diastereoisomer and enantioselectivity (94% ee, adduct yield 96%, diastereomer ratio 19: 1).

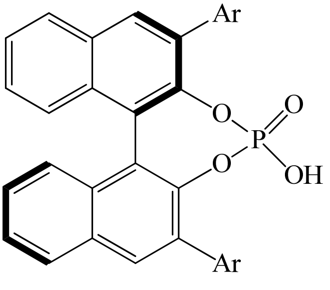
The catalyzed aza-reaction of D-A cyclic C-acylimines with cyclopentadiene catalyzed by new chiral acids of Brönsted [42]. As a result of the reaction, optically active aza-tetracycles with good yields and high diastereo- and enantiostereoselectivity are formed under moderate reaction conditions according to the scheme:

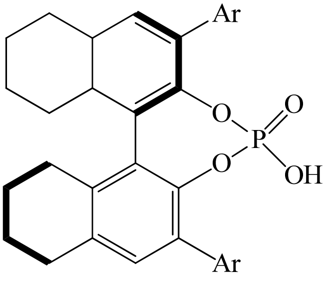


The reaction was carried out at a temperature of (-78^0) C and a duration of 2-16 hours in the presence of a solvent (toluene, a mixture of toluene and hexane, CH_2 Cl_2, $CHCl_3$). and 1-5 mol. % of catalyst.

The yield of the adduct was 73-91%, e.e. 8-94%.

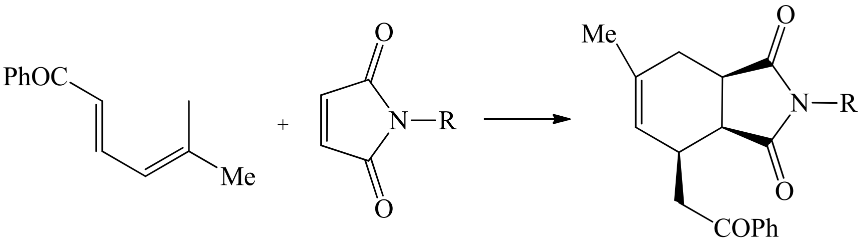
Trieneamine intermediates were used as chiral catalysts in the asymmetric reaction DA according to the scheme:

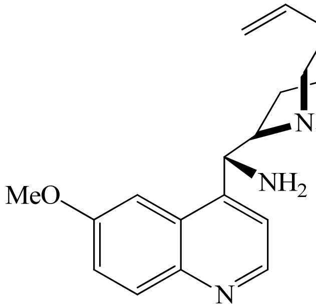




where R = H, CH_3, Ph.

The reaction was carried out at a temperature of 60^{0}C in toluene medium in the presence of the following catalyst:





Thus, the presented literature review shows that the use of chiral organic catalysts in the DA reaction continues to develop intensively and the number of works devoted to these studies is continuously growing.

In our studies, N-methylpyrrolizidone derivatives, which can be considered as one of the new versions of catalytic systems in the diene synthesis reaction, will be used as catalysts in the DA reaction.

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Резюме

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ДИЛЬС-АЛЬДЕР РЕАКЦИЯСЫНДАҒЫ ХИРАЛЬДЫ ОРГАНИКАЛЫҚ КАТАЛИЗАТОРЛАР

Диенді синтездеу реакциясында хиральды органикалық катализаторларды қолдану саласындағы ғылыми зерттеулерге талдау жүргізілді. Өндірістің әртүрлі салаларында синтезделген аддуктерді қолдану бағыттары көрсетілді. Қолданылған катализаторлардың стерео- және энантиоселективті реакцияларға әсері зерттелді.

Түйін сөздер: диенді синтез, хиральды органокатализаторлар, оптикалық белсенді қосылыстар.

Резюме

Э. Г. Мамедбейли, И. Г. Аюбов, Г. Э. Гаджиева, С. В. Исмайлова

ХИРАЛЬНЫЕ ОРГАНИЧЕСКИЕ КАТАЛИЗАТОРЫ В РЕАКЦИИ ДИЛЬСА-АЛЬДЕРА

Осуществлен анализ научных исследований в области применения хиральных органических катализаторов в реакции диенового синтеза. Показаны направления применения синтезированных аддуктов в различных отраслях промышленности. Изучено влияние использованных катализаторов на стерео- и энантиоселективность реакций

Ключевые слова: диеновый синтез, хиральные органокатализаторы, оптически активные соединения.

UDK 544.46:665.75:662.7

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THERMODYNAMICS AND MECHANISM OF OIL ADSORPTION PROCESS BY THERMOGRAPHITE

Abstract. In this work synthesis of the production of expanded graphite is proposed. It's used as a sorbent for the elimination of oil. It ́s characteristics, kinetics, and properties were investigated. The mechanism of oil adsorption is established. The magnetic properties of thermographite were also determined.

Keywords: thermographite, thermodynamics, kinetics, adsorption, oil absorption, reagent composition, ferromagnet.

It is common knowledge that cleaning surface and wastewater from oil is one of the cardinal problems of environmental protection, since oil and oil products cause enormous damage to the biosphere [1]. A common and substantial lack of all the known ways of running can practically be described as the absolute impossibility of the recovery of the collected from the water surface of the oil. It is completely burned down (method of monitoring combustion), or it falls on the bottom and is subject to dissipation (disincentives, secondary coils), or it can be unjustifiably depleted or completely removed from the reagents, emulsified water (floating adsorbents), or civil, mechanical take (with the reduction of mechanical constitution), and such oil will undo by burning with a rubbish or coil [2, 3].

The new effective sorbent synthesized in [4] on the basis of thermographite (TEG) is devoid of the aforementioned shortcomings. In the studies, natural flake graphite of the Chelyabinsk deposit of grade GL-1 0.4-0.8 mm in size was used (GOST 5279-74), the swelling agent was six-water ferric chloride [FeCl3 · 6H2O] and the initiating agent was metallic magnesium. Synthesized during the combustion of oil sorbents possessed high sorption and hydrophobic properties. It has been established that they can be reduced to the use of non-refined products and other pollutants to 80 g per 1 g of corn, which is facilitated by such properties of the TEG as a high-speed surplus surface (50-150 m^2/g), low density (1-10 kg·m^{-3}), microcrystalline structure, to improve the resistance of large clusters of substances. It should be noted that an easy and hygienic thermomagnet stabilizes the rate of release on the surface of the water in the course of the day, and after the use of non-ferrous products in the course of several sideways. At this time it can wipe the water with the surface, as well as out of the water. It is hydrated, chemically inert, electrolytic, ecologic clean, removes non-ferrous products as if they are reconstituted or emulsified, as well as in a gasoline state.

In the next paper [5], the investigation of the kinematics of the thermogenesis of the reagent composition on the output of gaseous and solid products in the frames of the classical ways to the operation of the heterogeneous reactions of the type S1 → S2 + gas is given.

The obtained results allowed to evaluate the effective thermodynamic resistance for different temperatures (table 1).

Table 1 – Effective components of the rapidity of the reagent composition for various temperatures

Temperature of thermolysis, °C	Effective constant of shortly, k h^{1}	Free member	Coefficient correlations
830	0,31 ± 0,01	0,23 ± 0,04	0,993
880	1,49 ± 0,04	-0,13 ± 0,06	0,990
1000	2,15 ± 0,09	0,43 ± 0,08	0,991

The calculated values of the effective energy of the activation of the reagent formulation are 176 kJ/mol and are close to the E_{act} values determined by other methods and presented in the literature.

The authors have proven that the main routes of the thermolysagic composition are the stages of dethermalization and ventilation (with the formation of OC and TRH, respectively), which appear paralleling. If we take into account the well-known literature [6, 7] and the obligatory for the synthesis of intercalated graphite compounds of the stages of electron transfer to the oxidizer and intercalation of graphite, it is possible to present the general scheme of the process and the destruction of SIG and, in the framework of this scheme, to consider this process as one.

The purpose of this study is to consider the thermodynamic possibility of forming thermographite using various crystalline hydrates at the interface: the solid surface of the reagent-air-oil film-water. Crystalline hydrates ($FeCl_3 \cdot 6H_2O$) can only be intermediate compounds and promote the formation of thermographite, and as the temperature rises, crystalline hydrates dissolve. Thermodynamic calculations of the values of the variation of isobaric-isothermal potentials at different temperatures.

At present, the most frequently used data are the changes in enthalpy (ΔH), heat capacity (Cp), entropy (S), Gibbs's energy (ΔG), and equilibrium constant (K) at constant pressure. Knowledge of such quantities, first of all, is necessary for determining the thermal balances of processes, in calculating the characteristics of equipment and for using them in theoretical works. Moreover, for the most part, on the basis of data on heat capacity, the effect of temperature on the enthalpy and entropy of substances and on their variation as a result of the reaction.

The values of the isobar potential are calculated for different temperatures by the formulas:

$$\Delta G_T = \left(\Delta H_{298} + \int_{298}^{T} C_p dT\right) - T\left(S_{298} + \int_{298}^{T} C_p \frac{dT}{T}\right) \quad (1)$$

$$\int_{298}^{T} C_p dT = a(T-298) + \frac{b}{2}(T-298)(T+298) + \frac{c}{3}(T-298)(T^2 + 2\cdot 298T + 298\cdot 298) \quad (2)$$

$$\int_{298}^{T} C_p \frac{dT}{T} = a\ln\frac{T}{298} + b(T-298) + \frac{c}{2}(T-298)(T+298) \quad (3)$$

$$\int_{298}^{T} C_p \frac{dT}{T} = a\ln\frac{T}{298} + b(T-298) + \frac{c}{2}(T-298)(T+298) \quad (4)$$

$$\int_{298}^{T} C_p \frac{dT}{T} = a\ln\frac{T}{298} + b(T-298) + \frac{c}{2}(T-298)(T+298) \quad (5)$$

The values of the standard values ΔH(298) = 0, S(298) and average molar heat capacity mean coefficients of the equation (mean = f (T) a = 4.1, b = $1.02\cdot10^{-3}$ and c = $-2.1\cdot10^{-5}$) are taken from the reference books [8-9]

Thermodynamic calculations of the values of the variation of isobaric-isothermal potentials at different temperatures (table 2).

Table 2 – Isobaric-isothermal potentials of ΔGT reactions of formation of thermogravenite and decomposition of crystalline hydrates at different temperatures.

T, K	$\int_{298}^{T} C_p dT$	$\int_{298}^{T} C_p \frac{dT}{T}$	ΔG_T, kcal/mol
873	-2581,6	-1,72	-2276,05
923	-3291,1	-2,36	-2377,33
973	-4100,8	-3,07	-2446,73
1023	5015,6	-3,82	-2509,21
1073	-6040,6	-4,61	-2564,10
1123	-7180,9	-5,46	-2587,88

As follows from the table, the formation of thermographites in the burning of oil at the interface between the solid surface of the reagent – air-oil film-water – is thermodynamically favorable and depends on the kinetic characteristics. The existence of crystalline hydrates at different ratios in natural graphite in the metastable state during the combustion of oil should be observed if the rate of formation of thermographite is sufficiently high. With increasing temperature, the dissolution rates of crystalline hydrates increase.

Thus, the thermodynamic characteristics of this process indicate its ability and direction towards the formation of individual compaction products, up to thermographite.

The establishment of the mechanism of the oil adsorption process, the nature of the adsorbing forces, is one of the important problems of physics and surface chemistry. Figure 1 shows a step-by-step sequence of interaction between the TEG and the oil film.

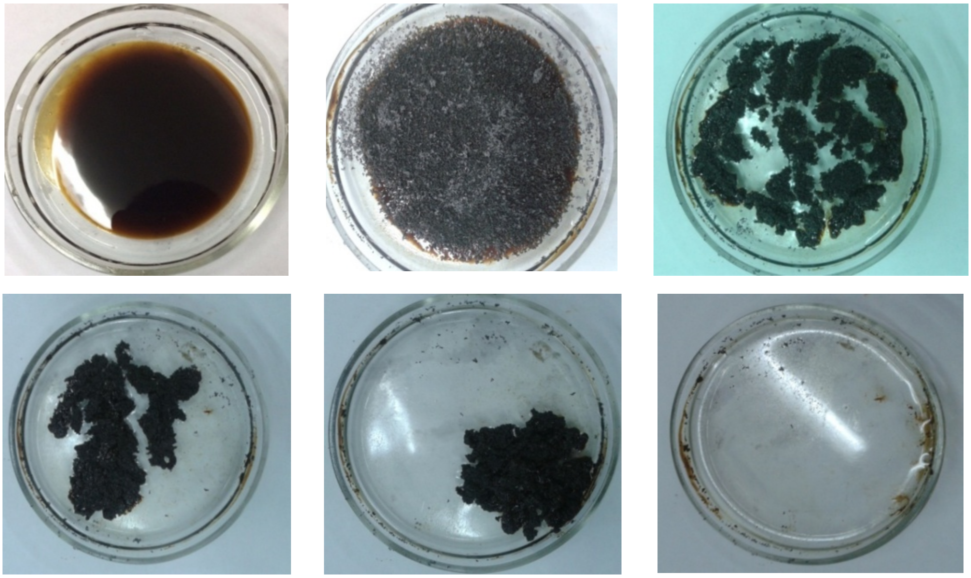


Figure 1 – Process of interaction of thermographite and oil film on the surface of water

The outer surface of the TEG is not homogeneous. In the places of contact of the particles of TEG and the oil film, interaction occurs due to intramolecular forces, which leads to a decrease in the density of the oil film. The increase in the magnetic moment of such sorbents enhances the effect of their attraction and the formation of dendrike-like structures. Such a structure ensures the stability of the position of the oil slick on the surface, at least in conditions of calm oil.

It is known [10] that the surface of any solid covers the double electrical layer, and the oil molecules are dipoles, and therefore there is interaction between the surface of the adsorbent and the oil film. Experimental studies of various adsorption cases show that the bond of the adsorbed molecule to the adsorbent can vary from weak molecular potentials to high values of chemical energy [11].

The whole process of water purification from oil contamination with an adsorbent can be presented in stages, beginning from the moment of the immersion of individual particles (or their conglomerates) of the sorbent into the oil film on water and interaction with it by the micellization scheme [12].

This process reduces to the fact that on the surface of a solid particle, due to its hydrophobicity, the process of adhesion of sorbate molecules (oil) begins and pulls them into dense colloidal formations enveloping the adsorbent particles as the core of the micelle. In addition, for the aggregates of the adsorbent there is a process of displacement and The introduction of oil into micellar complexes. The film of oil becomes thinner. Since the adsorbent particles have magnetic properties, the micelles formed also exhibit magnetic properties. Primary complexes begin to shrink together, forming the structure of a mixture of oil + sorbent. Simultaneously, the process of oil absorption by moving micelles complexes continues. The particles of the magnetic adsorbent are aligned, forming an internal fairly rigid "dendrite-like" structure inside the remaining oil film on the water surface. The number and branching of such colonies of micelles is determined by the ratio of the amount of spilled oil and the powder scattered over thermographite. With complete exhaustion of the sorption capacity of thermographite particles, a stable oil-powder structure is formed, which ensures the stability of this mixture on water.

The molecule and the sorption surface polarize each other and the dipole-dipole van der Waals interaction between these induced dipoles generates the heat of adsorption. The heat of adsorption in such cases is usually of the order of 5 kcal/mol.

A feature of adsorption interactions is that the adsorbed molecule interacts not with one center on the adsorbent surface, but with many neighboring centers. In this case, the total interaction of the adsorbate molecules with the entire adsorbent, due to the dispersive forces, is always greater than the interaction with one center of the adsorbent, and the total electrostatic interaction can be less than the electrostatic interaction with one center of the adsorbent.

The oil film does not spread, but is fixed on the surface of the water and becomes magnetically controlled. The molecules of the surface layer belong to both phases. But they experience the effect of intermolecular forces more on the liquid phase side than on the side of the solid phase (figure 2).

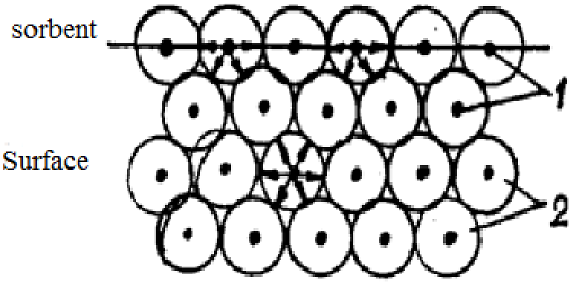


Figure 2 – Scheme of the action of intermolecular forces in the volume of a liquid and \on its surface: 1 – molecules; 2 – sphere of action of forces

To increase the effect of contraction and complete purification from oil, it is necessary either to add an additional amount of magnetic adsorbent, or to ensure the mobility of the remaining oil by "disturbing" the surface of the water. In this case, the oil completely coagulates with the sorbent. The resulting mixture exhibits magnetic properties and can be easily controlled when moving through water and collecting in a container in various ways, including by means of a magnetic conveyor.

The proposed mechanism of interaction of thermographite and oil film on the surface of water was confirmed by extended pilot testing of the reagent composition, and also by the analysis of the obtained TRG with sorbed oil.

Initially, water with a volume of 50 liters is poured into a container, then an oil layer 0.5-1 mm thick is poured onto the water surface. On the surface of the oil, a small amount of flammable liquid is sprayed, in this case gasoline, after which it is ignited (figure 3a). On the surface of burning oil the reagent composition is scattered. The high temperature of the oil heats it, as a result of which thermogravenite is formed over the oil and the burning of oil gradually decreases (Figure 3b). At the same time, the formation of thermographite on the surface of the oil ends and after a few seconds a complete adsorption of the oil product takes place (figure 3c).

a b c

Figure 3 – Formation and use of innovative reagent formulations as a sorbent for the elimination of oil in a pilot plant:a) burning of oil on the water surface with different reagent compositions in the pilot plant; b) formation of thermogranite and reduction of combustion; c) adsorption of petroleum products

The adsorption capacity of synthesized thermogranite is determined primarily by the state of the surface of the particles and by the dimensions of the adsorbing surface. Of the ophthalmic photographs, the thermographite, which is derived from the mechanical sample "20% graphite + 70% [$FeCl_3 \cdot 6H_2O$] + 10% magnesium," can see that the size of its particles varies from 100 to 1200 μm (figure 4).

The amount of oil absorbed by thermogravenite also depends on the free area of the sorbent and the properties of the surface. The increase in the surface area of the sorbent can be achieved by increasing the porosity.

In figure 5 shown of IR-spectra termographite before and afther oil sorption.

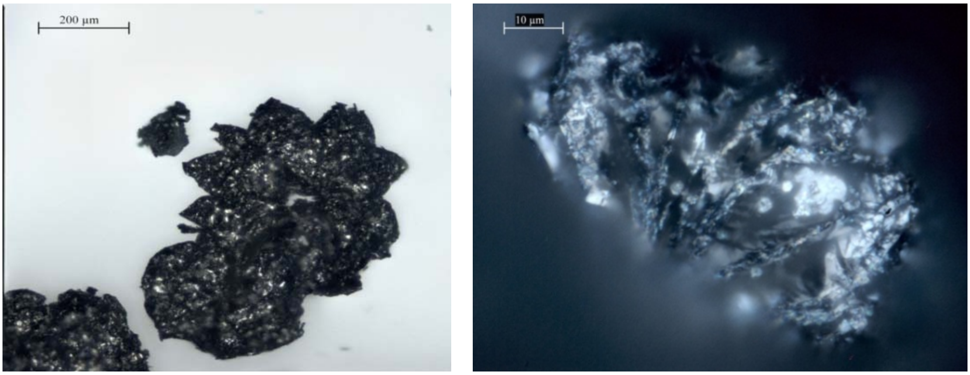


Figure 4 – Optical microcirculation of the thermomagnetic image, emitted from the mechanical "20% graphite + 70% [$FeCl_3 \cdot 6H_2O$] + 10% magnesium"

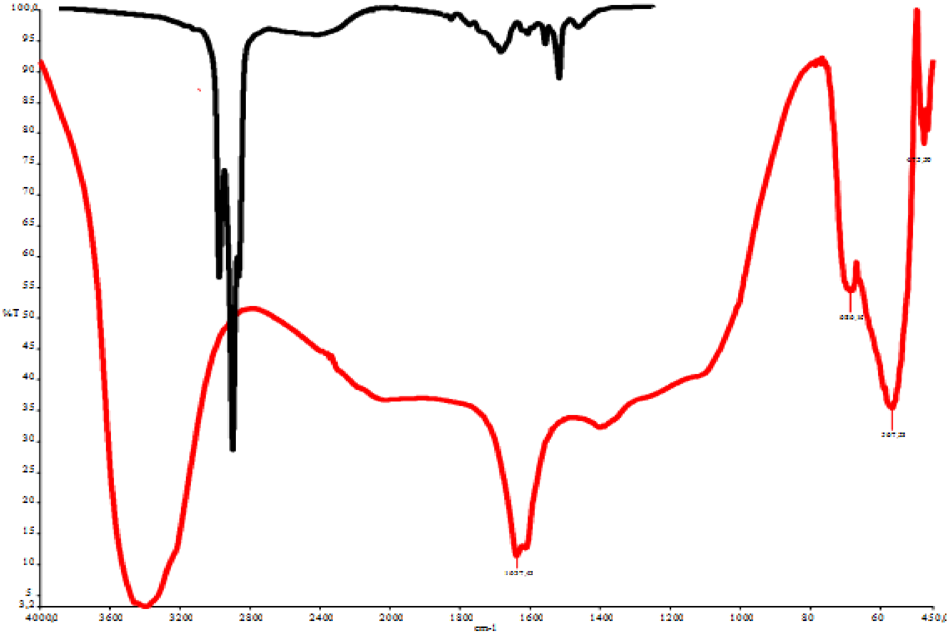
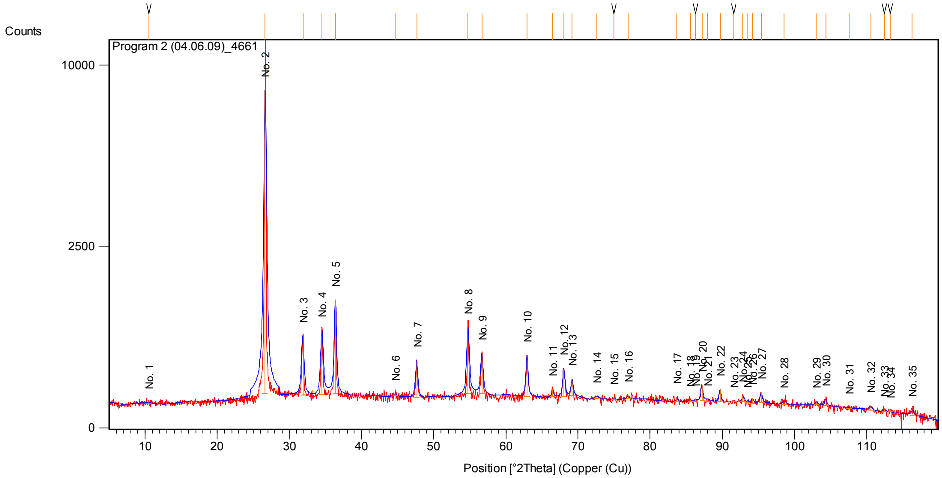


Figure 5 – IR spectra of thermographite before and after oil sorption

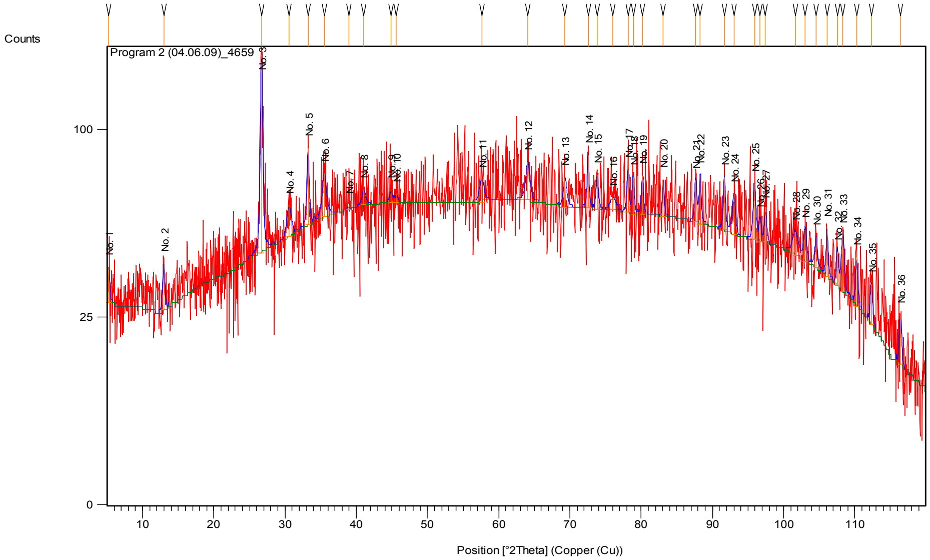
As it is seen, after the absorption of oil by thermogravenite, peaks with high inten- sity appear at the spectrum at 2955, 2923 and 2853 cm^{-1}, which are connected with symmetric valence and antisymmetric valence vibrations of the C-H bond on the surface. The presence of an impurity in these values of the alumina induces adsorption of the naphtha to thermogravenite. In addition, the method of IR spectroscopy established the presence of carbonylic, carboxyl groups on the surface of thermogravenite (intense absorption peaks in the 1600-1700 cm-region).

It was found that the properties of the carboxyl and carbonyl groups depend on such properties of thermogravenite as the capacity of absorption, the ability to exchange and form complex compounds, etc.

Additional orders on the structure of the samples of in-process and thermal gains are obtained by the method of retrogenic analysis. The retrograde phase analysis of the subterranean glare of the GL-1 mark (figure 6a) and the thermogranite obtained from the reagent composition grafit-$FeCl_3 \cdot 6H_2O$ (figure 6b) is shown on figure 6.



a – nature graphite



b – thermographite

Figure 6 – X-ray diffractograms of nature grafite and thermogranite

The blue Fourier line corresponds to the Bragg-Brentano transformation. The red line is an amorphous phase of carbon by the method of sliding X-rays. The trouble bumps of the diffraction are a characteristic black amorphous material, confirming that the thermodynamic transforms the crystal structure of the granite into an amorphous, exquisite (figure 6b) [13].

RFA also shows the magnitude of the defective phase of carbon along with the small crystal gland of the iron.

Thus, in the present study, thermodynamic calculations of the formation of thermogranite, as well as the mechanism of adsorption of oil on the surface of the synthesized sorbent, were proposed for consideration.

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Резюме

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ТЕРМОГРАФЕНИТ КӨМЕГІМЕН МҰНАЙ СОРБЦИЯСЫ ҮРДІСТЕРІНІҢ МЕХАНИЗМІ ЖӘНЕ ТЕРМОДИНАМИКАСЫ

Жұмыста кеңейтілген графит алу синтезі және оны мұнайды сіңіру сорбенті ретінде пайдалану ұсынылады. Оның сипаттамасы, кинетикасы және қасиеттері зертелінді.Мұнда мұнай адсорбциясы үрдісінің механизмі көрсетілген. Сондай-ақ, термографенитің магниттік қасиеттері анықталынды.

Түйін сөздер: термогранит, термодинамика, кинетика, адсорбция, мұнай сіңіру, реагент композициясы, ферромагнит.

Резюме

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Б. А. Байтимбетова, Е. К. Онгарбаев, З. А. Мансуров

ТЕРМОДИНАМИКА И МЕХАНИЗМ ПРОЦЕССА АДСОРБЦИИ НЕФТИ ТЕРМОГРАФЕНИТОМ

Предложен синтез получения вспученного графита и использование его как сорбента для ликвидации нефти. Были исследованы характеристики, кинетика и свойства. Установлен механизм процесса адсорбции нефти. Также были определены магнитные свойства термографенита.

Ключевые слова: термографенит, термодинамика, кинетика, адсорбция, нефтепоглощение, реагентный состав, ферромагнит.

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SYNTHESIS AND STRUCTURE OF 1,5-BIS(AMINOBUTYNILOXY)NAPHTHALINES

Abstract. New potentially biologically active 1,5-bis(aminobutynyloxy)naphthalenes were synthesized by the interaction of dipropynyloxynaphthalene with paraform and secondary amines under the catalysis of CuJ in dry dioxane at 45 °C.

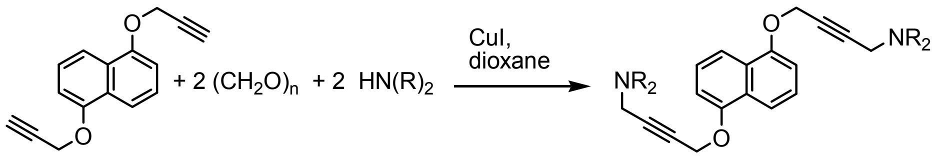
Keywords: Mannich reaction, 1,5-di(prop-2-ynyloxy)naphthalene, aminomethylation, 1,5-bis(aminobutynyloxy)naphthalenes, ^{1}H and ^{13}C NMR, PASS prediction.

The Mannich reaction, which takes place in the presence of copper monochloride in dioxane, is still one of the main methods of introducing an aminomethylene group to the neighboring position to a triple carbon-carbon bond. Authors of the article [1] give the results about the use of copper (II) acetate and ferric chloride (III) in aminomethylation reactions, the advantage of which is the use of ready-made salts of the corresponding metals in place of freshly-prepared copper monochloride. It is possible to use the Mannich reaction to prepare 2,6-diarylpiperidin-4-ones by a one-pot method by simultaneously reacting the ketone, benzaldehyde and amine component [2].

Previously, we investigated the reactivity of terminal acetylene hydrogen of 1,5-di(prop-2-ynyloxy)naphthalene in the aminomethylation reaction by some secondary amines under catalysis by copper monochloride [3] and copper monoiodide [4]. It was found that the use of copper monoiodide as a catalyst by heating of the reaction mixture to 45-50 °C in dry dioxane medium leads to less gum formation and allows reducing the reaction time to 3 hours.

In continuation of the di(prop-2-ynyloxy)naphthalenes terminal acetylene hydrogen reactivity investigation, we have now studied the aminomethylation of 1,5-di(prop-2-ynyloxy)naphthalene by diethylamine, dipropylamine, piperidine, morpholine, 3-morpholinopropane-1 -amine and methylpiperazine, shown in the figure 1 scheme.

The advantages of carrying out the reactions of aminomethylation under the catalysis by copper monoiodide include the increase of the reaction rate and the easy isolation of the products. Aminomethylated 1,5-bis(aminobutynyloxy) naphthalenes 1 – 6 are isolated by a simple treatment of the reaction mixture. After completion of the reaction, dioxane was distilled off, the precipitate was treated with ammonia (to remove copper iodide), extracted with benzene. The combined benzene extracts were dried by dry potassium. After distilling off the solvents, 1,5-bis(aminobutynyloxy)naphthalenes 1 – 6 were obtained in the form



1-6

1 $NR_2 = N(CH_2CH_3)_2$; 2 $NR_2 = N(CH_2CH_2CH_3)_2$; 3 $NR_2 = N(CH_2)_5$; 4 $NR_2 = NCH_2CH_2OCH_2CH_2$;

5 $NR_2 = NH(CH_2)_3N(CH_2CH_2)_2O$; 6 $NR_2 = N(CH_2CH_2)_2NCH_3$;

Figure 1 – Scheme of 1,5-di(prop-2-ynyloxy)naphthalene aminomethylation

of oils. As a result, 4,4'-(naphthalene-1,5-diylbis(oxy))bis(N,N-diethylbut-2-yn-1-amine) 1 (in 65% yield), 4,4'- (naphthalene-1,5-diylbis(oxy))bis(N,N-dipropylbut-2-yn-1-amine) 2 (in 87% yield), 1,5-bis(4- (piperidin-1-yl)but-2-ynyloxy)naphthalene 3 (in 82% yield), 1,5-bis(4-morpholinobut-2-ynyloxy)naphthalene 4 (in 50% yield), 4.4'-(naphthalene-1.5-diylbis(oxy))bis(N-(3-morpholinopropyl)but-2-yn-1-amine) 5 (in 52% yield) and 1,5-bis(4-(4-methylpiperazin-1-yl) but-2-ynyloxy)naphthalene 6 (in 76% yield) were obtained.

The results of the reactions of aminomethylation show that 1,5-di(prop-2-ynyloxy)naphthalene is easily aminomethylated by the secondary diamines having various structure under copper monoiodide catalysis.

The structure of synthesized compounds 1 – 6 was proved on the basis of IR, ^{1}H, ^{13}C, COSY (^{1}H-^{1}H) and HMQC (^{1}H-^{13}C) spectroscopy data.

In the IR spectra of 1,5-bis(aminobutynyloxy)naphthalenes 1 – 6, there is no absorption band in the 3300 cm^{-1} region, which is characteristic of the ≡CH terminal acetylenic group, but there is a weak band at 2118 cm^{-1}, which is characteristic for disubstituted C≡C bound, which confirms the aminomethylation reaction.

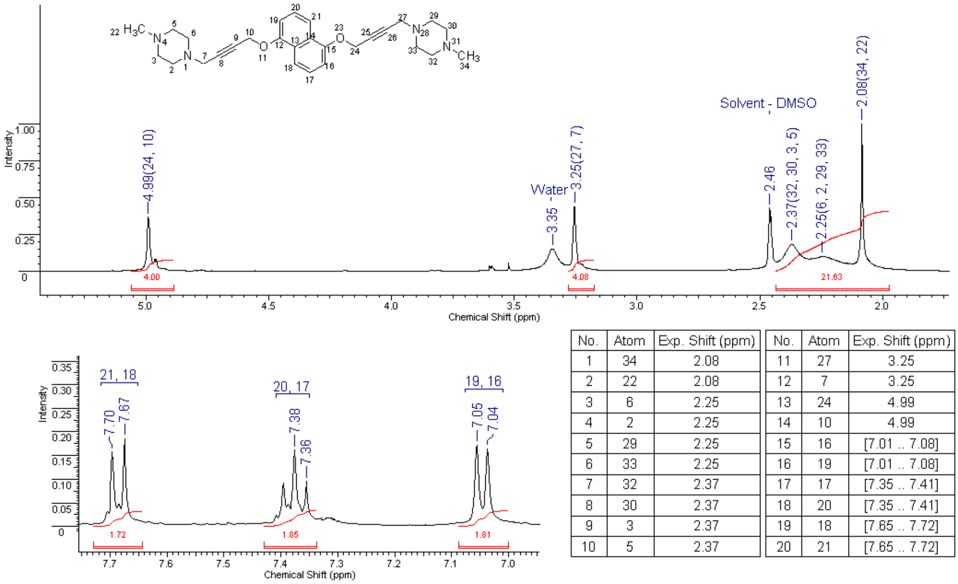
In the ^{1}H NMR spectra of 1,5-bis(aminobutynyloxy)naphthalenes 1 – 6, the data of which are given in table 1, the new resonance signals appear in the corresponding regions characteristic for an aminomethylene group (in a range 3.25 – 3.37 ppm) and for the substituents at a nitrogen atom.

Table 1 – NMR ^{1}H (δ, ppm) NMR spectra of 1,5-bis(aminobutynyloxy)naphthalenes 1 – 6

Comp.	Protons of naphthalene cycle			CH_2N	OCH_2	Protons of NR_2
	$H^{16}H^{19}$	$H^{17}H^{20}$	$H^{18}H^{21}$			$N(CH_2)_2$, $O(CH_2)_2$, CH_3
1	7,06	7,37	7,68	3,35	5,10	2,45; 0,94
2	7,06	7,34	7,67	3,32	4,91	2,46; 1,27; 0,71
3	6,98	7,34	7,88	3,27	4,85	2,49; 1,50; 1,54
4	6,90	7,30	8,07	3,27	4,89	2,71; 3,73
5	7,06	7,32	7,72	3,36	4,95	3,19; 3,54; 1,49
6	7,05	7,38	7,70	3,25	4,99	2,37; 2,25; 2,08

Note: The numbering of signals is given in accordance with figure 2.

For example, in the ^{1}H NMR spectra of 1.5-bis(4-(4-methylpiperazin-1-yl)but-2-ynyloxy)naphthalene 6 shown in a figure 2, signals at 2.08, 2,25, and 2.37 ppm, are assigned to signals of symmetrical methylene groups of two methylpiperazine rings. Singlets at 4.99 ppm correspond to protons of O-methylene groups. Protons of aminomethyl substituents appear at 3.25 ppm in form of a broadened singlet. In the weak-field part of the spectrum, the signals of protons of the naphthalene nucleus are appeared, resonating in the region of 7.04-7.70 ppm.



No.	Atom	Exp. Shift (ppm)	No.	Atom	Exp. Shift (ppm)
1	34	2.08	11	27	3.25
2	22	2.08	12	7	3.25
3	6	2.25	13	24	4.99
4	2	2.25	14	10	4.99
5	29	2.25	15	16	[7.01 .. 7.08]
6	33	2.25	16	19	[7.01 .. 7.08]
7	32	2.37	17	17	[7.35 .. 7.41]
8	30	2.37	18	20	[7.35 .. 7.41]
9	3	2.37	19	18	[7.65 .. 7.72]
10	5	2.37	20	21	[7.65 .. 7.72]

Figure 2 – ^{1}H NMR spectrum of 1,5-bis(4-(4-methylpiperazin-1-yl)but-2-ynyloxy)naphthalene 6

In the ^{13}C NMR spectra of 1,5-bis(aminobutynyloxy)naphthalenes 1-6, the data of which are given in table 2, new resonance signals appear in the corresponding regions, characteristic for the aminomethylene group (in the range 42 – 50 ppm) and for the substituents of a nitrogen atom.

For example, in the carbon spectrum of 1,5-bis(4-(4-methylpiperazin-1-yl)but-2-ynyloxy)naphthalene 6, shown in figure 3, the most characteristic chemical shifts of carbon atoms –C≡C– 80.55 and 83.69 ppm. Signals of oxymethylene carbon atoms are manifested at 56.71 ppm. In the weak-field region at 107.27-153.16 ppm the signals of the carbon atoms of the naphthalene ring are located. Signals of CH_3N and CH_2N groups are appeared in the strong-field region at 46.22 and 46.71. The carbon atoms of the piperazine rings are resonated at 51.68 and 55.02 ppm.

The results of the interpretation of the two-dimensional spectrum in the HMQC (^{1}H-^{13}C) format, shown in figure 4, allow us to determine the correlation between chemical shifts of protons and chemical shifts of carbon nuclei, spin-spin interactions between nuclei, which allows us to establish the nature of heteronuclear interactions.

Table 2 – NMR ^{13}C (δ, ppm) NMR spectra of 1,5-bis(aminobutynyloxy)naphthalenes 1 – 6

Соед.	OCH_2	–C≡C–	–C≡C–	≡CH_2	NR_2
1	56,83	83,37	80,29	47,03	47,03; 12,93
2	56,47	85,3	81,05	42,02	55,47; 20,59; 12,21
3	53,30	79,80	75,60	47,90	56,70; 23,80; 25,80
4	56,84	79,7	78,01	47,08	52,22; 66,58
5	56,32	79,5	78,80	50,35	48,6; 24,53; 56,32; 53,80; 66,61
6	56,71	83,69	80,55	46,71	51,68; 55,02; 46,22
Соед.	Carbon atoms of the naphthalene ring				
	$C^{12}C^{15}$	$C^{16}C^{19}$	$C^{17}C^{20}$	$C^{18}C^{21}$	$C^{13}C^{14}$
1	153,18	107,48	125,81	114,7	126,73
2	153,44	107,70	126,17	115,93	127,54
3	153,30	106,40	125,10	115,30	126,80
4	153,01	107,6	126,77	114,88	128,99
5	152,96	107,04	125,83	114,64	128,69
6	153,16	107,27	126,52	114,68	128,85
Note: The numbering of signals is given in accordance with figure 3.					

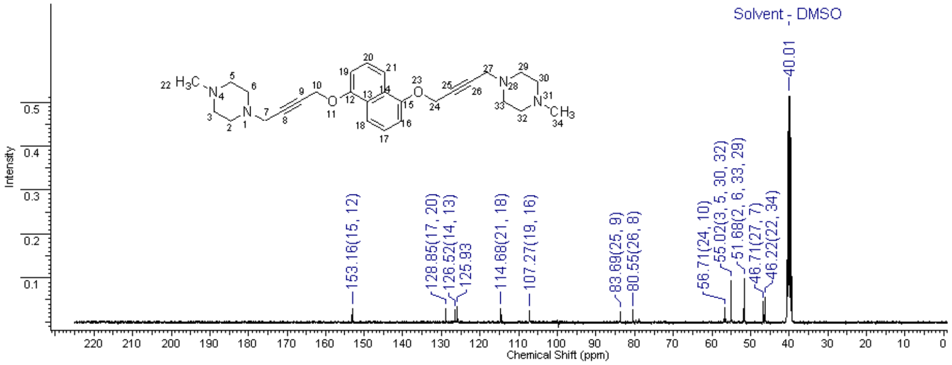


Figure 3 – ^{13}C NMR spectrum of 1,5-bis(4-(4-methylpiperazin-1-yl)-but-2-ynyloxy)naphthalene 6

The relationship "structure - biological activity" serves as a foundation for the purposeful creation of effective medicines. To determine the types of potential biological effects of synthesized compounds, a predictive assessment of the probable biological activity was carried out using the PASS (Prediction of Activity Spectra for Substance) computer program developed by the russian scientists V.V. Poroykov and D.A. Filimonov [5]. Using the computer program PASS - PharmaExpert, after analyzing the results of the forecast, it is possible to select those substances that are likely to possess the required set of activity types.

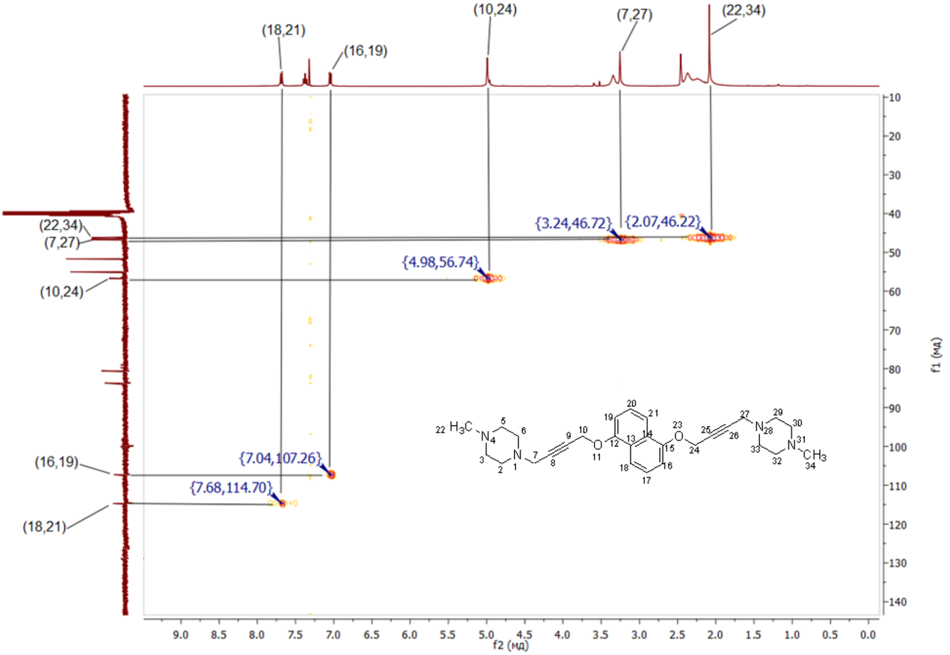


Figure 4 – Two-dimensional spectrum of 1,5-bis(4-(4-methylpiperazin-1-yl)but-2-ynyloxy) naphthalene 6 in the HMQC (^{1}H-^{13}C)

Analysis of data given in table 3 shows that 1,5-bis(aminobutynyloxy)naphthalenes 1 – 6 potentially with a probability above 90% are the substrates of cytochrome CYP2C12 families (cytochromes are responsible for the metabolism of endogenous steroids of the body). For compounds 1, 2, 3, 5 with a probability from 60% to 93%, it is predicted spasmolytic activity in the treatment of bladder hyperactivity.

Table 3 – Predicted biological activity of 1,5-bis(aminobutynyloxy)naphthalenes 1 – 6

Chemical compounds	Probability of occurrence of predicted activity, %							
	CYP2C12 substrate	Spasmolytic, urinary	Antiseborrheic	Antisecretoric	Antineurotic	Phobic disorders treatment	Membrane integrity agonist	Antidyskinetic
1	94	93	86				76	70
2	91	89	78	70			82	
3	74	60		61	66	72	73	
4	68				75	87		
5		81			73	84		
6	67			59	75	69		

It should also be noted that for the 4,4'-(naphthalene-1,5-diylbis(oxy))-bis(N,N-diethylbut-2-yn-1-amine) 1 and 4,4'-(naphthalene-1,5-diylbis(oxy))-bis(N,N-dipropylbut-2-yn-1-amine) 2 the highest probability from 78% to 86% of the antiseborrheic activity in the treatment of children and adults seborrheic dermatitis (seborrhea). With the introduction of piperidine, morpholine, 3-morpholinopropane-1-amine and methylpiperazine, activity for the treatment of phobic disorders treatment (neuroses) (69-87%) and antineurotic activity (66-75%) is manifested. In addition, the compounds obtained revealed the possibility of manifesting antisecretoric and antidyskinetic activity.

Thus, as a result of the research work, new potential biological active 1,5-bis(aminobutynyloxy)naphthalenes have been synthesized. The structure of the synthesized compounds was established by the methods of IR spectroscopy, ^{1}H and ^{13}C NMR spectroscopy.

Experimental part

The course of the reaction and the purity of the products were monitored by thin-layer chromatography on "Silufol UV-254" plates, the eluent was a mixture of benzene and ethanol (1:3) with the appearance of substances spots with iodine vapor. The IR spectra are recorded on a Nicolet 5700 spectrometer in KBr tablets. The ^{1}H and ^{13}C NMR spectra of the samples were taken in DMSO-D$_6$ using a JNM-ECA 400 (Jeol) spectrometer with operating frequencies 400 (^{1}H), 100 MHz (^{13}C).

4,4'-(Naphthalene-1,5-diylbis(oxy))bis(N,N-diethylbut-2-yn-1-amine) 1. Solution of 0.3 g (0.0042 mol) diethylamine in dioxane 10 ml was dropped while stirring to a reaction mixture consisting of 0.5 g (0.0021 mol) of 1,5-di(prop-2-ynyloxy)naphthalene, 0.12 g (0.004 mol) of paraform, 0.12 g (0.0042 mol) of copper monoiodide in 20 ml of dioxane, and heated to 45 °C in a three-necked reaction flask equipped with a reflux condenser and a stirrer. After the end of the reaction, dioxane was distilled off. The residue was treated by aqueous ammonia solution and extracted by benzene. The extract was dried with potash, and the solvent was distilled off. The residue was applied to a column of silica gel, eluting by benzene. Chromatographically homogeneous fractions were combined, benzene was distilled off under reduced pressure. 4,4'-(Naphthalene-1,5-diylbis-(oxy))bis(N,N-diethylbut-2-yn-1-amine) 1 was obtained as an oil 0.56 g (65%).

4,4'-(Naphthalene-1,5-diylbis(oxy))bis(N,N-dipropylbut-2-yn-1-amine) 2. Similarly, from 0.5 g (0.0021 mol) of 1,5-di(prop-2-ynyloxy)naphthalene, 0.12 g of paraform, 0.43 g (0.0042 mol) of dipropylamine in the presence of 0.1 g of copper monoiodide in dioxane (at 45 °C) was obtained 0.85 g (87%) of diamine 2 as an oil.

1,5-Bis(4-(piperidin-1-yl)but-2-ynyloxy)naphthalene 3. Similarly, from 0.5 g (0.0021 mol) of 1,5-di(prop-2-ynyloxy)naphthalene, 0.12 g of paraform, 0.36 g (0.0042 mol) of piperidine in the presence of 0.1 g of copper monoiodide in dioxane (at 45 °C), 0.75 g (82%) of diamine 3 was obtained as an oil.

1,5-Bis(4-morpholinobut-2-ynyloxy)naphthalene 4. Similarly, from 0.4 g (0.0016 mol) of 1,5-di(prop-2-ynyloxy naphthalene, 0.12 g of paraform, 0.35 g (0.0032 mol) of morpholine in the presence of 0.1 g copper monoiodide in dioxane (at 45 °C), 0.37 g (50%) of diamine 4 was obtained as an oil.

4.4'-(Naphthalene-1.5-diylbis(oxy))bis(N-(3-morpholinopropyl)but-2-yn-1-amine) 5. Similarly, from 0.5 g (0.0021 mol) of 1,5-di(prop-2-ynyloxy)naphthalene, 0.12 g of paraform, 0.61 g (0.0042 mol) of morpholine in the presence of 0.1 g copper monoiodide in dioxane (at 45 °C) gave 0.58 g (53%) of diamine 5 as an oil.

1,5-Bis(4-(4-methylpiperazin-1-yl)but-2-ynyloxy)naphthalene 6. Similarly, from 0.5 g (0.0021 mol) of 1,5-di(prop-2-ynyloxy)naphthalene, 0.12 g of paraform, 0.42 g (0.0042 mol) of methyl piperazine in the presence of 0.1 g copper monoiodide in dioxane (at 45 °C), 0.74 g (76%) of diamine 6 was obtained as an oil.

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Резюме

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СИНТЕЗ И СТРОЕНИЕ
1,5-БИС(АМИНОБУТИНИЛОКСИ)НАФТАЛИНОВ

Новые потенциально биологически активные 1,5-бис(аминобутинилокси)нафталины синтезированы путем взаимодействия 1,5-дипропинилоксинафталина с параформом и вторичными аминами (диэтиламином, дипропиламином, морфолином, 3-морфолинопропаном, метилпиперазином) при катализе CuJ в среде сухого диоксана при температуре 45 °С с выходами от 50 до 87%. Сделана прогнозная оценка вероятной биологической активности по компьютерной программе PASS (Prediction of Activity Spectra for Substance).

Ключевые слова: 1,5-ди(проп-2-инилокси)нафталин, аминометилирование, 1,5-бис(аминобутинилокси)нафталины, ЯМР ^{1}H и ^{13}C, PASS прогнозирование.

Резюме

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1,5-БИС(АМИНОБУТИНИЛОКСИ)НАФТАЛИНДЕРДІҢ СИНТЕЗІ ЖӘНЕ ҚҰРЫЛЫМДАРЫ

Жаңа потенциалды биологиялық белсенді 1,5-бис(аминобутинилокси)нафталиндер дипропинилоксинафталиннің параформмен және екіншілік аминдермен (диэтиламин, дипропиламин, морфолин, 3-морфолинопропан, метилпиперазин) CuJ катализі құрғақ диоксан ортасында 45 °С температурада әрекеттестіру жолы арқылы 50-ден 87 % дейінгі шығыммен синтезделген. PASS (Prediction of Activity Spectra for Substance) компьютерлік бағдарламасы бойынша ықтималды биологиялық белсенділікке болжаулар жүргізілді.

Түйін сөздер: 1,5-ди(проп-2-инилокси)нафталин, аминметилдеу, 1,5-бис(аминобутинилокси)нафталиндер, ЯМР ^{1}H және ^{13}C, PASS бағдарлау.

UDC 54.057:547

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OBTAINING PALLADIUM NANOPARTICLES AND THEIR APPLICATION AS CATALYST IN HYDROGENETION OF VEGETABLE OIL

Abstract. Palladium nanoparticles are obtained by reduction of palladium chloride with sodium borohydride. The obtained palladium particles are characterized by intense optical absorption in the region of λ=350 nm, which indicates the formation of particles with a size of 10-50 nm. Palladium nanoparticles are immobilized on activated carbon to increase the contact surface. The catalytic activity of the obtained catalyst has been studied in the hydrogenation reaction of vegetable oil at convection and microwave heating. It has been found that at the content of 1 % of the oil mass catalyst, a higher melting product is formed (38^{0}C. Decrease of temperature and duration reduction of the process results in low melting margarines of MLF and MLB grades). The use of microwave technology (power 700 W) reduces significantly the duration of the process (up to 30 minutes) to form a product with the melting point of 34^{0}C.

Key words: palladium nanoparticles, reduction, hydrogenation of vegetable oil, margarine, microwave activation.

Introduction. The colloids and clusters of platinum group metals exhibit high catalytic activity and selective capacity in relation to many reactions [1, 2]. In the work [3], it is reported that colloidal particles of platinum group metals synthesized by different methods differ markedly in their reaction and catalytic activity.

In the present work, obtaining of stable solutions of palladium nanoparticles, as well as the catalytic properties of immobilized Pd nanoparticles on activated carbon in the hydrogenation reaction of vegetable oil in margarine under the conditions of convection heating and microwave activation is described.

Depending on the melting point, consistency and appearance, margarines are divided into the following grades: hard (MH, MHC, MHF), soft (MS) and liquid (MLF, MLB). MH grade is used in bread, confectionery and culinary production and in home cooking. MHF - for the preparation of creams, fillings in flour confectionery goods, souffle, sweets and other sugary and flour confectionery goods (the melting temperature of MH and MHF grades should be 25-38^{0}C). MHC (the melting point is 36-44^{0}C) is used in the production of puff pastry. MS grade (the melting point is 25-36^{0}C) is directly used in food consumption, as well as in home cooking and in food industry. MLF grade is used for frying and cooking baked goods in home cooking, public catering network and industrial processing; and MLB is used for the mass production of bakery and baked confectionery products, as well as when frying products in the public catering network (the melting points of the grades MLF and MLB is not standardized) [4].

Experiment

UV spectra were recorded on a Shimadzu UV-1800 spectrometer (Japan). The melting point was determined on a PTP(M) device (Russia). Micrographs of the catalyst surface with 100-, 500- and 1000-fold increase were taken with a scanning electron microscope JSM-6510 LV of JEOL (Japan). The hydrogen generator GVCH-12M1 (Russia) was used to obtain hydrogen.

Obtaining of palladium nanoparticles supported on activated carbon. Prior to carrying out the reaction, solution of sodium borohydride and palladium chloride was prepared (2 drops of hydrochloric acid are added to the solution to dissolve the salt in water). At room temperature, to the reaction vessel containing 100 ml of $1\cdot10^{-3}$ mol/L of solution of palladium chloride, with constant stirring dropwise 100 ml of $1\cdot10^{-3}$ mol/L of solution of sodium borohydride is added. At the same time, colouration of the solution into whity brown is observed.

In order to prevent the agglutination process of nanoparticles into larger agglomerates, 2g of powdered pharmaceutical activated carbon is added to the reaction mixture and the solution is stirred for 6 hours. Then, the solution is filtered and the resulting solid mass is dried in a drying oven at a temperature of 110^0C for an hour.

Hydrogenation of vegetable oil.

a) 50 g of cottonseed oil is loaded and 0.5 g of catalyst (the palladium content in the catalyst is 0.53%) is added to a three-necked flask equipped with a stirrer, thermometer and hydrogen inlet tube. The process is carried out at 220-230^0C for 6 hours at a hydrogen flow rate of 0.2 l/min.

b) Mixture of 50 g of vegetable oil, 0.5 g of catalyst with constant hydrogen bubbling is irradiated with microwaves for 30 minutes.

Results and discussion

Synthesis of palladium dispersions has been carried out by reduction of palladium chloride with sodium borohydride [5].

The reduction reaction of palladium proceeds according to the following scheme:

$$2NaBH_4 + PdCl_2 + 6H_2O \rightarrow 2NaCl + 2H_3BO_3 + 7H_2 + Pd$$

The obtained palladium particles are characterized by intense optical absorption in the region of λ=350 nm (figure 1).

It is known [6] that a solution containing palladium nanoparticles with a particle size of 10 nm absorbs ultraviolet radiation in the region of 230 nm. With increase of the size of particles, the absorption bands shift into the visible region, for example, with an increase in the diameter of particles to 50 nm, a broad absorption band with a maximum of about 450 nm is observed. The obtained absorption spectrum data of palladium particles indicate the formation of particles with the sizes of 10-50 nm.

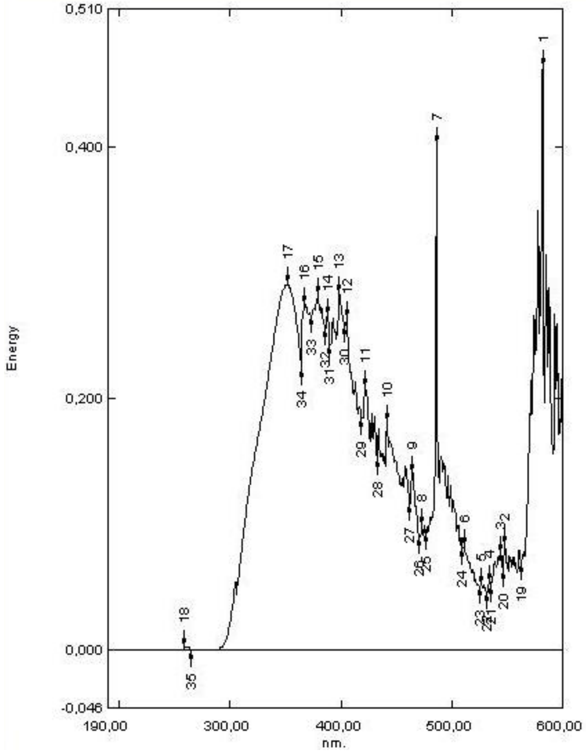
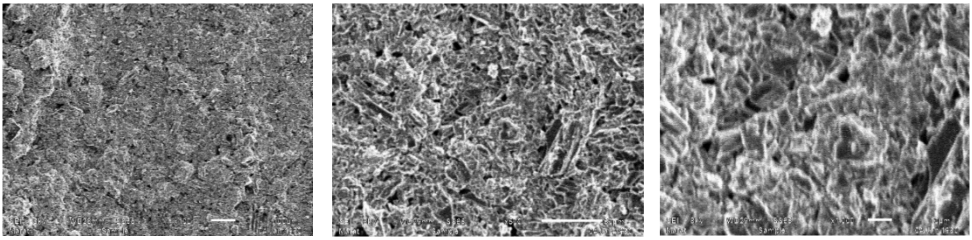


Figure 1 – Spectrum of the UV and visible region of the obtained palladium nanoparticles

The work [5] describes that palladium nanoparticles obtained by this method coagulate easily to form a precipitate. In order to prevent the agglutination process of nanoparticles into larger agglomerates, powdered pharmaceutical activated carbon was added to the reaction mixture. Micrographs of the obtained catalyst surface, taken with a scanning electron microscope JSM-6510 LV of JEOL (Japan) are shown in figure 2. Palladium nanoparticles (white dots) are fairly evenly distributed on the surface of activated carbon.

In addition to preventing the agglutination of nanoparticles, the contact surface of the catalyst increases.



100-fold increase 500-fold increase 1000-fold increase

Figure 2 – Micrographs of palladium nanoparticles immobilized on activated carbon

The hydrogenation process of vegetable oil has been carried out according to the known method [7]. The hydrogenation results on the obtained catalyst under various conditions are given in table.

The hydrogenation results of vegetable oil

No.	Hydrogenation duration, h	Process temperature, °C	Wt% of the catalyst from oil weight	The content of palladium nanoparticles in the catalyst, %	Wt% of palladium particles from oil weight	The melting point of a product, °C
1	6	220-230	0,1	0.053	$5{,}3\cdot10^{-4}$	8
2	6	220-230	0,5	0.265	$2{,}65\cdot10^{-3}$	10
3	6	220-230	1,0	0.53	$5{,}3\cdot10^{-3}$	38
4	6	200	1,0	0.53	$5{,}3\cdot10^{-3}$	15
5	5	220-230	1,0	0.53	$5{,}3\cdot10^{-3}$	9
6	0.5	MW radiation, 700 W	1,0	0.53	$5{,}3\cdot10^{-3}$	34

As the catalyst content is increased from 0.1 to 1 %, a higher melting product (38^0C) corresponding to the margarine of MHC grade is formed. Decrease of temperature and duration reduction of the process results in low melting margarines of MLF and MLB grades. The use of microwave technology (power 700 W) leads to a significant duration reduction of the process up to 30 minutes, while a product with the melting point of 34^0C, which meets the standards of MH, MHF AND MS grades, has been obtained.

Conclusions. Thus, hydrogenation catalyst of vegetable oil in which palladium nanoparticles are immobilized on activated carbon is obtained. The parameters of the hydrogenation process of vegetable oil, which allow obtaining various margarine grades are established.

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Резюме

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ПАЛЛАДИЙДІҢ НАНОБӨЛШЕКТЕРІН АЛУ ЖӘНЕ ОЛАРДЫ ӨСІМДІК МАЙЫН ГИДРЛЕУ КАТАЛИЗАТОРЫ РЕТІНДЕ ПАЙДАЛАНУ

Хлорлы палладийді натрий боргидридімен тотықсыздандыру арқылы палладийдің нанобөлшектері алынды. Алынған палладий бөлшектері λ=350 нм аумағында қарқынды оптикалық жұтылумен сипатталады, ол 10-50 нм өлшемді бөлшектердің түзілгендігін дәлелдейді. Жанасу бетін жоғарылату үшін палладийдің нанобөлшектері белсендірілген көмірге иммобилизацияланды. Алынған катализатордың каталитикалық белсенділігі өсімдік майын конвекциялық және микротолқындық қыздыру жағдайында зерттелді. Май массасынан катализатор мөлшері 1% болғанда жоғары температурада балқитын өнім түзіледі (38^{o}С. Температураны төмендеткенде және үрдіс ұзақтығын қысқартқанда МЖК және МЖП маркалы төмен температурада балқитын маргариндер түзіледі). Микротолқындық технологияны қолдану (қуаты 700 Вт) кезінде үрдіс ұзақтығы айтарлықтай қысқарып (30 мин-ке дейін), балқу температурасы 34^{0}С-ге тең өнім түзіледі.

Түйін сөздер: палладийдің нанобөлшектері, тотықсыздандыру, өсімдік майын гидрлеу, маргарин, микротолқындық активация.

Резюме

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ПОЛУЧЕНИЕ НАНОЧАСТИЦ ПАЛЛАДИЯ И ИХ ПРИМЕНЕНИЕ В КАЧЕСТВЕ КАТАЛИЗАТОРА ГИДРИРОВАНИЯ РАСТИТЕЛЬНОГО МАСЛА

Восстановлением хлористого палладия борогидридом натрия получены наночастицы палладия, которые характеризуются интенсивным оптическим поглощением в области λ=350 нм, что свительствует об образовании частиц размером 10-50 нм. Для увеличения контактной поверхности наночастицы палладия иммобилизованы на активированный уголь. Каталитическая активность полученного катализатора исследована в реакции гидрирования растительного масла при конвекционном и микроволновом нагреве. Найдено, что при содержании 1 % от катализатора массы масла образуется более высокоплавкий продукт (38^{o}С. Понижение температуры и сокращение продолжительности процесса приводит к низкоплавким маргаринам марок МЖК и МЖП). Использование микроволновой технологии (мощность 700 Вт) значительно сокращает продолжительность процесса (до 30 мин) с образованием продукта с т.пл. 34^{0}С.

Ключевые слова: наночастицы палладия, восстановление, гидрирование растительного масла, маргарин, микроволновая активация.

UDC 547.992 + 661.162.6

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APPLICATION OF MODIFIED HUMIC MATERIALS FOR GREENING CITIES AKTAU AND ZHANAOZEN

Abstract. Field trials of modified humic preparations at the sites of Expo-Trading LLP, Agrorost LLC (Aktau) and school No. 20 (Zhanaozen) have been shown their high efficiency in growing flower-decorative, deciduous, coniferous, vegetable and fruit-berry crops. It has been established that their application encourages the increase of seed germination (98.27-100.0%) and the survival of seedlings and plants (99.12-100.00%).

Keywords: modifiedhumicmaterials,growth stimulants, greening, open ground, field tests.

At present, the interest in humate-type fertilizers has increased all over the world, and there is extensive experience in the practical application of humic compounds as natural physiologically active substances under different agricultural cultures for different soil-climatic condition. They accumulate elements of nutrition and energy, participate in the migration of cations, reduce the negative effects of toxic substances, affect the development of organisms and the heat balance of the planet. The humic compounds are stable, high-molecular, polydisperse, contain various functional groups, amino acids, polysaccharides, benzoid fragments [1-4].

Climate of Aktau and Zhanaozen is characterized by large amplitude of temperature fluctuations throughout the year, a rapid transition from winter to hot summer. Its feature is the aridity, contrast and high variability over the years of the amount of precipitation and temperatures, a small amount of precipitation. This makes it necessary to use more frequent watering. It should be noted that the state of the ground in the cities of Aktau and Zhanaozen is extremely tense and pollution, degradation and depletion of soil is observed in most of the urban areas. There is also a negative change in the structure of the ground of the city, a decrease in the content of humus in it, which threatens the conservation of the biological diversity of urban plantations, the intensity of their survival and growth. Therefore, it is necessary to carry out a complex of measures to restore technogenic disturbed lands and gardening of Aktau and Zhanaozen. Growth stimulating, fertilizing, meliorative and humectant properties of composite humic materials allow using them to solve above problems.

Agrochemical experiments are laid on the sections of “Expo-Trading” LLP and “Agrorost” LLC (Aktau) and school No. 20 (Zhanaozen). Modified compositional humic materials are used for growing flower, deciduous, ornamental, vegetable and fruit-berry crops.

Composite humic materials have been used for seed treatment, root and foliar treatment of vegetative plants (figure 1).

“Expo-Trading” LLP sections

"Agrorost" LLC sections

Figure 1 – Humic growth-stimulants experiments layout

During the studies it was established that the use of humic growth stimulants promotes better survival, growth and development of test crops as compared to plants in control variants. The phenological observations showed that the degree of seed germination of the tested crops in the experimental version was 98.27-100.0%, and in the control one it was 93.70-94.80%, and the seedling and seedlings survival rate was 99.12-100.00 %, and in the control variant - 94.38-95.10%. Increasing the germination of seeds allows them to save them when planting (up to 15-20%). It should be noted that the application of these preparations leads to the development of the root system of plants, and the enhanced development of roots certainly increases the supply of water to the leaves and leads to improved water supply of plants.

The application of modified humic preparations promoted intensification of the color intensity of flowers in experimental variants, increase in the size of their leaf surface and the height of the stems, as well as inflorescences. In this case, for flower crops, a significant increase in the length of the stem, the leaf surface and the size of the buds, the color of the leaves and flowers becomes more intensive in comparison with the control variant. In ornamental crops, their application increases the number and size of leaves, the color becomes more vivid. Treatment with the drug also leads to an increase in their disease resistances.

Sites are located along busy urban roads with a large number of exhausts of cars and enterprises, characterized by extreme gas contamination and pollution. The entire vegetation of these areas is subject to severe environmental pressure, therefore, it grows poorly, develops slowly, is prone to disease, etc. The use of modified humic preparations has made it possible to solve these problems, and has helped to significantly save budget for the purchase of expensive plant protection products (fungicides, herbicides, etc.) and a large number of mineral fertilizers. These drugs can be used not only for gardening of Aktau city, but also in other settlements of the country.

In the plots of school No. 20 (Zhanaozen), in conditions of open ground, agrochemical experiments with the application of modified composite humic growth stimulants are laid. Were planted 100 pcs of elm seedlings, 9 pcs of ailanthus, 8 pcs of ash, 15 pcs of thuja, as well as various flower crops and lawn grass. The area of the tested site was 700 m^2. The carried out researches have shown that under the action of modified composite humic preparations the vegetation period in experimental plants is reduced by 10-15 days, mainly due to the reduction of the period from germination to flowering.

3 years analysis results showed that the application of composite humic preparations leads to an increase in the activity of physiological processes in plants, i.e. promotes better germination and survival of the experimental crops, growth of stem size, trunk and branch of tree cultures, increase in the leaf surface of plants, inflorescences and buds of flower crops (figure 2). Their root system becomes longer and branchy, increases chlorophyll content in leaves. For example, experimental plants were better branched (41-55 pieces), increased by an average of 1.23-3.49 m compared to the control ones, the diameter of the trunk was 19-32 cm. During the observation of plants, the color of leaves and flowers was revealed become more intense in comparison with control variants.

As noted above, meteorological conditions during the agrochemical tests were characterized by a very dry summer and low precipitation. The use of modified composite humic preparations promoted the increase of plant resistance to unfavorable environmental conditions and stressful influences.

Figure 2 – Modified humic preparations influence on plants growth and development (Sh. No. 20, Zhanaozen)

Conclusions. Field trials of compositional humic compounds have shown their high efficiency in the cultivation of flower-decorative, deciduous, vegetable and fruit-berry crops conducted on the sites of "Expo-Trading" LLP and "Agrorost" LLC and school No. 20 in conditions of open ground in Aktau and Zhanaozen. It has been established that their application contributes to the increase of seed germination and the survival of seedlings and saplings, the growth of flower, ornamental and other crops, the increase in the size of inflorescences, buds and leaves, the intensification of their coloration, and the resistance of test crops to diseases and unfavorable external conditions.Carried out tests have been demonstrated a possible significant savings in the Aktau and Zhanaozen cities budget by using composite humic preparations for gardening.

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Резюме

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ТҮРЛЕНДІРІЛГЕН ГУМИНДІ МАТЕРИАЛДАРДЫ АҚТАУ ЖӘНЕ ЖАҢАӨЗЕН ҚАЛАЛАРЫН КӨГАЛДАНДЫРУҒА ҚОЛДАНУ

Ақтау және Жаңаөзен қалаларының ашық топырақ жағдайларында түрлендірілген гуминді материалдарды әртүрлі өсімдіктерді өсіруге қолдануға болатындығы көрсетілді. Жүргізілген егістік сынақтар кезіндетүрлендірілген гуминді материалдарды қолдану өсімдіктердің өсіп-өнуін жылдамдататындығы, олардың вегетация уақытын қысқартатындығы анықталды.

Түйін сөздер: түрлендірілген гуминді материалдар, өсімдіктің өсуін тездеткіштер, көгалдандыру, ашық топырақ, егістік сынақтар.

Резюме

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ПРИМЕНЕНИЕ МОДИФИЦИРОВАННЫХ ГУМИНОВЫХ МАТЕРИАЛОВ ДЛЯ ОЗЕЛЕНЕНИЯ ГОРОДОВ АКТАУ И ЖАНАОЗЕН

Показана возможность применения модифицированных гуминовых материалов для выращивания различных зеленых насаждений в условиях открытого грунта городов Актау и Жанаозен. Установлено, что использование модифицированных гуминовых материалов ускоряет рост и развития растений, приводит к сокращению сроков их вегетации.

Ключевые слова: модифицированные гуминовые материалы, ростстимуляторы, озеленение, открытый грунт, полевые испытания.

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NEW INVESTIGATIONS IN ION-EXCHANGE MEMBRANES SYNTHESIS AND THEIR MODIFICATION

Abstract. Ion exchange membranes (IEMs) have great potential in diverse applications and play prominent roles in addressing energy and environment related issues. Over the past decade, the development of IEMs has attracted much research attention in terms of materials, preparation and applications, due to their academic and industrial values. In this review, the advances in diverse IEM materials are summarized, providing insights into the fundamental strategies to achieve targeted properties. Apart from the intrinsic features of materials, optimized preparation methods are crucial to improve the quality of IEMs, which are discussed in detail. New IEM materials bring new applications, which are summarized in this review. Finally, the opportunities and challenges in the chemical stability of IEM materials, controllable fabrication of IEMs, and integration applications of IEMs are identified.

Keywords: ion exchange, ion-exchange membranes, membrane technology.

Ion exchange membranes (IEMs) are typically composed of hydrophobic substrates, immobilized ion-functionalized groups, and movable counter-ions. Depending on the type of ionic groups, IEMs are broadly classified into cation exchange membranes (CEMs) and anion exchange membranes (AEMs). Naturally, the ion-functionalized groups attached onto the IEMs will dissociate after the penetration of sufficient water molecules, releasing cations or anions for the transfer of corresponding ions. The most commonly functional moieties in CEMs contain sulfonic acid, phosphoric acid and carboxylic acid groups. Quaternary ammonium cations, imidazole cations, and guanidinium cations are generally anchored onto the polymer backbones to obtain AEMs [1, 2].

Since last century, IEMs as a new type of material have received much research attention because of their applications in a variety of fields. IEMs are used in electrodialysis to concentrate or dilute aqueous or non-aqueous electrolyte systems, and in diffusion dialysis to recover acid or alkali from waste acid or alkali solutions. Recently, IEMs have significantly contributed to overcome the problems associated with energy and environment. Diverse electrochemical technologies such as polymer electrolyte membrane fuel cells, redox flow batteries, reverse electrodialysis cells, and water electrolysis utilize IEMs that separate and transport ions between the anode and cathode to balance the electron flow in the external circuit. Thus, there is an increasing worldwide interest in the use of IEMs to develop renewable energy sources [1].

Considering the importance of IEMs for contemporary developments, they have been extensively studied in academic and industrial fields. To satisfy various requirements of traditional and newly emerging IEM-related fields, research efforts have been devoted to developing novel IEMs or to modifying pristine IEMs for certain targeted activity. To date, most of the IEMs consist of polymeric backbones prepared by either post-functionalization of pre-existing polymers or direct polymerization of functionalized monomers. To convert the prepared polymers to IEMs, suitable membrane formation techniques are needed, and these techniques have been widely studied in the past. IEMs with excellent qualities can be assembled into various devices and processes. Materials, preparation methods, and final applications are all crucial in the field of IEMs.

In 2005, a review on IEMs was published in Journal of Membrane Science [3]. The review was extensively cited, indicating that the research enthusiasm on IEMs is ever-growing. In the current decade, great efforts have been devoted to upgrading IEMs, as illustrated by the chronology of IEM related publications over the past decade in figure 1. We realize a brand-new review to summarize the progresses of IEMs is given urgently. Particularly, with the rapid progress in nanoscience, the regulation and control of polymer structures make for the formation of ionic channels, which is a new development in this field. Newly emerging preparation methods are worthy of research attention. Over the past decade, most of the IEM applications are expected to solve issues related to energy and environment, and these aspects are becoming the hot topics in the present literature. Herein, the recent progress in IEMs along with the line of materials-preparation applications will be reviewed [1–3].

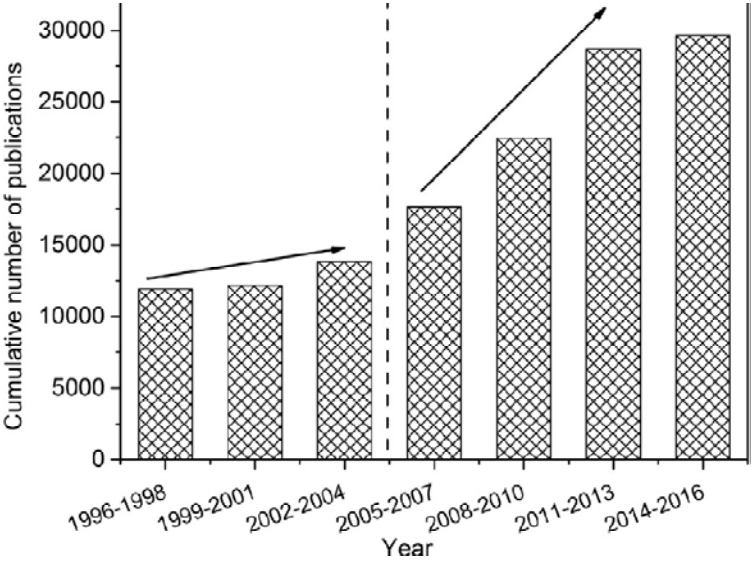

Figure 1 – Chronological advancement of ion exchange membrane in the past 20 years. Source: www.scopus.com; Search settings: ion exchange membrane including articles, conferences, notes, books and review papers; Last accessed: August 2016

Anion exchange membranes (AEMs). AEMs are generally prepared from positively charged polyelectrolytes and are designed to conduct anions while being impermeable to neutral molecules or cations. The major concerns of AEMs lie in anion conductivity, chemical stability and dimensional stability. To date, substantial research efforts have been devoted to this field, which can be classified into two main categories. The first category involves synthesis of new anion conducting groups (ACGs), while the second category involves design of a particular polymer architecture [4].

AEMs with new cationic head groups. Quaternized ammonium (QA) groups (figure 2a) are the conventional ACGs for AEMs because of their facile synthesis procedure by simply treating a polymer precursor bearing benzyl halide groups and trimethylamine (TMA) [1, 5]. However, the drawbacks of low anion conductivity and inadequate tolerance to highly alkaline environments have been blocking the AEMs' development and commercialization. In order to solve these problems, various tertiary amines with different chemical structures were investigated as precursors for ACGs. Some of these included 1,4- diazabicyclo[2.2.2]-octane (DABCO) (figure 2b), hexamethylenetetramine (figure 2c), N,N,N,N-tetramethyl-1,6-diaminohexane (figure 2d) (TMHDA), and N,N,N,N-tetramethyl-1,2-diaminoethylene etc. [6]. Interestingly, some of these functional reagents (such as TMHDA, and DABCO) contain two tertiary amine groups and thus can be utilized as cross-linking reagents to prepare AEMs with improved mechanical properties and dimensional stability.

Nitrogen containing conjugated molecules are potential ACGs for AEMs. Guanidinium cations (figure 2e) were firstly investigated as ACGs for AEMs by Zhang and co-works. Novel AEMs were easily prepared by functionalizing chloromethylated PAES with 1,1,2,3,3-pentamethyl guanidine. High basicity of pentamethylguanidine with a conjugated structure was considered to be responsible for the high anion conductivity and alkaline tolerance of this type of AEMs. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (figure 2f) is a kind of organic super bases which possesses a high pKa value in the order of 12. DBU based AEMs were prepared via the reaction between brominated poly(2, 6-dimethyl-1, 4-phenylene oxide) (BPPO) and DBU under mild conditions. More recently, extensive research efforts have been devoted to the development of imidazolium based AEMs (figure 2g) because of their easy synthesis procedure and versatile structures. It should be noted that substituents on the imidazole ring have a profound impact on the alkaline stability of imidazolium based AEMs. C2- unsubstituted imidazolium has proved to be unstable and undergoes ring opening degradation in strongly basic environments. Afterwards, Price and co-works investigated the effect of different C2 substituents on the chemical stability of imidazolium cations. Surprisingly, imidazolium with C2 position substituted by some bulky substituents (such as, tert-butyl and phenyl group) exhibits much inferior alkaline tolerance, verifying that steric hindrance protection is a less effective factor for stabilizing of the imidazolium cations. However, the authors think that acidity of the methyl protons at C2 position, which can provide alternative and reversible deprotonation

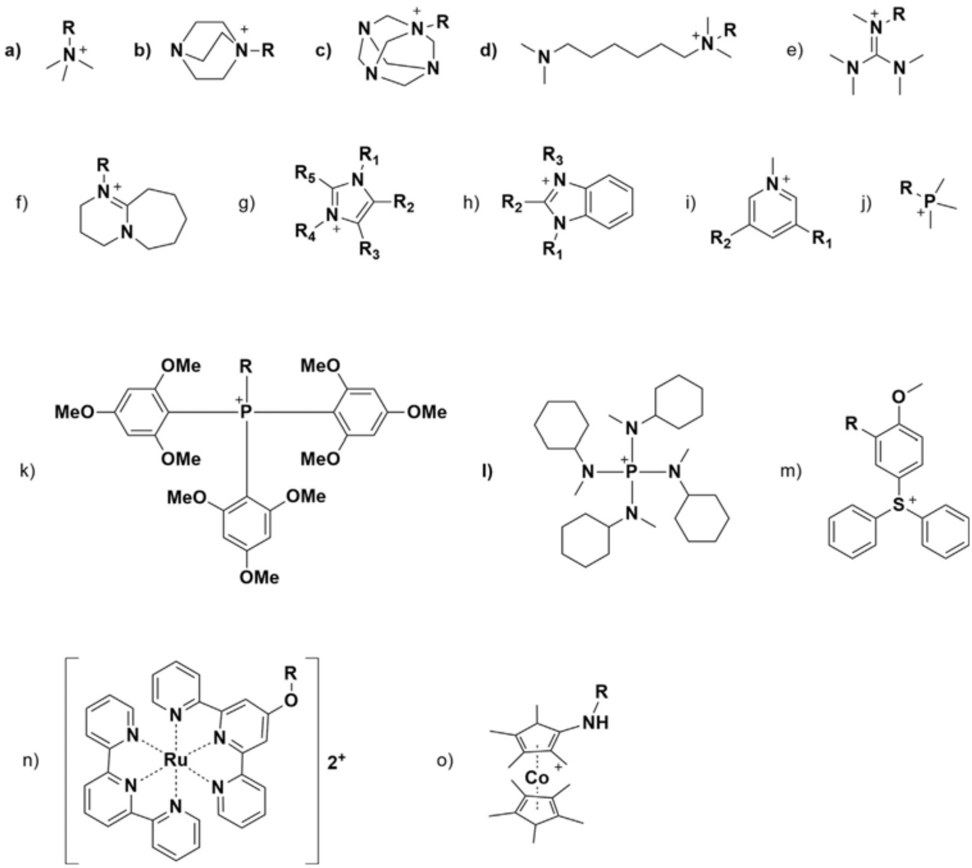

Figure 2 – Commonly encountered anion conducting groups for anion exchange membrane

reactions, is the key factor that decides the stability of imidazolium cations. On the other hand, Yan and co-workers reported that both steric hindrance and electro-donation effects have significant influences on the alkaline tolerance of imidazolium based AEMs. To support this, the imidazolium cation with 2,4,6-trimethoxyphenyl as C2 substituent was prepared and its chemical stability was compared with C2 unsubstituted one. As expected, this type of AEMs prepared from BPPO and trimethyl-2-(2,4,6-trimethoxyphenyl) imidazole exhibited both high anion conductivity and improved alkaline stability.

Benzimidazolium cations (figure 2h) hold great promise to serve as ACGs for AEMs. Holdcroft and co-workers synthesized benzimidazolium based AEMs by methylation of PBI. By introducing a bulky tirmethylphenyl ring to the C2 position of benzimidazole, stable main chain functionalized type AEMs were successfully synthesized. It is noteworthy that the introduction of adjacent bulky groups increases the steric hindrance around the reactive C2 position, would hinder nucleophilic attack by hydroxide ions, thus improving the stability of PBI based AEMs. Benzimidazolium based AEMs have shown advantages in dimensional, mechanical and thermal stabilities, while simultaneously exhibiting higher anion conductivity compared with the analogous AEMs bearing quaternary ammonium and imidazolium cations [7, 8].

Pyridine-based AEMs (figure 2i) were synthesized by our group and employed in the separation of various anions. Improved hydrophilicity and anion permeability were observed for pyridinebased AEMs compared with the conventional QA based AEMs. Besides, the membrane also exhibited good perm-selectivity for different anions.

Phosphonium cations are recognized as promising candidates for ACGs. AEMs based on phosphonium cations can be easily prepared by reacting polymer precursors containing benzyl halide with either trimethylphosphine (figure 2j) or triphenylphosphine. However, this type of AEMs have proved to be unstable in alkaline media because of severe nucleophilic attack by hydroxide ions. Yan and co-workers [9–12] found that by introducing three electro-donating methoxyl groups into each phenyl ring of triphenylphosphine (figure 2k), cation conductivity and alkaline tolerance of phosphonium based AEMs could be greatly enhanced. This can be ascribed to both steric hindrance and electro-donating effects of methoxyl groups. Another type of phosphonium cation with more complicated structure was synthesized and investigated by Coates and co-works (figure 2l). Despite its relatively low IEC values, this phosphonium based AEM exhibited satisfactory cation conductivity and outstanding alkaline tolerance. It is believed that steric hindrance protection to the central phosphonium cations and delocalization of positive charges to the carbon atoms are the principle reasons for their superior chemical stability.

Tertiary sulfonium cations (figure 2m) act as ACGs for AEMs. Yan and coworkers [11] synthesized the first base stable sulfoniumbased AEM by introducing one electro-donating methoxyl group to the phenyl ring connected to sulfonium cations. Hickner and co-workers [13, 14] prepared metal-cation functionalized AEMs by copolymerization and cross-linking of dicyclopentadiene and norbornene monomers bearing a water-soluble bis(terpyridine)ruthenium (II) complex (figure 2n). Hydroxide conductivity of 27 mS/cm and acceptable alkaline tolerance were observed, suggesting that the metal-cation based polyelectrolytes may serve as potential candidate for AEMs. Besides, Yan and coworkers reported permethyl cobaltocenium based AEMs (figure 2o), which have reduced positive charges on the metal center. This cobalt based AEM exhibited excellent stability.

Monovalent ion perm-selective membranes (MIPMs). A monovalent ion perm-selective membrane (MIPM) allows for rapid permeation of mono-valent ions, while blocking passage of multi-valent ions. Owing to the special functions of MIPMs in distinguishing mono-valent and multi-valent ions with the same charge, they are widely explored in a wide range of applications including seawater desalination, acid recovery in hydrometallurgy and removal of specific ions from liquid waste. The perm-selectivity between ions of the same charge in a mixture through MIPMs is governed by several factors, such as differences in ions' hydrated radii, affinities with IEMs and migration speeds in the membrane phase. The strategies used for regulating such factors have been reported in the literature. Some of these strategies are as follows [15].

Importing cross-linked moieties in IEM matrix or coating a cross-linked thin layer on the membrane surface is considered to be effective in obtaining MIPMs. With the introduction of crosslinked components, the IEM becomes denser. Therefore, the ions with different hydrated radii may be differentiated based on a size sieving effect. Apart from widely reported covalent cross-linking, acid-base cross-linking also demonstrates effective in improving the density of membrane matrix to obtain MIPMs. For example, an MIPM with this type of cross-linking was constructed by our group using imidazole groups and sulfonic acid groups (figure 3). The formation of hydrogen bonding networks based on the acid-base interaction makes the membranes more compact and also holds the ability to limit the passage of Zn^{2+}. Meanwhile, the channels along with the hydrogen bonding networks promote the transfer of H^+, leading to desired high H^+ flux. Crystalline is another type of cross-linking. Recently, our group completed the preparation of a MIPM by adding crystalline domains into IEMs [16, 17].

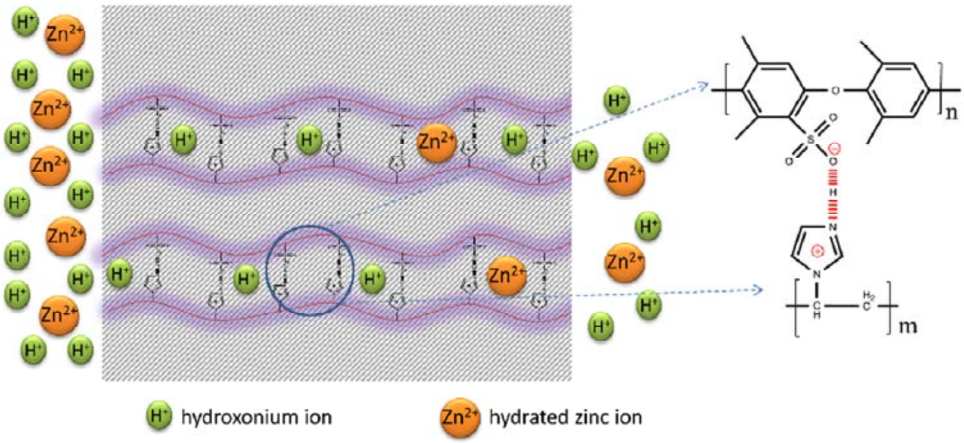

Figure 3 – Constructing H^+ transfer channels through the formation of acid-base pairs

Although cross-linking is especially fascinating in preparing MIPMs, high electrical resistance caused by the cross-linking is an inevitable issue. To decrease the detrimental influence of cross-linking, conducting layers are introduced onto the MIPM surface. Gohil and co-workers developed a MIPM by means of the polymerization of pyrrole on the membrane surface. The poly-pyrrole layers could both reject multi-valent ions and reduce the resistance during the electro-dialysis operation.

Depositing an oppositely charged layer relative to the nature of bulk IEM' charge also enables the preparation of MIPMs. For this type of MIPMs, multi-valent ions with the same charge as the membrane surface are rejected due to the relatively large electrostatic repulsion, while mono-valent ions are still able to pass through the skin layer. Lambert et al. [18] modified a Nafions membrane by electro-depositing highly protonated polyethyleneimine (PEI) on its surface. The PEI layer is positively charged in acidic media and has the potential to block the passage of multi-valent ions. More recently, with the development of layerby-layer (LBL) technique, alternating adsorption of poly-cations and poly-anions has become a potential method to form an ultrathin layer for repelling multi-valent ions. For example, S. Mulyati et al. [19] deposited poly(sodium 4-styrene sulfonate) (PSS) and poly(allylamine hydrochloride) (PAH) alternatively on a NEOSEPTA AMX membrane by the LBL technique. With the increasing number of layers, the selectivity for the mono-valent anions is greatly improved.

Polymerization grafting of cationic/anionic vinyl monomers on the membrane surface is also an attractive option to obtain MIPMs through the surface modification means. Ogumi et al. [20] prepared monovalent cation perm-selective membranes by surface polymerization of 4-vinypyridine monomers initiated by the generated radicals during the oxygen plasma treatment. The resultant membrane showed high monovalent cation perm-selectivity and low membrane resistance.

Regulating the compositions of ionic functional groups and IEM matrices can be applied in achieving selective permeation of mono-valent ions. This is due to the fact that the perm-selectivity among ions with same valence state is not only governed by the difference in size, but also decided by the difference in affinity forces of ions with the membranes. Nagarale et al. [21] investigated a series of CEMs having different functional groups including sulfonic acid, phosphonic acid, and carboxylic acid groups. The results showed that an IEM with phosphonic acid groups is the most suitable for the electro-driven separation of ions with identical charges. Furthermore, a few recent studies tried to prepare MIPMs by varying the hydrophobic and hydrophilic characters of the membranes. For example, Gohil et al. [22] adjusted the hydrophilic-hydrophobic property of pristine sulfonated PES by adding sulfonated poly ether ether ketone (SPEEK). It was observed that the perm-selectivity of mono-valent ions relative to di-valent ions increased with decreasing SPEEK contents.

The above-mentioned methods may be combined in a reasonable way to improve the monovalent perm-selectivity of IEMs. Although a large number of optional IEMs are widely reported in various industrial fields, the comprehensive properties of MIPMs can still not meet some requirements set for applications on an industrial scale. The limitations rely on low perm-selectivity, insufficient ion flux, and high electrical resistance. More research attention should be given to further improve the membranes.

Bipolar membranes (BPMs). Over the last decade or so, IEMs have evolved from a laboratory tool to industrial products with significant technical and commercial impacts. Among these IEMs, the bipolar membrane (BPM), which is composed of one cation exchange layer (CEL), one anion exchange layer (AEL) and an interfacial layer (IL) between the two layers, occupies a special position due to its ability for generating protons and hydroxide ions from water molecules under direct current polarization. In 1956, this type of IEM was referred to as BPM in an academic literature for the first time [23]. Since then, intensive studies have been conducted on BPMs, which focus on a number of BPMs' industrial applications, such as electrodialysis for environmentally clean technologies and treatment of salt water effluents. It is worth mentioning that a well-established milestone in this field is the understanding of the mechanism of electric field enhanced (EFE) water molecule dissociation in BPMs.

BPMs are analogous to p-n junction semiconductors, whereas the junction formed at the BPM interfacial layer (IL) constitutes a depletion region and thus contains a built-in potential. Figure 4a shows a schematic illustration of the structure and function of BPMs. When a potential (40.83 V) is applied across the mem-brane, a very large electric field (108 V/m) is generated in the IL. The water mo-lecules residing in the IL become sufficiently polarized and hence, get dissociated. Figure 4b shows a typical steady current density-voltage (I-V) curve, which presents the operation of a BPM. The curve clearly presents the water splitting process during the passage of an increased current density through the membrane. In the first region, the current is very low and is mainly transported by the diffusion of salt ions. In the second region, water dissociation occurs and the current is transported by protons and hydroxide ions, which are generated in the interphase. In the third region, the generation rate of protons and hydroxide ions is limited by the transport of water molecules into the interphase, leading to an increase of the operating voltage and the destruction of the membrane. It is worth mentioning that the water dissociation in the BPMs is seven orders of magnitude higher than that in the free solution. The actual water dissociation mechanism is still not fully understood and needs extensive research attention [1, 24].

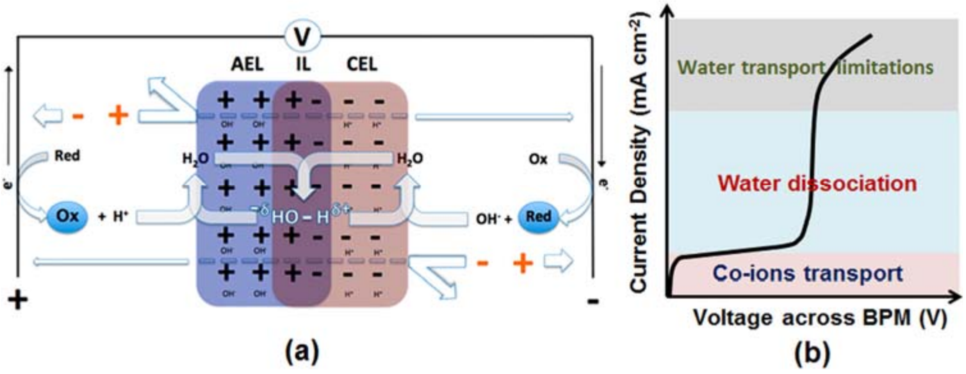

Figure 4 – Schematic illustrations of (a) the structure and function of a BPM;
(b) a typical I-V curve of a BPM in a salt solution

Various mechanisms have been proposed to explain the accelerated water dissociation in BPMs. A well-established mechanism, which is supported by theoretical and experimental evidences, is the so-called reversible proton transfer reaction mechanism. According to the model, the generation of protons and hydroxide ions at the interfacial region are believed to be the result of protonation and deprotonation of the reaction between the water molecules and fixed charge groups. This model can explain the acceleration of water dissociation in the interphase of BPMs and also serve as a theoretical basis for the development of BPMs.

Typically, BPMs have been commonly prepared by LBL casting of CEL and AEL materials, or pasting CEL and AEL together by external addition of heat and pressure or by using adhesives. During these processes, a thin, modified IL is formed between CEL and AEL to generate protons and hydroxide ions. Available materials for both CEL and AEL need to transport ions effectively. The water dissociation materials for the IL are sought to control the BPM potential to a value as close to the thermodynamic potential of 0.83 V as possible so that the energy consumption could be reduced. The chemical composition and structure of the IL are elaborately designed, following the mechanism of the proton transfer reaction. One promising strategy is to immobilize catalysts in the IL to provide alternative reaction paths for the dissociation reaction by forming very active complexes. Previous studies have reported that weak acid and base with an equilibrium constant close to that of the water dissociation reaction constant pKa¼7, e.g. amino groups (primary, secondary or tertiary amine), and pyridines could be incorporated into the IL. Our previous work have demonstrated the catalytic activities of hydrophilic macromolecules, including polyethylene glycol (PEG), PVA, and hyper-branched polymers. Additionally, inorganic substances, such as GO, and heavy metal ions complexes could also been incorporated into IL for enhancing the water dissociation [25].

In summary, tremendous progresses have been made in screening suitable catalysts for the water dissociation and improvement of membrane preparation techniques in the past several decades. It is worth mentioning that high performance commercial BPMs are available and are widely used in industrial scale application. However, there are still a lot of open questions regarding the development of chemical stable polymer candidates, precise control of micro-morphology and in-depth understanding of water dissociation and ions transport mechanism within BPMs. In practical applications, BPMs are required to possess low electrical resistance at high current density, high water dissociation ratio, low co-ion transport rate, high ionic selectivity, and most importantly, good chemical stability against acid and base due to direct contact of CEL with the acid solution and that of AEL with the alkaline solution. However, highly alkaline stable AEL candidates are rarely reported. Additionally, precise control of thickness and architecture of the catalytic interphase is still unsatisfactory. Further systematic studies on these points will continue to push forward the industrial application of BPMs.

Ion exchange membranes emerging as renewable materials play prominent roles in promoting the development of traditional industry and innovative energy technologies. To date, most of the attention has been focused on exploring promising materials, developing diverse preparation methods, and expanding a wide variety of applications related to ion exchange membranes.

Over the past ten years, such field has significantly bloomed and a large number of achievements have been gained. To date there are a tremendous number of ionic polymer candidates available for the preparation of various kinds of ion exchange membranes, including cation exchange membranes, anion exchange membranes, monovalent ion perm-selective membranes, mixed matrix membranes, and bipolar membranes. Although progresses in exploring new ion exchange membranes are prominent, there are still a few challenges, which need to be urgently addressed. For example, the chemical stability of the membranes should be promoted furthermore to ensure the longevity of their lifetime in various applications.

Apart from the intrinsic characteristics of materials, choosing appropriate preparation methods is also of pivotal importance to accomplish desired membrane performances. Currently, a series of techniques such as polymer blending, pore filling, in-situ polymerization and electro-spinning, have shown promise in preserving and occasionally improving the elegant properties of pristine polymers. To date, the studies on the preparation methods are not very detailed and only the feasibility of these methods has been demonstrated. Further exploration and optimization of operating conditions are essential to achieve precise control in structure and composition of improved ion exchange membranes.

Along with the advancements of materials and preparation methods for ion exchange membranes, the corresponding applications have also made rapid progress. Typical applications involving IEMs include diffusion dialysis, electrodialysis, bipolar membrane electrodialysis, reverse electrodialysis, fuel cells, and redox flow batteries. Although some of them have come true or may come true from the viewpoints of industries, their integration of these applications is still scarce and some technical puzzles need to be solved.

Besides, more available ion conducting mechanisms should be proposed after achieving a deeper understanding towards the transport issues within confined space. Porous ion exchange membranes from polymers of intrinsic microporosity and Troger's Base [26] as well as porous fillings such as metal-organic framework, and covalent organic framework also deserve special attention, as these may achieve extremely high separation effi- ciency and beat the “trade-off” effect in IEMs-based process. Finally, it should be emphasized that materials, preparation methods, and potential applications in the area of ion exchange membranes need to be synergistically explored and taken forward.

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Резюме

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ИОНАЛМАСТЫРҒЫШ МЕМБРАНАЛАРДЫҢ ЖАҢА ЗЕРТТЕУЛЕР СИНТЕЗДЕУ ЖӘНЕ МОДИФИКАЦИЯЛАУ

Ионалмастырғыш мембраналар әртүрлі қолданыстарда үлкен әлеуетке ие және энергетика мен қоршаған ортаға қатысты мәселелерде үлкен рөл атқарады. Соңғы онжылдықта ионалмастырғыш мембраналардың дамуы академиялық және өндірістік құндылықтары арқасында материал, дайындау және қолдану тұрғысынан зерттеушілердің аса назарын аударды. Бұл шолу мақаласында негізгі стратегияларды түсінуді және қойылған мақсаттарға қол жеткізуді қамтамасыз ете отырып, ионалмастырғыш мембраналардың синтезі мен түрленулері туралы жаңа зерттеулерге арналған әртүрлі жұмыстардағы жетістіктер талданып қорытылған. Дайындаудың оңтайландырылған әдістері мембраналардың сапасын жақсарту үшін өте маңызды. Ионалмастырғыш материалдар осы шолу мақаласында жинақталған синтезге және түрленуге жаңа зерттеулерді енгізеді.

Түйін сөздер: ион алмасу, ион алмасу мембраналар, мембраналық технология.

Резюме

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НОВЫЕ ИССЛЕДОВАНИЯ В СИНТЕЗЕ И МОДИФИКАЦИИ ИОНООБМЕННЫХ МЕМБРАН

Ионообменные мембраны обладают большим потенциалом в различных применениях и играют огромную роль в вопросах, касающихся энергетики и окружающей среды. За последние десятилетия развитие ионообменных мембран привлекло большое внимание исследователей с точки зрения материалов, подготовки и приложений, благодаря их академических и промышленных ценностей. В этом обзоре обобщены достижения в различных работах, посвященных новым исследованиям в синтезе и модификации ионообменных мембран, обеспечивая понимание основных стратегий и достижения поставленных задач. Оптимизированные методы подготовки имеют решающее значение для повышения качества мембран. Ионообменные материалы предполагают новые исследования в синтезе и модификации, которые обобщены в этом обзоре.

Ключевые слова: ионный обмен, ионообменные мембраны, мембранная технология.

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CATALYTIC PROPERTIES OF V_2O_5-TiO_2 AND V_2O_5-ZrO_2 BINARY SYSTEMS IN THE VAPOR-PHASE OXIDATION OF 3-METHYLPYRIDINE INTO NICOTINIC ACID

Abstract. The results of catalytic activity of V_2O_5-TiO_2 and V_2O_5-ZrO_2 binary catalysts in the partial oxidation of 3-methylpyridine were investigated. It was found that the V-Ti-O catalyst prepared using highly dispersed titanium dioxide particles (200 nm) and V-Zr-O catalyst significantly exceeds both vanadium pentoxide and TiO_2 (Rutile) based vanadium-titanium contact by its activity. Nicotinic acid is obtained with the yield of 78-80% at 300 °C and a molar ratio of 3-MP:O_2:H_2O = 1:13:94.

Key words: oxidation, 3-methylpyridine, nicotinic acid, catalysts.

Introduction. Nicotinic acid (NA) is widely used in medicine as a vitamin PP, a general stimulant for life-supporting processes in the body, a drug that reduces toxic effects, a starting material for the synthesis of cardiac agents such as cordiamine, nicodane, etc., as well as in plant growing as a stimulator for the growth of wheat, cotton, cultures, livestock breeding and, especially, poultry farming.

The vapor-phase oxidation of 3-methylpyridine (3-MP) by air oxygen is the most cost-effective method of nicotinic acid synthesis. In Bekturov Institute of Chemical Sciences, with the purpose of creating a one-stage technological process for the NA production, the research is being conducted for searching the efficient catalysts of 3-MP vapor-phase oxidation.

The vanadium-titanium systems are widely used as catalysts for such an industrially important process as the partial oxidation of hydrocarbons. Titanium dioxide (TiO_2) is one of the components for catalysts of redox processes. Close to titanium dioxide by its chemical properties, zirconium dioxide (ZrO_2) is also widely used in the synthesis of highly selective catalysts, for example, the dehydrogenation of hydrocarbons. The structure and phase composition of oxidized vanadium-titanium and vanadium-zirconium catalysts were studied by Petrov I.Ya. et al. [1] using physicochemical methods (XRD, IR spectroscopy, UV and visible spectroscopy, EPR spectroscopy). It was found that the nature of the TiO_2 supporter has little effect on the structure of the supported vanadium-oxide catalyst. Comparison of samples of V_2O_5-TiO_2 catalysts, based on rutile and anatase, showed that the crystal structure of TiO_2 does not affect the activity of V-Ti-O catalysts in *o*-xylene oxidation [2].

Earlier, we noted the effect of the crystalline modification of TiO_2 on the catalytic properties of V-Ti-O catalysts in the oxidation of 3- and 4-methylpyridines [3]. It was found that V_2O_5-TiO_2 (Anatase) is more active and selective in the formation of pyridine carboxylic acids.

The purpose of this work was to test the new V-Ti-O binary catalyst prepared with highly dispersed titanium dioxide particles (200 nm) and V-Zr-O catalyst in 3-MP oxidation.

Experiment

In this work, dried and distilled 3-MP with boiling point of 140 °/ 692 mm, $d_4^{20} = 0.9568$, $n_D^{20} = 1.5050$ was used. These characteristics corresponded to the reference data.

As initial components of the catalysts, we used vanadium pentoxide, titanium and zirconium dioxides. The initial oxides in a molar ratio of 1:4 were ground in a porcelain mortar to form a homogeneous batch, which was then compressed into tablets of 15 mm in diameter and 3-4 mm in thickness and calcined at 350 and 640 °C for 4 hours. After cooling, the tablets were crushed into grains of 3-5 mm in size.

The oxidation of 3-MP was carried out in a continuous installation of reaction tube made of stainless steel with a diameter of 20 mm and a length of 150 mm into which 9 ml of a granular catalyst was loaded.

The unreacted 3-MP and reaction products were trapped in air-lift type scrubbers filled with water and analyzed by gas-liquid chromatography. NA was titrated with 0,035 N alkali using phenolphthalein.

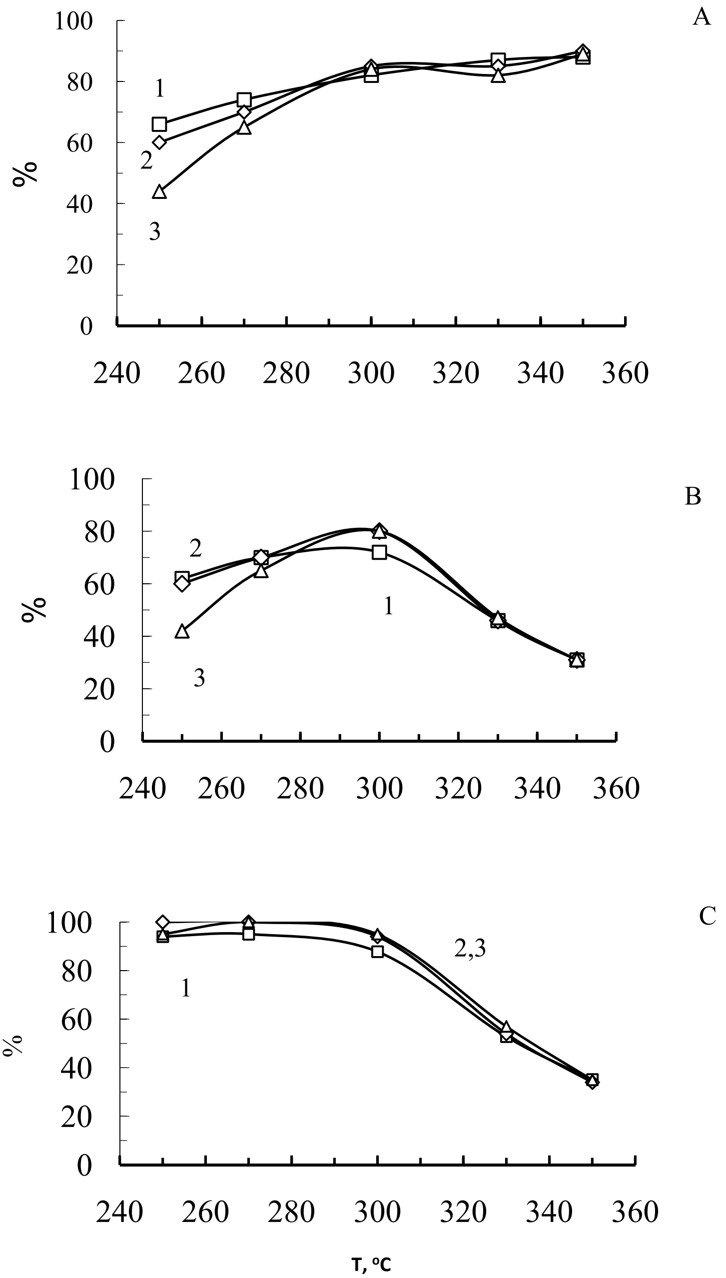
The deep oxidation products were analyzed by LXM-8MD chromatograph with a thermal conductivity detector. The stainless steel columns had a length of 3,5 m and an inner diameter of 3 mm. The adsorbent for CO detection was an AG-5 mk. activated carbon (0,25-0,50 mm), for CO_2 – polysorbent-1 (0,16-0,20 mm). The temperature of the thermostat was 40 °C.

Results and discussion

The purpose of this article is to compare the catalytic activity and selectivity of V_2O_5-TiO_2 (Anatase), V_2O_5-TiO_2 (Rutile) and V_2O_5-ZrO_2 binary catalysts in 3-MP oxidation.

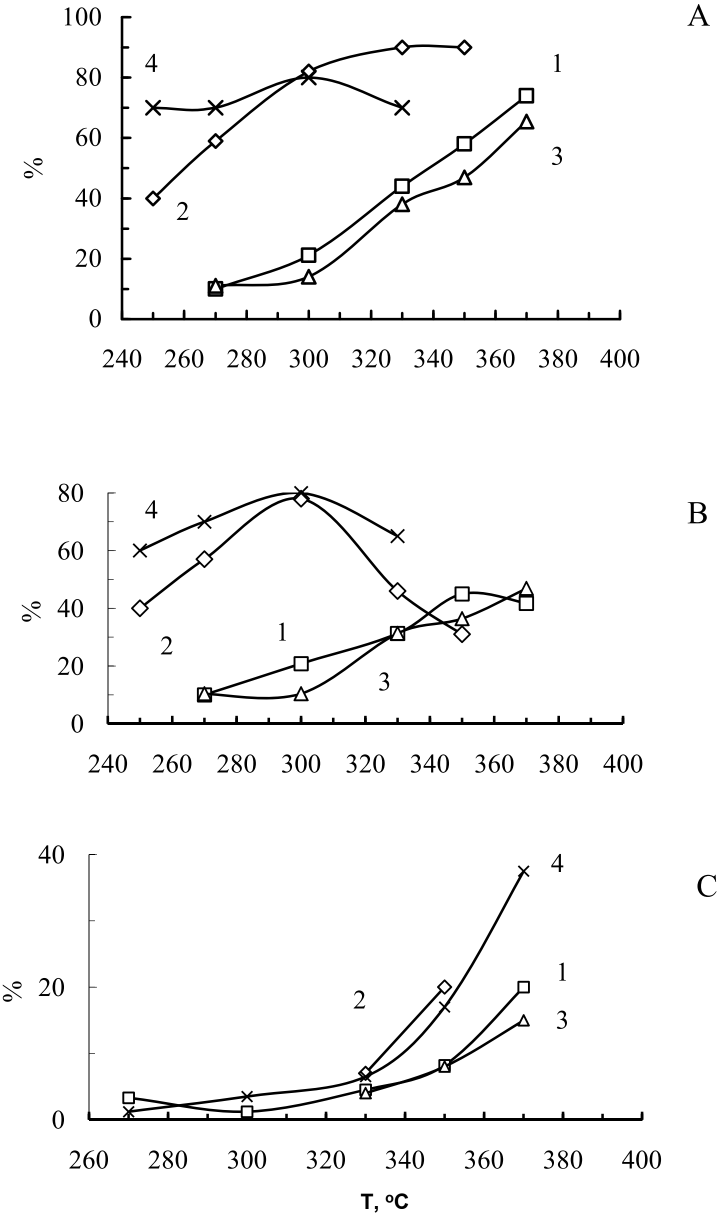
We investigated the general laws of the reaction, in particular, the effect of temperature, the amount of oxygen and water on the yield of the main products of the reaction.

The test of the vanadium-titanium oxide catalyst prepared using titanium dioxide with particle size of 200 nm showed that the feeding of initial substance (36,6 g), 550 L of air per 1 L of catalyst per hour in a temperature range of 250-350 °C, the conversion of 3-MP increases from 40 to 90%. The main product of the reaction was NA, the yield of which passes through a maximum with increasing temperature. While at 250 °C the yield of NA was 40-50%, then at 300 °C it reached 75%, a further increase in temperature causes a decrease in the yield of the targeted acid. It was noted that in the low-temperature region (250-300 °C) the selectivity for NA formation was 95%.



The feed rate of 3-MP – 36.6 g, air 420 L per 1 L of the catalyst in hour.
Mole ratio of initial substance:O_2:H_2O = 1:10:25.5 (1), 1:10:73 (2), 1:10:94 (3)

Figure 1 – Influence of temperature and amount of water on the conversion of 3-MP (A), yield (B) and selectivity of NA formation (C) under oxidation conditions over the $V_2O_5 \cdot 4TiO_2$ catalyst



The feed rate of 3-MP – 36,6 g, air 550 L, water 654,8 g. per 1 L of the catalyst in hour.
Mole ratio of 3-MP:O_2:H_2O = 1:13:94

Figure 2 – The effect of temperature and catalyst composition on the conversion of 3-MP (A), NA yield (B) and CO_2 (C) under oxidation conditions over the V_2O_5 (1), V_2O_5-TiO_2(Anatase) (2), V_2O_5-TiO_2(Rutile) (3), V_2O_5-ZrO_2 (4)

The variation in the water amount supplied to the reaction zone from 25 to 94 moles per mole of 3-MP practically does not affect the main parameters of the process: the conversion of the initial substance, the yield and the selectivity of the formation of the desired product. Figure 1 shows the results of the experiments with a lower air flow rate of 420 L per liter of catalyst in hour, corresponding to 10 moles of oxygen. It is shown that the conversion of 3-MP increased by 15% in the low-temperature region. At 250-270 °C, the yield of NA also increased. The selectivity of NA formation remained as high as 95%.

The tests of the binary vanadium-zirconium catalyst ($V_2O_5 \cdot 4ZrO_2$) were carried out in conditions comparable to the vanadium-titanium catalyst. The results obtained are shown in figure 2. Comparison of 3-MP conversion over two samples of the catalysts showed that when air was supplied at a rate of 550 L per liter of the catalyst in hour and at 250-270 °C, the activity of the vanadium-zirconium catalyst was higher than that in the vanadium-titanium catalyst. Somewhat higher was the yield of NA, the highest yield (70%) was obtained at 300 °C with feeding of water 76,0 and 97,0 moles per mole of 3-MP. The selectivity of NA formation at 270-300 °C was above 88%.

The injection of a smaller amount of air into the reaction zone (420 L per 1 L of catalyst in hour) resulted in a slight decrease in the conversion of the initial substance and the yield of NA. Despite this, the selectivity of NA formation even under these conditions remained high. In the oxidation products of 3-MP, in addition to NA, pyridine and nicotinic acid nitrile were present, but pyridine-3-aldehyde was not formed over both catalysts.

Figure 2 shows the comparison of 3-MP oxidation on the individual vanadium pentoxide and vanadium-titanium catalyst prepared on the basis of TiO_2 (Rutile). It is clearly seen that the V-Ti-O catalyst prepared using titanium dioxide with a higher dispersion particles (200 nm) and V-Zr-O catalyst significantly exceeds both vanadium pentoxide and vanadium-titanium contact containing TiO_2 (Rutile). These catalysts showed the high selectivity in the desired product formation and can be recommended for 3-MP oxidation into nicotinic acid.

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Резюме

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3-МЕТИЛПИРИДИННІҢ НИКОТИН ҚЫШҚЫЛЫНА БУКҮЙІНДЕ ТОТЫҒУЫНА ҚОЛДАНЫЛАТЫН БИНАРЛЫ V_2O_5–TiO_2 ЖӘНЕ V_2O_5–ZrO_2 КАТАЛИЗАТОРЛАРЫНЫҢ БЕЛСЕНДІЛІГІ

3-Метилпиридиннің парциалды қолданатын кейбір бинарлы V-Ti-O және V-Zr-O катализаторлардың каталитикалық белсенділігін зерттеу нәтижелері талқыланады.

Түйін сөздер: парциалды тотығу, 3-метилпиридин, никотин қышқылы, катализаторлар.

Резюме

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КАТАЛИТИЧЕСКИЕ СВОЙСТВА БИНАРНЫХ СИСТЕМ V_2O_5–TiO_2 И V_2O_5–ZrO_2 В ПАРОФАЗНОМ ОКИСЛЕНИИ 3-МЕТИЛПИРИДИНА В НИКОТИНОВУЮ КИСЛОТУ

Обсуждены результаты исследования каталитической активности бинарных V-Ti-O и V-Zr-O катализаторов в парциальном окислении 3-метилпиридина.

Ключевые слова: окисление, 3-метилпиридин, никотиновая кислота, катализаторы.

УДК 541.64

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СИНТЕЗ И ИССЛЕДОВАНИЕ НАНОЧАСТИЦ АЛЬБУМИНА, ИММОБИЛИЗОВАННЫХ ПРОТИВОТУБЕРКУЛЕЗНЫМ ПРЕПАРАТОМ «П-АМИНОСАЛИЦИЛОВАЯ КИСЛОТА»

Аннотация. Приведены результаты исследования наночастиц (НЧ) серного альбумина, иммобилизованных противотуберкулезным препаратом «п-аминосалициловая кислота» (ПАСК). Введение лекарства в матрицу полимера проведено двумя способами: адсорбцией лекарства на пустых наночастицах альбумина и включением ПАСК в наночастицы в процессе сшивки макромолекул альбумина. Получены НЧ альбумина с удовлетворительными физико-химическими характеристиками и достаточно высоким содержанием лекарства. Изучен процесс высвобождения лекарственного вещества из полимерных наночастиц серного альбумина. Степень высвобождения лекарственного препарата имеет высокие значения и составляет 88 и 80 % в случаях адсорбции и включения соответственно. Таким образом, полученные результаты позволяют надеяться на пролангацию действия п-аминосалициловой кислоты и снижение разовой дозы лекарства при терапии туберкулеза.

Ключевые слова: полимерные наночастицы, альбумин, противотуберкулезный препарат, п-аминосалициловая кислота, адсорбция, включение.

В настоящее время лечение такого заболевания, как туберкулез остается одной из главных проблем современной медицины. Туберкулез сегодня широко распространен в странах Африки и Азии и по статистическим данным приводит к смертности каждого третьего инфицированного в мире [1, 2]. Интенсивное лечение этого заболевания с применением высоких доз лекарств оказывает сильное токсическое действие, а неоднократное введение препарата в течение дня вызывает неудобство у пациентов. К тому же, использование сильнодействующих антибиотиков в комплексе приводит к проявлению множественной лекарственной устойчивости. В связи с этим, проблема создания терапевтической системы, позволяющей осуществить направленный транспорт лекарства в место назначения в заданные сроки, особенно важна в химиотерапии туберкулеза. Одним из лекарственных препаратов, используемых в терапии туберкулеза, является *п*-аминосалициловая кислота (ПАСК) (рисунок 1), несмотря на то, что это лекарство само по себе является препаратом умеренного действия, т. е. относится ко II ряду, ПАСК с ее натриевой солью широко используется как в моно-, так и в комплексной терапии и является одним из первых антибиотиков, применяемых в лечении туберкулеза. Препарат обладает бактериостатическим действием только против туберкулезных бактерий.

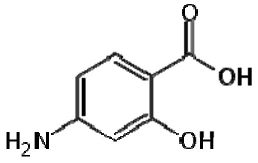


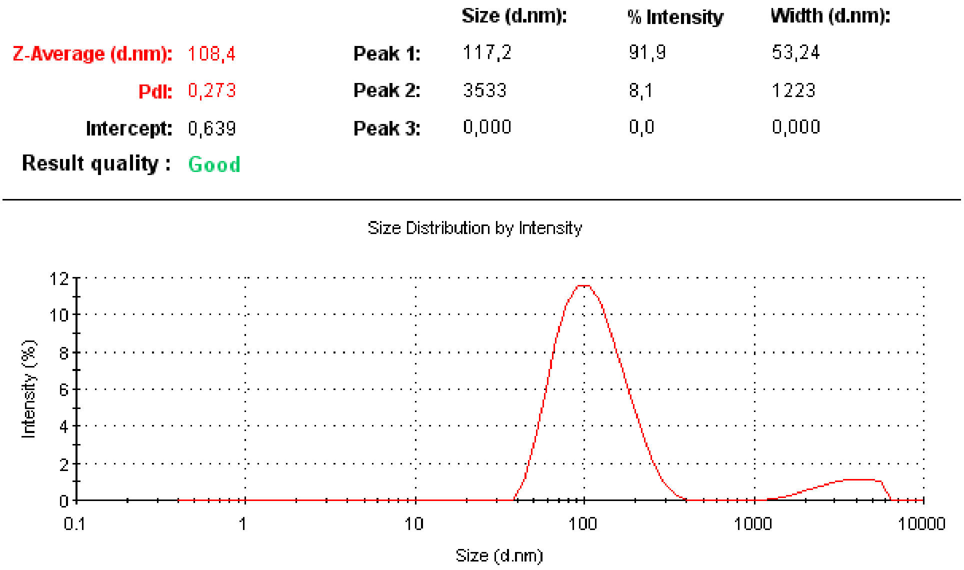
Рисунок 1 – Структурная формула ПАСК

Как и при применении других химиотерапевтических препаратов, в процессе лечения ПАСК образуются лекарственно-устойчивые формы бактерий. Кроме того, период полувыведения данного лекарственного препарата составляет всего 45-60 мин, что обуславливает необходимость назначения его по 5-12 г в сутки, а иногда и более высокие дозы. Разработка новых форм для транспорта противотуберкулезного препарата ПАСК в виде полимерных НЧ позволит обеспечить пролонгированное высвобождение лекарства с поддержанием эффективной концентрации лекарственного вещества (ЛВ) в крови в течение заданного промежутка времени, снизить побочные действия лекарственного препарата, таким образом повышая его терапевтический эффект.

Из литературных источников известно, что НЧ получают как из природных (альбумин, желатин, декстран и др.), так и из синтетических (полиметилметакрилат, полистирол, полиалкилцианоакрилат и др.) полимеров [3]. Сывороточный альбумин является одним из перспективных и широко используемых биополимеров для получения НЧ, который уже зарекомендовал себя в качестве полимерного носителя для многих лекарственных препаратов. В работе [4] показано, что альбумин аккумулируется в зараженных тканях, а НЧ, полученные на основе альбумина, не токсичны и хорошо переносятся человеческим организмом. Наличие в структуре альбумина множества реакционноспособных центров (тиоловые, имидазольные, карбоксильные и аминогруппы) дает возможность связывания его молекул бифункциональным соединением – глутаровым альдегидом. В частности, возможно сшивание по аминным связям с образованием иминов. Кроме того, функциональные группы (карбоксильные и аминные), присутствующие в структуре альбумина, позволяют модифицировать поверхность НЧ, прикрепляя «узнающие» (направляющие) молекулы, что позволит обеспечить целенаправленную доставку лекарства [5, 6]. В связи с этим, с целью повышения терапевтического эффекта противотуберкулезного препарата ПАСК нами исследована возможность связывания данного лекарства с НЧ сывороточным альбумином.

Пустые НЧ альбумина синтезировали методом десольвации, описанным ранее учеными университета им. Й. Гете [5-7]. Суть данного метода заключается в следующем: растворенный в воде сывороточный альбумин подвергают десольвации этанолом с последующей стабилизацией частиц; затем макромолекулы альбумина сшивают глутаровым альдегидом.

Синтез НЧ осуществляли при температуре 25 °С. Скорость подачи десольватирующего агента (этанола) в среду регулировали с помощью мининасоса, значение pH поддерживали в пределах 8,0-8,5 [8]. От непрореагировавшего сывороточного альбумина раствор очищали трехкратной промывкой водой и последующим центрифугированием в течение 15 мин при 14500 об/мин на приборе Eppendorf 14500 Miniplus (Германия). Физико-химические характеристики полученных пустых НЧ альбумина определяли фотонной корреляционной спектроскопией, данные которого приведены на рисунке 2.



			Size (d.nm):	% Intensity	Width (d.nm):
Z-Average (d.nm):	108,4	**Peak 1:**	117,2	91,9	53,24
PdI:	0,273	**Peak 2:**	3533	8,1	1223
Intercept:	0,639	**Peak 3:**	0,000	0,0	0,000
Result quality :	Good				

Рисунок 2 – Размер пустых НЧ серного альбумина

Из рисунка 2 видно, что синтезированные частицы имеют малый размер (108,4 нм) и достаточно узкое распределение (PDI = 0,273), а доля частиц нанометрического размера составляет практически 92 %, что удовлетворяет требованиям полимерных носителей лекарственных препаратов.

В продолжение исследования нами рассмотрена возможность связывания НЧ альбумина с противотуберкулезным препаратом ПАСК методом адсорбции. Адсорбцию ЛВ на НЧ сывороточного альбумина осуществляли в две стадии: получение пустых НЧ и последующее связывание их с ПАСК. Связывание *п*-аминосалициловой кислоты с пустыми НЧ проводили непосредственным смешением соответствующих растворов при перемешивании (650 об/мин) при температуре 25 °С. При этом концентрацию лекарства в растворе варьировали в пределах 0,02-0,1 г/мл. Данные о физико-химических характеристиках частиц после сорбции ПАСК разных концентраций на НЧ альбумина сведены в таблицу 1.

Таблица 1 – Характеристики НЧ сывороточного альбумина, иммобилизованных ПАСК методом адсорбции

Концентрация ПАСК, г/мл	Характеристики НЧ			
	Средний диаметр частиц, нм	Поли-дисперсность	Выход частиц с размером до 1000 нм, %	Степень связывания, %
0,02	758,6	0,184	100,0	10,0
0,04	512,0	0,165	100,0	23,4
0,06	635,2	0,201	97,7	12,0
0,08	670,4	0,246	100,0	36,5
0,1	998,4	0,196	100,0	14,7

По результатам, приведенным в таблице 1, видно, что размер частиц значительно увеличился после адсорбции ПАСК на пустых НЧ альбумина, значение полидисперсности варьирует в пределах 0,165-0,246, что указывает на достаточно узкое распределение частиц по размерам.

Следующим этапом работы было определение степени связывания лекарства с НЧ альбумина, для чего полученные частицы отделяли от маточного раствора ультрацентрифугированием при 14500 об/мин и промывали водой. Содержание несвязавшегося лекарства определяли кондуктометрическим методом, результаты которого также приведены в таблице 1. Как видно, наиболее высокой степени связывания можно достичь при использовании концентрации лекарства 0,08 г/мл. Учитывая также относительно малый размер и значение степени связывания, которое превышает 20 % при адсорбции 0,4 г ЛВ, нами для дальнейших исследований выбраны НЧ с адсорбированным ПАСК концентрациями 0,04 и 0,08 г/мл.

Немаловажным фактором применимости полимер-иммобилизованных форм лекарственных препаратов является возможность биодеградации полимера с высвобождением ЛВ. Известно, что высвобождение лекарства из полимерных микро- и наночастиц может происходить посредством десорбции лекарства, находящегося на поверхности полимера и/или диффузии ЛВ в результате эрозии полимерной матрицы. Поэтому в продолжение исследований нами изучена кинетика высвобождения ПАСК из матрицы полимерных НЧ альбумина. Скорость высвобождения лекарства из НЧ альбумина изучали в in vitro условиях (pH 7,4, температура 37^0С) в течение 24 ч. Сравнительные данные по степени высвобождения ПАСК при адсорбции 0,4 и 0,8 г лекарства приведены на рисунке 3.

Из графика зависимости количества высвободившегося ПАСК от концентрации лекарства видно, что выделение лекарства в среду из НЧ, иммобилизованных 0,4 г ПАСК, происходит быстрее по сравнению с высвобождением лекарства из полимерных НЧ, иммобилизованных 0,8 г ПАСК. В целом, как и следовало ожидать, в обеих случаях скорость процесса высвобождения достаточно высокая на начальном этапе: так, при адсорбции

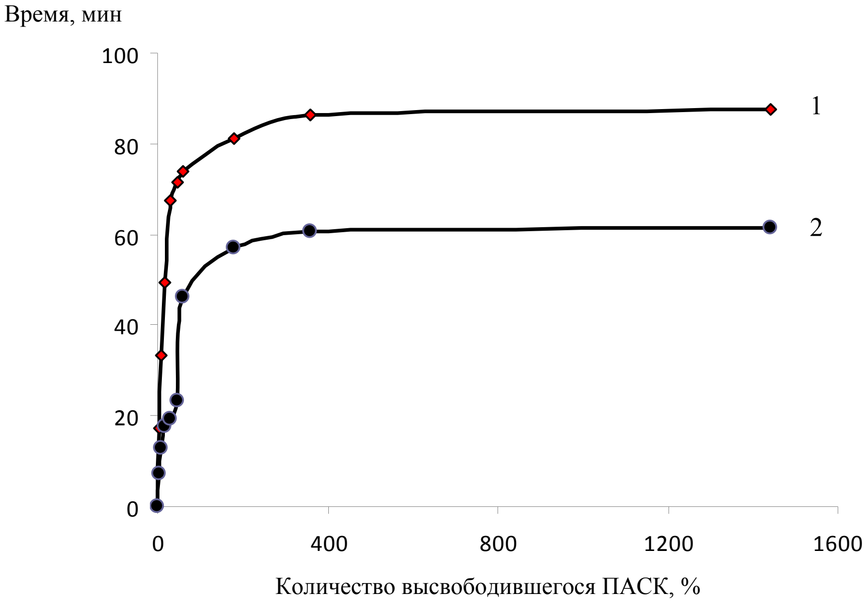


Рисунок 3 – Зависимость количества высвободившегося лекарства из матрицы НЧ сывороточного альбумина, иммобилизованных 0,4 (1) и 0,8 г (2) ПАСК, от времени

0,4 г лекарства в течение первых 10 мин в среду выделяется около 30 % ПАСК, а через 30 мин – более 60 % ЛВ.

Однако далее высвобождение лекарства идет медленнее с выделением около 80 % лекарства за 3 ч, а через сутки количество высвободившегося ЛВ составило 88 %. Высвобождения оставшегося количества ПАСК в модельную среду не наблюдалось, что, по-видимому, связано со сшитой структурой макромолекул альбумина.

Несмотря на общее сходство характера высвобождения ПАСК из НЧ альбумина с 0,8 г лекарства, выделение ЛВ в среду в этом случае проходит медленнее: так, за 10 мин высвободилось только 13 % лекарственного вещества, а за 30 мин – только 19% ; за час выделилось 46 % ПАСК, а через 3 ч количество выделившегося лекарства достигло 57 %. Однако максимально высвободившееся количество ЛВ за сутки составило только 62 %.

Быстрое высвобождение основного количества лекарства в среду в начале процесса можно объяснить выделением адсорбированного ПАСК, главным образом, с поверхности НЧ. Дальнейшее высвобождение происходит, по всей видимости, за счет выделения ЛВ из внутренней части НЧ в результате их частичной деструкции.

При адсорбции существует риск потери некоторого количества лекарства десорбцией с поверхности частиц, в связи с этим, на следующем этапе нами исследовано присоединение лекарства в процессе получения частиц. В этом случае ПАСК предварительно растворяли в водном растворе альбумина, затем проводили десольвацию. Концентрацию лекарства в исходном растворе поддерживали как и в случае адсорбции (0,02-0,1 г/мл). Физико-химические характеристики частиц, полученных включением ПАСК, показаны в таблице 2.

По данным фотоннной электронной спектроскопии можно увидеть (таблица 2), что наилучшие результаты получены при иммобилизации 1 г лекарства: средний диаметр частиц составил 211,5 нм, а значение полидисперсности (0,524) указывает на достаточно узкое распределение частиц по размерам. Кроме того, из таблицы также видно, что 86 % системы составляют частицы нанометрического размера.

Степень связывания ПАСК с НЧ альбумина, полученных методом включения, определяли по значениям электропроводности, которые также показаны в таблице 2. Можно сделать вывод о том, что иммобилизация 1 г лекарства в матрицу сывороточного альбумина позволяет связать до 38 % ПАСК, что является достаточно высоким показателем. Также в этом случае были получены НЧ с удовлетворительными физико-химическими характеристками, поэтому нами изучена кинетика высвобождения лекарственного вещества из полимерных НЧ альбумина, полученных включением 1 г ПАСК.

Таблица 2 – Характеристики НЧ сывороточного альбумина,
иммобилизованных ПАСК методом включения

Концентрация ПАСК, г/мл	Характеристики НЧ			
	Средний диаметр частиц, нм	Поли-дисперсность	Выход частиц с размерами до 1000 нм, %	Степень связывания, %
0,02	1332,0	0,402	100	11,9
0,04	2022,0	0,467	0	18,7
0,06	2330,0	1,0	0	20,6
0,08	1684,0	0,409	5,5	21,8
0,1	211,5	0,524	86,8	38,2

Скорость высвобождения лекарства из матрицы НЧ альбумина изучали в условиях, моделирующих биологические (pH 7,4, температура 37^0С), а количество выделившегося в среду лекарства также определяли кондуктометрическим методом. График зависимости количества высвободившегося ПАСК от времени показан на рисунке 4.

Из приведенного графика видно, что высвобождение ПАСК из НЧ альбумина, иммобилизованных методом включения, относительно медленная: так, за первые 15 мин в среду выделяется только около 8 % лекарства, и еще через 15 мин – 25 %, а за час – всего 32 % ПАСК. Далее менее 50 % связанного лекарства высвобождается за 3 ч.

Следует отметить, что период полувыведения самого лекарства составляет 45-60 мин, что позволяет сделать вывод о перспективности иммобилизации противотуберкулезного препарата ПАСК в матрицу НЧ сыворо-

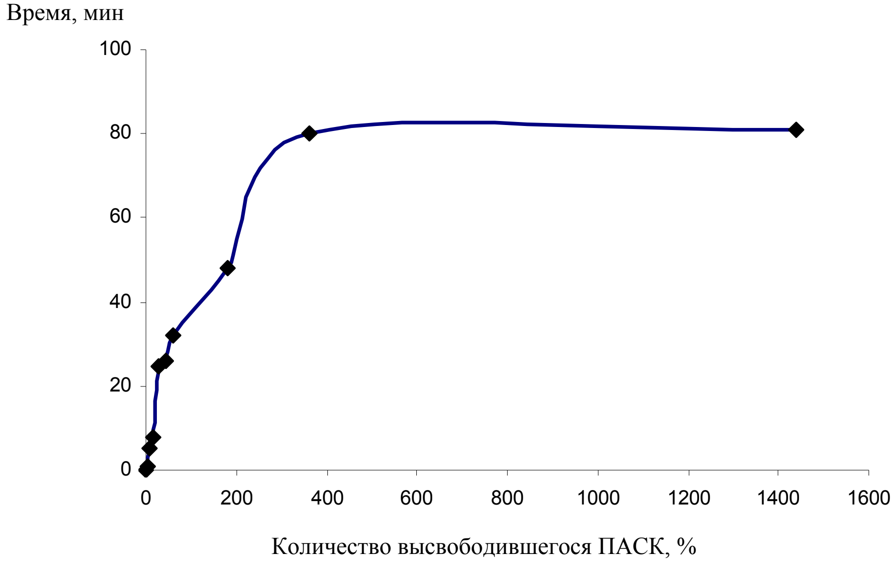


Рисунок 4 – Зависимость количества высвободившегося ПАСК из матрицы НЧ сывороточного альбумина, иммобилизованных 1,0 г лекарства, от времени

точного альбумина методом включения, при этом концентрацию лекарства можно еще значительно повысить для того, чтобы добиться необходимого терапевтического эффекта. Как видно из рисунка 4, высвобождение лекарства прекращается по достижении 80 %; оставшаяся часть ПАСК, по-видимому, не выделяется из матрицы альбумина из-за сшитой структуры НЧ.

Таким образом, в настоящей работе получены НЧ сывороточного альбумина, иммобилизованные противотуберкулезным препаратом ПАСК двумя способами: адсорбцией лекарства на пустых НЧ альбумина и растворением ПАСК в среде непосредственно в процессе сшивки макромолекул альбумина. По результатам исследований можно заключить, что полученные методом включения НЧ имеют удовлетворительные характеристики и дают возможность пролонгации действия лекарства до 3-х раз, что может быть использовано в дальнейшем для транспорта противотуберкулезного препарата ПАСК.

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Резюме

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ТҮБЕРКҮЛЕЗГЕ ҚАРСЫ ПРЕПАРАТ «П-АМИНОСАЛИЦИЛ ҚЫШҚЫЛЫМЕН» ИММОБИЛИЗАЦИЯЛАНҒАН АЛЬБУМИНДІ НАНОБӨЛШЕКТЕРДІ СИНТЕЗДЕУ ЖӘНЕ ЗЕРТТЕУ

Жұмыста түберкүлезге қарсы препарат п-аминосалицил қышқылының терапевтік әсерін жоғарылату мақсатымен оны күкіртті альбуминнің нанобөлшектерімен байланыстыру мүмкіндігі зерттелді. Адсорбция және енгізу әдістерімен дәрілік затпен иммобилизацияланған нанобөлшектердің физика-химиялық сипаттамалары келтірілді. Альбуминнің полимерлі матрицасынан п-аминосалицил қышқылының босап шығуының кинетикасы зерттелді.

Дәрілік затпен иммобилизацияланған альбуминді нанобөлшектердің оңтайлы физика-химиялық сипаттамалары және байланысу дәрежесінің жоғары мәндерге ие болуы түберкүлезге қарсы препарат п-аминосалицил қышқылының наносомалы үлгілерін қолданудың келешегі зор екендігін көрсетеді.

Түйін сөздер: полимерлі нанобөлшектер, альбумин, түберкүлезге қарсы препарат, п-аминосалицил қыщқылы, адсорбция, енгізу.

Резюме

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SYNTHESIS AND INVESTIGATION OF ALBUMIN NANOPARTICLES LOADED WITH ANTITUBERCULOSIS DRUG "P-AMINOSALICYLIC ACID"

In this work the possibility of binding antituberculosis drug p-aminosalicylic acid with the nanoparticles of serum albumin with the aim of increasing the therapeutic efficacy of the drug is studied. The results of the investigation of physicochemical characteristics of nanoparticles loaded with the drug obtained by adsorption and incorporation methods are shown. Drug release kinetics of p-aminosalicylic acid from polymeric matrix of albumin is studied.

Optimal physicochemical characteristics of albumin nanoparticles loaded with the drug and high meanings of binding degree points on perspective of the use of nanosomal forms of antituberculosis drug "p-amino salicylic acid".

Keywords: polymeric nanoparticles, albumin, antituberculosis drug, p-aminosalicylic acid, adsorption, incorporation.

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SYNTHESIS OF (3-MORPHOLYL)PROPYLDITHIOCARBAMIC ACID ALKYL ESTERS

Abstract. The alkylation of potassium (3-morpholyl)propyldithiocarbamate with haloalkylswas studied. Conditions for the synthesis of new alkyl esters of (3-morpholyl)-propyldithiocarbamic acid were developed. Hexyl, heptyl, octyl, nonyl, decyl and dodecyl esters of (3-morpholyl)propyldithiocarbamic acid were synthesized in67, 68, 91, 81, 67 and 87 % yield. Structure of alkyl esters of (3-morpholyl)propyldithiocarbamic acid was established based on IR and ^{13}C NMR spectroscopic data.

Keywords: alkylation reaction, potassium (3-morpholyl)propyldithiocarbamate, alkyl esters of (3-morpholyl)propyldithiocarbamic acid.

The chemistry of sulfur compounds is an important and intensively developing field of organic synthesis. Most of the reactions involving sulfur are associated with the use of various sulfurizing reagents. So, a special place in the synthesis of organic sulfur compounds is occupied by carbon disulfide, which is a sulfurizing reagent in the synthesis of dithiocarbamates and dithiocarbamic acids. Dithiocarbamates are widely used in various fields of practice: chemistry and chemical technology, mineral processing, agriculture, medicine and technology.

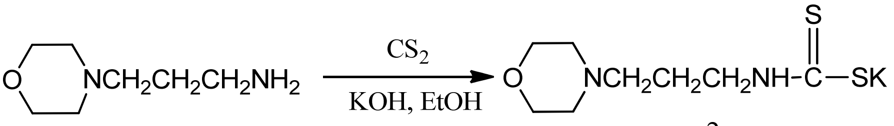
Dithiocarbamatesare used in analytical chemistry to detect p- and d-elements having affinity to sulfur, as well as for separation, masking and extraction photometric determination of many metals, for example, Cu, Ag, Bi, Cd, Co, As (III), for gravimetric definition of In, titrimetric – Hg, Pb, Pt, Te. Thus, morpholindithiocarbamateis used for the photometric determination of Cu, Co, and Ni in an aqueous methanol medium. Diethanoldithiocarbamateis used for photometric determination of Cu, Co and Ni or pairs of elements Cu and Ni, Cu and Coin aqueous solutions, for the determination of Cu in lubricating oils, alloys, steels and aluminum alloys [1].

Derivatives of thio- and dithiocarbamic acids are widely used as herbicides and fungicides.By the transition from the derivatives of thiocarbamic acid to the derivatives of dithiocarbamic acid decreases herbicidal activity, whereas fungicidal and bactericidal activity increases.Salts of dithiocarbamic acids with different metals have the practical importance, which are used as fungicides for combating plants diseases [2].Many derivatives of dithiocarbamic acids are usedalso as flotation reagents in the flotation of polymetallicsulphide ores [3].

The diverse activity of the dithiocarbamates and their derivatives, the increased stability of many of them to the action of radiation, as well as the use in mineral processing, agriculture and medicine, all contribute to the urgency of our studies on the synthesis of new dithiocarbamic acid derivatives.

With a view to the synthesis of new derivatives of alkyl esters of dithiocarbamic acids containing in their structure the saturated hydrocarbonic chain was taken (3-morpholyl)propylditiocarbamate potassium as the starting substrate.

Potassium (3-morpholyl)propyldithiocarbamate was synthesized by the interaction of equimolar amounts of 4- (3-aminopropyl)morpholine**1** with carbon disulfide at a temperature of 0-5 °C in the presence of potassium hydroxide in ethyl alcohol. Potassium dithiocarbamate**2**was formed as a white crystalline substance, which was isolated by filtration from the reaction mixture and washed with methylene chloride. The potassium (3-morpholyl)propyldithiocarbamate **2** was synthesized in 96% yield.

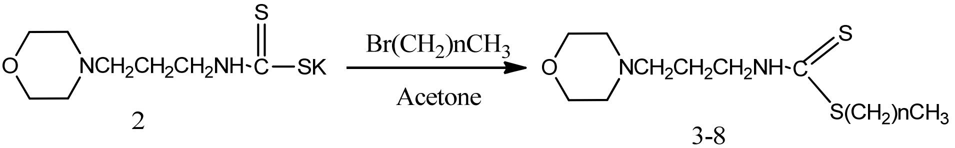


1

2

The composition and structure of the potassium dithiocarbamate**2**were established bythe elemental analysis and IR spectroscopy. The physicochemical characteristics of the compound **2** are shown in the table 1. An absorption band of the valence vibrations of the NH group is presentin the IR spectrum in the region of 3299 cm^{-1}. The absorption bands in the region 2962, 2918, 1241-1448 cm^{-1} refer to the valence vibrations of the CH_2 groups. The valence vibrations C = S correspond to absorption in the region of 1027 cm^{-1}. In the region of 816 cm^{-1}appears an absorption band of the C-S bond.

Conditions of alkylation of potassium (3-morpholyl)propyldithiocarbamate were studied and new alkyl esters of (3-morpholyl)propyldithiocarbamic acid were synthesized. The alkylation reaction of potassium (3-morpholyl)propyldithiocarbamate**2** with saturated haloalkylswas carried out at room temperature in acetone.



2

3-8

n = 5, 6, 7, 8, 9, 11

As a result of isolation from reaction mixtures were obtained in the individual form hexyl, heptyl, octyl, nonyl, decyl and dodecyl esters of (3-morpholyl)propyldithiocarbamic acid **3-8**in 67, 68, 91, 81, 67, 87 % yield, respectively.

The elemental analysis, TLC and IR spectral data confirm composition and individuality of the synthesized compounds. The yield and physicochemical constants are presented in table 1. Structure of the synthesized alkyl esters of (3-morpholyl)propyldithiocarbamic acid **3-8** is established based on the ^{13}C NMR spectra, thespectral data of which are presented in table 2.

Table1 – Physicochemical constants for compounds **2-8**

№	Yield, %	m.p., °C	R_f acetone : hexane (1:7)	ИК-spectra, υ, cm^{-1}		
				NH	C=S	C-S
1	**2**	**3**	**4**	**5**	**6**	**7**
2	96	193-195	0.14	3299	1027	816
3	67	Oil	0.86	3234	1117	939
4	68	Oil	0.85	3234	1120	936
5	91	Oil	0.83	3240	1115	868
6	81	34-36	0.82	3234	1120	936
7	67	oil	0.81	3236	1115	869
8	87	38-40	0.79	3238	1115	998

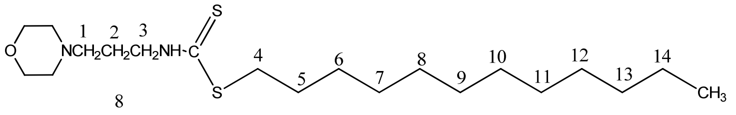
Continious of the table 1

№	Found, %				Formula	Calculated, %			
	C	H	N	S		C	H	N	S
1	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
2	37.30	5.57	10.62	25.03	$C_8H_{15}KN_2OS_2$	37.18	5.85	10.84	24.81
3	55.45	9.03	9.50	21.36	$C_{14}H_{28}N_2OS_2$	55.22	9.27	9.20	21.06
4	56.32	9.27	8.55	20.31	$C_{15}H_{30}N_2OS_2$	56.56	9.49	8.79	20.13
5	57.57	9.50	8.20	19.05	$C_{16}H_{32}N_2OS_2$	57.78	9.70	8.42	19.28
6	58.75	9.68	8.31	18.29	$C_{17}H_{34}N_2OS_2$	58.91	9.89	8.08	18.50
7	59.80	10.28	7.53	17.53	$C_{18}H_{36}N_2OS_2$	59.95	10.06	7.77	17.78
8	61.37	10.25	4.04	19.13	$C_{19}H_{38}N_2OS_2$	61.58	10.03	4.22	19.34

In the IR spectra of compounds **3-8** in the region of3234 $cm^{-1}$is found an absorption band of the stretching vibrations of the NH group. An absorption band of the valence vibrations of the C = S group is present in the region of 1115-1120 cm^{-1}. The absorption band of the C-S bond is present in the region of 543-669 cm^{-1}.

Analysis of the^{13}C NMR spectra (table 2) of the compounds **3-8** confirms their structure. In the ^{13}C NMR spectrum, the signal of the carbon atom of the methyl group is manifested in the strong-field spectral region δ 14.11-14.24 ppm. Chemical shifts of carbon atoms of methylene groups of the alkane chain appear in the range of δ 22.55-58.60 ppm. The carbon atoms of morpholine are resonated in the range of δ 53.40-53.60 ppm. (-N (CH2) 2) and δ 66.54-67.04 ppm. (O (CH2) 2). The carbon atom of the C = S group resonates in the weak-field region δ 197.43-197.77 ppm.

Table 2 – ^{13}C NMR(δ, ppm) spectraldataforcompounds **3-8**

Carbon atom						
	3	**4**	**5**	**6**	**7**	**8**
$O(CH_2)_2$-	67,02	66,61	66,54	66,85	67,04	66,71
$N(CH_2)_2$-	53,60	53,42	53,40	53,53	53,60	53,47
-C=S	197,43	197,73	197,77	19762	197,44	197,73
C^1H_2	58,57	58,17	58,12	58,46	58,60	58,30
C^2H_2	22,67	22,68	22,72	22,77	22,77	22,79
C^3H_2	48,50	47,84	47,75	48,27	48,55	48,01
C^4H_2	35,23	35,24	35,24	35,27	35,24	35,27
C^5H_2	29,34	29,34	29,32	29,56	29,00	29,75
C^6H_2	28,63	28,94	28,98	29,00	29,28	29,01
C^7H_2	31,43	28,94	29,22	29,29	29,40	29,37
C^8H_2	22,60	31,78	29,22	29,36	29,63	29,73
C^9H_2	–	22,55	31,88	29,38	29,60	29,70
$C^{10}H_2$	–	–	22,55	31,96	29,40	29,62
$C^{11}H_2$	–	–	–	22,55	31,97	29,44
$C^{12}H_2$	–	–	–	–	22,64	29,30
$C^{13}H_2$	–	–	–	–	–	32,09
$C^{14}H_2$	–	–	–	–	–	22,54
CH_3	14,11	14,19	14,20	14,23	14,22	14,24

Experiment

Control of the reaction was carried out by TLCon Silufol UV-254 plates, eluent acetone-hexane (1: 7). IR spectra of synthesized compounds are recorded on a Nicolet 5700 device in tablets with KBr, with 0.25% and in a thin layer. NMR spectra were obtained on a JNM-ECA 400 (JEOL) spectrometer.

Potassium (3-morpholyl)propyldithiocarbamate 2. Solution of potassium hydroxide (8.4 g, 0.15 mol) in water (5 ml) was addedto the mixture of of 4-(3-aminopropyl) morpholine1 (21.63 g, 0.15 mol) in 50 ml of alcohol. Then a solution of carbon disulfide (12.16 g, 0.16 mole) in alcohol (10 ml) was added-dropwise at 0-5 ° C with stirring. The reaction mixture was stirredat 0-5° C for 3 hours. The resulting white crystals were filtered on a Shott funnel and washed with methylene chloride. Potassium (3-morpholyl)propyldithiocarbamate was obtained in 35 g (96%) yield.

Hexyl(3-morpholynolpropyl)carbamodithioate 3. Solution of 1-Bromohexane (4.95 g, 0.03 mol)in acetone (5 ml)was added dropwiseto the mixture of Potassium (3-morpholyl)propyldithiocarbamate 2in acetone (25 ml)with stirring. The reaction mixture was stirred at room temperature for 16 hours. The precipitate formed was filtered out, the solvent was distilled off in a vacuum of the water jet pump.The resulting mass as an oil was dried in a vacuum of the oil pump. Product was obtained in6.12 g (67%) yield.

Heptyl(3-morpholynolpropyl)carbamodithioate 4 was synthesized by the similar procedure. The yield was 6.5 g (68%).

Octyl(3-morpholynolpropyl)carbamodithioate 5 was synthesizedby the similar procedure. The yield was 9.11 g (91%).

Nonyl(3-morpholynolpropyl)carbamodithioate6 was synthesized by the similar procedure. The yield was 7.02 g (81%).

Decyl(3-morpholynolpropyl)carbamodithioate*7* was synthesized by the similar procedure. The yield was7.19 g (67%).

Dodecyl(3-morpholynolpropyl)carbamodithioate 8 was synthesized by the similar procedure. The yield was 10.17 g (87%).

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Резюме

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(3-МОРФОЛИЛ)ПРОПИЛДИТИОКАРБАМИН ҚЫШҚЫЛЫНЫҢ АЛКИЛ ЭФИРЛЕРІНІҢСИНТЕЗДЕУ

Калий (3-морфолил)пропилдитиокарбаматын галогеналкилдермен алкилдеу зерттелінді. (3-морфолил)пропилдитиокарбамин қышқылының жаңа алкил эфирлері синтезінің жағдайлары жасалынды. (3-морфолил)пропилдитиокарбамин қышқылының гексил, гептил, октил, нонил, децил және додецил эфирлері сәйкесінше 67, 68, 91, 81, 67, 87% шығыммен синтезделінді. ИҚ-спектроскопиясы және ЯМР 13С спектроскопия әдістері арқылы (3-морфолил)пропилдитиокарбамин қышқылының алкил эфирлерінің құрылысы анықталынды.

Түйін сөздер: алкилдеу реакциясы, калий (3-морфолил)пропилдитиокарбаматтар, (3-морфолил)пропилдитиокарбамин қышқылының алкил эфирлері.

Резюме

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СИНТЕЗ АЛКИЛОВЫХ ЭФИРОВ (3-МОФОЛИЛ)ПРОПИЛДИТИОКАРБАМИНОВОЙ КИСЛОТЫ

Изучено алкилирование(3-морфолил)пропилдитиокарбамата калиягалогеналкилами. Разработаны условия синтеза новых алкиловыхэфиров (3-морфолил)пропилдитиокарбаминовой кислоты. Синтезированы гексиловый, гептиловый, октиловый, нониловый, дециловый и додециловый эфиры (3-морфолил)пропилдитиокарбаминовой кислоты с выходами 67,68, 91, 81, 67, 87%, соответственно.Методами ИК-спектроскопии и спектроскопии ЯМР ^{13}C установлена структура алкиловых эфиров (3-морфолил)пропилдитиокарбаминовой кислоты.

Ключевые слова: реакция алкилирования, (3-морфолил)пропилдитиокарбамат калия, алкиловые эфиры(3-морфолил)пропилдитиокарбаминовой кислоты.

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THE INFLUENCE OF SORBENT NORM AND TIME ON THE PROCESS OF PURIFICATION OF PHOSPHORIC ACID FROM CATION OF LEAD (II) BY ACIDOMODIFICATED ZEOLITE FROM SHANKANAY DEPOSIT

Abstract. The effect of the norm of the acid-modified zeolite of the Shankanay deposit and the time on its sorption capacity with respect to the Pb (II) cations in 26 and 83% H_3PO_4 was studied. It was found that in 26 and 83% phosphoric acid, the modified zeolite exhibits a high sorption ability with respect to the Pb^{2+} cations, with the optimal ratio "acid-modified zeolite: H_3PO_4" equal to 10: 100. 26% and 83% of H_3PO_4 acid, respectively, are cleared at 98.94 and 99.60%. It has been established, that the curves of the residual content of Pb^{2+} cations after purification with 83% H_3PO_4 in time for all investigated temperatures and C_{Pb} are rectilinear and decrease with increasing duration of the process. The highest degree of sorption of Pb (II) by sorbent is achieved in 60 minutes of the process.

Key words: heavy metals, lead cations, acid-modified zeolite, sorption, phosphoric acid.

Introduction. At present, pollution of the environment with heavy metals is one of the problems of ecology and public health. The flow of heavy metals (HM) into the biosphere occurs for various reasons. The natural source of their entry into the aquatic environment is the dissolution and leaching of rocks. However, in recent years, the main contribution has been made by liquid discharges of ore-dressing factories, chemical and metallurgical enterprises, galvanic industries, as well as the production of mineral paints, fertilizers, man-made fibers, the booming oil-producing and oil-refining industry. Another cause of pollution of the HM environment is the involvement of low-grade and off-balance raw materials, in particular low quality phosphorites and phosphorus waste (phosphorus slags and sludges). The phosphoric acid obtained from such raw materials is contaminated with dissolved impurities in the form of various compounds and salts that have passed from the composition of phosphate raw materials, including HM salts [1]. Heavy metals pass into phosphorus fertilizers and then migrate to the soil, ponds, atmosphere. In phosphoric acid, the content of HM of the hydrogen sulfide group, namely Pb, is strictly regulated by the corresponding GOST: mass for Pb in Thermic phosphoric acid (TPhA) of grade A is no more than 0.0005%, grade B: grade 1 is 0.002%, grade 2 is 0.005% [2]. These requirements are due to the fact that, soluble lead salts are not biodegradable and accumulate in living organisms [3], causing various diseases and disorders such as anemia with reproductive, genotoxic, carcinogenic, and neurological consequences, especially for children [4].

The purity of the final product and the absence of certain impurities in it are some of the basic requirements for phosphoric acid, so there is a need for its purification. The problem of cleaning various media, including phosphoric acid, from HM and recycling spent sorbents can be solved by developing new technologies, obtaining promising sorption materials that can effectively extract them. Very promising new sorption materials are sorbents that combine ion-exchange, sorption and filtering properties. At the same time, they must possess a stable chemical nature, the presence of a large number of surface functional groups, good physicochemical characteristics, the possibility of regeneration without a significant loss of sorption capacity and utilization of the spent sorbent, and also a relatively low cost [5]. To date, such materials can include natural zeolites, kaolinites, activated carbons, bentonites and many others. First, zeolites, which are widely used as ion exchangers, deserve attention. This is facilitated by factors such as the granular structure of the zeolite, which makes it possible to carry out the ion exchange process under dynamic conditions, as well as a significant increase in the exchange capacity of the zeolite as a result of various pretreatment methods. Therefore, the work uses an acid-modified zeolite with a sufficiently high sorption activity to cations, in which the statistical exchange capacity (SEC) cation exchanger (0.984 meq/g) is 3.83 times higher than that of the SEC anion exchanger (0.2568 meq/g) [6].

Experiment

The purpose of this work was to study the influence of the sorbent rate and time on the sorption capacity of the zeolite of the Shankanay deposit, modified with hydrochloric acid (0.1n), with respect to Pb^{2+} ions in phosphoric acid. To eliminate the effect of impurities, a study of the sorption of lead (II) cations with a modified zeolite was carried out on the model system "Pb^{2+}–H_3PO_4-acid-modified zeolite" The specified concentration of lead (II) cations was created by introducing into the phosphoric acid a calculated amount of lead salt $Pb(CH_3COO)_2 \cdot 3H_2O$.

The sorption capacity of the sorbent was studied under agitation conditions. A sample of H_3PO_4 was placed in a thermostated, heated to a specific temperature and a lead salt was injected. Then, a modified zeolite was added to the lead-containing phosphoric acid solution at a predetermined ratio "the modified zeolite (Solid-S): H_3PO_4 (Liquid-L)" and mixed for a predetermined time. Sampling of the phosphoric acid to be purified from the reactor was carried out regularly at regular intervals. An aliquot was weighed on an analytical scale to the fourth digit, then the mixture was quantitatively transferred to a 250 ml volumetric flask and filtered through a paper filter. The resulting filtrate was analyzed for the content of lead ions, the determination of which was carried out on an absorption spectrometer (AAC).

The degree of sorption (R,%) was found from the difference between the initial and residual concentrations of metals in solution by the formula:

$$R = \frac{Co - Cp}{Co} \cdot 100\%,$$

where C_0 is the initial concentration of metal ions in solution, mg/l; C_p is the concentration of metal ions in the solution after purification by sorbent, mg/l.

The effect of the sorbent's rate on its sorption capacity was investigated in dilute (26%) and concentrated (83%) phosphoric acids with a content of 48.4 mg/l Pb^{2+}. The sorbent consumption was from 5 to 30 g per 100 g of purified phosphoric acid.

The degree of purification of various media depends significantly on the duration of contact of the sorbent with the acid to be purified. The effect of the process time on the sorption of Pb^{2+} cations by an acid-modified zeolite was studied in 83% of H_3PO_4 with a concentration of cations of Pb^{2+} equal to (10-100) mg/l in the range (20-70)°C at a constant ratio of S:L = 10:100.

Results and discussion

The obtained results on the effect of the rate of acid-modified zeolite on its sorption capacity in dilute and strongly concentrated phosphoric acid are presented in the table. From the data obtained, it follows that in dilute H_3PO_4 (26%) with an increase in the rate of acid-modified zeolite from 5 g to 30 g per 100 g of the purified solution, the purification rate increases by 1.28%. When purification of concentrated H_3PO_4 (83%) with an increase in sorbent consumption from 5 g to 10 g per 100 g of purified acid purification rate R is increased by 0.15%, with a further increase in the sorbent load, a tendency to a slight decrease in the sorbent appears. Perhaps the acid-modified zeolite undergoes greater structural changes in concentrated H_3PO_4 than in dilute H_3PO_4 [7], which affects its sorption ability. This explains why, at a low sorbent rate (S:L = 5: 100), the degree of sorption in concentrated H_3PO_4 is 1.43% higher than that of dilute phosphoric acid.

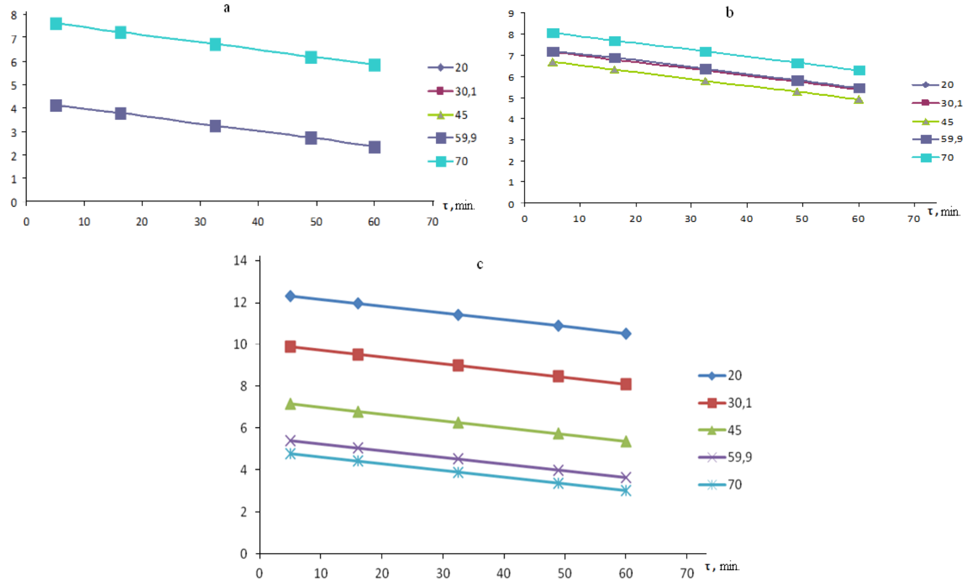
Based on the results obtained, it follows that the acid-modified zeolite in the acids under study shows a high sorption ability with respect to the Pb^{2+} cations.

The effect of the modified zeolite norm on the sorption of lead (II) ions from phosphoric acids

C_{H3PO4}, %	26		83	
S:L	Residual content Pb^{2+}, mg/l	R, %	Residual content Pb^{2+}, mg/l	R, %
5:100	0,99	98,02	0,27	99,45
10:100	0,53	98,94	0,19	99,60
20:100	0,37	99,25	0,23	99,53
30:100	0,35	99,30	0,23	99,52

The degree of sorption reaches 98.0-99.6%. Regardless of the concentration of phosphoric acid for all temperatures, the optimal ratio of "acid-modified zeolite: H_3PO_4" is 10:100. Under these conditions, the concentration of phosphoric acid does not have a significant effect on the degree of purification. Thus, 26% and 83% phosphoric acid with acid-modified zeolite is purified at 98.94 and 99.60%.

Analysis of the obtained data on the sorption ability of the acid-modified shankanese zeolite revealed that in the investigated temperature range and concentrations of lead (II) cations, the sorption curves have the same type of character (figure).



Residual content Pb^{2+} on time

a – 10 mg/l Pb^{2+}; b – 55 mg/l of Pb^{2+}; c – 81.8 mg/l Pb^{2+}

The influence of duration time on the residual content of Pb (II) cations in the system "Pb^{2+} – H_3PO_4 – acid-modified zeolite"

The curves of the residual content of Pb^{2+} ions are of a rectilinear nature and decrease with increasing duration of the process. That is, as the time increases, the degree of lead sorption increases. For example, in an acidic medium with a concentration of Pb^{2+} ions equal to 55 mg/l at 20°C, 85.45% is sorbed for 5 minutes, 86.0% for 85 minutes, 87.0% for 30 minutes, 60 minutes - 88.7%.

Under the investigated conditions, an increase the duration time of the process has a positive effect on the purification of phosphoric acid. The highest degree of sorption of Pb (II) cations with an acid-modified zeolite is achieved in 60 minutes of the process.

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Резюме

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ШАҢҚАНАЙ КЕН ОРНЫНЫҢ ҚЫШҚЫЛМЕН МОДИФИКАЦИЯЛАНҒАН ЦЕОЛИТІ АРҚЫЛЫ ФОСФОР ҚЫШҚЫЛЫН ҚОРҒАСЫН (II) КАТИОНДАРЫНАН ТАЗАРТУ ПРОЦЕСІНЕ СОРБЕНТ МӨЛШЕРІ МЕН УАҚЫТТЫҢ ӘСЕРІ

Шаңқанай кен орнының қышқылмен модификацияланған цеолиті мөлшерінің және уақыттың 26 және 83 % H_3PO_4 қышқылындағы Pb (II) катиондарына қатысты сорбциялық қабілетіне әсері зерттелді. 26 және 83 %-ды фосфор қышқылында модификацияланған цеолит Pb^{2+} катиондарына қатысты жоғары сорбциялық қасиет көрсететіні анықталды. «Қышқылмен модификацияланған цеолит: H_3PO_4» қатынасы оңтайлы, яғни 10:100 тең болғанда 26 және 83 % H_3PO_4 қышқылы сәйкесінше 98,94 және 99,60 %-ға тазарады.

83 % H_3PO_4 қышқылы тазарғаннан кейін Pb^{2+} катиондарының қалған мөлшерін көрсететін уақытқа тәуелді қисық зерттеліп отырған барлық температура және C_{Pb} үшін тік сызықпен сипатталады және процесс уақытын арттырған сайын төмендейді. Сорбент арқылы Pb (II) катионы ең жоғары сорбциялану дәрежесіне 60 минутта жетеді.

Түйін создер: ауыр металдар, қорғасын катиондары, қышқылмодифицирленген цеолит, сорбция, фосфор қышқылы.

Резюме

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ВЛИЯНИЕ НОРМЫ СОРБЕНТА И ВРЕМЕНИ НА ПРОЦЕСС ОЧИСТКИ ФОСФОРНОЙ КИСЛОТЫ ОТ КАТИОНОВ СВИНЦА (II) КИСЛОТОМОДИФИЦИРОВАННЫМ ЦЕОЛИТОМ МЕСТОРОЖДЕНИЯ ШАНКАНАЙ

Исследовано влияние нормы кислотомодифицированного цеолита месторождения Шанканай и времени на его сорбционную способность по отношению к катионам Pb (II) в 26 и 83 % H_3PO_4. Выявлено, что в 26 и 83 % фосфорной кислоте модифицированный цеолит проявляет высокую сорбционную способность по отношению к катионам Pb^{2+}. При оптимальном соотношении «кислотомодифицированный цеолит: H_3PO_4» равном 10:100. 26 и 83 % H_3PO_4 кислота очищается соответственно на 98,94 и 99,60 %. Установлено, что кривые остаточного содержания катионов Pb^{2+} после очистки 83 % H_3PO_4 во времени для всех исследуемых температур и C_{Pb} носят прямолинейный характер и с увеличением продолжительности процесса снижаются. Наибольшая степень сорбции Pb (II) сорбентом достигается за 60 мин процесса.

Ключевые слова: тяжелые металлы, катионы свинца, кислотомодифицированный цеолит, сорбция, фосфорная кислота.

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ANALYSIS OF SOME PRIMARY AND SECONDARY METABOLITES OF THE AERIAL PART OF *TAMARIX HISPIDA*

Abstract. The article provides an analysis of the quantitative and qualitative content of some groups of primary and secondary metabolites contained in the aerial part of the plant Tamarixhispida harvested during flowering in 2016 in the territory of the Almaty region of the Republic of Kazakhstan. We carried out a qualitative determination of the presence of various groups of BASs in the aerial part of Tamarixhispida. Then the quantitative content of BAS groups interested in us was determined, in particular, the quantitative content of the sum of alkaloids, polysaccharides, carotenoids and riboflavin was reduced, and finally we studied the ethilacetate extract from the aboveground masses of Tamarixhispida by high-performance liquid chromatography with a mass-selective detector.

As a result, in the aboveground part of the plant Tamarixhispida we detected the presence of tannins, alkaloids, polysaccharides, flavonoids, coumarins, anthraquinones, carotenoids, organic acids, carbohydrates, amino acids and riboflavin. We also determined the quantitative content of the sum of alkaloids, polysaccharides, carotenoids and riboflavin.

Finally, by the method of high performance liquid chromatography with a mass-selective detector. WE was 15 compounds in the ethyl acetate extract. The dominant of which was dicyclohexylphthalic acid ester with a content of more than 50%, a significant amount of morphine derivatives (Morphinan-4,6-diol, N- formyl-6-acetate), some halogen and sulfur-containing compounds (Milbemycin B, 6.28-anhydro-15-chloro-25-isopropyl-13-dehydro-5-O-demethyl-4-methyl, 2-methoxy-N methyl-4- (methylsulfanyl) -N-phenyl-benzamide, 5-(2-Chloro -6-fluorobenzyl) -6-methyl-2- (2-propinilsulfanil) -4-pyrimidinol, oryzalin, Alkometazon).

Key words: *Tamarixhispida*, BAS, *Tamaricaceae*, metabolites, HPLC-MS.

Introduction. Organs of higher plants contain many primary and secondary metabolites belonging to different classes of organic substances; many of them exhibit different types of biological activity and have different effects on the human body. In particular, compounds of the alkaloid class exhibit, anesthetic or stimulating action, flavonoids and tannins substances have an antioxidant and astringent effect; some types of sulfur-containing compounds affect the growth of pathogenic organisms and exhibit actericidal properties. In this connection, knowledge of the qualitative and quantitative composition of various plants is of obvious practical interest [1].

We studied the qualitative and quantitative composition of the aerial mass of *Tamarixhispida* family *Tamaricaceae* harvested in 2016 in the Almaty region during the flowering period.

From the work on the aerial mass of the *Tamarixhispida* of the family Tamaricaceae. Itwas found out that in the aerial part of *Tamarixhispida* a significant amount of flavonoids, tannins and terpenoid.

Was found, and the structure of a number of new compounds, such as (octane, genicosan, docosane, tricano, heptadecane, nonadecane, hexacosane, pentacosane) terpenoids (α-copene, g-element, g-cadien, isophytol, phytol, β-cubenene, 3-α- [3'', 4'' -dihydroxy-trans-cinamoyl] -oxy-D -fridolean-14-ol-28-xylitol, β-systenrol, α-cadinol, d-cadinol, α-bisabolol) and their derivatives, polar acid esters (hexanoic acid, heptanoic acid, 2-ethylhexanoic acid, methyl palminat, hexadecanoic acid, octanoic, dodecanoic), aromatic compounds (vanillin, benzyl, benzoate, benzyl tsinamat) and alcohols (tridecanol, eugenol) [2].

Of the aerial mass directly *Tamarixhispida*, compounds of various classes were isolated, such as: ursolic acid-1, 2 methyl ester of 3β-al-D-freeoolean-14-ene-28-one acid, 3-α- [3 '' 4''-dihydroxy-transcinamoloxy] -D-firdoolean-14-ene-28-tartaric acid (isotamarixene) -3,3-α-hydroxy-D-fridooleane-14-ene-28-tartaric acid 4-, 3- - [4''-hydroxy-transcamolamoxy] -D-firdoolean-14-ene-28-olal kilo-5. isoramnetin, 3,5-dihydroxy-4 ', 7-dimethoxyflavone, rhamnocetri, afzelin, 5,3'-dihydroxy-7,4'-dimethoxyflavone 3-O-β-D-glucopyranoside, 4-hydroxy-3,5-O-dimethyl benzo 7'-tetrahydrofuran, 3,7,4'-trihydroxy-5-methoxyflavone, 3,5,7-trihydroxy-3 ', 4'-dimethoxyflavone, Kampferid-3- O-β-glucopyranoside [3].

It was also proved that the extract from the aboveground mass *Tamarixhispida* has antibacterial and antioxidant activity [4].

Methods. After the study, previously published by *Tamarixhispida*, we decided to determine the quantitative composition of the least studied *tamarix* metabolites, namely alkaloids, polysaccharides, carotenoids and riboflavin

For which the following methods were used.

Determination of the quantitative content of alkaloids. About 10 grams (accurately weighed) of the crushed material are placed in a 250 ml flask, 100 ml of chloroform or ethyl acetate are added, 5 ml of concentrated ammonia solution, covered with a stopper and shaken on a vibrating apparatus for 2 hours or left at room temperature for 15 hours, after which they shake another 30 minutes. Chloroform extraction is filtered through cotton wool. 50 ml of the filtrate is transferred to a 100 ml flask and the chloroform is distilled to a volume of 1-2 ml. The remaining chloroform is removed by blowing air. To the remainder, add 2 ml of sodium hydroxide solution (0.1 mol/l) with a pipette and rub with a stick until the lumps disappear completely, then add 8 ml of water and mix 2-3 minutes. 10 ml of a solution of hydrochloric acid (0.1 mol/l) are added to the contents, pipetched gently and left for 8-10 minutes, then shaken on a vibratory shaker for 8-10 minutes and filtered through a triple paper filter, 7 cm in diameter. 10 ml The filtrate is transferred to a 50 ml flask, 10 ml of water, 2 drops of methyl red solution are added and the excess acid is titrated with a solution of sodium hydroxide

(0.01 mol/l) until a yellow color appears. At the same time, they conduct a control experiment. Add 1 ml of sodium hydroxide solution (0.1 mol/l) to a 50 ml flask, add 4 ml of water and 5 ml of hydrochloric acid (0.2 mol/l), mix, add 2 drops of methyl red solution and titrate excess acid sodium hydroxide solution (0.1 mol/l) until yellow coloration appeared. The content of the sum of alkaloids in terms of thermopsin and absolutely dry feedstock (X) in percent is calculated by the formula:

$$X = \frac{(V1 - V2) \times 0.0244 \times 4 \times 100 \times 100}{m \times (100 - W)},$$

where 0.0244 – the number of alkaloids in terms of thermopsin, corresponding to 1 ml of a solution of hydrochloric acid (0.1 mol/l), g; V1 is the volume of a solution of sodium hydroxide (0.1 mol/l), which has gone for titration of the control experiment, ml; V2 is the volume of a solution of sodium hydroxide (0.1 mol/l), which has gone for titration of the test solution, ml; m is the mass of the raw material, g; W is the loss in mass when the raw material is dried,%.

Determination of the quantitative content of polysaccharides. Approximately 5 grams (accurately weighed) of the crushed raw material are placed in a 100 ml flask, 50 ml of purified water are added, the flask is attached to a reflux condenser and boiled while stirring in a water bath for 1 hour, cooled. Extraction with water is repeated twice for 30 minutes under the same conditions. Water extracts combine and filter into a volumetric flask with a capacity of 250 ml ml through 3 layers of gauze. The filter is rinsed with purified water and the volume of the solution is adjusted with water purified to the mark. 25 ml of the resulting solution are placed in a centrifuge tube, 75 ml of ethyl alcohol 95% is added, mixed, heated in a water bath at a temperature of 60 ° C for 5 minutes. After 30 minutes, the contents are centrifuged at a rotation speed of 5000 rpm for 30 minutes. The supernatant is filtered under vacuum through a glass filter POR 16 dried to a constant weight. The precipitate is then quantitatively transferred to the same filter and washed with 15 ml of ethyl alcohol 95%. The filter with the precipitate is dried at a temperature of 100-105 ° C to constant weight. The content of polysaccharides in terms of absolutely dry raw materials in percent (X) is calculated by the formula:

$$X = \frac{(m2 - m1) \times 250 \times 100 \times 100}{m \times 25 \times (100 - W)},$$

where m1 - filter weight, g; m2 - filter weight with precipitate, g; 32 m - weight of the sample of raw materials, g; W is the moisture content in the mass when the raw material is dried, %.

Determination of the quantitative content of carotenoids. Approximately 5 grams (accurately weighed) of the crushed plant material are placed in a conical flask with ground glass stopper of 100 ml capacity, 50 ml of a mixture of hexane-alcohol ethyl 96% (1: 1) are poured, kept for 2 hours with constant stirring, filtered. 15 ml of the filtrate is placed in a 25 ml volumetric flask and the volume is adjusted to a label with a mixture of hexane-ethyl alcohol 96% (1: 1). [Approximately 1 g (exact sample) of the preparation is dissolved in a mixture of these solvents in a 50 ml volumetric flask, the volume of the solution is brought to the mark with the same mixture and mixed.] * The optical density of the solution is measured at a wavelength of 450 nm in a cuvette with a layer thickness of 10 mm , using a mixture of hexane-ethyl alcohol 96% (1: 1) as the reference solution. In parallel, the optical density of the potassium dichloride CO solution is measured. The content of carotenoids in terms of β-carotene in mg% (X) is calculated by the formula:

$$X = \frac{D1 \times 0.00208 \times 25 \times 50 \times 100 \times 100}{D0 \times m \times 15 \times (100 - W)}$$

where D1 - optical density of the solution under study at a wavelength of 450 nm; D0 is the optical density of the solution of potassium bichromate CO at a wavelength of 450 nm; 0,00208 - the amount of β-carotene in milligrams, in a solution corresponding to the color of the solution of potassium bichromate CO; m is the weight of the sample of raw materials, g; W - loss in mass during drying of raw materials,%

Preparation of potassium bichromate (CO) solution: 0.0036 g (exact sample) of potassium bichromate potassium salt is dissolved in water, purified in a volumetric flask with a capacity of 1 liter, the volume of the solution is adjusted with water purified to a mark, and mixed. The color of the solution corresponds to a solution containing 0.00208 mg of β-carotene in 1 ml.

Determination of the quantitative content of riboflavin. 0.06 g of the plant material is placed in a 1000 ml flask, 20 ml of glacial sulfuric acid are added, 500 ml of purified water, heated in a water bath, then cooled to room temperature, filtered and the volume of the solution is adjusted to the mark with water. 10 ml of filtrate are taken from the resulting solution, placed in a 100 ml volumetric flask, 3.5 ml of 0.1 mol/l sodium acetate solution is added and the volume of the solution is adjusted to the mark with water. 34 The optical density of the resulting solution is measured at a wavelength of 270 nm in a cuvette with a layer thickness of 10 mm. The content of riboflavin in percent (X) is calculated by the formula

$$X = \frac{D \times 10000}{a \times 850}$$

Where D is the optical density of the test solution at a wavelength of 270 nm; 850 - specific absorption index of riboflavin at a wavelength of 270 nm; a - the mass of the sample of raw materials, g.

The quantitative content of alkaloids, polysaccharides, carotenoids and riboflavin is given in table 1.

Next, we studied the ethylacetate extract obtained from the aerial mass of Tamarixhispida family Tamaricaceae according to the following procedure.

Vegetable raw materials are harvested in the southern region of the Republic of Kazakhstan (Almaty region). The ground air dry powder (500 g) was extracted with ethyl acetate into the feed / reagent ratio (1:10) in a Soxhlet apparatus. The resulting extract was concentrated under mild conditions (water bath temperature 40-450 °C).

The extract was examined by a high-performance liquid chromatograph with a mass selective detector of Aligent Technologies 6400 Series Triple Quadrupole LC/MS.

We was use: a Poroshell 120 EC-C18 column (50 mm in length, 3 mm in diameter, 4.0, 2, 7 and 1.9 μm) with 10% methanol with an aqueous solution of methanol as the starting solvent and 90% methanol as the final solvent at a pressure of 11.5 mPa and a temperature of 40 °C.

The components were identified by mass spectra and retention times, using the NIST library and Wiley LC / MS.

The results are shown in table 2.

Results and discussion

Chemical analysis of the aerial mass of *Tamarixhispida* family *Tamaricaceae* showed that in the investigated object there are alkaloids in the amount of 0.32%, polysaccharides (1.22%), carotenoids, 10.32% and riboflavin (2.09%), the data prompted us to further study the aboveground masses of Tamarixhispida already using the methods of mass spectrometry and high-performance liquid chromatography.

Table 1 – Content of alkaloids, polysaccharides, carotenoids and riboflavin in the aerial part of *Tamarixhispida* family *Tamaricaceae*

№	BAS Group	Content, (%)
1	Alkaloids	0.32
2	Polysaccharides	1.22
3	Carotenoids	10.32
4	Riboflavin	2.09

As a result of studying the hexane extract, 96.93% of the substances were identified. It was found that in the above-ground part of the *Tamarix hispida* family *Tamaricaceae* is dominated by dicyclohexyl ester of phthalic acid contained in an amount of 54.58%, of the compounds of the alkaloid class is dominated by Morphinan-4,6-diol, N-formyl-6-acetate (6.49%), total fraction of nitrogen-preserving compound is 14.17%, in addition to the derivatives of morphine, we classified benzenamine, 4-methyl-N, N-bis (4-methylphenyl) (1.94%), 6H-benzo [b] naphtho [2,3-H] carbazole (3 , 46%), 44-t-butyl-2- (4-methoxyphenyl) -6-p-tolyl-pyridine (1.27%), pyrrole, 2- (2-naphthyl) -3,5-diphenyl (1.01 %).

In addition to the nitrogen-containing compounds, we have identified some compounds related to terpenoids, namely (6E, 8E, 10E, 12E, 14E, 16E, 18E, 20E, 22E, 24E, 26E, 28E) -31-methoxy-2,6,10, 14,19,23,27,31-octamethyldotriaconta-6, 8,10,12,14,16,18,20,22,24,26,28-dodecaen-2-ol (3.68%), and the produced heterocycles 3 , 5-progesterol acetate (2.93%).

Table 2 – Component composition of the ethyl acetate extract
of the aboveground mass *Tamarixhispida* Willd.

№	ConnectionName	Formula	Molecular weight	RT	Content, %
1	Milbemycin B, 6.28-anhydro-15-chloro-25-isopropyl-13-dehydro-5-O-demethyl-4-methyl	$C_{33}H_{47}ClO_7$	590	0,48	3.06
2	Morphinan-4,6-diol, N-formyl-6-acetate	$C_{19}H_{23}NO_4$	329	5,85	6.49
3	(6E, 8E, 10E, 12E, 14E, 16E, 18E, 20E, 22E, 24E, 26E, 28E) -31-methoxy-2,6,10,14,19,23,27,31-octamethyldotriaconta-6, 8,10,12, 14,16,18,20,22,24,26,28-dodecen-2-ol	$C_{41}H_{60}O_2$	584	6,97	3.68
4	3,5-progesterol acetate	$C_{23}H_{32}O_3$	356	7,48	2.93
5	2-methoxy-N-methyl-4-(methylsulfanyl) -N-phenylbenzamide	$C_{16}H_{17}NO_2S$	287	8,07	8.57
6	Benzenamine, 4-methyl-N, N-bis (4-methylphenyl)	$C_{21}H_{21}N$	287	8,40	1.94
7	5- (2-chloro-6-fluorobenzyl) -6-methyl-2- (2-propynylsulfanyl) -4-pyrimidinol	$C_{15}H_{12}ClFN_2OS$	322	8,78	0.65
8	6H-benzo [b] naphtho [2,3-H] carbazole	$C_{24}H_{15}N$	317	8,92	3.46
9	4- (dipropylamino) -3,5-dinitrobenzenesulfonamide	$C_{12}H_{18}N_4O_6S$	346	9,37	4.51
10	Alclomethasone	$C_{28}H_{37}ClO_7$	520	9,73	0.65
11	4-t-Butyl-2- (4-methoxy-phenyl) -6-p-tolyl-pyridine	$C_{23}H_{25}NO$	331	10,03	1.27
12	Pyrrole, 2- (2-naphthyl) -3,5-diphenyl	$C_{26}H_{19}N$	345	10,76	1.01
13	2-methyl-4- (1,1,3,3-tetramethylbutyl) phenol	$C_{15}H_{24}O$	220	11,64	3.36
14	2,4,6-decathrienoic acid, 1a, 2,5,5a, 6,9,10,10a-octahydro-5,5a-dihydroxy-4- (hydroxymethyl) -1,1,7,9-tetramethyl-11 -oxo-1H-2,8a-methanocyclopenta [a] cyclopropa [e-cyclodecene-6-yl ester, [1aR-(1aα, 2α, 5β, 5aβ, 6β, 8aα, 9α, 10aα)]	$C_{30}H_{40}O_6$	496	12,81	0.77
15	dicyclohexyl ester of phthalic acid	$C_{20}H_{26}O_4$	330	13,88	54.58

A significant amount of organo-halogen compounds has been identified with a total content of 4.36% and includes the following compounds: Milbemycin B, 6.28-anhydro-15-chloro-25-isopropyl-13-dehydro-5-O-demethyl-4-methyl (3.06 %), 5- (2-chloro-6-fluorobenzyl) -6-methyl-2- (2-propynylsulfanyl) -4-pyrimidinol (0.65%), alclometasone (0.65%).

In addition, we identified a number of sulfur-containing compounds of various classes with a total fraction of 13.73% in the ethylacetnane extract, the following compounds were dentified: 22-methoxy-N-methyl-4- (methylsulfanyl) -N-phenylbenzamide (8.57%) and 4- (dipropylamino) -3,5-dinitrobenzenesulfonamide (4.51%).

Some of the identified compounds were not previously found in representatives of the tamarix family, in particular halogen-containing organic compounds have been detected for a while for the metabolites of a plant in the family of Tamaricaceae [5-9].

Conclusion. Thus, we determined the quantitative content of 4 groups of metabolites in the aerial part of *Tamarixhispida*, namely, alkaloids, carotenoids, polysaccharides and riboflavin, and the presence of alkaloids was confirmed by HPLC mass spectrometry.

In addition to the groups of substances by the method of high-performance liquid chromatography with a mass-selective detector. In the ethylacetate extract from the aboveground weight of *Tamarixhispida*, we found 15 compounds of various classes. 2 of them ether, 1 phenolic compound, pyrolysis derivative, pyridine derivative, pyromadyl derivative and morphine derivatives, also identified 3 sulfur-containing compounds including the class of sulfonamides; in addition, 3 halogen-containing compounds, namely Milbemycin B, 6.28-anhydro-15-chloro-25-isopropyl-13-de 5-O-demethyl-4-methyl, 5- (2-chloro-6-fluorobenzyl) -6-methyl-2- (2-propynylsulfanyl) -4-pyrimidinol, which had not previously been identified in plants of the tamarix genus [11].

The data obtained are in general consistent with the results of the literature review, since the identified BAS groups have anti-inflammatory and bactericidal activity

In particular, the sulfamide class compounds are known as highly effective antibiotics, and in a number of literature it is claimed that the *tamarix* aerial extract has a tonic and anesthetic effect, which is confirmed by the presence in the composition of alkaloids-derivatives of morphine, known for their high therapeutic efficacy w [12-15].

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Резюме

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TAMARIXHISPIDA БӨЛІГІНІҢ КЕЙБІР БАСТАПҚЫ ЖӘНЕ ЕКІНШІ МЕТАБОЛИТТЕРІН ТАЛДАУ

Мақалада бастапқы және қайталама метоболиттердің кейбір топтарының сандық және сапалық мазмұнын талдау. 2016 жылы Алматы облысының аумағында гүлдену кезінде жиналған *Tamarix hispida* жер асты бөлігінде орналасқан. Біз *Tamarix hispida*жоғары бөлігінде әртүрлі топтардың болуын сапалы анықтауды жүзеге асырдық. Және бізді қызықтыратын БАВ топтарының сандық ортасы анықталды. Атап айтқанда, соманың сандық мазмұны алкалоидтар,полисахаридтер, каротиноидтар және рибофлавина.Қорытындысында біз жер асты массасынан алынған Tamarix hispida этилацетаттың экстрактісін, селективті-масса детектормен жоғары сапалы сұйық хромотография әдісімен зерттедік.

Нәтижесінде жерасты *Tamarix hispida* өсімдігі дубилді заттардығ қатысында анықталды, алкалоидтық, полисахаодтік, флаваноидтық, кумариндық, антрахинондық, каротиноидтық, органикалық қышқылдық, көміртектік аминқышқылдық және рибофлавиндік. Және де алкалоидтардың, полисахаридтердің, каротиноидтардың және рибофлавиндердің

Түйін сөздер: *Tamarix hispida, БАВ, Tamaricaceae,* метаболитырын*, HPLC-MS.*

Резюме

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АНАЛИЗ НЕКОТОРЫХ ПЕРВИЧНЫХ И ВТОРИЧНЫХ МЕТАБОЛИТОВ НАДЗЕМНОЙ ЧАСТИ *TAMARIXHISPIDA*

Анализ количественного и качественного содержания некоторых групп первичных и вторичных метаболитов, содержащихся в надземной части растения *Tamarixhispida*, заготовленного в период цветения в 2016 г. на территории Алматинской области Республики Казахстан. Нами было проведено качественное определение присутствия различных групп БАВ в надземной части *Tamarixhispida*, затем было определено количественное содержание заинтересовавших нас групп БАВ. В частности, было пороеделено количественное содержание суммы алкалоидов, полисахаридов, каротиноидов и рибофлавина и в заключение мы изучили этиацетатный экстракт из надземной масс *Tamarixhispida* методом высокоэффективной жидкостной хроматографии с масс-селективным детектором.

В результате в надземной части растения *Tamarixhispida* нами было обнаружено присутствие дубильных веществ, алкалоидов, полисахаридов, флаваноидов, кумаринов, антрахинонов, каротиноидов, органических кислот, углеводов, аминокислот и рибофлавина. Также нами было определено количественное содержание суммы алкалоидов, полисахаридов, каротиноидов и рибофлавина.

В завершении методом высокоэффективной жидкостной хроматографии с масс-селективным детектором в этилацетатном экстракте было идентифицировано 15 соединений, доминирующим из которых являлся дициклогексиловый эфир фталевой кислоты с содержанием более 50%, также обнаружено значительное количество производных морфина (Морфинан-4,6-диол, N-формил-6-ацетат), некоторое количество галоген и серосодержащих соединений (Милбемицин B, 6,28-ангидро-15-хлор-25-изопропил-13-дегидро-5-O-деметил-4-метил, 2-метокси-N-метил-4- (метилсульфанил) -N-фенилбензамид, 5-(2-Хлор-6-фторбензил) -6-метил-2- (2-пропинилсульфанил) -4-пиримидинол, Оризалин, Алкометазон).

Ключевые слова: *Tamarixhispida, БАВ, Tamaricaceae,* метаболиты*, HPLC-MS.*

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PROCESSING OF OIL SLUDGE AND OIL CONTAMINATED SOIL

Abstract. In this article examines the existing modern methods for processing oil sludge and oil-contaminated soil. On the basis of comparative economic and environmental characteristics of purification processes, the preference is given to physical-chemical methods for processing oil wastes.

Keywords: oil sludge, oiled soil, processing, purification, cleaning methods, target product.

Today in the market relations, many states and large transnational oil and gas companies pay serious attention to the real needs of the world economy in energy carriers, especially in hydrocarbon resources, to develop key guidelines for their future development. Despite of the positive dynamics of oil production and the growing demand for petroleum products, Kazakhstan is one of the last places in the world in terms of the ratio of the total capacity of the refinery and the volume of production. So, in 2013, oil processing reached the level of 15.3 million tons, the processing/production ratio was only 18.7% [1]. At the same time, oil refining and petrochemicals are an attractive sector of manufacturing industry, taking into account market prospects, economic effect and competitiveness of the Republic of Kazakhstan. Priority commodity groups are defined based on the volumes of the markets of Kazakhstan and the macroregion, the technological "complexity" of product groups, as well as the possibility of their production, taking into account the requirement to reduce environmental emissions [1]. In this regard, environmental security is one of the main strategic components of the national security of the Republic of Kazakhstan and the most important aspect of state priorities. As many national and foreign researchers believe, pollution of the environment has become a serious obstacle to the socio-economic development of the country [2]. On the territory of the republic there are about 2.5 thousand enterprises that belong to the 1-2 highest risk classes among 5 existing classes [3]. According to the Environmental Code of the Republic of Kazakhstan dated January 9, 2007, the requirements to environmental standards and increasing the responsibility of industrial enterprises for the state of the environment are tightened. This is also relevant because the republic, implementing the "Strategy 2030", "The concept of transition to sustainable development for 2007-2024" aims to long-term environmental strategy - the harmonization of interaction between society and the environment, as well as the creation of an environmentally friendly safe, well-bred environment. Implementing the strategic goals of the Concept, Kazakhstan, increasing the efficiency of resource use, increasing life expectancy, providing an increase in the index of environmental sustainability, will create an opportunity is on the level of quality of life among the most competitive and developed countries in the world [4].

The growth of oil production in Kazakhstan, the volumes of its processing and transportation is accompanied by an increase in volumes of oil pollution and other toxic waste. Every year in our country during the processing or transportation of oil, as a result of spills and accidents, about 400 thousand tons of oil waste are generated, and resources in earthen barns are estimated at 4.5 million tons [5]. According to these authors, a memorandum of cooperation was signed between the ministries of environment and oil and gas protection, NC KazMunaiGas and KMG EP, according to which 400 thousand tons of planned for disposal in the contract area of “JSC”OzenMunaiGas will be liquidated for a year until 2021, almost 1.3 million cubic meters of "historical" waste. Also, KMG is studying advanced world technologies: positive results, for example, were given by pilot-industrial tests of the hydrodynamic cleaning method. In the framework of GP FIIR, the company built the first in the region plant for the processing of oil-containing waste "Shyryn", which is included in the Map of Industrialization of Kazakhstan. At the same time, oil producing and oil refining companies can not balance all available oil sludge in the country, as only the volumes of environmental payments for them will significantly exceed profit figures. But practice shows that in many cases it is more profitable to pay environmental fees or even hide the amount of pollution. With a view to environmental safety, oil giants should seriously engage in their disposal and support of state bodies and partial or full financing of oil-slime utilization from the state budget is necessary. The state should move from point and spontaneous actions to a comprehensive and balanced program of actions, including a system of environmental monitoring and audit of accumulated damage, the amount and volume of slurry barns, the terms of mandatory recycling and fines for non-compliance with regulations.

It is common knowledge that the main sources of pollution by oil and oil products are mining enterprises, pumping and transportation systems, oil terminals and oil depots, oil products storage facilities, railway transport, river and sea oil tankers, refueling complexes and stations. In the Mangystau region, as in other regions of the country, there is still no system for preventing and eliminating the consequences of emergencies associated with oil spills and oil products, there is also no system for collecting, processing and utilizing oily waste that meets modern standards and protection requirements environment. This problem requires an immediate solution, since the accumulation of oily waste affects not only the ecological state of the natural environment, but also the sanitary well-being of the inhabitants of the region. When oil is produced, strong contamination of soil and water with drill cuttings containing hydrocarbons, and oil spills during its extraction are associated with a number of negative phenomena leading to "oiled" and degradation of the soil of huge areas. Naturally, after such an impact, the useful properties of the land are disturbed and need to restoration, that is, remediation. Reclamation is a complex of measures aimed at restoring the former fertile qualities of the land, its biological and economic value, as well as improving the environmental conditions. The creation of a high-performance technology for processing oil-contaminated soils will solve the problem of their complete elimination with the return of land to the user, reduce environmental pollution and enable rational use of organic raw materials from waste. Accordingly, in order to carry out measures for reclamation and restoration of land, it is necessary, initially, to collect and dispose of oil-containing waste. It should be understood that the presence of oil sludge collection in barns increases the risk of animal death, pollution of groundwater, air. To improve the ecological status and return to the economic circulation of lands contaminated with oil sludge, various environmental technologies for processing and utilization are proposed [6-10].

One of the methods is using hydrocarbon oxidizing microorganisms for neutralizing the soil from oily waste (biological method). Using the oil-degrading organisms to clean the environment today is the central problem in petroleum microbiology [11]. One of the important aspects of remediation (cleaning) of contaminated soil by oil is the microorganisms (MO) of the soil. The rate of their decomposition is due to oxidation-reduction conditions, hydrothermal regime, microorganism activity and a number of other conditions [11]. In this article, the main aspects of the current state of environmental problems in the locations of enterprises of the oil and gas complex, the problems of soil contamination with oil, methods for cleaning the soil from oil and oil products contamination, using microbial biotechnologies are examined. The result of scientific works in this field have been various developments in the bioremediation of oil, including active strains - oil destructors and their consortia, on the basis of which commercial biopreparations for the liquidation of hydrocarbon contamination are produced. In [5] it is noted that despite of the efforts of scientists and oil workers, a unified method of processing for all types of oil was not found yet. It is clear that oil products should not be burned (this is harmful to the environment), and buried. On the scientific and practical side, the method of bioremediation is not bad, but the effect of bacteria takes several years and does not always give a positive result. On such costly methods as washing with ultrasound or injection into the seam, there is still no question. It is necessary to search for suitable combinations of technologies, taking into account their cost, productivity, mobility, compliance with environmental requirements and environmental safety. And in this article, a new complex is proposed that works with any oil-contaminated soil, with any oil sludge, including in the bare steppe. Own fuel is used as fuel. As a result of complex impact on oil waste, they are separated into washed sand, which can be used for pouring roads, for technical water suitable for building or dusting roads, and for a mixture of oil waste. The universal complex installation STORM-15, mentioned in the article, has much in common with the installation of oil-contaminated soil (UZG), noted in [12]. For processing and utilization of oil-contaminated soils and solid combustible oil-containing waste, incl. non-recyclable methods of washing, bioprocessing or other methods, as well as in cases where other methods are economically less advantageous, the types of oiled soil installation are used (UZG, Patent RU 2341547, Certificate No. ROCC RU.HO01.B00158). The unit provides utilization of soils with a degree of contamination from 2% to 16%. Processing is carried out at a temperature of 500-900 °C. To reduce the emission of suspended solids into the atmospheric air, the "UZG-1M" set includes a Cyclone off-gas treatment unit and an irrigation unit, which allows to minimize the emissions of harmful substances as compared to the utilization of open burning. The cleaning factor of the cyclone at the initial stage of loading of detoxified waste into the furnace is 97.3% (dry cleaning), and in the maximum load mode "UZG-1M" the cyclone purification factor is 88.4%. However, the heat almost completely destroys the fertility of the soil being cleaned.

One of the modern methods in processing oil sludge is the use of the ST-150 system, where it is possible to obtain commercial grade oil, industrial water and solid residue, which can later be used in the production of building materials. [13] Along with such methods, oil-containing waste is pumped in layer. The process is to collect the waste, homogenize it into a homogeneous pulp and pump it into the selected reservoir for the safe disposal of waste. However, the waste remains waste, and the cost of pumping into the reservoir is high, that this technological process is economically inexpedient and environmentally unsafe. In addition to these, there are many patented methods for processing and utilization of oil sludge such as wave combustion, vibration reduction, electromagnetic cavitation, etc., which in practice are not widely used. In all these ways, the key factor is the economic feasibility of processing oil sludge expressed in profits when implementing this process.

Oil slimes consist of three distinct fractions: **water, oil** and **solid**. With all the variety of characteristics of different oil waste in the most general form, all can be divided into the following main groups or types:

- Oiled soil - oil spilled on it and its components in the process of extraction and its purification from salts, solid hydrocarbons and mechanical impurities;
- Bottom sludge**-** formed on the bottom of various reservoirs after the oil spill occurred and contain a lot of water;
- Products formed as a result of stripping of reservoirs that are formed during the storage and transportation of oil in a wide variety of reservoirs (oil sludge);
- Water-oil emulsion;
- Trapping oil;
- Drilling cuttings;
- Ambar top layer.

Such wastes are generated as a result of the following activities:

- Extraction and exploitation of oil and gas fields;
- Preparation, transportation and processing of oil;
- Cleaning of tanks at refineries and filling stations;
- Wastewater treatment with oil products, etc.

However, they differ significantly in their composition and properties, depending on the quality and composition of the raw crude oil.

For the processing of oil sludge, biotechnologies, chemical-technologies, acoustic, thermal and purely fire technologies, as well as combined technologies are used. A common disadvantage of all these technologies for utilization and processing of oil sludge is their low productivity and high material, energy and financial costs. In addition, they do not allow complete refining and degassing of oil sludge and do not provide environmental safety for the environment. The problem of processing granary oil sludge in the oil-producing and oil-refining industry has not yet been completely solved. This is due to the high stability of ambar emulsions, the features of their composition and properties, constantly changing under the influence of the atmosphere and the various processes taking place in them [14]. Among the reservoir type, one can also include trapped oil. Accumulation of trapped oil takes place in closed reservoirs - reservoirs where there is no direct contact with air, there is no influence of atmospheric precipitation, storage time is limited to months and only in exceptional cases for several years, i.e. they are not subject to such long and hard aging as ambar emulsions. In this regard, possessing many characteristic common features (high content of mechanical impurities of organic and inorganic origin, paraffins with a high melting point, high viscosity and density), potting emulsions are generally less are stable than granary ones, and the values of the indicators for the parameters listed above are an order of magnitude lower. The trapping oils are stored during storage in tanks. It is noted in [12] that when storing oil sludge in tanks after the expiration of time they are stratified into four layers:

- the top layer represents the water-in-oil emulsion, where the water content does not exceed 5-8%, 70-80% oils, 6-25% asphaltenes, 7-20% ashes, 1-4% paraffins and fine impurities up to 5 %;
- the middle layer, relatively small, is an oil-in-water emulsion and contains 70-80% water, 1.5-15% mechanical impurities;
- the last layer entirely consists of mineralized water with a density of 1.01-1.19 g / cm^3;
- the bottom layer or bottom silt represents a heterophasic system consisting of 45% organic matter, 50-88% mechanical impurities and 25% water.

Spilled oil and petroleum products in the course of physico-chemical interactions with the components of the environment form oil sludge, and with soil of oil-contaminated soil. Over time, partial evaporation, oxidation and condensation occur to form resin-like compounds.

Well-known and one of the available methods is the utilization of liquid slurries with the help of sawdust. This method is effective where sawdust is available, however, the high fire hazard of recycled products requires compliance with fire safety. In turn, the slimes stored in pits and earth sediment basins are usually "weathered" and contain more solids, and their interaction with water leads to the formation of a "water-oil" emulsion, with mechanical impurities - suspensions and mineral dispersions. Effective ways of processing oil waste and rational use of natural resources are important for ensuring sustainable development of the country. The main factors on which the economic efficiency of the utilization of oily waste depends. are: oil content in oil sludge, the degree of its extraction from oil sludge, the distance of transportation of oil waste to the place of utilization, etc. The technical and economic efficiency of processing oil sludge depends significantly on the concentration of oil in them. At low concentrations of oil in oil sludge, their processing with extraction of oil becomes unprofitable. For the processing of such oil sludge, old oil sludge in barns, as well as waste oil sludge plants that are formed after the extraction of hydrocarbons from oil sludge, it is required to build additional facilities for their utilization or landfilling. This requires additional capital investment and operating costs. In [15] it is noted that the economic efficiency (***E***) from rational use consists of prevented damage (***D***) and cost Returned to the turnover of oil minus the costs of implementing the recommended activities is determined by the formula:

$$E = D + P_{ad} - E_{exp}$$

where P_{ad} - the additional income from returned oil, E_{exp} - expenses for realization of the recommended technology. In the case of complete processing of oil-bearing soils and oil sludge, the developed technology eliminates the need to construct a landfill for disposal of waste.

The presence of waste forces enterprises to incur additional costs, which certainly worsens the economic performance of production. To solve the problem, it is necessary to solve the problem of introducing non-waste technology, that is, in this case the processing of oil sludge. However, despite the efforts of scientists, a unified way of processing oil sludge has not yet been found. Incineration of oil waste violates the ecology of the air basin, dig in, means the destruction of the flora of the environment, the method of bioremediation requires appropriate climatic conditions and the action of bacteria takes several years. Washing with ultrasound or injection into the reservoir is not economically viable. Consequently, suitable combinations of technologies, given their cost, productivity, mobility, compliance with environmental requirements and safety. Based on these factors and the criteria that determine the choice of technology for processing and utilization of oil sludge, it can be concluded that the most effective is the physicochemical method. On the other hand, oil sludge is a source of valuable raw materials - and it is necessary to use them for the designated purpose as energy resources and building materials. The determining factor in making a decision on the processing of oil sludge is the composition of the waste and its physical and chemical properties. In any case, this process allows us to return to life of the earth and prevent pollutants of organic origin from entering the environment.

Slimes should not simply be disposed of, but processed into targeted products of the economy. In Europe and Russia, such technologies are already working. We must give credit, there are such examples in Kazakhstan. Small, however, in terms of the volume of the work of the enterprise, but with quite innovative cleaning methods from time to time appeared in Mangistau oblast, WKO, Kyzylorda, the construction of a mini-plant in Pavlodar is planned.

To clean the soiled soil with the preservation of fertile soil properties, the most appropriate way is to propose a patent [16]. These authors of the invention, under the supervision of First Deputy Director General of the Institute of Chemical Sciences. named after A Bekturov, Corresponding Member of NAS of the Republic of Kazakhstan U. Zh. Dzhusipbekov developed a unique new technology for cleaning oil-contaminated soil using humate-containing compounds. Depending on the characteristics of the soiled soil, the latter can be used as a road construction material, and the extracted oil for processing in an economically expedient variant (fuel, oil, complex, etc.). At the same time, humates have a positive effect on improving soil fertility - cleaned soil. Investigations of the effect of oiled soils on cleaning and impact on soil characteristics are of scientific and practical value. Today the work of cleaning oil-contaminated areas in the basin "Ozenmunaigas" continues.

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Резюме

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МҰНАЙ ШЛАМЫН ЖӘНЕ МҰНАЙМЕН ЛАСТАНҒАН ТОПЫРАҚТЫ ӨҢДЕУ

Мақалада мұнай шламын және мұнаймен ластанған топырақты өңдеудің қазіргі заманғы әдістері қарастырылған. Тазарту процестерінің салыстырмалы экономикалық және экологиялық сипаттамалары негізінде мұнай қалдықтарын өңдеудің физика-химиялық әдістеріне артықшылық беріледі.

Түйін сөздер: мұнай шламы, майлы топырақ, өңдеу, тазалау, тазалау әдістері, мақсатты өнім.

Резюме

Б. Абайылданов

ПЕРЕРАБОТКА НЕФТЯНОГО ШЛАМА И ЗАМАЗУЧЕННОГО ГРУНТА

Рассматриваются существующие современные методы переработки нефтяного ила и загрязненной нефтью почвы. На основе сравнительных экономических и экологических характеристик процессов очистки предпочтение отдается физико-химическим методам переработки нефтяных отходов.

Ключевые слова: нефтяной шлам, замазученный грунт, обработка, очистка, способы очистки, целевой продукт.

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ANALYSIS OF CYTOTOXIC ACTIVITY AND QUANTITY OF BIOLOGICALLY ACTIVE METALS OF THE AERIAL MASS OF *TAMARIX HISPIDA*

Abstract. This article considers the quantitative content of bioactive metals, and the cytotoxic activity of the aboveground mass of the plant Tamarixhispida of the family Tamaricaceae harvested in September 2016 in the Almaty region. Determination of the number of metals was carried out by atomic absorption spectroscopy, and cytotoxic activity using the larvae of Artemiasalina shrimps in concentrations of 10, 100 and 1000 μl in aqueous medium by the LD 50 method, that is, determination of the concentration level of the substance in which more than 50 subjects do not survive organisms.

As a result, we found out that the content of biometals in the above-ground mass of Tamarixhispida does not exceed the parameters specified in the State Pharmacopoeia as permissible, and the cytotoxic activity of 50% ethanol, 70% ethanol, ethyl acetate, hexane and dichloromethane extract is practically absent, while 90 % the extract showed a relatively high level of cytotoxic activity

Key words: *Tamarixhispida, Tamaricaceae, Artemiasalina*, cytotoxic activity, alcohol extracts.

Introduction. It is known that indicators of good quality and safety are an extremely important parameter of the good quality of medicinal plant raw materials and the possibility of its use in medicine.

The medicinal raw materials contain many compounds that are potentially capable of harming the human body, such as mineral components, for example, salts of heavy metals, and various organic substances, both natural metabolites of plants, and those that have fallen into the raw materials from the environment (pesticides used in agriculture or emissions from industrial enterprises).

As an object of research, we chose the aboveground mass of the plant *Tamarixhispida* of the family *Tamaricaceae* harvested in September 2016 in the Almaty region.

The genus *Tamarix* belongs to the family *Tamaricaceae*. Types of *Tamarix* are ornamental shrubs or trees, mostly related to evergreen plants.

Tamarix can grow on highly saline soils due to the ability to regulate the salt balance by extracting excess Salt through the deciduous glands and consuming large amounts of water from underground sources.With the help of a developed root system, which facilitates the accumulation of a large number of mineral components in the overground mass of the plant [1-3].

In folk medicine, decoctions of the aerial part are used for rheumatism, gastrointestinal diseases, treatment of inflammation of the oral cavity. In the review of Sharma there is information about the use of representatives of the family *Tamarix* as an antioxidant for cosmetic purposes [4, 5].

To determine the content of heavy metals, we selected the method of atomic emission spectroscopy [6, 7], the cytotoxic activity was determined using larvae of Artemiasalina. Eggs of *Artemiasalina* are easily accessible, as a food for fishes in pet shops. When placed in artificially obtained sea water, eggs are opened within 48 hours, which provides a large number of larvae. This is a fast, inexpensive, general Biological Analysis that was developed for screening, fractionation and monitoring of physiologically active natural products.

Methods

Determination of heavy metals. The initial medicinal plant material was analyzed for the presence of heavy metals by atomic absorption spectroscopy using the following procedure

About 3-5 g of crushed medicinal plant raw materials (exact weighed portion) are placed in a pre-calcined and precisely weighed porcelain crucible.

The crucible is then gently heated, giving the substance first to burn or to evaporate at the lowest possible temperature. With incomplete combustion of coal particles, the residue is cooled, wetted with water or a saturated solution of ammonium nitrate, evaporated in a water bath and the residue is calcined. If necessary, repeat this operation several times.

Calcination leads to about 500 ° C to constant mass, avoiding the fusion of ash, and sintering with the walls of the crucible. At the end of the calcination, the crucible is cooled in a desiccator and then, the resulting ash is burned again at 600 ° C until a uniform gray color is obtained.

Finally, the precipitate is dissolved in 5 ml of HNO_3. The resulting solution must be heated on the tile to wet salts. The result is dissolved in 10-15 ml of 1H HNO_3 and transferred to a 25 ml volumetric flask, bring the volume to the mark. In parallel, prepare a blank sample with 1N HNO_3 solution

The analysis was carried out on the Atomic Absorption Spectrophotometer Shimadzu 6200

With a wavelength range of 190-900 nm with a measurement step of 0.2 nm

The results of determination of the concentration of heavy metals are given in the table1

Determination of cytotoxic activity. Test specimen, *Artemiasalina*, sea salt (38 g / l D / W, pH 7.4), Honed tray with a perforated septum, lamps for attracting larvae in brine, micro pipettes (10, 100, 1000 μl) , a tray for bottles, 9 bottles with samples of organic solvents (methanol / ethanol / acetone / water), distilled water.

Getting the larvae. Tray for the reproduction of larvae (rectangular dish (22x32 cm)) is half filled with filtered saline solution then *Artemiasalina* (50 mg) eggs are introduced. Incubate at 37° C for 48 hours.

Sample preparation. Dissolve the test sample (20 mg) in 2 ml of the appropriate solvent at concentrations of 10, 100 and 1000 μg / ml, respectively, and leave under the traction for 24 hours to remove the solvent. After 2 days from hatching and maturation, how to select 10 larvae, using a Pasteur pipette. Then place in 5 ml with seawater. Incubate the selected group at 25-27 ° C for 24 hours, under constant illumination. Add samples to the medium with the test substance.

Parallel to the same procedure, prepare positive and negative samples.

Data analysis is performed using the Finney computer program to determine LD 50 values with 95% confidence intervals.

The results of the determination of cytotoxic activity are shown in table 2.

Results and discussion

As a result of studying the aboveground mass of *Tamarixhispida* family *Tamaricaceae*, we determined that the lead content is 1.11 mg/kg that does not exceed the maximum permissible standards in accordance with the requirements of the State Pharmacopoeia [8].

The content of other metals is also within safe limits.

Table 1 – The content of heavy metals medicinal plant raw materials
(aboveground mass *Tamarixhispida* Wild.)

Metal	Cu	Fe	Ni	Pb	Mn	Zn	Cd
Number of metals in mg/kg	0.62	40.36	0.51	1.11	3.13	2.26	0.01

For the most complete determination of cytotoxic activity in order to further develop several technologies for obtaining the substance based on the aboveground masses of *Tamarixhispida*, we prepared several extracts, namely, ethanol extracts with an ethyl alcohol concentration of 70, 50 and 90 percent, dichloromethane, hexane and ethyl acetate extracts [9].

As a result of the comparison of this cytotoxic activity, we see that in all the samples, in addition to 90% of the ethanol extract, mortality does not exceed 20% of the total number of organisms. Which allows us to speak about a sufficiently low level of toxicity and as a result of safety of preparations based on *tamarix* overground weight, 90 % alcohol extract the concentration at which more than 50% of the test organisms die is more than 400 μl. Which, given the sensitivity of *Artemiasalina* larvae to toxic compounds, is not an absolute proof the danger of 90% of the extract for humans and requires additional research.

Conclusion. As a result, we found out that the above-ground mass of the *Tamarixhispida* family of *Tamaricaceae* and preparations based on it are sufficiently safe for humans.The content of metals such as cadmium, lead, manganese, nickel, iron, copper and zinc is in acceptable concentrations and meets the requirements State Pharmacopoeia, the cytotoxic activity of both polar (various alcohol extracts) and nonpolar fractions is relatively low and does not prevent the

Table 2 – Cytotoxic activity of various extracts obtained
from the aerial mass of *Tamarixhispida* Wild.

Dose	Number of organisms (initial)	Number of surviving organisms	LD 50	Standard drug	LD 50
70% ethanol					
10	30	30	–	Etoposite	7.4625
100	30	30			
1000	30	29			
50% ethanol					
10	30	29	–	Etoposite	7.4625
100	30	29			
1000	30	26			
90% ethanol					
10	30	28	489.6056	Etoposite	1.4625
100	30	27			
1000	30	0,9			
Dichloromethane					
10	30	21	–	Etoposite	1.4625
100	30	26			
1000	30	26			
Hexane					
10	30	29	–	Etoposite	1.4625
100	30	29			
1000	30	28			
Ethylacetate					
10	30	30	–	Etoposite	1.4625
100	30	29			
1000	30	29			

use of *tamarix* preparations in medicine, even at high concentrations. The analysis of the cytotoxic activity of various extracts of *Tamarixhispida*was performed for the first time.

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Резюме

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АНАЛИЗ ЦИТОТОКСИЧЕСКОЙ АКТИВНОСТИ И КОЛИЧЕСТВА БИОЛОГИЧЕСКИ АКТИВНЫХ МЕТАЛЛОВ НАДЗЕМНОЙ МАССЫ *TAMARIXHISPIDA*

Рассмотрено количественное содержание биоактивных металлов и цитотоксическая активность надземной массы растения Tamarixhispida семейства Tamaricaceae, заготовленного в сентябре 2016 г. в Алматинской области. Определение количества металлов проводилось методом атомно-абсорбционной спектроскопии, а цитотоксической активности с применение личинок рачков вида Artemiasalina в концентрациях 10, 100 и 1000 мкл в водной среде по методу LD 50, то есть определения уровня концентрации вещества, при котором не выживает более 50 испытуемых организмов.

В результате выяснено, что содержание биометаллов в надземной массе Tamarixhispida не превышает параметры, указанные в Государственной Фармакопее, как допустимые, а цитотоксическая активность 50% этанольного, 70% этанольного, этилацетатного, гексанового и дихлорметанового экстракта практически отсутствует, в то время как 90% экстракт проявил сравнительно высокий уровень цитотоксической активности

Ключевые слова: *Tamarixhispida, Tamaricaceae, Artemiasalina,* цитотоксическая активность, спиртовые экстракты.

Резюме

Д. Саматкызы, Е. С. Ихсанов, Н. А. Султанова, Ж. А. Абилов, М. И. Чоудхари

БЕЛСЕНДІ МЕТАЛЛ ЖЕР ҮСТІ МАССАСЫНЫҢ ЦИТОТОКСИКАЛЫҚ БЕЛСЕНДІЛІГІН ЖӘНЕ СОМАСЫН ТАЛДАУ

Мақалада қарастырамыз: сандық мазмұны бар биоактивті металдар және активті цитотоксикалық жер үсті массасының өсімдігі Tamarix hispida тұқымдасы Tamaricaceae; 2016 қыркүйек айында Алматы облысында дайындалған. Металдардың санын атомдық – адсорбциялық спекртоскопия әдісі арқылы жүргізілді, цитотоксикалық белсенділік Artemia salina құрттарын пайдаланып, олардың концертициялары 10,100 және 1000 мкл сулы ортада LD50 әдісімен жүргізу, яғни заттың концентрациясын анықтау,онда 50-ден астам организмдер өмір сүрмейді.

Нәтижесінде; биометалдар құрамын, жер үсті массасында Tamarix hispida, мемлекеттік Фармакопия ұсынған параметрлерден аспайды, ол цитотксикалық белсенділік 50%-дық этанолдық, 70 %-дық этанолдық, этилацетаттың, гексанның және дихлорметанның экстракты іс-жүзінде жоқ, сол уакытта 90% экстракт салыстырмалы жоғары деңгейде цитотоксикалық белседілігін көрсетті.

Түйін сөздер: *Tamarix hispida, Tamaricaceae, Artemia salina,* цитотоксикалық белсенділігін, этанолдық экстракт.

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RELEASE OF ANESTHETIC DRUGS FROM POLYMERIC FILMS

Abstract. The release of anesthetic drug from polymeric medicinal films with the prolonged therapeutic action is studied. Local anesthetic lidocaine is used as anesthetics agent. The films are obtained by watering of polyvinyl alcohol solution of different concentration on the horizontal glass surface with their subsequent drying during 2-3 days. Kinetics of drug release from films in model biological environments is investigated. Lidocain, evenly dissolved in polymeric matrix, is released by the mechanism of diffusion with rate reduction. The clinical tests of polymeric anesthetic films are conducted at treatment of periodontal pathology.

Keywords: release, polymeric films, polyvinyl alcohol, lidocaine, periodont treatment.

Medical films have found wide application in the clinic of ophthalmology, dentistry, cardiology and the treatment of wounds and burns [1, 2]. Film therapeutic system is obtained by dissolving polymer carrier and drug substance in common solvent, the resulting solution was poured onto substrate, heated and molded film by evaporation of solvent. The obtained film was cut into samples of the required size. The simplicity of this technological scheme is obviously, another advantage consists in the possibility of using a broad range of drugs. As materials for manufacture of film dosage forms use variety of synthetic and natural polymers. To control the rate of release of drugs from medicinal films used either their limited permeability through polymer membrane (membrane systems), or slow diffusion of the drug dissolved in polymer matrix (solid system).

Dosage forms, traditionally used in therapeutic dentistry, have several disadvantages, the main of which can be attributed the short period of therapeutic action, the inability to ensure the sustainability concentration of drug in oral cavity, discomfort and duration of treatment. A promising direction is development new drug forms, capable of continuously release the drug in the local area, to have high adhesion to wet and hard tissues, to ensure dosing accuracy and constancy of concentration of drug for long time. Successful therapy of inflammatory periodontal diseases is only possible while maintaining constant concentration of drug long time within the ideal "therapeutic corridor" between the lower borders of toxic and effective concentrations [3-6].

An example of adhesive mucosal dosage form is medicinal films obtained on the basis of biocompatible polymers. Medical films containing various pharmacological drugs are already used in dental practice. Prolonged effect in such films is achieved by immobilization of local anesthetics on various polymeric carriers. Application of essentially new medicinal forms on the basis of polymeric films opens new era in pain therapy.

In this work release of local anesthetic lidocaine from polymeric films in model biological environments is studied. The application of polymeric medicinal films with the prolonged therapeutic action for treatment of periodontal diseases is briefly described.

Experimental part

Local anesthetic lidocaine was used pharmaceutical grade purity. Polyvinyl alcohol (PVA) with MM 70 000 company "Aldrich" (USA) was used without further purification.

Polymer films were obtained from the corresponding solution of polymer and drug substance by evaporation of the solvent (water). Amount of 10,0 % PVA in distilled water kept on magnetic stirrer at 80°-90°C until complete dissolution. After obtaining homogeneous solution it cooled to room temperature and was added a calculated amount of substance of lidocaine. After mixing the resulting solution was poured onto a glass substrate and dried in the box, installed horizontally level, at room temperature to constant weight. Received dosage form had the appearance of thin elastic transparent film, which with the help of die cut standard discs with a diameter of 0.45-0.5 cm or squares with thickness of 0.2-0.5 mm. The calculation of dose of drug was carried out at the minimum dose.

The release of drug from polymer samples was studied under conditions *in vitro* at 37°C with help of the UV-spectroscopy. Spectra were recorded in quartz cuvette with thickness of 1 cm at spectrophotometer "Specord UV-VIS” (Japan).

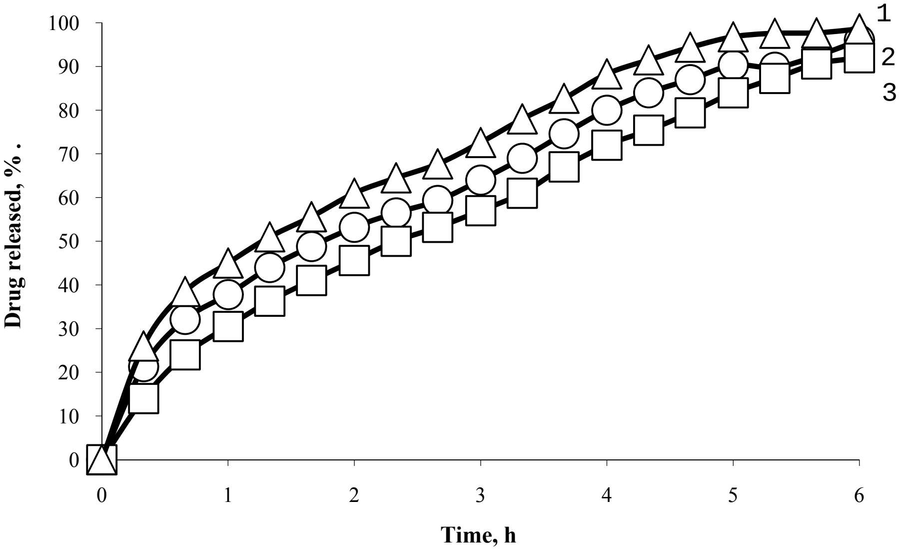
Results and discussion

Polyvinyl alcohol represents considerable interest as drug carrier in developing the anesthetizing films. This polymer has been widely used in medicine as plasma substitutes, stabilizer for suspensions, film-forming agent for capsules and tablets, component of ointment [7].

The medical films on the basis of PVA containing different doses of anesthetic drug lidocaine are developed. The effect of various physical-chemical factors on the process of drug release in model biological environment is studied. Dependence of lidocaine release at various drug loading is presented in figure.

Lidocaine is uniformly dispersed in polymer matrix and released in model environment on the mechanism of diffusion with rate reduction. The process of diffusion is described by Fick law and follows first order kinetics, i.e. the amount of drug released per unit time is proportional to its concentration in polymer. It is shown that drug diffused from polymer at 85-90% for 5-6 hours.

With the increase of film thickness, the diffusion of drugs slows down. So if the system is 1.0 mm thick the 50% of drug released per 1,0-1,5 h, at a film thickness of 2.5 mm the same amount of anesthetic diffuses for 4.0-4.5 h. It is found that with increase of drug loading from 100 to 300 mg per 1 g of polymer diffusion coefficients is reduced.



Release of lidocaine from PVA-films at various drug loading:
25 mg/1 g of PVA (1), 50 mg /1g of PVA (2), 100 mg /1 g of PVA (3)

Release parameters of lidocaine from PVA-films

Loading, мg/g	Time of 50% release, h	Time of max release, h	$D \cdot 10^{-7}$, cm^2/s
25	1,5	5,0	2,9
50	2,0	5,5	2,6
100	2,5	6,0	2,2

Clinical observations on patients with periodontal disease inflammatory and inflammatory-destructive nature showed significant advantages of using polymer film forms of lidocaine. Clinical efficacy was confirmed in statistically significant reduction of terms of treatment of patients with generalized periodontal disease, improvements of the test of Kulagina, gingival index of Loe, hygienic condition of the mouth, a higher percentage of remission of the disease in the early and late periods.

The main advantage of film is long and effective therapeutic effects of small drug doses in the area of pathology. The regulation process is carried out by slow diffusion of oral fluid in polymer, followed by swelling, biodegradation and slow release of the drug from swelling polymer. The sustained drug release from films provides prolonged therapeutic effect. Using variety of techniques, it is possible in a wide range to change the physical-chemical properties of the matrix and respectively the kinetics of release of drug substance. The one of advantages of new dosage form of lidocaine should also be attributed to the lack of irritating action on the mucous membrane of the mouth, absence of allergic reactions and change the function of salivary glands, whereas the imposition of hardening of the gingival dressing is always associated with salivation, unpleasant taste of the dressing and aesthetic discomfort.

The analysis of direct, immediate and remote results of treatment and long-term observation of patients who have taken courses of treatment using medicinal films, expanded range of therapeutic and preventive measures, give experimental and clinical substantiation of their use in dental practice.

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Резюме

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ПОЛИМЕРЛІК ҚАБЫРШАҚТАН АНЕСТЕТИКТЕРДІ БОСАТУ

Емдік әсері ұзақ полимерлік қабыршақтан анестетиктерді босату зерттелді. Ауруды сездірмейтін дәрі ретінде лидокаин қолданылады. Қабыршақ үлгілері әртүрлі концентрациядағы поливинил спирт ерітіндісінің көлденең шыны бетке құйып, оны ары қарай 2-3 күн шамасында кептіру арқылы алынады. Анестетиктің қабыршақтан модельді биологиялық ортаға босату кинетикасы анықталды. Полимерлі қалыпта бірыңғай еріген дәрілік зат жылдамдықтың төмендеуімен диффузия механизмі бойынша модельді ортаға шығады. Қабынған түрдегі пародонт ауруын емдеуге арналған полимерлі ауруды сездірмейтін қабыршақтар клиникалық бақылаудан өткізілді.

Түйін сөздер: босату, полимерлі қабыршақтар, поливинил спирті, лидокаин, парадонт емдеу.

Резюме

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ВЫСВОБОЖДЕНИЕ АНЕСТЕТИКОВ ИЗ ПОЛИМЕРНЫХ ПЛЕНОК

Изучено высвобождение анестетиков из полимерных пленок с пролонгированным лечебным действием. В качестве обезболивающего агента использован местный анестетик – лидокаин. Образцы пленок получали поливом раствора поливинилового спирта различной концентрации на горизонтальную стеклянную поверхность с последующим их высушиванием в течение 2-3 сут. Исследована кинетика высвобождения местного анестетика из пленок в модельные биологические среды. Установлено, что лекарственные вещества, равномерно растворенные в полимерной матрице, высвобождаются в модельные среды по механизму диффузии с уменьшением скорости. Проведены клинические испытания полимерных обезболивающих пленок при лечении патологии пародонта.

Ключевые слова: высвобождение, полимерные пленки, поливиниловый спирт, лидокаин, лечение пародонта.

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SELECTIVITY OF INTERGEL SYSTEM BASED ON HYDROGELS OF POLYMETHACRYLIC ACID AND POLY-4-VINYLPYRIDINE TO LANTHANUM AND CERIUM IONS

Abstract. Process of lanthanum and cerium ions sorption by intergel system hydrogel of polymethacrylic acid (hPMAA) – hydrogel of poly-4-vinylpyridine (hP4VP) is studied. Found that intergel system hPMAA-hP4VP has selectivity to lanthanum and cerium ions. PMAA hydrogel doesn't have high values of extraction degree in relation to lanthanum and cerium ions (66.28% and 60.33% respectively). P4VP hydrogel also has low values of La^{3+} and Ce^{3+} ions sorption degree (66.05% and 56.67% respectively). In intergel system hPMAA-hP4VP selectivity can be controlled by changing hydrogels ratio. Maximum extraction degree of lanthanum ions is observed at 17%hPMAA:83%hP4VP ratio, sorption degree is 90.34%. Maximum sorption degree of cerium ions is observed at 50%hPMAA:50%hP4VP ratio, extraction degree is 89.33%. Individual PMAA and P4VP hydrogels also do not have high polymer chain binding degree. Polymer chain binding degree (in relation to lanthanum ions) of hPMAA and hP4VP is 55.17% and 55.00% respectively. Binding degree (in relation to cerium ions) of hPMAA and hP4VP is 50.05% and 47.00%. Maximum values of polymer chain binding degree (in relation to lanthanum ions) in intergel system hPMAA-hP4VP are observed at 17%hPMAA:83%hP4VP ratio, binding degree is 75.33%. Maximum values of binding degree (in relation to cerium ions) are observed at 50%hPMAA:50hP4VP ratio, binding degree is 74.10%. At 17%hPMAA:83%hP4VP and 50%hPMAA:50hP4VP ratios effective dynamic exchange capacity (in relation to lanthanum and cerium ions) is higher almost on 30% comparatively with individual PMAA and P4VP hydrogels. Mutual activation of PMAA and P4VP hydrogels provides transition into highly ionized state and, as a result, significant increase of sorption properties in intergel pairs.

Keywords: intergel system, sorption, selectivity, La^{3+} ions, Ce^{3+} ions, polymethacrylic acid, poly-4-vinylpyridine.

Effect of mutual activation of polymer structures of different nature on electrochemical and volume-gravimetric properties is described in previous works [1-6]. It is found that remote interaction of hydrogels provides transition of initial polymers into highly ionized state and, as a result, significant changes in electrochemical and conformational properties. After that, it was found that mutual activation provides significant increase of sorption properties of initial hydrogels [7-11]. Levels of ionization in intergel systems are in dependence from hydrogels ratios. Consequently, changing hydrogels ratio in certain intergel system will provide opportunity to re-orientate intergel system to maximum sorption of another ion. In this regard, goal of this work is to study impact of hydrogels ratio on selectivity of intergel system hPMAA-hP4VP.

Experiment

Equipment. For measurement of optical density of solutions for further calculation of La^{3+} and Ce^{3+} ions concentration spectrophotometer Jenway-6305 was used.

Materials. Investigations was carried out in solutions of lanthanum and cerium nitrate solutions. Hydrogels of polymethacrylic acid were synthesized in presence of cross-linking agent N,N-methylene-bis-acrylamide and red-ox system $K_2S_2O_8$–$Na_2S_2O_3$. Hydrogel of poly-4-vinylpyridine (hP4VP) (2% of cross-linking agent) was synthesized by «Sigma Aldrich» company. Synthesized hydrogels in an aqueous medium were put to create intergel system polymethacrylic acid hydrogel – poly-4-vinylpyridine hydrogel (hPMAA-hP4VP). Swelling degrees of hydrogels are: $\alpha_{(hPMAA)}=20.65$ g/g; $\alpha_{(hP4VP)}=2.65$ g/g.

Experiment. Experiments were carried out at room temperature. Study of the intergel system was made as follows: calculated amount of each hydrogel in dry state was put in special glass filters, pores of which permeable for low-molecular ions and molecules, but non-permeable for hydrogels dispersion. Then the filters were put in glass in which salt solution presents. After that, aliquots were taken.

Methodology of lanthanum ions determination in solution is based on formation of colored complex compound of organic analytic reagent arsenazo III with La^{3+} ions [12].

Extraction (sorption) degree was calculated by equation:

$$\eta = \frac{C_{\text{initial}} - C_{\text{residual}}}{C_{\text{initial}}} * 100\%$$

where $C_{initial}$ – initial concentration of lanthanum in solution, g/L; $C_{residue}$ – residual concentration of lanthanum in solution, g/L.

Polymer chain binding degree was determined by calculations in accordance with equation:

$$\theta = \frac{\nu_{\text{sorbed}}}{\nu} * 100\%$$

where ν_{sorbed} – quantity of polymer links with sorbed lanthanum, mol; ν – total quantity of polymer links (if there are 2 hydrogels in solution, it is calculated as sum of each polymer hydrogel links), mol.

Effective dynamic exchange capacity was calculated by formula:

$$Q = \frac{\nu_{\text{sorbed}}}{m_{\text{sorbent}}}$$

where ν_{sorbed} – amount of sorbed metal, mol; $m_{sorbent}$ – sorbent mass (if there are 2 hydrogels in solution, it is calculated as sum of their masses), g.

Results and discussion

Lanthanum ions sorption. Dependence of lanthanum ions extraction degree of the intergel system hPMAA-hP4VP from hydrogels ratios is shown on figure 1. Obtained results point to the fact that mutual activation provides significant increase of sorption properties of the polymer hydrogels in the intergel system. Initial hydrogels of polymethacrylic acid and poly-4-vinylpyridine do not have high extraction degree of lanthanum ions. Extraction degree is 66.28% for polymethacrylic acid hydrogel and 66.05% for poly-4-vinylpyridine hydrogel.

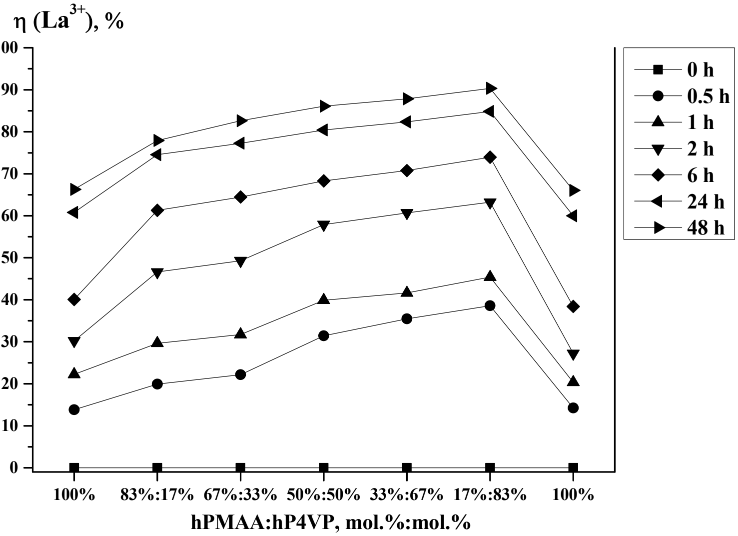

Figure 1 – Dependence of lanthanum ions extraction degree of intergel system hPMAA-hP4VP from hydrogels ratios

As seen from figure 1, maximum sorption of lanthanum ions occurs at 17%hPMAA:83%hP4VP ratio. Extraction degree of lanthanum ions at this ratio in the intergel system hPMAA-hP4VP is 90.34%. Main reason of such high sorption degree is high ionization of polymer structures due to their mutual activation.

Figure 2 shows dependence of polymer chain binding degree from time. Intergel pairs have higher values of binding degree comparatively with individual hydrogels. Polymer chain binding degree of individual hydrogels of polymethacrylic acid and poly-4-vinylpyridine is 55.17% and 55.00% respectively. Not very intensive sorption occurs at 83%hPMAA:17%hP4VP and 67%hPMAA:33%hP4VP ratios. Such binding degree indicates to not sufficient ionization degree of polymer structures at remote interaction in mentioned above intergel pairs. Maximum values of binding degree are observed at 17%hPMAA:83%hP4VP. As seen from the figure, at this ratio binding of lanthanum by the polymers is significantly higher, polymer chain binding degree is 75.33%.

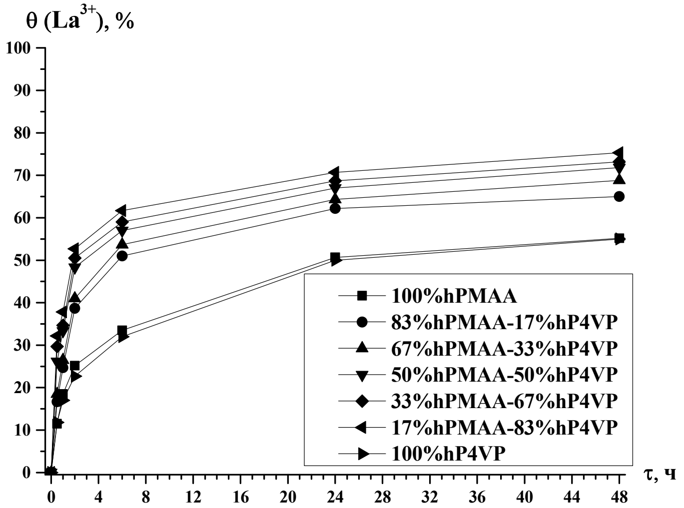

Figure 2 – Dependence of polymer chain binding degree of intergel system hPMAA-hP4VP from hydrogels ratios

Dependence of effective dynamic exchange capacity of the intergel system based on hydrogels of PMAA and P4VP from hydrogels molar ratios is shown on figure 3. Remote interaction of hPMAA and hP4VP provides significant increase of exchange capacity of polymer structures. The highest values of exchange capacity are observed at 33%hPMAA:67%hP4VP and 17%hPMAA:83hP4VP

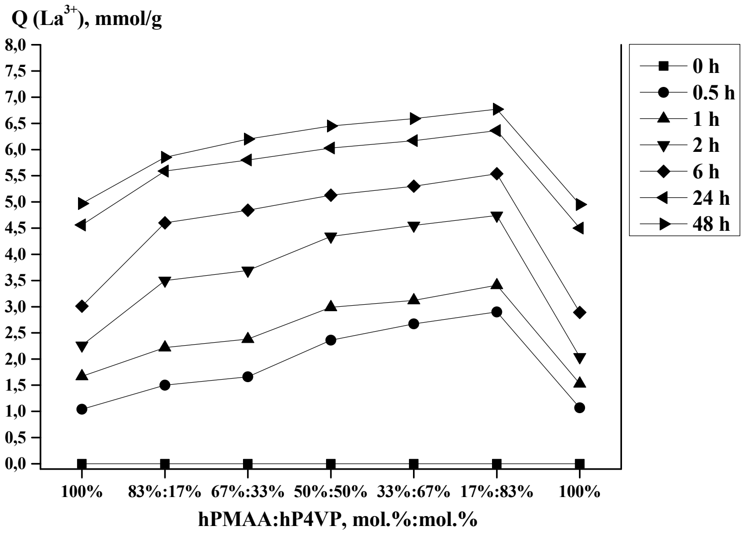

Figure 3 – Dependence of effective dynamic exchange capacity of intergel system hPMAA-hP4VP from hydrogels ratios

ratios. Maximum values of exchange capacity is reached at 48 hours at 17%hPMAA:83hP4VP ratio, at this ratio exchange capacity is on 30% higher in comparison with individual hydrogels. Minimum values of capacity are seen in presence of polyacid or polybasis, wherein values of exchange capacity are almost the same.

Cerium ions sorption. As seen from figure 4, extraction degree of cerium ions of the intergel system hydrogel of polymethacrylic acid – hydrogel of poly-4-vinylpyridine increases with time. Values of sorption degree are higher in intergel pairs than in case with individual hydrogels. Cerium ions extraction degree reaches maximum values at 48 hours of remote interaction of hydrogels at 50%hPMAA:50%hP4VP ratio. Maximum values point to high ionization degree of polymer structures at their mutual activation. Extraction degree of cerium ions at this ratio is 89.33%. Individual hydrogels of polymethacrylic acid and poly-4-vinylpyridine have low values of extraction degree of cerium ions. Extraction degree of cerium ions by PMAA hydrogel is 60.33%, by P4VP hydrogel – 56.67%.

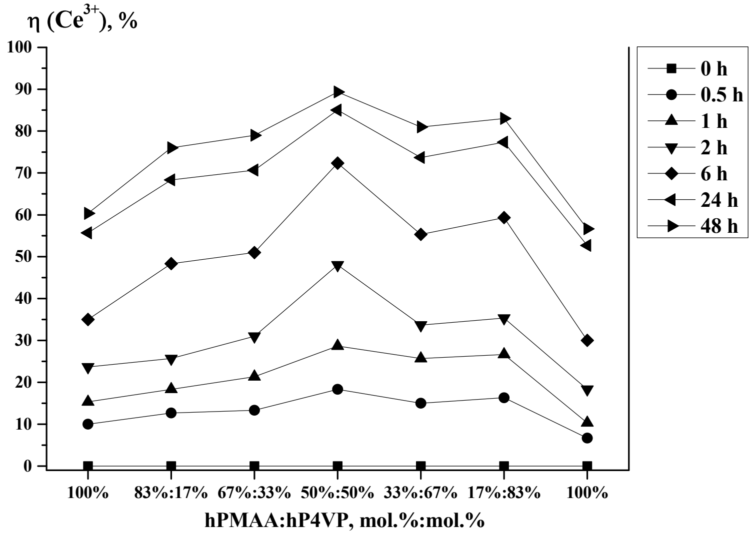

Figure 4 – Dependence of cerium ions extraction degree of intergel system hPMAA-hP4VP from hydrogels ratios

Figure 5 represents dependencies of polymer chain binding degree (in relation to cerium ions) of the intergel system hPMAA-hP4VP from time. The highest values of binding degree are observed at 50%hPMAA:50%hP4VP ratio, binding degree is 74.10%. Other intergel pairs also have high polymer chain binding degree values comparatively with individual hydrogels of polymethacrylic acid and poly-4-vinylpyridine. Initial hydrogels of PMAA and P4VP have the following values of polymer chain binding degree: 50.05% for hPMAA and 47.00% for hP4VP. Such significant difference of polymer chain binding degree values of

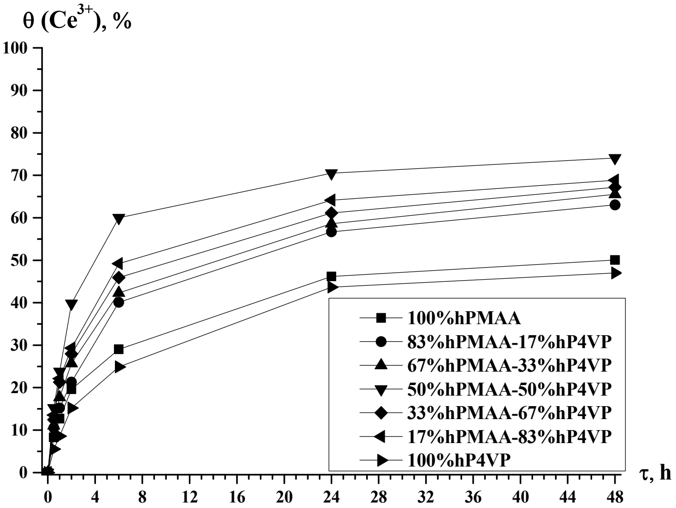

Figure 5 – Dependence of polymer chain binding degree of intergel system hPMAA-hP4VP from hydrogels ratios

intergel pairs and individual hydrogels is due to highly ionized state of hydrogels in intergel pairs due to their mutual activation at remote interaction in intergel system.

Figure 6 shows dependence of effective dynamic exchange capacity of the intergel system hPMAA-hP4VP from hydrogel ratios in time. Increase of exchange capacity occurs with time.

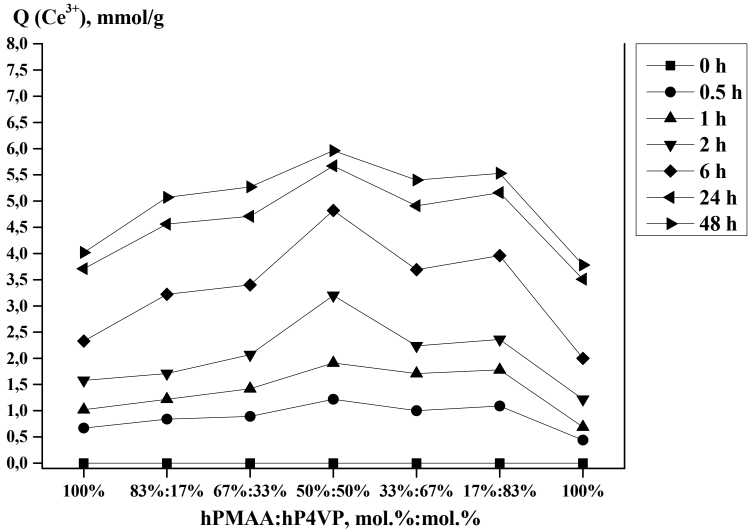

Figure 6 – Dependence of effective dynamic exchange capacity of intergel system hPMAA-hP4VP from hydrogels ratios

As seen from the figure, result of remote interaction of polymethacrylic acid and poly-4-vinylpyridine hydrogels is significant increase of effective dynamic exchange capacity of polymer hydrogels of PMAA and P4VP. Area of maximum values of effective dynamic exchange capacity is 50%hPMAA:50hP4VP ratio. At this ratio exchange capacity is over on 30% higher comparatively with individual PMAA and P4VP hydrogels.

Conclusion.

1. Intergel system based on rare-crosslinked polymer hydrogels of polymethacrylic acid and poly-4-vinylpyridine has selectivity to lanthanum and cerium ions.
2. Mutual activation of PMAA and P4VP hydrogels provides transition into highly ionized state and, as a result, significant increase of sorption properties in intergel pairs.
3. Polymethacrylic acid hydrogel doesn’t have high values of extraction degree in relation to lanthanum and cerium ions (66.28% and 60.33% respectively). Poly-4-vinylpyridine hydrogel also has low values of sorption degree (66.05% and 56.67% respectively).
4. In intergel system hPMAA-hP4VP selectivity can be controlled by changing hydrogels ratio. Maximum extraction degree of lanthanum ions is observed at 17%hPMAA:83%hP4VP ratio, sorption degree is 90.34%. Maximum sorption degree of cerium ions is observed at 50%hPMAA:50%hP4VP ratio, extraction degree is 89.33%.
5. Individual PMAA and P4VP hydrogels also do not have high polymer chain binding degree. Polymer chain binding degree (in relation to lanthanum ions) of hPMAA and hP4VP is 55.17% and 55.00% respectively. Binding degree (in relation to cerium ions) of hPMAA and hP4VP is 50.05% and 47.00%.
6. Maximum values of polymer chain binding degree (in relation to lanthanum ions) in intergel system hPMAA-hP4VP are observed at 17%hPMAA:83%hP4VP ratio, binding degree is 75.33%. Maximum values of binding degree (in relation to cerium ions) are observed at 50%hPMAA:50hP4VP ratio, binding degree is 74.10%.
7. Transition into highly ionized state of PMAA and P4VP hydrogels due to mutual activation also provides significant increase of effective dynamic exchange capacity. At 17%hPMAA:83%hP4VP and 50%hPMAA:50hP4VP ratios exchange capacity (in relation to lanthanum and cerium ions) is higher almost on 30% comparatively with individual PMAA and P4VP hydrogels.

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Резюме

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ПОЛИМЕТАКРИЛ ҚЫШҚЫЛЫ ЖӘНЕ ПОЛИ-4-ВИНИЛПИРИДИН ГИДРОГЕЛДЕРІ НЕГІЗІНДЕГІ ИНТЕРГЕЛДІ ЖҮЙЕЛЕРДІҢ ЛАНТАН ЖӘНЕ ЦЕРИЙ ИОНДАРЫНА СҰРЫПТЫЛЫҒЫ

Полиметакрил қышқылы гидрогелімен (ПМАҚг) поли-4-винилпиридин (П4ВПг) гидрогелі негізінде алынған интергелді жүйемен лантан және церий иондарын сіңіру процесі зерттелді. ПМАҚг-П4ВП интергелді жүйесінің лантан мен церий иондарына сұрыптылық қасиет көрсететіні анықталды. ПМАҚ гидрогелінің лантан және церий иондарын шығару дәрежесі аса жоғары емес (сәйкесінше 66,28% және 60,33%). П4ВП гидрогелінінде La^{3+} және Ce^{3+} иондарын шығару дәрежесі төмен. (сәйкесінше 66,05% және 56,67%). Интергелді жүйеде гидрогелдердің қатынастарын өзгерту арқылы сұрыптылықты басқаруға болады. 17%ПМАҚг:83%П4ВПг қатынасында лантан иондарын шығару дәрежесі жоғары екені байқалады, сіңіру дәрежесі 90,34%-ке тең. 50%ПМАҚг:50%П4ВПг қатынасында церий иондарын шығару дәрежесі жоғары екені байқалады, сіңіру дәрежесі 89,33%-ке тең. Сонымен қатар ПМАҚ және П4ВП жекелеген гидрогелдерінде полимерлік тізбектерінің байланысу дәрежесі төмен болып келеді. ПМАҚг және П4ВПг полимерлік тізбектерінің байланысу дәрежесі (лантан иондарына қатысты) сәйкесінше 55,17% және 55,00%-ті, ал (церий иондарына қатысты) сәйкесінше 50,05% және 47,00%-ті құрайды. ПМАҚг-П4ВП интергелді жүйесінің 17%ПМАҚг:83%П4ВПг қатынасында полимерлік тізбектерінің байланысу дәрежесі (лантан иондарына қатысты) жоғары, байланысу дәрежесі 75,33%-ке тең. Ал 50%ПМАҚг:50%П4ВПг қатынасында (церий иондарына қатысты) байланысу дәрежесі жоғары, яғни 74,10%-ке тең. ПМАҚ мен П4ВП жекелеген гидрогелдерімен салыстырғанда 17%ПМАҚг:83%П4ВПг және 50%ПМАҚг:50%П4ВПг қатынастарында (лантан және церий иондарына қатысты) тиімді динамикалық алмасу сыйымдылығы шамамен 30%-ға жоғары. ПМАҚ мен П4ВП гидрогелдерінің өзара активтілігі олардың жоғары иондалған күйге көшуіне алып келеді, нәтижесінде интергелді жұптарда сіңіру қасиеттерінің анағұрлым өсуіне әсер етеді.

Түйін сөздер: интергелді жүйе, сіңіру, сұрыптылық, La^{3+} иондары, Ce^{3+} иондары, полиметакрил қышқылы, поли-4-винилпиридин.

Резюме

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СЕЛЕКТИВНОСТЬ ИНТЕРГЕЛЕВОЙ СИСТЕМЫ НА ОСНОВЕ ГИДРОГЕЛЕЙ ПОЛИМЕТАКРИЛОВОЙ КИСЛОТЫ И ПОЛИ-4-ВИНИЛПИРИДИНА К ИОНАМ ЛАНТАНА И ЦЕРИЯ

Исследован процесс сорбции ионов лантана и церия интергелевой системой гидрогель полиметакриловой кислоты (гПМАК) – гидрогель поли-4-винилпиридина (гП4ВП). Установлено, что интергелевая система гПМАК-гП4ВП проявляет селективность к ионам лантана и церия. Гидрогель ПМАК не обладает высокой степенью извлечения ионов лантана и церия (66,28 и 60,33% соответственно). Гидрогель П4ВП также имеет невысокие значения степени извлечения ионов La^{3+} и Ce^{3+} (66,05 и 56,67% соответственно). В интергелевой системе возможно управлять селективностью путем изменения соотношений гидрогелей. Максимальная степень извлечения ионов лантана наблюдается при соотношении 17%гПМАК:83%гП4ВП, степень сорбции равна 90,34%. Максимальная степень сорбции ионов церия наблюдается при соотношении 50%гПМАК:50%гП4ВП, степень извлечения равна 89,33%. Также индивидуальные гидрогели ПМАК и П4ВП не обладают высокими значениями степени связывания полимерной цепи. Степень связывания полимерной цепи (по отношению к ионам лантана) гПМАК и гП4ВП составляет 55,17 и 55,00% соответственно. Степень связывания (по отношению к ионам церия) гПМАК и гП4ВП равна 50,05 и 47,00%. Максимальные значения степени связывания полимерной цепи (по отношению к ионам лантана) в интергелевой системе гПМАК-гП4ВП наблюдаются при соотношении 17%гПМАК:83%гП4ВП, степень связывания равна 75,33%. Наибольшие значения степени связывания (по отношению к ионам церия) наблюдаются при соотношении 50%гПМАК:50%гП4ВП, степень связывания равна 74,10%. При соотношениях 17%гПМАК:83%гП4ВП и 50%гПМАК:50%гП4ВП эффективная динамическая обменная емкость (по отношению к ионам лантана и церия) практически на 30% выше по сравнению с индивидуальными гидрогелями ПМАК и П4ВП. Взаимная активация гидрогелей ПМАК и П4ВП приводит к переходу в высокоионизованное состояние и, как результат, к значительному росту сорбционных свойств в интергелевых парах.

Ключевые слова: интергелевая система, сорбция, селективность, ионы La^{3+}, ионы Ce^{3+}, полиметакриловая кислота, поли-4-винилпиридин.

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CONSTANTS AND PARAMETERS OF RADICAL COPOLYMERIZATION OF POLY(ETHYLENE GLYCOL FUMARATE) WITH ACRYLIC ACID

Abstract. In the present work, the binary radical copolymerization of poly(ethylene glycol fumarate) with acrylic acid in a dioxane medium was investigated for the first time at various mole ratios of the initial monomer mixture. The kinetics of the copolymerization reaction was studied. Kinetic curves show that with increasing mole fraction of acrylic acid in solution, the reaction rate and sorption capacity of copolymers also increase.

The synthesized copolymers composition was determined by chromatography-mass spectroscopy. The constants and parameters of radical copolymerization were calculated using the integral methods of Mayo-Lewis, Fineman-Ross and Kelen-Tüdos. The Q-e parameters were calculated by the Alfray-Price equation on the basis of copolymerization constants.

A lower reactivity characterization of poly(ethylene glycol fumarate) were found at copolymerization of it with acrylic acid. Direct proportionality of the unsaturation degree of copolymers to the content of poly(ethylene glycol fumarate) in the composition of the initial monomer mixture was shown.

Key words: poly(ethylene glycol fumarate), acrylic acid, radical copolymerization, kinetics, copolymerization.

Unsaturated polyesters are interesting for theoretical and practical studies, since along with the simplicity, the economics of production, and they contain unsaturated double bonds in their composition, which makes it possible to obtain on their basis of spatially cross-linked structures. On the other hand, unsaturated polyesters provide the widest opportunity for directional modification due to polymerization reactions with various ionic monomers and, consequently, open the way to obtaining materials including composite ones with a predetermined valuable complex of properties.

The interaction of polyesters with unsaturated compounds was firstly called the copolymerization reaction by Benig [1], so copolymerization with vinyl acetate, styrene and methyl methacrylate, simple and complex allyl ethers, vinyl formates was investigated. As a result of the studies carried out, the role of unsaturated polyesters macromolecule as a "skeleton" at large formations was shown. From the literature analysis, only comonomers of hydrophobic nature were involved in the copolymerisation with unsaturated polyester resins [1-3], when the matter of hydrophilic monomers lay over until recently, which opens up prospects for new "intelligent" polymers.

The preparation of polymers based on unsaturated polyesters with the required combination of properties is possible only on the knowledge basis of the processes kinetics and mechanism of their radical copolymerization with ionic monomers. It seemed interesting and expedient to fill in the marked gap since the study of the kinetics, constants, and parameters of unsaturated polyesters copolymerization with ionic monomers remains undetermined and actual.

We synthesized earlier copolymers susceptible to changes in external factors by radical copolymerization reaction of polyglycol maleates with a number of unsaturated carboxylic acids, acrylamide [4, 5]. Hence, it seemed interesting to continue the research in this direction.

This paper demonstrates the first studies on the reactions of radical copolymerization of poly(ethylene glycol fumarate) (p-EGF) with acrylic acid (AA).

Experiment

The initial p-EGF was obtained by the polycondensation reaction of fumaric acid and ethylene glycol at a temperature of 403-453 K [6]. The course of the reaction was monitored by determining the acid number and the volume of water released. The synthesized polyester is a light-yellow, resinous, fusible substance, soluble in chloroform and dioxane. The resulting resin was purified from the initial monomers by repeated washing with acetone. The composition of the obtained product was determined from elemental analysis data: m.p. of p-EGF is 80°C.

The molecular weight of the p-EGF was determined by light-scattering methods on the nephelometer 2100 AN by NACH and by the method of determining the end group fraction, which is 2500 amu.

Radical copolymerization of p-EGF with AA was carried out in the dioxane solution at various initial molar ratios of comonomers in the presence of an initiator – benzoyl peroxide (BP) at a temperature of 333 K. The synthesized polymers were repeatedly washed with dioxane and dried under vacuum until constant mass for purifying them from unreacted monomer residues.

The compositions of the obtained copolymers were determined by potentiometric titration and by the residual amount of monomers by chromatography-mass spectroscopy on Agilent 7890A using the Agilent 5975C mass selective detector [7, 8]. A bromate-bromide method was used to quantify unreacted double bonds (the degree of unsaturation) of the copolymers [9].

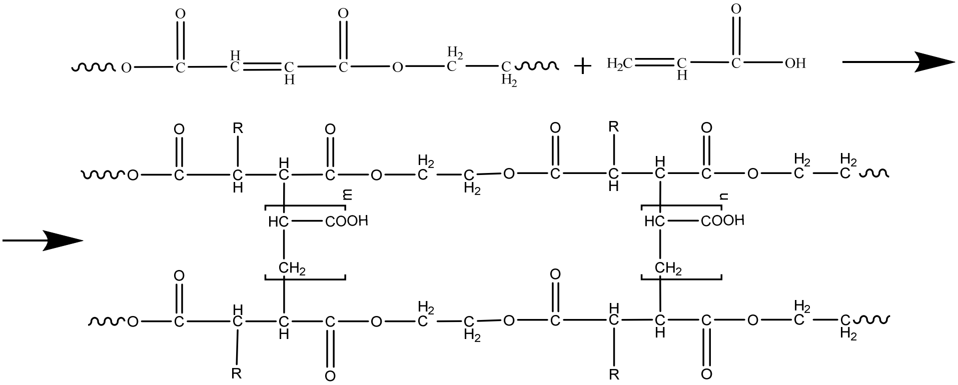
The kinetics of radical copolymerization of p-EGF with AA was studied by dilatometric method in the dioxane solution. The copolymerization constants r_1 and r_2 were determined on the basis of the copolymer compositions obtained at deep conversion ratios using the Mayo-Lewis integral equation [10], as well as the standard methods of Fineman-Ross and Kelen-Tüdos [11, 12].

Results and discussion

The intensive development of fundamental research in the field of radical copolymerization, which allows to regulate the properties, structure and molecular mass of polymers, the speed of the process, opens up new ways of obtaining polymers with given properties. Products based on unsaturated polyesters cured with vinyl monomers having specific physical-chemical and physical-mechanical properties are of considerable interest. The presence of unsaturated double bonds in the p-EGF molecule provides an opportunity to use it as a polymer matrix for the preparation of spatially cross-linked polymers by copolymerization with reactive acrylic acid.

P-EGF is obtained by the polycondensation reaction of fumaric acid and ethylene glycol [6].

As a result of radical copolymerization of the oligomeric molecule of p-EGF with AA in the presence of the initiator - BP the formation of the spatially cross-linked copolymer can be represented by the following scheme:



The values of constants and copolymerization parameters are important characteristics when considering the relative reactivity of the monomers depending on their structure. However, more complete information on the relative reactivity of the monomers during copolymerization can be obtained on the basis of kinetic data (figure 1).

However, more complete information on the relative reactivity of the monomers during copolymerization can be obtained on the basis of kinetic data (figure 1).

The kinetics of radical copolymerization of p-EGF with AA at various initial molar ratios was studied in detail to assess the relative activity of the monomers (figure 1). Increase of the reaction rate and yields of the copolymers was found with the growth in the content of AA in the initial monomer mixture, also these parameters decrease with the increase of the p-EGF content in the reaction mixture. This is apparently due to the presence of a functional -COO carboxyl group in the AA chain that capable of participating in elementary polymer transfer

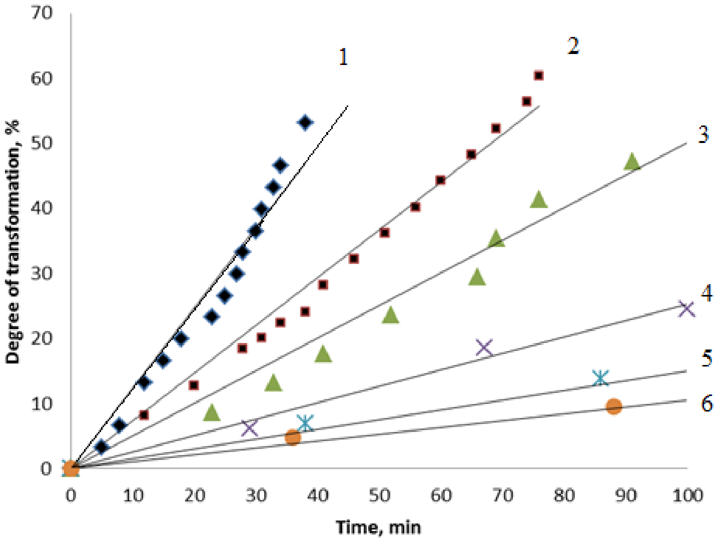


Figure 1 – Kinetic curve of the copolymerization of p-EGF:AA:
1 – 7,95:92,05; 2 – 11,95:88,05; 3 – 21,03:78,97;
4 – 44,05:55,95; 5 – 68,96:31,04; 6 – 89,05:10,95 mol.%

reactions, accompanied by an increase in the molecular weight due to branching processes. Figure 1 shows the kinetic data of radical copolymerization indicating a regular acceleration of the process with increasing molar fraction of AA in the initial monomer mixture.

The radical copolymerization of p-EGF with AA forms insoluble polymers of the network structure in the entire range of the studied comonomer ratios.

The experimental data obtained as a result of studying the processes of radical copolymerization in p-EGF-AA systems are presented in table 1. The yield of the copolymers was 83-74%.

Table 1 – Composition dependence of the copolymers on the initial mixture composition in the copolymerization of p-EGF (M_1) with AA (M_2) [BP] = 8 mol/m^3, T=333 K

The initial ratio of monomers, mass %		Copolymer composition, mass %		Yield, %	Degree of unsaturation
M_1	M_2	m_1	m_2		
10,09	89,91	7,95	92,05	83,23	41,3
15,06	84,94	11,95	88,05	78,98	42,5
25,02	74,98	21,03	78,97	76,22	46,8
50,01	49,99	44,05	55,95	75,32	49,6
75,06	24,94	68,96	31,04	75,05	52,1
90,08	9,92	89,05	10,95	73,83	54,4

Enrichment of the p-EGF-AA copolymers with AA units throughout the investigated range of the initial mixtures was seen from Table 1, while the content of the AA units in the copolymer composition increases sympathetically its amount in the initial monomer mixture. The copolymer yield and the swelling degree increase with increasing concentration in the initial AA mixture, which is apparently due to a sufficient degree of branching and cross-linking. Since the fumarate groups are not capable of homopolymerization reactions, the branching and cross-linking reactions diminish with a decrease in the molar AA concentration, respectively, while the unsaturation degree of the copolymer increases. Also, the above reactions are difficult with the increase of the p-EGF concentration in the initial monomer mixture, which in turn leads to the viscosity growth.

The composition diagram demonstrates more clearly the dependence of the copolymer composition on the initial mixture composition (figure 2).

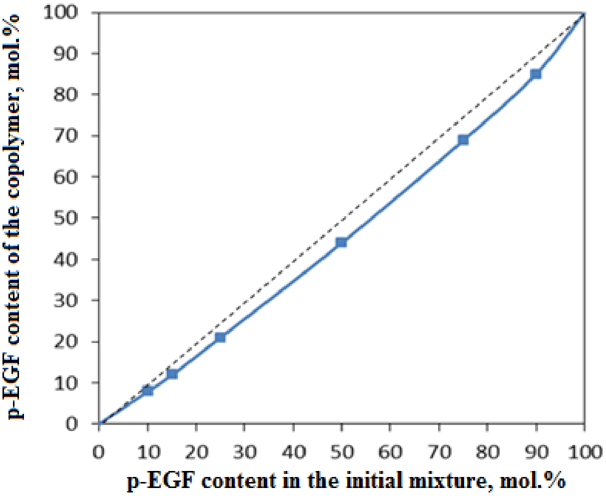


Figure 2 – The dependence of the p-EGF-AA copolymers composition on the composition of the initial monomer mixture

The relative activities of the comonomers were calculated using the integral Mayo-Lewis equation [9], the standard Fineman-Ross and Kelen-Tüdos methods on the basis of the copolymer and the initial monomer mixture compositions data. Table 2 shows the results of calculations. There was an assumption that p-EGF

Table 2 – Constants and parameters of radical copolymerization of p-EGF-AA binary systems

Method	r_1	r_2	$r_1 \cdot r_2$	$1/r_1$	$1/r_2$	e_1	Q_1	e_2	Q_2
Mayo-Lewis	0,84±0,076	1,18±0,050	0,99	1,19	0,85	0,86	0,90	0,77	1,15
Fineman-Ross	0,72±0,006	1,25±0,140	0,90	1,39	0,80	1,09	1,18	0,77	1,15
Kelen-Tüdos	0,83±0,038	1,02±0,094	0,85	1,21	0,98	1,18	1,34	0,77	1,15
Average	0,80±0,04	1,15±0,095	0,91	1,26	0,88	1,04	1,14	0,77	1,15

had a lower reactivity in radical copolymerization compared to AA. The obtained values of the relative activities of the copolymers confirm this assumption. The calculated values of the copolymerization constants indicate a greater AA activity in radical copolymerization. The data from Table 2 demonstrate the relative activity r_1 in the p-EGF-AA system that is less than one. It may indicate more activity of macroradical ending in the p-EGF unit towards the "foreign" monomer or radical, while the macroradical ending in the second comonomer AA (r_2> 1) unit reacts much more easily with its "own" monomer. The product of copolymerization constants ($r_1 \cdot r_2$) close to unity indicates the possibility of copolymers to the formation of statistical structures.

Various internal factors as conjugation, steric hindrance, polarity of the monomer and radical, influence on the monomers reactivity. The Q-e parameters were calculated by the Alfray and Price equations based on the values of copolymerization constants [10]. Both p-EGF and AA monomers have different polarities of the double bond (see table 2). The Q values for these monomers are significantly different. The degree of conjugation in the double bond with the substituents is also different due to the less value of Q for p-EGF. This determines the high propensity of monomers and radicals ending in the p-EGF units to attach more "foreign" monomers under the polymerization conditions.

Thus, a brief review of the studies in the paper shows a possibility to obtain new polymers of the spatially cross-linked structure as a result of radical copolymerization of poly(ethylene glycol fumarate) and acrylic acid. The obtained results demonstrate the ability to control the physical-chemical properties of the copolymers based on poly(ethylene glycol fumarate) and acrylic acid, induced by the polymer composition, which allows the creation of new materials with a predefined program of behavior.

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Резюме

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ПОЛИЭТИЛЕНГЛИКОЛЬФУМАРАТТЫҢ АКРИЛ ҚЫШҚЫЛЫМЕН РАДИКАЛДЫҚ СОПОЛИМЕРЛЕНУДІҢ КОНСТАНТАЛАРЫ МЕН ПАРАМЕТРЛЕРІ

Жұмыста алғаш рет диоксан ортасында бастапқы мономер қоспасының әртүрлі мольдік қатынасында полиэтиленгликольфумараттың акрил қышқылымен бинарлы радикалды сополимерленуі зерттелінген. Сополимерлену реакциясының кинетикасы зерттелді. Кинетикалық қисықтар ерітіндідегі акрил қышқылының мольдік мөлешерінің көбейген сайын реакция жылдамдығы мен сорбциялық сыйымдылығы артатыны көрсетілді. Хроматография-масс-спектроскопияны қолдану арқылы синтезделген сополимерлердің құрамы анықталды. Радикалды сополимерленудің константалары мен параметрлері Майо-Льюис, Файнман-Росс және Келен-Тюдоштың интегралды әдісімен есептеледі. Сополимерлену тұрақтыларының негізінде Q-e параметрлері Алфрей-Прайс теңдеуі бойынша есептелінді. Акрил қышқылының полиэтиленгликольфумаратпен сополимерлену кезінде соңғысының төмен реактивтілікпен сипатталатыны анықталды. Сополимерлердің қанықпағандығы бастапқы мономер қоспасы құрамындағы полиэтиленгликольфумараттың мөлшеріме тура пропорцианалды екеніндегі көрсетілді.

Түйін сөздер: полиэтиленгликольфумарат, акрил қышқылы, радикалды сополимерлену, кинетика, сополимерлену.

Резюме

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КОНСТАНТЫ И ПАРАМЕТРЫ РАДИКАЛЬНОЙ СОПОЛИМЕРИЗАЦИИ ПОЛИЭТИЛЕНГЛИКОЛЬФУМАРАТА С АКРИЛОВОЙ КИСЛОТОЙ

Впервые исследована бинарная радикальная сополимеризация полиэтиленгликольфумарата с акриловой кислотой в среде диоксана при различных мольных соотношениях исходной мономерной смеси. Изучена кинетика реакции сополимеризации. Кинетические кривые показывают, что с повышением мольной доли акриловой кислоты в растворе увеличиваются скорость реакции и сорбционная способность сополимеров. С применением хромато-массспектроскопии определен состав синтезированных сополимеров. Интегральным методом Майо-Льюиса, Файнмана-Росса и Келена-Тюдоша рассчитаны константы и параметры радикальной сополимеризации. На основании констант сополимеразации по уравнению Алфрея-Прайса рассчитаны параметры Q-e. Установлено, что при сополимеризации акриловой кислоты с полиэтиленгликольфумаратом последний характеризуется меньшей реакционной способностью. Показано, что степень ненасыщенности сополимеров прямо пропорциональна содержанию полиэтиленгликольфумарата в составе исходной мономерной смеси.

Ключевые слова: полиэтиленгликольфумарат, акриловая кислота, радикальная сополимеризация, кинетика, сополимеризация.

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ИЗУЧЕНИЕ РАСТВОРИМОСТИ В СИСТЕМЕ ТРИМЕТИЛЕНТЕТРАТИОМОЧЕВИНА – АЦЕТАТ МЕДИ – АЦЕТАТ ЦИНКА ПРИ 25 И 75 °С. Сообщение 1

Аннотация. Целью настоящего исследования является разработка технологии препарата протравителей семян хлопчатника. На основе физико-химического анализа установлено равновесие между компонентами $HOCH_2NHCON\ (CH_2OH)_2$-$Cu(CH_3COO)_2$-H_2O.

Ключевые слова: растворимость, температура, протравитель, триметилолмочевина, ацетат меди, ИК-спектр.

Изучение тройных систем, растворимости физиологически активных соединений обусловлено тем, что взаимное растворение бинарных компонентов даст возможность предсказать и определить технологические параметры синтеза новых веществ и фаз [1, 2].

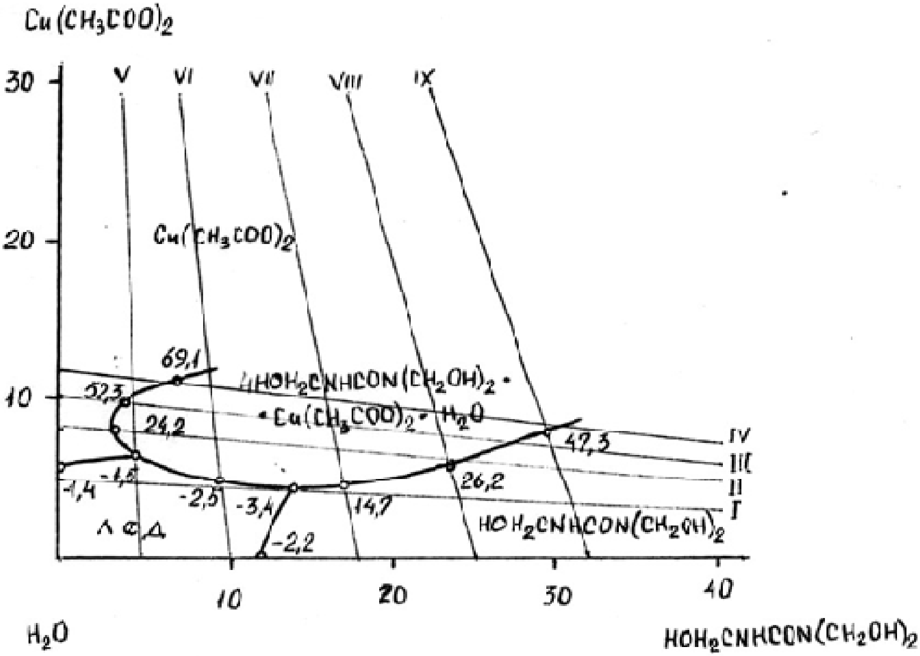
Сведения по растворимости и химическому взаимодействию в водных системах, включающих триметилолмочевину и ацетаты двухвалентных металлов, в литературе отсутствуют. Поэтому для выявления совместного поведения триметилолмочевины и ацетата меди в водной среде визуально - политермическим методом изучена растворимость в тройной системе в широком температурном и концентрационном интервале.

Данные химического анализа жидких и твердых фаз, проведенного общеизвестными методами аналитической химии, использовали для определения составов твердых фаз по Скрейнемакерсу [3, 4]. Триметилолмочевину синтезировали по методикам, описанным в работе [5].

Диаграмма растворимости бинарной системы триметилолмочевина-вода, входящая в состав исследуемой системы, состоит их ветвей кристаллизации льда и триметилолмочевины, перемыкающихся в криогидратной точке, соответствующей 11,8% $HOH_2CNHCON(CH_2OH)_2$ и 82,2% H_2O при температуре - 2,2°С.

Политерма растворимости системы $HOH_2CNHCON(CH_2OH)_2$-$Cu(CH_3COO)$ - H_2O изучена с помощью девяти внутренних разрезов. Из них I-IY проведены со стороны $Cu(CH_3COO)_2$ - H_2O к вершине $HOH_2CNHCON(CH_2OH)_2$, а с Y-IX со стороны $HOH_2CNHCON(CH_2OH)_2$ - H_2O к вершине $Cu(CH_3COO)_2$.

На основе политерм растворимости бинарных систем и внутренних разрезов построена диаграмма растворимости системы



Политерма растворимости системы триметилолмочевина – ацетат меди – вода

$HOH_2CNHCON(CH_2OH)_2$ - $Cu(CH_3COO)_2$-H_2O от -3,4 до 70° С (рисунок), на которой разграничены поля кристаллизации льда, триметилолмочевины, ацетата меди и нового соединения состава $4HOH_2CNHCON(CH_2OH)_2$ - $Cu(CH_3COO)_2$ - H_2O. Указанные поля, сходясь в двух тройных точках системы, для которых установлены температуры кристаллизации и состав равновесного раствора (таблица).

На политермической диаграмме нанесены изотермы растворимости через каждые 10°С, полученные интерполяцией данных по разрезам. Построены проекции политермических кривых растворимости на боковые стороны диаграммы триметилолмочевина – вода и ацетат меди – вода. Анализ диаграммы растворимости показал, что соединение $4HOH_2CNHCON(CH_2OH)_2$ - $Cu(CH_3COO)_2$ - H_2O - инконгруэнтно растворимое в воде.

ИК-спектры поглощения исходных компонентов – триметилолмочевины, ацетата меди и исследованных комплексов регистрировали на спектрофотометре ИК-20 в области частот 4000-400 см$^{-1}$. Образцы готовили прессованием с KBr в виде таблеток [6, 7]. Сравнение ИК-спектра свободной триметилолмочевины и спектров её соединений с ацетатом меди показывает, что при переходе от нескоординированного лиганда к комплексу определенные изменения претерпевают полосы валентных колебаний (N – C = O), (C - N), s(OH). В области (N – C = O) для комплекса наблюдается уменьшение частот на 14 см$^{-1}$. На спектре происходит смещение

Двойные и тройные точки системы триметилолмочевина – ацетат меди – вода

Состав раствора, масс %			Температура кристаллизации, °С	Твёрдая фаза
Триметилол мочевина	Ацетат меди	Вода		
–	5,6	94,4	-1,4	Лёд + $Cu(CH_3COO)_2 \cdot H_2O$
5,0	6,7	88,3	-1,5	То же
9,5	4,9	85,6	-2,5	Лёд + $Cu(CH_3COO)_2 \cdot H_2O$ + $4HOH_2CNHCON(CH_2OH)_2 \cdot Cu(CH_3COO)_2 \cdot H_2O$
14,0	4,3	81,7	-3,4	Лёд + $4HOH_2CNHCON(CH_2OH)_2 \cdot Cu(CH_3COO)_2 \cdot H_2O$ + $HOH_2CNHCON(CH_2OH)_2$
11,8	–	82,2	-2,2	Лёд + $4HOH_2CNHCON(CH_2OH)_2$
3,6	7,7	87,7	24,2	$Cu(CH_3COO)_2 \cdot H_2O$ + $4HOH_2CNHCON(CH_2OH)_2 \cdot Cu(CH_3COO)_2 \cdot H_2O$
4,0	9,5	86,5	52,3	То же
7,2	11,1	81,7	69,4	То же
17,1	4,5	78,4	14,7	$HOH_2CNHCON(CH_2OH)_2 \cdot 4HOH_2CNHCON(CH_2OH)_2 \cdot Cu(CH_3COO)_2 \cdot H_2O$
23,6	5,8	70,6	26,2	То же
29,3	8,0	62,7	47,3	То же

амидного карбоната в низкочастотную область, этим показано возможное участие NH – C = O группы в существовании комплекса и является дополнительным подтверждением его образования.

Таким образом, впервые визуально-политермическим методом изучена тройная система растворимости триметилолмочевина – ацетат меди – вода и построена диаграмма растворимости тройной системы. Результаты исследований подтверждают образование нового двойного соединения состава $4HOH_2CNHCON(CH_2OH)_2 - Cu(CH_3COO)_2 - H_2O$.

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Резюме

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25 ЖӘНЕ 75 °С ТЕМПЕРАТУРАДА МЫРЫШ ЖӘНЕ МЫС АЦЕТАТТАРЫНЫҢ ТРИМЕТИЛЕНТЕТРАТИОМОЧЕВИНА ЖҮЙЕСІНДЕГІ ЕРІГІШТІКТІ ЗЕРТТЕУ

Зерттеудің мақсаты $HOCH_2NHCON(CH_2OH)_2$-$Cu(CH_3COO)_2$-H_2O компоненттері арасындағы тепе-теңдіктің физика-химиялық талдау негізінде мақта тұқымдарын дәрілейтін препарат технологиясын жасау.

Түйін сөздер: ерігіштік, температура, дәрілегіш, триметилолмочевина, мыс ацетаты, ИҚ-спектр.

Summary

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N. Abdurahimova, K. Kabylbek

STUDYING OF SOLUBILITY IN THE TRIMETILENTETRA SYSTEM OF THIOUREA OF ACETATES OF COPPER AND ZINC AT 25 AND 75 °C

The research is the present purpose development of technology of medicine of etchant of seeds of a cotton. On the basis of the physical and chemical analysis is established balances between components. $HOCH_2NHCON\ (CH_2OH)_2$-$Cu(CH_3COO)_2$-H_2O.

Keywords: solubility, temperature, protectant, trimethyl urea, copper acetate, IR-spectrum.

УДК 541.49:546.73.547

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ИЗУЧЕНИЕ РАСТВОРИМОСТИ В СИСТЕМЕ ТРИМЕТИЛЕНТЕТРАТИОМОЧЕВИНА – АЦЕТАТ МЕДИ – АЦЕТАТ ЦИНКА ПРИ 25 И 75 °С. Сообщение 2

Аннотация. Методом изотермического насыщения при 25 и 75 °С изучены растворимость и химическое взаимодействие компонентов в тройной водной системе с участием ацетатов меди, цинка и триметилентетратиомочевины.

Ключевые слова: растворимость, температура, регуляторы, триметилентетратиомочевина, ацетат меди, ИК-спектр.

Интерес к изучению гетерогенных равновесий в системах с участием ацетатов микроэлементов и тиомочевиноформальдегидных соединений обусловлен практическим значением исходных компонентов и их комплексов, так как в последнее время синтезированы и выявлены регуляторы роста растений на основе солей микроэлементов и низкомолекулярных метиленовых производных тиомочевины [1-5].

В связи с этим методом изотермического насыщения при 25 и 75 °С изучены растворимость и химические взаимодействия компонентов в тройных в водных системах с участием ацетатов меди цинка и триметилентетратиомочевины (ТМТМт). Триметилентетратиомочевину синтезировали по методикам, описанным в работе [6]. Химическое равновесие в системах с участием ТМТМт устанавливалось через 2,5, 3,0 сут при 25 и 75^{o}С соответственно. Несколько меньшее время установления равновесия при 25^{o}С объясняется минимальным гидролизом ТМТМт, увеличивающимся с повышением температуры. Данные химического анализа жидких и твердых фаз, проведенного общеизвестными методами аналитической химии, использовали для определения составов твердых фаз по Скрейнемакерсу [7]. Результаты изучения тройной системы ацетат меди - ТМТМ - вода 25 и 75^{o}С приведены в таблице 1.

При изучении растворимости и взаимодействия ТМТМт с ацетатами меди и цинка в водной среде выявлено образование четырех новых соединений, которые были выделены в кристаллическом виде. Химический анализ соединений, проведенный по методу [8, 9], подтверждает их образование в изученных системах: найденный состав соединений хорошо согласуется с вычисленным (таблица 2).

Выделенные новые соединения были также идентифицированы ИК-спектроскопическим методом физико-химического анализа [10-12]. ИК-спектры поглощения исходных компонентов - ТМТМт и ацетатов меди,

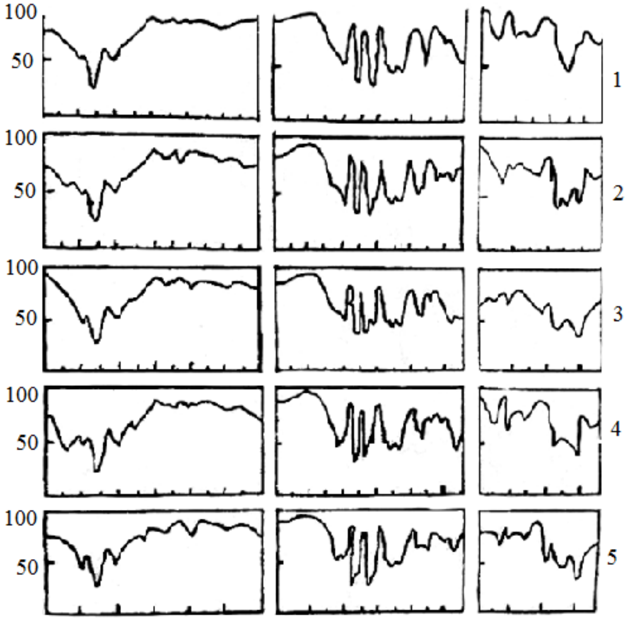
Таблица 1 – Данные по растворимости
в системе ацетат меди - триметилентетратиомочевина - вода 25 и 75 °C

Температура, °C	Состав жидкой фазы, мас.%			Состав твердого остатка, мас%			Твердая фаза
	$Cu(CH_3CO_2)_2$	ТМТМт	H_2O	$Cu(CH_3CO_2)_2$	ТМТМт	H_2O	
25	--			--	96,15		ТМТМт
	1,55	1,15		0,43	91,23		Тоже
	1,60	1,17		10,39	79,19		$Cu(CH_3CO_2)_2$·4ТМТМт ·H_2O
	3,82	1,56		10,75	76,34		То же
	5,89	2,85		11,17	78,65		То же
	5,91	2,87		20,44	70,16		$Cu(CH_3CO_2)_2$ ·4ТМТМт ·H_2O + $Cu(CH_3CO_2)_2$ ·ТМТМт ·H_2O
	5,93	2,88		31,21	58,35		$Cu(CH_3CO_2)_2$·ТМТМт ·H_2O
	7,94	2,71		30,65	55,82		То же
	9,45	3,61		31,44	55,05		То же
	9,44	3,64		54,60	22,03		$Cu(CH_3CO_2)_2$ ·ТМТМт ·H_2O + $Cu(CH_3CO_2)_2$ ·H_2O
75	9,46	3,62		84,12	0,69		$Cu(CH_3CO_2)_2$ ·H_2O
	9,48	1,82		79,63	0,38		То же
	9,56	--		86,27	--		То же
	--	--		--	95,84		ТМТМт
	1,16	2,35		10,67	79,96		$Cu(CH_3CO_2)_2$·4ТМТМт ·H_2O
	4,24	2,06		11,13	80,40		То же
	7,27	2,73		11,26	78,63		То же
	11,22	3,91		11,61	77,59		То же
	14,39	5,18		12,06	78,81		То же
	14,40	5,20		48,63	39,19		$Cu(CH_3CO_2)_2$ ·4ТМТМт ·H_2O + $Cu(CH_3CO_2)_2$ ·H_2O
	14,37	5,16		83,31	0,84		То же
	14,23	2,65		82,55	0,51		То же
	14,20	--		86,24	--		То же

Таблица 2 – Данные по растворимости
в системе ацетат цинка -триметилентетратиомочевина - вода 25 и 75^{o}C

Тем-пера-тура	Состав жидкой фазы, мас.%			Состав твердого остатка, мас%			Твердая фаза
^{0}C	$Zn(CH_3CO_2)_2$	ТМТМт	H_2O	$Zn(CH_3CO_2)_2$	ТМТМт	H_2O	
	--	--		--	96,15		ТМТМт
	1,53	1,87		10,75	80,76		$Zn(CH_3CO_2)_2$·4ТМТМт ·H_2O
	6,80	2,51		11,16	80,13		То же
	11,59	2,96		12,01	80,78		То же
	11,61	3,00		20,35	72,49		$Zn(CH_3CO_2)_2$ ·4ТМТМт + $Zn(CH_3CO_2)_2$ ·ТМТМт ·H_2O
	11,60	3,03		31,43	53,81		$Zn(CH_3CO_2)_2$ ·ТМТМт ·H_2O
	16,85	2,67		33,35	57,03		То же
	22,05	2,58		32,86	56,07		То же
	26,15	3,53		33,45	56,77		То же
	26,20	3,61		47,71	37,45		$Zn(CH_3CO_2)_2$ ·ТМТМт ·H_2O + $Zn(CH_3CO_2)_2$ ·ТМТМт ·H_2O
	26,13	3,57		76,25	0,76		$Zn(CH_3CO_2)_2$ ·ТМТМт ·H_2O
75	25,56	1,43		72,47	0,39		То же
	25,00	--		78,59	--		То же
	--	--		--	95,84		ТМТМт
	0,95	1,56		0,66	89,12		То же
	2,07	2,18		10,23	76,93		$Zn(CH_3CO_2)_2$ ·4ТМТМт
	8,81	2,11		11,81	75,62		То же
	20,88	2,18		12,25	79,02		То же
	31,29	2,31		13,05	77,96		То же
	39,05	3,38		15,12	76,87		То же
	39,11	3,42		54,07	31,15		$Zn(CH_3CO_2)_2$ ·4ТМТМт + $Zn(CH_3CO_2)_2$ ·$2H_2O$
	39,15	3,49		79,03	1,06		$Zn(CH_3CO_2)_2$ ·$2H_2O$
	39,24	1,65		72,16	0,76		То же
	39,40	--		79,61	--		То же

цинка, исследуемых комплексов регистрировали на спектрофотометре ИК-20 в области частот 4000-400 см$^{-1}$. Образцы готовили прессованием с КВч в виде таблеток. Полученные результаты представлены на рисунке и в таблице 3.



ИК-спектры:
1 – ТМТМт; 2 – $Cu(CH_3CO_2)_2$ ·ТМТМт ·H_2O; 3 – $Cu(CH_3CO_2)_2$ ·4ТМТМт ·H_2O;
4 – $Zn(CH_3CO_2)_2$ ·ТМТМт ·H_2O; 5 – $Zn(CH_3COO)_2$ ·4ТМТМт

По данным ИК-спектроскопических исследований, спектры ТМТМт и ацетатов меди, цинка содержат все присущие им полосы валентных и деформационных колебаний. Как следует из результатов анализа ИК-спектров комплексных соединений ТМТМт с ацетатами меди, цинка, они характеризуются интенсивным и широким поглощением в области частот 3600-2800,

Таблица 3 – Содержание компонентов в соединениях ТМТМт с ацетатами меди и цинка

Соединения	Найдено, мас.%			Вычислено, мас.%		
	$Me(CH_3CO_2)_2$	ТМТМт	H_2O	$Me(CH_3CO_2)_2$	ТМТМт	H_2O
$Cu(CH_3CO_2)_2$ ·ТМТМт ·H_2O	33,71	62,94	3,35	33,64	63,02	3,34
$Cu(CH_3CO_2)_2$ ·4ТМТМт·H_2O	11,69	87,16	1,15	11,64	87,21	1,15
$Zn(CH_3CO_2)_2$ ·ТМТМт ·H_2O	33,79	62,86	3,35	33,88	62,80	3,32
$Zn(CH_3CO_2)_2$ ·4ТМТМт	11,93	88,07	--	11,88	88,12	--

1700-900 и 300-400 см$^{-1}$, то есть имеют основные характеристические полосы поглощения, соответствующие колебаниям свободной молекулы исходных компонентов. При сравнении ИК-спектров существенным является высокочастотный сдвиг. Полоса поглощения $\upsilon\alpha s(NH_2)$, $\upsilon(NH)$, $\delta(NH_2)$, $\upsilon(CN)$ соединений относительно чистой триметилентетратиомочевины. Из этого следует, что связи NH и CN стали более прочными.

Смещение полос поглощения валентных колебаний N-П связи в области высоких частот обусловлено разрывом межмолекулярных водородных связей, характерных для свободных молекул ТМТМт. На ИК-спектрах исследуемых соединений полоса поглощения, соответствующая валентным колебаниям связи C=S, происходит понижение частоты поглощения с 635-655 см$^{-1}$ у лигандов до 565-597 см$^{-1}$ у соединений. В то время как полоса поглощения $\upsilon(CN)$ при 1520 см$^{-1}$, наблюдаемая в спектрах свободной молекулы ТМТМт, смещается в высокочастотной области на 4-10 см$^{-1}$. Такие изменения колебательных частот в спектрах комплексах ТМТМт ацетатами меди, цинка относительно исходных компонентов позволяет предположить, что координация в них осуществляется через атом серы тиокарбонилъной группы ТМТМт. На ИК-спектрах гидратированных комплексов в области 1648-1630 см$^{-1}$ соответственно полоса поглощения, обусловлена валентными и деформационными колебаниями кристаллизационной воды.

Полученные новые соединения были также идентифицированы и охарактеризованы рентгенофазовым [13] и термическим методами физического анализа [14, 15]. Таким образом, изучением растворимости в тройных системах ТМТМт –ацетат меди цинка вода выявлено образование новых комплексных соединений:

$$Cu(CH_3COO)_2\ ТМТМт\cdot H_2O\ Zn(CH_3COO)_2\cdot\ ТМТМт\cdot H_2O$$

$$Cu(CH_3COO)_2\cdot 4ТМТМт\ H_2O\ Zn(CH_3COO)_2\cdot 4ТМТМт,$$

обладающих ярко выраженной индивидуальной особенностью.

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Резюме

Х. Исаков, С. Усманов, И. Р. Аскаров, К. Кабылбек, Х. С. Усманов

25 ЖӘНЕ 75 °С ТЕМПЕРАТУРАДА МЫРЫШ ЖӘНЕ МЫС АЦЕТАТТАРЫНЫҢ ТРИМЕТИЛЕНТЕТРАТИОМОЧЕВИНА ЖҮЙЕСІНДЕГІ ЕРІГІШТІКТІ ЗЕРТТЕУ

Изотермиялық қаныққан әдіспен 25 және 75°С температурада триметилентетратиомочевина, мырыш және мыс ацетаттарының қатысуымен үшсулы жүйедегі компоненттердің химиялық өзара әрекеттесуі және ерігіштігі зерттелді.

Түйін сөздер: ерігіштік, температура, регулятор, триметилентетратиомочевина, мыс ацетаты, ИҚ-спектр.

Summary

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STUDYING OF SOLUBILITY IN THE TRIMETILENTETRA SYSTEM OF THIOUREA OF ACETATES OF COPPER AND ZINC AT 25 AND 75 °C

The solubility and chemical interaction of the components in the ternary aqueous system with the participation of copper, zinc and trimethylenetetriothiourea acetate have been studied by isothermal saturation at 25 and 75 ° C.

Keywords: solubility, temperature, regulators, trimethylenethiourea, copper acetate, IR spectrum.

УДК 631.895:631.85:631.812.1

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ИССЛЕДОВАНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ НОВОГО ОРГАНОМИНЕРАЛЬНОГО УДОБРЕНИЯ НА ОСНОВЕ МАГНИЙСОДЕРЖАЩЕГО ФОСФОРНОГО УДОБРЕНИЯ И БИОПРЕПАРАТА

Аннотация. На основании исследований установлено, что новое органоминеральное удобрение на основе магнийсодержащего фосфорного удобрения и биопрепарата, содержащего растительный экстракт и борат калия, имеет малую равновесную влажность, высокую влагоемкость, неслеживается, что является теоретическим обоснованием для бестарного хранения, способов перевозки в зимних, весенних, летних, осенних условиях, а также внесения в почву.

Ключевые слова: оргономинеральное удобрение, магнийсодержащий фосфорный тук, растительный экстракт, физико-химические свойства.

Для организации правильного хранения, транспортировки и внесения в почву удобрений необходимо исследовать их основные физико-химические свойства.

Ниже приведены характеристики важных взаимосвязанных показателей этих свойств удобрений.

Гигроскопичность характеризует способность удобрений поглощать влагу из воздуха. При повышенной гигроскопичности удобрения отсыревают, слеживаются, ухудшается их сыпучесть и рассеиваемость, гранулы теряют свою прочность.

Влажность поставляемых сельскому хозяйству промышленных удобрений (ее максимально допустимый уровень) должна составлять для азотных удобрений 0,15–0,3%, фосфорных – 3–4%, остальных удобрений – 1–2%. От влажности зависят все основные физико-механические свойства удобрений.

Предельная влагоемкость характеризуется максимальной влажностью удобрения, до появления тонкой пленки жидкой фазы на поверхности гранул.

Слеживаемость – склонность удобрений переходить в связанное и уплотненное состояние. Она зависит от влажности и влагоемкости удобрений, размера и формы частиц, их прочности, давления в слое, условий и продолжительности хранения.

В связи с вышеизложенным в данной статье представлены результаты изучения гигроскопичности, слеживаемости, влагоемкости, равновесной влажности органоминерального удобрения (ОМУ) на основе магнийсодержащего фосфорного (МФ) удобрения и биопрепарата, содержащего растительный экстракт и борат калия.

Склонность продуктов поглощать атмосферную влагу влияет на условия производства и сушки, качество продукции при хранении, транспортировке и применении. Критерием оценки гигроскопичности зернистых и порошкообразных химических продуктов является гигроскопическая точка и равновесная влажность W.

На рисунке 1 приведены кривые влагопоглощения МФ удобрения во времени (сутки) при относительной влажности атмосферы 40, 60 и 80%.

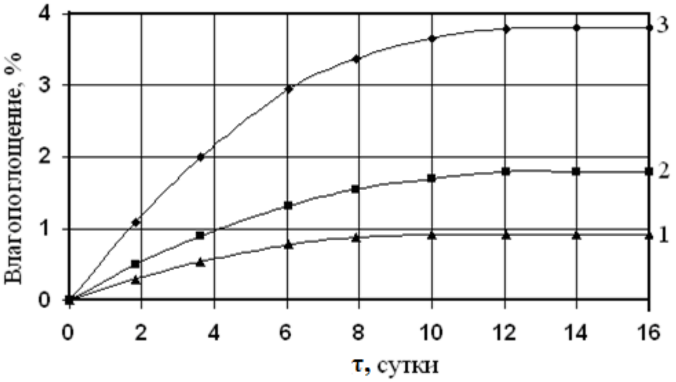

Рисунок 1 – Динамика влагопоглощения МФ удобрения во времени:
1 – относительная влажность атмосферы – 40; 2 – 60; 3 – 80%

Из полученных данных следует, что в случае относительной влажности атмосферы 40%, что соответствует летнему периоду южных регионов, равновесная влажность W МФ удобрения составляет 0,92 мас.%, т.е. при данной относительной влажности атмосферы не происходит влагопоглощения. При относительной влажности атмосферы 60% (весенне-летний период) равновесная влажность наступает при влагосодержании 1,7 мас.%, а при 80% (осенне-зимний период) – 3,7 мас.%.

Исследования по определению влагоемкости МФ удобрения показали, что образование свободной влаги наступает при его влагосодержании 7,8 мас.%.

Изучение слеживаемости МФ удобрения при его максимальном влагосодержании 3,7 масс.%, соответствующем осенне-зимнему периоду хранения, показали, что образцы весом 100 г после 12 ч хранения под нагрузкой 2 кг при температуре 80°С не подверглись слипанию и комкованию.

Результаты исследований свидетельствуют о том, что МФ удобрения можно хранить под навесом навалом и перевозить бестарно, даже в осенне-зимний периоды.

Определено, что равновесная влажность W биопрепарата при относительной влажности 40 % наступает при влагосодержании 0,15 масс.%, при 60 % – 0,5 масс.% и при 80 % – 0,9 масс.%. Исследования влагоемкости и слеживаемости биопрепарата показали его высокую влагоемкость – 10,2 масс.%. Биопрепарат до влагосодержания 8,5 масс.% не слеживается.

Большое практическое значение имеют данные по динамике влагопоглощения, равновесной влажности W, влагоемкости и слеживаемости обогащенного биопрепаратом МФ удобрения.

На рисунке 2 представлены данные по поглощению влаги МФ удобрения, обогащенным биопрепаратом в количестве: 1,5; 2,0; 2,5 масс.% в сравнении с необогащенным МФ удобрением при относительной влажности атмосферы 40%.

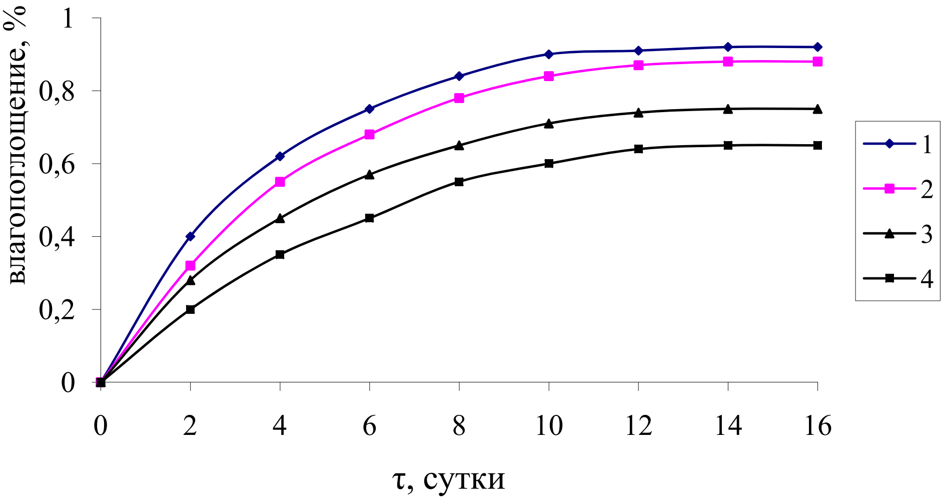

Рисунок 2 – Динамика влагопоглощения МФ удобрения и МФ удобрения, обогащенного биопрепаратом, во времени при относительной влажности атмосферы 40%:
1 – МФ удобрение;
2 – МФ удобрение обогащенное биопрепаратом, 1,5 масс.%;
3 – МФ удобрение обогащенное биопрепаратом, 2,0 масс.%;
4 – МФ удобрение обогащенное биопрепаратом, 2,5 масс.%.

Если в случае МФ удобрения равновесная влажность W наступает при влагосодержании 0,92 масс.% (рисунок 2, кривая 1), то биопрепарат в количестве 1,5 масс.% способствует снижению влагосодержания на 0,75 масс.% (рисунок 2, кривая 2), при котором наступает равновесная влажность W. Увеличение содержания биопрепарата до 2 и 2,5 масс.% приводит к дальнейшему снижению точки равновесной влажности W, которая имеет значение 0,73 масс. % (рисунок 2, кривая 3) и 0,70 масс.% (рисунок 2, кривая 4).

Аналогичная закономерность прослеживается и при относительной влажности атмосферы 60 (рисунок 3) и 80% (рисунок 4). Так, если в случае МФ удобрения, при относительной влажности атмосферы 60 %, равновесная влажность W наступает при влагосодержании 1,7 масс.% (рисунок 3, кривая 1), то с биопрепаратом в количестве: 1,5; 2,0; 2,5 масс.%, способствует снижению точки равновесной влажности до 1,3 масс.% (рисунок 3, кривая 2); 1,25 масс.% (рисунок 3, кривая 3); 1,0 масс.% (рисунок 3, кривая 4) соответственно.

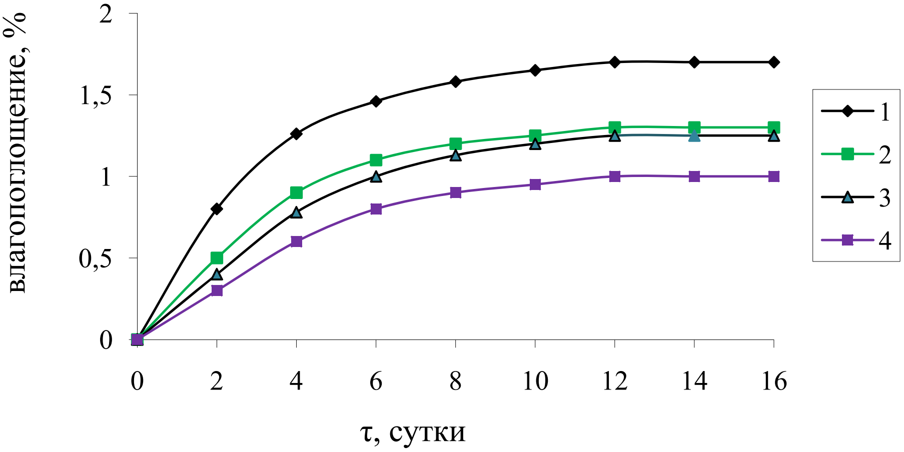

Рисунок 3 – Динамика влагопоглощения МФ удобрения и МФ удобрения, обогащенного биопрепаратом, во времени при относительной влажности атмосферы 60%:
1 – МФ удобрение;
2 – МФ удобрение, обогащенное биопрепаратом, 1,5 масс.%;
3 – МФ удобрение, обогащенное биопрепаратом, 2,0 масс.%;
4 – МФ удобрение, обогащенное биопрепаратом, 2,5 масс.%

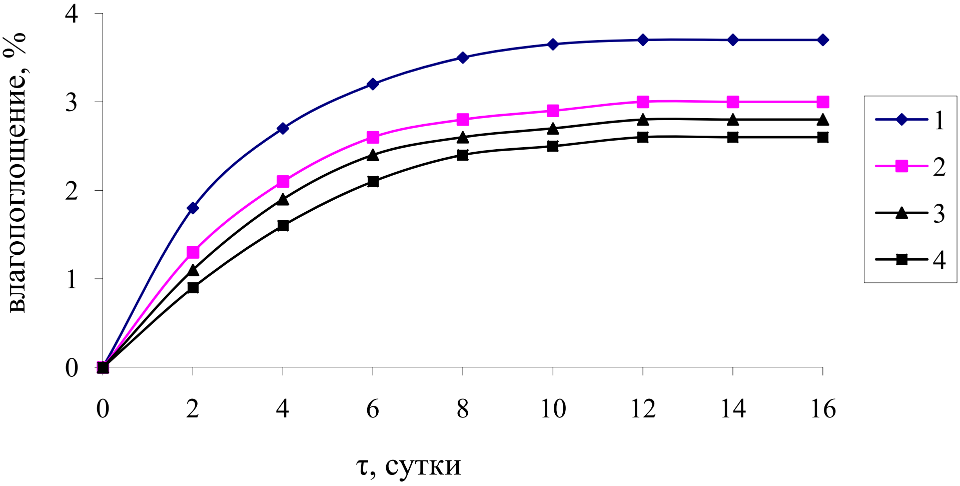

Рисунок 4 – Динамика влагопоглощения МФ удобрения и МФ удобрения, обогащенного биопрепаратом, во времени при относительной влажности атмосферы 80%:
1 – МФ удобрение;
2 – МФ удобрение, обогащенное биопрепаратом, 1,5 масс.%;
3 – МФ удобрение, обогащенное биопрепаратом, 2,0 масс.%;
4 – МФ удобрение обогащенное биопрепаратом, 2,5 масс.%

При относительной влажности атмосферы 80% равновесная влажность W МФ удобрения наступает при его влагосодержании 3,7 масс.% (рисунок 4, кривая 1), а МФ удобрения, обогащенного биопрепаратом в количестве 1,5, 2,0 и 2,5 масс.%, при влагосодержании 3,0 масс.% (рисунок 4, кривая 2), 2,9 масс.% (рисунок 4, кривая 3) и 2,8 масс.% (рисунок 4, кривая 4) соответственно.

Влагоемкость МФ удобрения, обогащенного биопрепаратом в количестве 1,5, 2,0 и 2,5 масс.%, имеет значение 8,2, 8,3 и 8,5 масс.% соответственно.

Повышение значения влагоемкости МФ удобрения, обогащенного биопрепаратом в сравнении с необогащенным (7,8 мас.%), объясняется высокой влагоемкостью биопрепарата (10,2 мас.%). Удобрение не слеживается до влагосодержания 7,5 мас.%.

Сводные данные гигроскопических характеристик МФ удобрения и МФ удобрения, обогащенного биопрепаратом, в сравнении с биопрепаратом представлены в таблице.

Гигроскопические свойства МФ удобрения и МФ удобрения, обогащенного биопрепаратом

Удобрения	Гигроскопические свойства						
	отн. влажн. атм., %	равн. влажн. W, %	отн. влажн. атм., %	равн. влажн. W, %	отн. влажн. атм., %	равн. влажн. W, %	влагоемкость Wк, %
МФ удобрение	40	0,92	60	1,7	80	3,7	7,8
Биопрепарат	40	0,15	60	0,5	80	0,9	10,2
МФ удобрение, обогащенное биопрепаратом							
МФ удобрение, обогащен. биопрепаратом, 1,5 масс.%	40	0,90	60	1,6	80	3,5	8,0
МФ удобрение, обогащен. биопрепаратом, 2 масс.%	40	0,88	60	1,55	80	3,4	8,1
МФ удобрение, обогащен. биопрепаратом, 2,5 масс.%	40	0,85	60	1,3	80	3,3	8,3

Таким образом, на основании исследований установлено, что удобрения имеют малую равновесную влажность, высокую влагоемкость, неслеживаются. Результаты исследования явились научной основой для бестарного хранения, перевозки и механизированного внесения в почву в летних, осенне-весенних, зимних погодных условиях.

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ЛИТЕРАТУРА

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Резюме

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БИОПРЕПАРАТ ЖӘНЕ ҚҰРАМЫНДА МАГНИЙ БАР ФОСФОРЛЫ ТЫҢАЙТҚЫШ НЕГІЗІНДЕ ОРГАНОМИНЕРАЛДЫ ТЫҢАЙТҚЫШТЫҢ ФИЗИКА-ХИМИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

Құрамында калий бораты, өсімдік сығындысы бар, биопрепарат және құрамында магний бар фосфорлы тыңайтқыш негізінде алынғын органоминералды тыңайтқыштардың тепе-теңдік ылғалдылық, ылғал сыйымдылық, жабысқақтық, гигроскопиялық нәтижелері келтірілген.

Түйін сөздер: органоминералды тыңайтқыш, құрамында магний бар фосфорлы тыңайтқыш, өсімдік сығындысы, физика-химиялық қасиеттері.

Summary

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INVESTIGATION OF PHYSICAL AND CHEMICAL PROPERTIES OF NEW ORGANOMINERAL FERTILIZER ON THE BASIS OF MAGNESIUM CONTAINING PHOSPHORUS FERTILIZER AND BIOPREPARATE

The results of hygroscopicity, caking, moisture capacity, equilibrium moisture of organomineral fertilizer based on magnesium-containing phosphorus fertilizer and biopreparatie containing plant extract, potassium borate are presented.

Keywords: organomineral fertilizer, magnesium-containing phosphorus fertilizer, plant extract, physical-chemical properties.

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AGROCHEMICAL, ECONOMIC AND ECOLOGICAL EFFICIENCY OF THE COMPOSITION OF POLYFUNCTIONAL ACTION ON THE BASIS OF DIMETHYLOLUREA PHYTO-CONNECTIONS OF COPPER AND ZINC ON CROPS OF A COTTON-PLANT

Abstract. In this paper, it was shown that by application of the composition of the polyfunctional action based on dimethylolurea, phyto-connections of copper and phyto-connections of zinc as a material for preplans treatment of cotton-plant was observed in comparison with the standard reducing the incidence of plants by root rot and gommos on 10-16%, respectively increase of the preservation of plants for harvesting at 6000-9000 pieces / ha, obtaining an additional yield of raw cotton -2.6-4.8 c/ha, the quality of cotton fiber indicators are increased by 0.3-0.6%, its length is 0.2 -0.3 mm and yield of oil 1.8-4.2%. The income form additional raw cotton is equal to 38.700-71.700 tg/ha. After harvesting in the soil, the content of easily hydrolysable nitrogen increases – 1.5-2.8 mg/kg, assimilable forms of phosphorus pentoxide – 1.3-3.7 mg/kg soil and soil organic matter – 3.6-4.8 t/ha.

Keywords: etchant, composition of polyfunctional action, dimethylolurea, phyto-connections of copper, phyto-connections of zinc, cottonplant, increase, income, qualitative indicators.

An important factor in the intensification of crop production is protection of agricultural crops from harmful objects [1]. All over the world, annually every year about 35% of the crop were lost from pests, diseases and weeds [2]. The concept of integrated protection of plant against diseases provides for integrated use of modern agricultural technology, sustainable varieties, as well as rational use of chemical and biological means of protection. Necessity use of pesticides which caused by increasing losses from harmful organisms and weeds, deterioration of the quality of crop products and at the same time absence of real alternative methods, a lack of steady grades, their high economic efficiency [3, 4]. Cotton plant – one of the main agricultural crops in South Kazakhstan region. In the complex events to increase its yields the significant place occupied protection of cotton plant against harmful organisms.

Chemical methods of struggle were led to a number of negative consequences of environmental pollution and others. The severe consequences of the "pesticide syndrome" urgently required the search of an alternative existing cotton plant protection strategy, which created prerequisites for developing the principles of integrated management of the number of harmful and useful species in cotton agrobiocenoze, based on widespread use of ecological approach for plant protection [5].

The main purpose of the work was to study the technological methods for application of compositions of polyfunctional action on cotton crops to protect seeds from diseases, to increase yields, to improve the condition of the soil and the quality of products, as well as economic efficiency.

In the vegetation period 2016 in the Maktaaralsky region of South Kazakhstan area at the experimental site of LLP "Hazrat-Ali-Akbar" was carried out field experiment on cotton crops in order to determine the biological, agrochemical and economic efficiency of preparative form of composition polyfunctional action based on dimethylolurea (DMU) and phyto-connections of copper (PCC) and dimethylolurea (DMU) and phyto-connections of zinc (PCZ).

Field experiment with a triple repetition, placed in one tier, size of the plots of 0.1 hectares, the area under the study were -1.5 hectares.

The main plowing on the trial plot was done on November 23, 2015. Harrowing held on April 22, 2016, after following by a 2-fold chilling. Seeding of cotton seeds, treated with Sunkar-3 disinfectant and the effective substance of the composition of polifunctional action were made on April 28, 2016, combination with harrowing. Ammonium nitrate was introduced into the soil on June 27, 2016 at the beginning of the budding phase.

Agrotechnics of experience is common for Maktaaral cotton-growing zone. Cotton seeds Mactaaral-4005, the first reproduction. Watering 2 times. Preparations before processing of cotton seeds were diluted with water with calculation of 15 liters of working solution on 1 ton of seeds. The degree of soil salinity was 0.075% for Cl-ions (a strong degree of salinity).

Scheme of field experience, the cultivation of cotton plants are following: introduction of ammonium nitrate into the phase of budding – 200 kg/ha (N-68); in the reference version, Sunkar-3 was used in an amount of 0.5 l/ha, in experimental variants, l/ha: 4DMU·PCC – 0.25, 0.5; 4DMU·PCZ – 0.5.

Table 1 shows, the results of biological studies to determine the degree of affection of cotton plants by root rot and gummosis in mid – May, as well as the preservation of plants for harvesting (the beginning of month of September).

Table 1 – Effect of seed Protestants on the degree of plant damage by disease and preservation for harvesting

Variants	Degree of disease affection, %		Preservation of plants for harvesting, thousand pieces/ha
	root rot	gommoz	
1. Control	17	21	103
2. Sunkar-3 (0,5 l/ha)	1,8	2.0	117
3. 4DMU · PCC (0,25 l/ha)	1,5	1.75	123
4. 4DMU · PCC (0,5 l/ha)	1,40	1.70	125
5. 4DMU · PCZ (0,5 l/ha)	1,42	1.69	126

It was shown that in the season of 2016, cotton plants on the experimental plot in the control variant were destroyed by root rot by 17% and gummosis – 21%, the preservation of plants for harvesting 103 thousand pieces / ha. In variant where used the seed dressing Sunkar-3 root rot was destroyed only 1.8% of the plants and gommoz – 2.0%, and the safety of the plant to harvest – 117 thousand units/ha. It is established that compositions of multifunctional action in comparison with Sunkar-3 lower a disrupt of plants by 10-16% root decay and gommoz, ensure larger safety of plants to harvesting on 6-9 thousand pieces/ha.

Table 2 presents the results of phenological observations, plant growth and development and the raw cotton crop.

Table 2 – Growth, development of plants and harvest of raw cotton

Variants	Height of the main stalk by dates of vegetation, cm		Number of buds, piece / plant	Number of fruit branches, piece/plant	Number of boxes, piece / plant	Harvest of raw cotton, c/ha	Harvest of raw cotton	
	date							
	1.06	1.09	1.07	1.08	1.09	20.10	c/ha	%
1	11.4	62.1	7.3	5.3	6.3	25.2	–	–
2	11.9	65.7	7.5	6.0	6.5	28.7	3.5	13.88
3	12.5	66.9	8.9	6.5	7.7	31.3	6.1	24.20
4	12.8	67.1	9.0	6.7	7.9	33.5	8.3	32.90
5	12.75	67.2	9.1	6.7	7.9	33.4	8.2	32.50

The obtained data indicate that seed treatments Sunkar-3 and preparative form of polyfunctional action on the basis 4 DMU·PCC and 4 DMU·PCZ positively affect growth and development of plants, accumulation of fruit elements and ultimately provide the increases of cotton yields.

It should be noted that the compositions of polyfunctional action can save more boxes at the end of the vegetation and consequently increase the yield of raw cotton.

If in case of option with Sunkar-3 number of boxes of 6.3 pieces/ plant and an increase of harvest were made 3.5 c/ha, then compositions of polyfunctional action on the basis of double connections 4 DMU·PCC and 4 DMU·PCZ at the same rate provide accumulation of boxes of 7.7 and 7.9 pieces/ plant and an respectively increase of harvest makes 8.2 and 8.3 c/ha. Reducing the norm of the composition in 2 times to led obtain an additional crop raw cotton 6.1 c/ha.

Economic indexes of the application of composition of multifunctional action on the basis of double connections 4 DMU·PCC and 4 DMU·PCZ on crops of a cotton are presented in table 3.

From obtained data follows that, the economic efficiency due to additional harvest in a case of Sunkar-3 with the deduction of its value compiled 51 300 tg/ha, in case of polyfunctional composition action this index matters were 90 000 – 123 000 tg/ha.

Table 3 – Economic indexes of application of composition on cotton crops

Va-riants	Harvest of cotton-raw, c/ha		Economic efficiency in comparison with monitoring at the expense of a harvest increase with deductions of cost of preparation, tg/ha
	in all	increase harvest	
1	25.2	–	–
2	28.7	3.5	51 300
3	31.3	6.1	90 000
4	33.5	8.3	123 000
5	33.4	8.2	122 500
Note. Value Sunkar-3 – 1200 tg/ha, compositions based on 4 DM · PCC (PCZ) is – 1500 tg/ha, raw cotton cost is– 150.0 thous. tg/t.			

Table 4 shows qualitative indicators of cotton fiber and oiliness seeds. It is established that in variants by using the composition of polyfunctional action, the qualitative indicators of cotton fiber and oiliness seeds have the best indicators.

Table 4 – Average date of qualitative indicators of cotton fiber and oiliness of seeds

Variants	Fiber output, %	Fiber length, mm	Varieties	Oiliness of seeds, %
1	32.0	32.1	first	16.3
2	32.5	32.3	selective	16.5
3	32.8	32.5	selective	16.8
4	33.1	32.6	selective	17.2
5	33.0	32.6	selective	17.2

The greatest theoretical and practical significance have the content of movable forms of nutrients elements and humus at the end of vegetation. From the obtained data of table 5 follows that the etchant of seeds Sunkar-3 and compositions of polyfunctional action not only increased productivity the of cotton plant, but also contributed greater accumulation in the soil at the end of the vegetation of movable forms of nutritive elements and humus.

Table 5 – Contents of movable forms of nutritive elements and humus in the soil (0.0-30.0 cm) at the end of vegetation

Variants	Nutrient elements content, mg/kg soil			Humus, %
	N	P_2O_5	K_2O	
1	17.5	10.9	210	1.09
2	22.4	12.8	215	1.10
3	23.9	14.1	216	1.19
4	25.1	16.4	220	1.21
5	25.2	16.5	219	1.22

So if at the end of vegetation in the case of a control variant readily hydrolyzable nitrogen was 17.5 mg/kg of soil, movable forms of phosphorus pentoxide was – 10.9 mg/kg of soil , exchangeable potassium dioxide was – 210 mg/kg of soil and humus – 1.09%, then in the variants with seed dresser Sunkar-3 and compositions of polyfunctional action with readily hydrolyzable nitrogen value were 22.4-25.2 mg/kg of soil, movable forms of phosphorus pentoxide was 12.8-16.5mg/kg of soil and exchangeable potassium dioxide – 215-220 mg/kg of soil, humus – 1.10-1.22%. It should be emphasized that the compositions of polyfunctional action favorably differ from Sunkar-3 seed dressing by additional content of mobile forms of nutrients, especially by accumulation of humus, which was 3.6-4.8 t/ha.

Conclusions. Application of as a material for preplant treatment of cotton seeds by compositions of polyfunctional action in comparison with Sunkar-3 disinfection were provided:

– decrease damage to plants root rot and gomos on 10-16%, accordingly, the safety of plants for harvesting more than 6-9 thousand piece/ha;

– receiving additional harvest of raw cotton 2.6-4.8 c/ha;

– economic efficiency due to additional harvest was 38 700 - 71 700 tg/ha;

– increase after harvesting in soil, (mg/kg of soil): easily hydrolysable nitrogen - 1.5-2.8, easily hydrolysable nitrogen – 1.5-2.8, assimilable forms of phosphorus pentoxide were – 1.3-3.7;

– accumulation in the soil 3,6-4,8 t/ha of humus;

– increase in fiber output – 0,3-0,6%, its length – 0,2-0,3 mm, oiliness of seeds were – 1,8-4,2%.

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Резюме

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МАҚТА ЕГІСТІГІНДЕГІ ДИМЕТИЛОЛМОЧЕВИНА, МЫРЫШ ЖӘНЕ МЫС ФИТОҚОСЫЛЫСЫ НЕГІЗІНДЕ АЛЫНҒАН КӨПФУНКЦИОНАЛДЫ ӘСЕРІ БАР КОМПОЗИЦИЯНЫҢ БИОЛОГИЯЛЫҚ, АГРОХИМИЯЛЫҚ, ЭКОНОМИКАЛЫҚ ЖӘНЕ ЭКОЛОГИЯЛЫҚ ТИІМДІЛІГІ

Жұмыста мақта егістігіндегі диметилолмочевина, мыс және мырыш фитоқосылысы негізінде алынған көпфункционалды әсері бар композицияның биологиялық, агрохимиялық, экономикалық және экологиялық тиімділіктерінің нәтижелері келтірілді.

Түйін сөздер: дәрілегіш, көпфункционалды әсері бар композиция, диметилолмочевина, мыс фитоқосылысы, мырыш фитоқосылысы, мақта, өсім, кіріс, сапалық көрсеткіштер.

Резюме

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АГРОХИМИЧЕСКАЯ, ЭКОНОМИЧЕСКАЯ, ЭКОЛОГИЧЕСКАЯ ЭФФЕКТИВНОСТЬ КОМПОЗИЦИИ ПОЛИФУНКЦИОНАЛЬНОГО ДЕЙСТВИЯ НА ОСНОВЕ ДИМЕТИЛОЛМОЧЕВИНЫ, ФИТОСОЕДИНЕНИЙ МЕДИ И ЦИНКА НА ПОСЕВАХ ХЛОПЧАТНИКА

Приведены результаты исследований биологической, агрохимической, экономической и экологической эффективности композиции полифункционального действия на основе диметилолмочевины, фитосоединения меди и фитосоединения цинка на посевах хлопчатника.

Ключевые слова: протравитель, композиция полифункционального действия, диметилолмочевина, фитосоединение меди, фитосоединение цинка, хлопчатник, прибавка, доход, качественные показатели.

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INFLUENCE THE TEMPERATURE AND CONCENTRATION OF LEAD (II) ON ITS SORPTION BY ACIDOMODIFICATED ZEOLITE FROM CONCENTRATED PHOSPHORIC ACID

Abstract. The sorption of lead (II) cations from concentrated phosphoric acid (85.2 %) was studied by the acid-modified zeolite of the Shankanay deposit. The mutual influence of temperature and concentration of Pb^{2+} cations on the process of their sorption is revealed, the time has no significant effect.

The sorption curves of the dependence of the residual content of lead (II) on the temperature in phosphoric acid with a content of 10 and 55 mg/Pb have a minimum at 43 °C, corresponding to its maximum absorption. in phosphoric acid with C_{Pb} equal to 28 mg/l with increasing temperature, the sorption curves increase, and with C_{Pb} equal to 100 mg/l - decrease, respectively, the degree of sorption decreases and increases. The curves for the residual content of lead (II), depending on its concentration up to 30 °C, have a minimum at C_{Pb} of 28 mg/l, corresponding to a high degree of lead sorption (99.0-99.6 %), and in the range from 45 to 70 °C - a maximum characterizing the lower degree of Pb absorption. Moreover, the maximum on the sorption curves with increasing temperature shifts to a region of solutions less concentrated in lead content. The appearance of a maximum or minimum on the sorption curves of Pb^{2+} cations is due to the desorption process, when under the conditions under study the sorbed cations from the zeolite exit to the solution.

Keywords: heavy metals, lead cations, acid-modified zeolite, sorption, phosphoric acid.

Introduction. Studies of the adsorption properties of natural zeolites to a number of heavy metals in aqueous media have been widely performed in [1-4]. Structural features of natural zeolites determine the penetration of not only metal cations with large radii, but also molecules into the crystalline structure of natural zeolite [1, 5]. During sorption, the ions (molecules) of the sorbate migrate from the volume of the medium to the surface of each body and pass into its adsorption layer. Adsorbed ions migrate in this layer, diffuse into the body volume or are desorbed. If the interaction of sorbate molecules with each other is sufficiently strong, they are assembled into two-dimensional clusters that can expand along the surface until they come into contact with neighboring clusters [6]. Migrating along the surface, the molecules for some time are in some adsorption center, and then jump to the next center. In this case, the residence time of a molecule on the vertices, edges or steps on the faces of a single crystal can differ by a factor of tens. The difference in the residence of molecules in adsorption centers located on crystalline faces with different atomic relief is equally great. Therefore, faces with an unequal number of steps have different sorption capacity: each face is characterized by its own local adsorption coefficient and sorption capacity.

In recent years, sorption purification methods using activated zeolites have become widespread [7, 8]. The acid activation of natural zeolites is accompanied by a process of dealumination, which is caused by the unblocking of the channels of the zeolite framework, which leads to an increase in the Si/Al ratio and the formation of silanol groups, an increase in the effective size of micropores, and an increase in the capacity of zeolite exchange [9-13]. Along with the appearance of active in the sorption of H^+ exchange acid sites and the displacement of aluminum (Al^{3+}) in the exchange positions, as a result of acid activation, the arrangement of active sites is more favorable for the interaction of reacting substances. In addition, when acidizing zeolite, the liberated silica increases the specific surface area and porosity of the activated samples and removes impurities blocking the channels. The stability of the silica-alumina skeleton of high-silica zeolites to the action of acids has increased the possibilities of regulating their properties by decationizing and dealumination under various conditions of acid treatment.

A significant number of works are devoted to IR spectroscopic investigation of clinoptilolite after hydrochloric acid activation [14-19]. According to the obtained data, silanol groups Si-OH, bound by hydrogen bonds, removal of aluminum from the sorbent framework, and formation of "hydroxyl nests" associated with the formation of Al-O vacancies occur in the structure of the natural zeolite after acid treatment. In this case, an increase in the amount of loosely bound water and a decrease in water molecules involved in the formation of hydrogen bonds with silanol groups and the hydration of out-of-frame cations occur.

It has been found that acid-activated clinoptilolite tuffs exhibit high sorption properties, for example with respect to phenylalanine [20], formaldehyde [21], NH_4^+ ions [22], and SO_2 molecules [23]. Acid modification of natural zeolite allows to obtain efficient sorbents with respect to cations of heavy metals in aqueous media [24, 25]. It can be seen from the review that the applications of zeolites in various industries can be significantly expanded by modifying them. The aim of this work was to study the sorption of Pb (II) cations by the acid-modified zeolite from the Shankanay deposit from concentrated phosphoric acid.

Experimental part

Lead-containing phosphoric acid with a predetermined concentration of Pb^{2+} cations was prepared by introducing in the H_3PO_4 (85.2 %) the calculated amount of lead acetate $Pb(CH_3COO)_2 \cdot 3H_2O$ of the grade "chemical pure". As a sorbent, the zincite of the Shankanay deposit, modified with 15 % hydrochloric acid, was used. The sorption of lead (II) cations was carried out in a thermostated reactor under the conditions of mixing the sorbent (Solid) with lead-containing phosphoric acid (Liquid), taken in a ratio of S:L equal to 10:100. The initial and final concentrations of lead ions in solutions were determined on an atomic absorption spectrophotometer type AA-7000, the company "Shimadzu Corporation", Japan, No. A30664901456. The relative standard deviation of the output signal is 2 %.

Sorption was assessed by the change in the content of Pb^{2+} cations in solution, i.e. by the difference between the initial concentration and its residual concentration. The degree of sorption (extraction) is the ratio of the difference between the initial and reached the concentration of the cation Pb (II) to its original content reached at a fixed time.

The degree of purification of various media, including phosphoric acid, depends significantly on the main parameters of the sorption process (temperature, cation concentration Pb^{2+}, time). A study of the mutual influence of these technological factors on the process of purification of phosphoric acid from lead ions ((II)) with the acid-modified zeolite of the Shankanay deposit was carried out using the method of mathematical planning of the orthogonal rototable 3 factor experiment of the 2nd order [26].

Variable (input) factors of the process were: Z_2- temperature (20 -70°C); Z_3 - C concentration of cations Pb^{2+} (10-100 mg / l); Z_1 - time (5 - 60 minutes). These changes in the concentration of Pb (II) cations correspond to a possible range of their presence in acidic effluents and other contaminated solutions, as well as in thermal and extraction phosphoric acid.

The determined (output) parameter Y1 (response) was the residual content of Pb^{2+} ions in the liquid phase of the "Pb^{2+} acid acid-acid-modified zeolite" system under investigation after its purification by the sorbent.

The coordinates of the center of the plan, the variation intervals and the study levels are represented by the natural values Z_1, Z_2, Z_3 in table 1.

Table 1 – Coordinates of the center of the plan, levels of variation

Value of variables			
Coded	Natural		
	Z_1, time, min	Z_2, T°C	Z_3, mg / l Pb^{2+}
The upper level (+1)	48,9	59,9	81,8
The center of the plan is the zero level (Zi^0)	32,5	45	55
The lower level (-1)	16,1	30,1	28,2
Interval of variation along the axis (ΔZi)	16,4	14,9	26,8
Star shoulder (+1,682)	60	70	100
Star shoulder (-1.682)	5	20	10

The experimental conditions and the results obtained in table 2.

With the use of computer processing of experimental data, a regression analysis of the results was carried out. A regression equation describing the dependence of the residual lead content in an acid medium after its removal by an acid-modified zeolite on the process parameters under study was obtained by correlation analysis after elimination of insignificant coefficients.

Table 2 – Process conditions, content of Pb^{2+} sorption cations and the degree of their sorption by acid-modified zeolites in acid medium

No. of experience	The intrinsic value of experiments			Content of Pb^{2+} after sorption, mg/l	The degree of sorption (R), %
	X_1, min	X_2, °C	X_3, mg/l		
1	16,1	30,1	28,2	4,03	85,71
2	48,9	30,1	28,2	4,13	85,35
3	16,1	59,9	28,2	4,42	84,32
4	48,9	59,9	28,2	5,21	81,52
5	16,1	30,1	83,7	9,36	88,81
6	48,9	30,1	83,7	9,42	88,74
7	16,1	59,1	83,7	9,46	88,69
8	48,9	59,1	83,7	1,05	98,74
9	5	45	55	5,78	89,49
10	60	45	55	5,94	89,20
11	32,5	20	55	6,41	88,34
12	32,5	70	55	7,74	85,92
13	32,5	45	10	1,16	88,40
14	32,5	45	100	1,04	98,96
15	32,5	45	55	5,44	90,11
16	32,5	45	55	5,69	89,65
17	32,5	45	55	3,20	94,18
18	32,5	45	55	5,82	89,41
19	32,5	45	55	7,14	87,01
20	32,5	45	55	6,51	88,16

Results and discussion

After processing the obtained data and excluding the insignificant factors, the regression equation is given below, in which six coefficients are significant:

$$У=5{,}793-0{,}527X_1+0{,}493X_2+1{,}805X_3-1{,}326X_3^2-2{,}238X_2X_3 \qquad (1)$$

The adequacy of the regression equation was verified by the Fisher criterion. As a result of optimization of the calculations, it was found that the calculated value of the Fisher test is less than the tabulated value:

$$F<F_{1-p} \qquad (2)$$

namely 4.2728734016 <4,69999998, therefore, the equation adequately describes the experiment.

An analysis of the regression equation obtained showed that the temperature and concentration of Pb^{2+} ions have the greatest influence on the sorption of

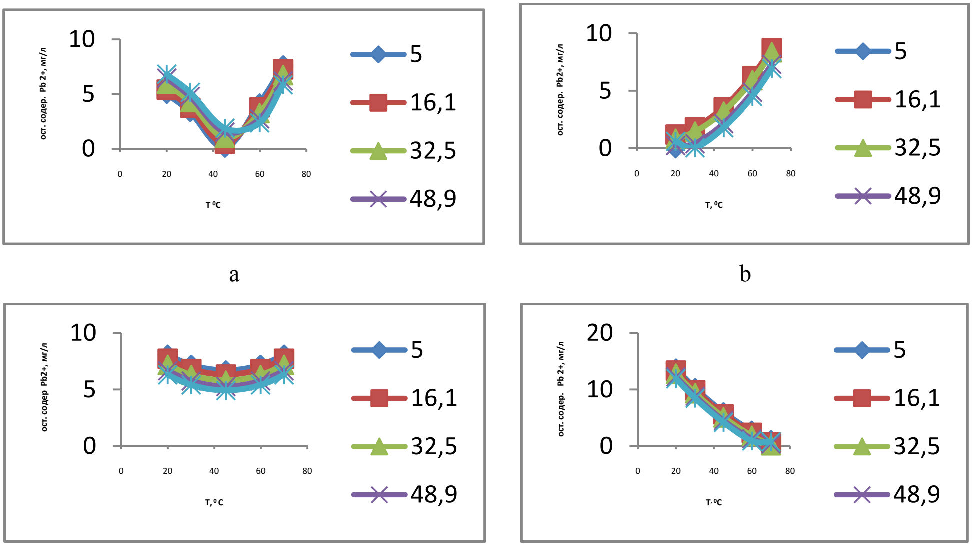
Pb (II) cations. Comparison of the coefficient values showed that the time has no significant effect on the output parameter.

As already noted, temperature has a significant effect on sorption purification processes, using both natural aluminosilicate sorbents and their modified forms as sorbents. According to the regression equation 1 describing the sorption of Pb^{2+} cations by an acid-modified zeolite in phosphoric acid, the effect of temperature on the output parameter is complex and is represented by positive linear (X_2) and double interaction of process temperature and lead cation (X_2X_3) concentration with a minus sign. In the regression equation, before the variable temperature coefficient (X_2) there is a plus sign. That is, the temperature factor affects the output parameter not only as a double interaction with the third factor (X_2X_3), but also independently, and directly proportional. A comparison of the values of the coefficients showed that the greatest influence on the output parameter is exerted by a double interaction of the process temperature and the concentration of Pb^{2+} cations. It follows from the regression equation 1 that the double interaction (X_2X_3) has a minus sign at a coefficient. That is, a decrease in the value of only one factor (either temperature or Pb concentration) can increase the purity of phosphoric acid. The simultaneous decrease or increase in the values of both factors in the regression equation when they multiply gives a plus sign and, as a result, a decrease in the degree of purification. Simultaneous decrease in the values of temperature and concentration leads to poor purification of the acid medium, and a simultaneous increase in their values may contribute to the desorption (exit) of lead ions from the sorbent solution.

The graphical dependence of the obtained dependences of the residual content of Pb^{2+} ions in the liquid phase of the "Pb^{2+} -H_3PO_4-acid-modified zeolite" system on temperature is shown in Fig. 1. It can be seen that in low- and medium-concentrated lead-containing solutions (10 and 55 mg / l Pb) cations of Pb^{2+} are extreme with a minimum at 45°C, which is most pronounced in solutions obtained with C_{Pb} equal to 10 mg/l, and corresponds to the highest degree of sorption of Pb^{2+} cations (figure 1a, c). For example, 47.5 % Pb is sorbed from an acidic solution with C_{Pb} equal to 10 mg / l at 20 ° C for 16 minutes, 99.5 % Pb at 45 ° C, 63 % Pb at 60 ° C, and Pb at 60°C, 28 % Pb. Moreover, in low-concentration solutions of lead, an increase in the duration of the process has a slight negative effect on the sorption capacity of the sorbent. That is, with decreasing phase contact time, the degree of sorption somewhat increases as the temperature decreases. Thus, 99.5 % Pb sorbed in 5 min at 45 ° C, 95 % Pb in 16 min, 91 % Pb in 32 min, 84 % Pb in 50 min and 81 % in 60 min, 3 % Pb.

In solutions with a lead content of 28 mg/l, the extreme dependence of the sorption curves on temperature is smoothed (figure 1b), i.e. As the temperature rises, the residual content of Pb (II) cations constantly increases, so the degree of sorption decreases. Thus, 95.7 % Pb is sorbed in this solution for 5-16 min at 20 ^{0}C, 94.04 % Pb at 30 ^{0}C, and 69.85 % Pb for 60 min.

In solutions with a lead concentration of 82-100 mg/l, an increase in the process temperature has a positive effect. Under the investigated conditions, the



a b

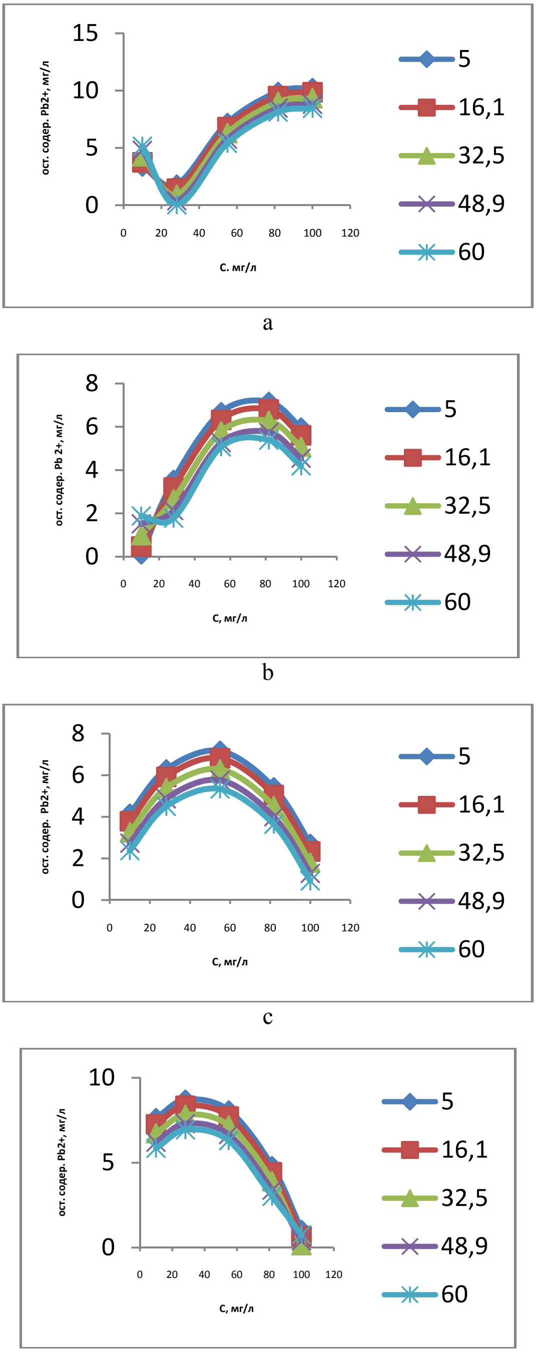
c d

Figure 1 – Effect of temperature on the residual content of Pb (II) cations in the system «Pb^{2+} - H_3PO_4 - acid-modified zeolite»: a – 10 mg/l Pb^{2+}; b – 28 mg/l Pb^{2+}; c – 55 mg/l Pb^{2+}; d – 100 mg/l Pb^{2+}

residual content of Pb^{2+} cations in the liquid phase of the system decreases with increasing temperature, and the degree of their sorption increases accordingly (figure 1d). For example, in a solution with C_{Pb} equal to 100 mg/l at 20°C and 16 min, the sorption degree of Pb^{2+} ions reaches 86.9%, at 40 ^{0}C - 94.2%, at 70 ^{0}C - 99.1 %.

The effect of the concentration of Pb^{2+} cations on its residual content in the system under study is complex and is represented in the regression equation 1 by a positive linear concentration factor of lead (X_3) and its negative quadratic term (X_3^2). In this case, the values of the coefficients of the factor under consideration are C_{Pb} (X_3) higher than in X_1 (time), which indicates a significant influence of lead concentration on the process of its sorption compared with time.

It should be taken into account that in the regression equation 1 the influence of C_{Pb} is also represented by a negative double factor of its interaction with the process temperature (X_2X_3). A comparison of the values of the X_2X_3 coefficients showed that a double interaction of the Pb^{2+} cation concentration and the process temperature has a significant effect on the output parameter. The minus sign at the coefficient of variables X_2X_3 in the regression equation shows that the simultaneous increase or decrease of the values of these factors will not lead to the purification of the acidic environment. On the contrary, a decrease in the value of one of the factors with an increase in the value of the other leads to an increase in the degree of sorption of lead. The considered interference of factors and their effect on the response is well demonstrated by the graphs below (figure 2). In the



a

b

c

d

Figure 2 – Influence of the concentration of cations of Pb (II) on its residual content in the system «Pb^{2+} - acidic medium - acid-modified zeolite»:
a – 30 °C; b – 45 °C; c – 60 °C; d – 70 °C

regression equation 1, the plus sign is used before the coefficient of variable lead concentration (X_3). That is, the concentration factor of lead (II) affects the output parameter not only in the form of negative quadratic and double interaction with the second factor (temperature), but also independently, and directly proportional. The higher the concentration of lead in solution, the more it remains after the end of the sorption process. At the same time, the value of the coefficient X_3 shows a greater effect than the influence of its quadratic factor X_3^2, but a slightly smaller effect compared to the double factor X_2X_3. That is, even in lead-concentrated solutions, the acid-modified zeolite will exhibit rather high sorption properties.

The curves of the residual content of Pb^{2+} ions as a function of their concentration over the whole time interval studied at 20-30^{0}C have a minimum in phosphoric acid with C_{Pb} equal to 28 mg/l, which corresponds to the maximum absorption of Pb^{2+} cations by acid-modified zeolite 99.0-99.9 % (figure 2 a).

The sorption curves of lead depending on its concentration at elevated temperatures from 45 to 70^{0}C are characterized by a clearly pronounced maximum, which is due to the influence of the double factor X_2X_3 (figure 2b, c, d). The sorption capacity of the acid-modified zeolite under these conditions increases slightly with the increase in the concentration of Pb^{2+} cations, and then increases. For example, the degree of sorption in a system with C_{Pb} equal to 10 mg/l reaches 90 %, with C_{Pb} equal to 40 mg/l – 86 %, C_{Pb} equal to 73.5 mg/l - 91.4 %, and with C_{Pb} equal to 100 mg/l -94.8 % at 45 ^{0}C for 16 minutes. Moreover, the maximum on the sorption curves shifts to the region of lower concentrations with increasing temperature. So the maximum is prescribed in H_3PO_4 with a concentration of 73.5 mg/l Pb^{2+} at 45 ^{0}C, with C_{Pb} equal to 52.6 mg/l Pb^{2+} at 60 ^{0}C, and with C_{Pb} equal to 31.6 mg /l Pb^{2+} at 70^{0}C. At the same time, a high degree of sorption of 99.0-99.8 % is already achieved in phosphoric acid with C_{Pb} equal to 100 mg/l. It is possible that at an elevated temperature in concentrated phosphoric acid the process of dealumination continues, which causes an increase in the sorption capacity of the acid-modified zeolite with phosphoric acid with a high content of Pb^{2+} cations. That is, in the purification of lead-containing phosphoric acid by acid-modified zeolite, the concentration of lead must be taken into account. A high degree of purification can be achieved practically in the entire investigated range of Pb (II) ion concentrations, selecting the process temperature.

It should be noted that the presence of a maximum or minimum on the sorption curves appears to be due to the saturation of the zeolite and, as a consequence, the deterioration of its sorption properties. This process, in turn, may be caused by the system's striving for equilibrium, in which the concentration of lead in both phases is equalized. That is, the appearance of a maximum on the sorption curves is due to the desorption process, when under these conditions the sorbed cations from the zeolite exit to the solution.

Thus, when choosing the optimal conditions for the purification of concentrated phosphoric acid from cations of Pb^{2+} with an acid-modified zeolite, the temperature of the process and the concentration of lead (II) cations should be taken into account first. On the basis of the studies, optimum conditions for the maximum hollow purity of a low-concentration lead (10 mg/l Pb) of phosphoric acid were found: time - 16 min, temperature – 45 ^{0}C; more concentrated in lead (28-100 mg/l Pb) of H_3PO_4, the time is 50 minutes, and the temperature is 40 ^{0}C, and in high-concentrated for lead H_3PO_4 the temperature needs to be raised to 70^{0}C.

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Резюме

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ҚЫШҚЫЛМЕН МОДИФИКАЦИЯЛАНҒАН ЦЕОЛИТ АРҚЫЛЫ КОНЦЕНТРЛІ ФОСФОР ҚЫШҚЫЛЫНАН ҚОРҒАСЫННЫҢ СОРБЦИЯЛАНУЫНА ТЕМПЕРАТУРА МЕН ҚОРҒАСЫН (II) КОНЦЕНТРАЦИЯСЫНЫҢ ӘСЕРІ

Шаңқанай кен орнының қышқылмен модификацияланған цеолиті арқылы концентрлі фосфор қышқылынан (85,2 %) қорғасын (II) катиондарын сорбциялау процесі зерттелді. Температура мен Pb^{2+} катиондары концентрациясының олардың сорбциялану процесіне өзара әсер ететіні анықталды, ал уақыт онша әсер етпейді.

Құрамында 10 және 55 мг/Pb бар фосфор қышқылындағы қорғасынның (II) қалған мөлшерінің температураға тәуелді сорбциялық қисықтарының 43°С-та минимумы бар, яғни бұл оның ең көп мөлшерде сорбцияланғанын көрсетеді. Құрамында 28 мг/л C_{Pb} бар фосфор қышқылында температура артқан сайын сорбция қисықтары жоғарылайды, ал құрамында 100 мг/л C_{Pb} бар фосфор қышқылында төмендейді, яғни сәйкесінше сорбция дәрежесі азаяды және артады. Қорғасынның (II) концентрацияға тәуелді қалған мөлшері 30 °С C_{Pb} концентрациясы 28 мг/л тең болғанда минимумы бар, ол қорғасынның жоғарғы сорбциялану дәрежесіне (99,0-99,6 %) сәйкес келеді, ал 45-тен 70 °С-қа дейінгі температура аралығында қорғасынның төменгі сорбциялану дәрежесін көрсететін максимум бар. Сорбциялық қисықтарда температура артқан сайын пайда болатын максимум қорғасын мөлшері бойынша аз концентрлі ерітінділер жаққа қарай ығысады. Pb^{2+} катиондарының сорбциялану қисықтарында максимумның немесе минимумның пайда болуы десорбциялану процесімен түсіндіріледі, яғни зерттеліп отырған жағдайларда сорбцияланған катиондардың цеолиттен қайтадан ерітіндіге өтуі орын алады.

Түйін сөздер: ауыр металдар, қорғасын катиондары, қышқылмен модификацияланған цеолит, сорбция, фосфор қышқылы.

Резюме

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ВЛИЯНИЕ ТЕМПЕРАТУРЫ И КОНЦЕНТРАЦИИ СВИНЦА (II) НА ЕГО СОРБЦИЮ КИСЛОТОМОДИФИЦИРОВАННЫМ ЦЕОЛИТОМ ИЗ КОНЦЕНТРИРОВАННОЙ ФОСФОРНОЙ КИСЛОТЫ

Исследован процесс сорбции катионов свинца (II) из концентрированной фосфорной кислоты (85,2%) кислотомодифицированным цеолитом месторождения Шанканай. Выявлено взаимовлияние температуры и концентрации катионов Pb^{2+} на процесс их сорбции, время не оказывает существенного влияния.

Сорбционные кривые зависимости остаточного содержания свинца (II) от температуры в фосфорной кислоте с содержанием 10 и 55 мг/ Pb имеют минимум при 43°С, соответствующий его максимальному поглощению. в фосфорной кислоте с C_{Pb} равной 28 мг/л с повышением температуры кривые сорбции возрастают, а с C_{Pb} равной 100 мг/л – снижаются, соответственно степень сорбции уменьшается и увеличивается. Кривые остаточного содержания свинца (II) в зависимости от его концентрации до 30°С имеют минимум при C_{Pb} равной 28 мг/л, соответствующий высокой степени сорбции свинца (99,0-99,6 %), а в области от 45 до 70°С - максимум, характеризующий более низкую степень поглощения Pb. Причем максимум на сорбционных кривых с ростом температуры смещается в область менее концентрированных по содержанию свинца растворов. Появление максимума либо минимума на кривых сорбции катионов Pb^{2+} обусловлено процессом десорбции, когда в исследуемых условиях происходит выход сорбировавшихся катионов из цеолита обратно в раствор.

Ключевые слова: тяжелые металлы, катионы свинца, кислотомодифицированный цеолит, сорбция, фосфорная кислота.

UDC 34

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EQUIVALENCE OF ENERGY AND MASS OF SUBSTENCES

Abstract. In this article the transfer of thermal energy is considered by elementary particles- "theplotrons". The equation between the mass and energy indicates their equivalence. This statement means that the mass does not become energy, and energy is a property of matter that characterizes its movement. The temperature of system is determined by "pulsation" of the " teplotron ."

Keywords: energy, mass, heat, "teplotron", temperature, "chemical individual", Gibbs's equation.

Introduction. The study of the forms of transfer of thermal energy between material objects is one of the important tasks of natural science. Historically, to explain the transfer of thermal energy, German chemists I.I. Beher and G. E. Stahl, the creators of "phlogiston theory" [1], believed that the carriers of heat are the smallest particles - "corpuscles of phlogiston." In their opinion, the "corpuscles of phlogiston" can not be detected materially, and air is an object that contributes to the release of particles of "phlogiston" from various substances and to absorb them. However, most scientists advanced the notion of heat as a movement of internal parts of bodies with a refutation of "phlogiston theory" [2]. Currently, there are various types of heat transfer, the main types of which are [3]:

- convective heat exchange between liquid or gas flows and the surface of a solid body;
- heat transfer from a hot medium (liquid, gas or solid) to the cold part of the system through the dividing partitions;
- joint heat transfer by radiation (radiant) and convection.

In all cases, the transfer of thermal energy from one material part of the system to another, differing in temperature, before the onset of thermodynamic equilibrium. There are many points of view on the mechanism of energy exchange when contacting between material objects [3-7]. And the first person who realized that the allocation of heat during the movements of contacting 0bodies is the direct result of bringing mechanical energy to the rubbing parts was B. Thompson known as the graph of Rumford [7]. But how does the transformation of mechanical energy into heat occur during friction? There is still no exhaustive answer to this question. And despite the rich accumulated material on heat, as a form of energy transfer, the mechanism of its transmission and the physical meaning of temperature-the quantitative evaluation of the degree of heating of the system-remains unclear. In this paper, an attempt was made to discover the mechanism of heat transfer between material objects based on the molecular-kinetic, thermodynamic, and quantum-mechanical theory and the quantitative criterion of the thermal state-temperature.

Discussion. Energy is an inalienable property of matter, expressing its movement and constituent elements from microscopic to macroscopic formation. Massive bodies are characterized by potential and kinetic energies, which ensure the fulfillment of mechanical work. Similarly, the elementary particles entering the microstructure of the "chemical individual" [8] in the set represent the internal energy, the change of which is transmitted in the form of heat, light, work, etc. in the system of material objects under consideration. In this case, the material characteristics of micro- and macroobjects of the surrounding world, is characterized by a rest mass or mass in motion. In [9] there is a correlation between "energy", "momentum" and mass, which are manifested in nature in two qualitatively different ways, which gives grounds for subdividing it into two varieties:

- inert mass, which characterizes the inertness of bodies in the aggregate of constituent elements of a given kind of matter under given conditions;
- the gravitational mass shows the interaction of the body with the external gravity fields, which is the basis for measuring the mass by weighing.

Despite of this, it should be noted that the material object exists in the given system with its constituent elements regardless of the measure being measured and represents the nature of this individual. Indeed, with the generally accepted choice of units, the gravitational and inertial masses of the body are equal to each other [10]. In this connection, the mass of the body expresses a physical quantity that is a measure of the inert properties of matter and at the same time a measure of its gravitational properties, i.e. it is a question of the same individual of a material object. In turn, a conceptual expression "energy" is introduced - for describing quantitative and qualitative of movement of material object with its corresponding mass ,i.e. the movement is the characteristic property of matter. The well-known equation of the interrelation between energy and mass in the form of kinetic $(\varepsilon = mv^2/2)$, potential ($\varepsilon = mgh$) energies , momentum (mv) and $\varepsilon = mc^2$ and express their equivalence. In addition, the change in the energy characteristics of material objects as a result of the physicochemical process for open systems is described by the fundamental Gibbs's equation:

$$dU = TdS - pdV + \Sigma\mu_i dn_i$$

$$dH = TdS + Vdp + \Sigma\mu_i dn_i$$

$$dA = - pdV - SdT + \Sigma\mu_i dn_i$$

$$dG = VdP - SdT + \Sigma\mu_i dn_i$$

The state functions ***U, H, A, G*** and ***S*** express energy characteristics that directly relate to a certain type and number of material objects constituting the system. And on the right side of the equation, the term - $\Sigma\mu_i dn_i$ shows the change in the energy characteristic of an open system due to a change in the amount of matter (particles, ions, etc.). According to the properties of the total differential of functions, their partial derivatives with respect to the i-th amount of a material object, with the constancy of other variables, express the corresponding types of potentials (thermochemical, electrochemical, etc.), the sum of which represents the chemical potential of the system. Consequently, the partial derivative with respect to the number of elementary particles related to thermal phenomena, with the constancy of other parameters of the system, expresses the chemical potential (μi) of thermal particles, ie:

$$\mu_i = (\partial U / \partial ni)_{S, V, nj} = (\partial H / \partial ni)_{S, p, nj} = (\partial A / \partial ni)_{T, V, nj} = (\partial G / \partial ni)_{T, p, nj}$$

It follows from these expressions that the thermal energy is transmitted by an elementary particle with a certain mass and a "thermochemical" potential μ_i. It should be noted that only in the process manifest forms of energy transfer in the form of heat, light, electricity, work, etc. In this connection, it is quite difficult to study phenomena, determine the rest masses of energy carriers, which end with the termination of the process. The question arises, in what form are the carriers of heat and light in the material object? However, this issue is beyond the scope of this article and on the accumulation of elementary energy carriers will be reported in the following publications.

In [11] we used classical laws of thermodynamics and molecular-kinetic theories to determine the mass of elementary heat carriers based on thermochemical data of hydrogen combustion with formation of water. The heat of combustion of hydrogen is **285.8 kJ/mol** and calculations show that out of this amount **114.4 kJ/mol** of heat dissipates into the environment. According to the equation $\varepsilon = mc^2$, with a loss of **114.4 kJ** of heat from the system, a loss of $\mathbf{12.7 \cdot 10^{-13}}$ **kg** of the mass of the "elementary particles" of the heat carriers is equivalent. The calculations on the calculation of the mass of elementary heat carriers have shown that this value is $\mathbf{5.15 \cdot 10^{-36}}$ **kg**, and according to the wave optics data $\mathbf{3.87 \cdot 10^{-36}}$ **kg** [11-14]. These heat carriers are called "teplotrons". The values given are determined by two different methods ($5.15 \cdot 10^{-36}$ kg and $3.87 \cdot 10^{-36}$ kg), which shows quite good agreement in the absence of purposeful experimental data. However, in [11] we showed inconsistencies in the energy values of the system of thermal chaotic motion of water molecules calculated for kinetic energy at 3173 K (**39.54kJ**) and experimentally determined thermal energy from thermochemical data (**285.8kJ)** at the same temperature (this temperature corresponds to the maximum combustion temperature of hydrogen in oxygen). The large difference in the values of the heats determined by two different traditional methods means that in addition to the thermal motions of the molecules, one should take into account the contribution to the kinetic energy of the heat carriers of the "teplotrons". Under thermal equilibrium conditions of the system, the total value of the contributions of the kinetic energy of the elementary particles of the heat carriers ($\Sigma x_i kT$) should equal the energy of the quanta of thermal radiation ($h\nu$), ie for the same particle the following equality holds:

$$\Sigma x_i kT = h\nu.$$

In contrast to the frequencies (v) in M. Planck's equations, $\varepsilon = h\nu$, in the proposed article "ν" refers to the frequency of "pulsations" of elementary particles proposed in [15]. To determine the number Σx_i, we use the spectroscopic data of IR radiation. It follows from the above formula that the temperature of the system is proportional to the frequency of the "pulsations" of the elementary particle,

$$T = h\nu / \Sigma x_i\, k = 6{,}6261 \cdot 10^{-34}\nu / (\Sigma x_i \cdot 1{,}3806 \cdot 10^{-23}) = 4{,}7994 \cdot 10^{-11} \cdot \nu / \Sigma x_i$$

where v is the frequency of the "pulsations" of the elementary particle, c-1;

The total kinetic energy of the thermal motion of an elementary particle:

$$\Sigma x_i kT = 5kT.$$

Hence, for a system in thermal equilibrium with the surrounding medium with thermal radiation, it is valid:

$$5\, kT = h\nu.$$

The left-hand side of the equation expresses the total contribution of the kinetic energy of the motion of the elementary particle to the thermal particle, and the right-hand side characterizes the thermal radiation (Planck's equation). We determine the mass of the particle with allowance for the Einstein equation from the formula $\varepsilon = mc^2$ [16]:

$$\mathbf{m = 2.189 \cdot 10^{-19} / (3 \cdot 10^{8})\ 2 = 2.432 \cdot 10^{-36}\ kg}$$

Consequently, the temperature of the system depends on the frequency of pulsations of elementary particles responsible for the thermal state, i.e.:

$$T = h\nu / \Sigma x_i\, k = 0.959 \cdot 10^{-11} \cdot \nu,$$

where $h / \Sigma x_i \cdot k = 0{,}959 \cdot 10^{-11} K{\cdot}s$ is the temperature constant of the elementary particle - the heat carrier of "teplotrons". From here we can draw a conclusion: the thermal state of the system is determined by the frequency of pulsations of elementary particles of heat carriers - "teplotrons", proportional to temperature, and the arrangement of the structural elements of the "chemical individual" is characterized by the entropy factor. The thermal state of the system is characterized by the formation of "combinations of heat sources" with the structural elements of the "chemical individual". The free concentration of "teplotrons" determines the temperature of the system.

Conclusion. The new fundamental concepts - heat transfer by "teplotrons", the possibility creating "combinations" between elementary particles, "pulsation" of micro-objects are proposed. The development of these fundamental provisions for their practical use promises a breakthrough in technologies aimed at creating new materials, saving energy and protecting the environment.

The transfer of heat by "teplotrons" indicates the equivalence of energy and mass. Energy is the characteristic value of matter and is determined by it. This statement means that the mass does not turn into energy and vice versa. If there was no material world, then there would be no question of energy. On the basis of the universal law of conservation and transformation of matter and energy, we can confidently assume that the named forms of energy transfer realized by "elementary particles", when interacting with material objects, form other kinds or combinations of the material world.

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Резюме

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ЗАТ МАССАСЫ МЕН ЭНЕРГИЯ ЭКВИВАЛЕНТТІЛІГІ

Қарастырылып отырған мақалада жылу энергиясының элемантар «жылу тасымалдағыш» бөлшектер «теплотрондар» арқылы тасымалданатындығы баяндалады. Масса және энергия арасындағы байланысты өрнектейтін теңдеу тек олардың эквиаленттілігін сипаттайды, яғни масса мен энергия өзара бір-біріне түрлене алмайды.Энергия материалдық дүниеліктің қозғалысын сипаттайтын шама. Жүйе температурасы «теплотрондардың» пішін жиілігі өзгерісімен (пульсация) анықталынады.

Түйін сөздер: энергия, масса, жылу, «теплотрон», температура, «химиялық индивид», Гиббс энергиясы.

Резюме

Б. Т. Утелбаев, Э. Н. Сулейменов, А. Б. Утелбаева

ЭКВИВАЛЕНТНОСТЬ МАССЫ И ЭНЕРГИИ ВЕЩЕСТВ

Рассматривается передача тепловой энергии элементарными частицами носителями теплоты – «теплотронами». Уравнение, показывающее взаимосвязь массы и энергии, указывает на их эквивалентность, но не равенство массы и энергии. Энергия является свойством материи, характеризующей его движение и означает невозможность взаимного превращения. Температура системы определяется «пульсацией» «теплотронов».

Ключевые слова: энергия, масса, теплота, «теплотрон», температура, «химический индивид», уравнение Гиббса.

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