S. M. Turabdzhanov[1], B. Sh. Kedelbaev[2], P. I. Kushnazarov[1],
F. M. Badritdinova[1], T. V. Ponamaryova[1], L. S. Rakhimova[1]

[1]Tashkent State Technical University named after Islam Karimov, Tashkent, Uzbekistan,
[2]M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan.
E-mail: tur_sad@mail.ru, kedelbaev@yandex.kz, latofat.2011@mail.ru,
polat.komol@mail.ru, tatyana111183@mail.ru

NEW APPROACH TO THE SYNTHESIS
OF POLYCONDENSATION ION-EXCHANGE POLYMERS
FOR WASTEWATER TREATMENT

Abstract. New ion-exchange polymers based on furfural and diphenyloxide were synthesized, followed by sulfonation for the introduction of functional groups. The mechanism and duration of the polycondensation reaction, the nature of the catalysts of the desulfurizing agents, were studied. The images of ion exchangers on a scanning electron microscope are obtained. Elemental analysis carried out as follows: a common area of the sample surface taken and elemental analysis was carried out, in the selected common site was re-conducted element analysis of the selected area. Due to the formation of a polymer matrix, diphenyloxide molecules retain oxygen atoms that play the role of a bridgehead between benzene rings, and oxygen atoms are also retained in the heterocyclic furan nucleus. In the sulfonation process, to introduce sulfo groups, sulfur atoms penetrate the interior of the polymer. The finished products also contain sorbed atoms of sodium, calcium, magnesium and copper, indicating selective, as well as selective properties of the resulting ion exchanger. Determination of the polymer composition for high-performance express analysis in spectrometer with an attachment of internal reflection. The results of study have shown that the knocked – out polymer matrixes have a three – dimensional structure and possess sorption properties due to the presence of functional groups in polymer. It was found that synthesized ion exchange polymers are suitable for the application of wastewater treatment from heavy metal ions.
Keywords: sorbent, selectivity, mechanism, porous structure, elemental analysis, sulfonating agent, catalyst, polycondensation, sorption, exchange capacity.

Introduction. There has been a number of extensive researches in the field of sorbents synthesis [1], the search for new methods of synthesis – ion exchange polymers for wastewater treatment, solutions of hydrometallurgical industries, seems to be an extremely topical problem. One of the available materials for the synthesis of new ion exchangers are furfural and diphenyloxide [2-4]. This work is devoted to the synthesis of a polymer matrix with subsequent sulfonation in order to create ionic groups, since sorbents based on it have greater mechanical, chemical and thermal strength [5-7].

The aim of the work was to develop and synthesize new ion exchangers with functional groups, which have sorption properties to non – ferrous metal ions and for wastewater treatment [8].

As a result of a number of researches conducted on the synthesis of ion – exchange polymers, which investigated their operational properties and the use in the treatment of wastewater from chemical industries, around the world, scientists have been able to obtain a number of scientific outcomes, including: a new generation of ion exchangers with a uniform granulometric composition of the ceramics (Dow Chemical Co USA, Bayer AG Germany and Purolite international Ltd, U.K) [9]; methods of obtaining ion – exchange polymers of a polycondensation type have been developed by modifying a sulfur – containing oil product with an epoxy resin. Methods for obtaining ion-exchange polymers of a polycondensation type have been developed by modifying a sulfur-containing product with a petroleum epoxy resin [10], Japanese scientists [11] describe the process of obtaining phosphorus-containing ion exchangers based on copolymers of glycidyl methacrylate and divinylbenzene in the presence of 40-160%

pore-formers, followed by phosphorylation of the copolymer with phosphoric acid. The properties of ionites (porosity, capacity for inorganic ion-selectivity) are determined and it is shown that some two and three valence ions during sorption on the obtained phosphorus-containing ion exchangers differ in the absorption coefficient from solutions containing impurity ionometals of the first group; complex-forming low-basic anion exchangers with selective properties for copper and molybdenum ions by polycondensation of furfural, benzoguanidine in the presence of polyethylenepolyamine, as well as macropor sulfocationite of polycondensation type based on furfural and diphenyloxide [12].

Methods. A 45% solution of sulfuric acid was added to a three-necked flask equipped with a reflux condenser and a mechanical stirrer with a bolt and a thermometer, and 17 g (0.1 mole) of diphenyloxide was added and, at 30-40°C furfural 14.4 g (0.15 mole). The temperature was raised to 70-80°C, and at this temperature, after 90 minutes, a gel was formed which was further transferred to a porcelain dish and placed in a drying cabinet, at first, dryed at 80-90° C, then at 100°C until it reached the air – dry state. The dried polymer was milled to a grain diameter d_g = 0.25-0.5 mm, then it was cleared from unreacted substances by washing with solutions – 5% HCl and distilled water, then with 5% solution of NaOH, and again distilled water sequentially until a neutral reaction. The finished polymer subjected to the process of sulfonation. The polymer swelled in concentrated sulfuric acid was placed in a three-neck flask with a mechanical stirrer and reflux condenser. The sulfonation was performed with 92-95% sulfuric acid, the molar ratio of polymer and acid was 1:6, at 70°C for 6 hours. To avoid deformation of the polymer matrix after sulfonation, the cooled polymer was washed with sulfuric acid, decreasing the concentration successively to 75, 50, 25 and 10% and then washed with distilled water until neutral wash water, then the resulting cation exchanger was dried at 80-90°C in a drying cabinet.

The samples of the obtained ion exchange polymers were examined on a scanning electron microscope (SEM-EVO MA 10) which zoomed 500 times, 1000 times and 3000 times. Elemental analysis on the device (Aztec Energy Advanced) (SEM/EDS). Samples mounted on the surface of the holder. Then the surface was deposited with a layer of carbon 5-20 bc. Each sample was examined for SEM element analysis as follow: a common sample surface area was taken and element analysis was performed, in the selected common site, an elemental analysis of the isolated site was re-performed.

The copper content have been determined by a chemical analysis. The synthesized product has also been investigated by the IR spectroscopy and differential-thermal analysis methods [13].

Results and discussion. Industrial polycondensation cation exchangers are mainly derived from phenols and formaldehyde. The use instead of formaldehyde furfural and together phenols of diphenyl oxide will allow us to solve cardinally the problem of increasing the thermochemical and radiation resistance and mechanical strength of ion exchanges. From this point of view, as a polymer matrix for the introduction of ionic groups. A polycondensation product of diphenyl oxide and furfural was used [14]. The choice of diphenyl oxide instead of phenols is due to the fact that: 1) the presence of aromatic nuclei and the absence of hydroxyl groups make it possible to obtain polymers with high thermochemical resistance. 2) The molecule of diphenyl oxide contains 6 mobile hydrogen atoms, which make it possible to obtain ionite with a high content active groups; 3) The presence of an oxygen bridge between the aromatic rings promotes an increase in the selectivity to ions of certain metals; 4) Diphenyloxide is relatively inexpensive and available [15, 16]. The formation of the polymer is due to the reaction of the aldehyde group of furfural with the most reactive hydrogen of diphenyloxide in the ortho- and para positions, which agrees with the data obtained from IR spectroscopic studies of the obtained polymer [17].

The absorption bands in the 1200-1600 cm^{-1} region in the cationite spectrum correspond to SO$_3$H groups. The absorption bands in the 3200-3500 cm^{-1} region correspond to stretching vibrations-COOH groups. The absorption bands in the 644 cm^{-1} region correspond to the presence of diphenyloxide groups. The absorption bands in the 1033 cm^{-1} region correspond to the 1.2.3.4-substituted benzene ring. The absence of absorption bands in the 1670 cm^{-1} region indicates that furfural reacts with diphenyloxide due to its carbonyl group. The absorption bands in the region 740. 810. 870 cm^{-1} correspond to the vibrations of the furan ring.

The study is further directed to the effects of nature and the concentration of the sulfonating agent on the properties of the cation exchanger. As sulfonating agents, chlorosulfonic acid, 5% oleum, concentrated 70% and 92% sulfuric acid were used. When chlorosulfonic acid is used, the degree of conversion corresponds to about 50%, which leads to a decrease in the exchange capacity of 0.1 N solution of caustic
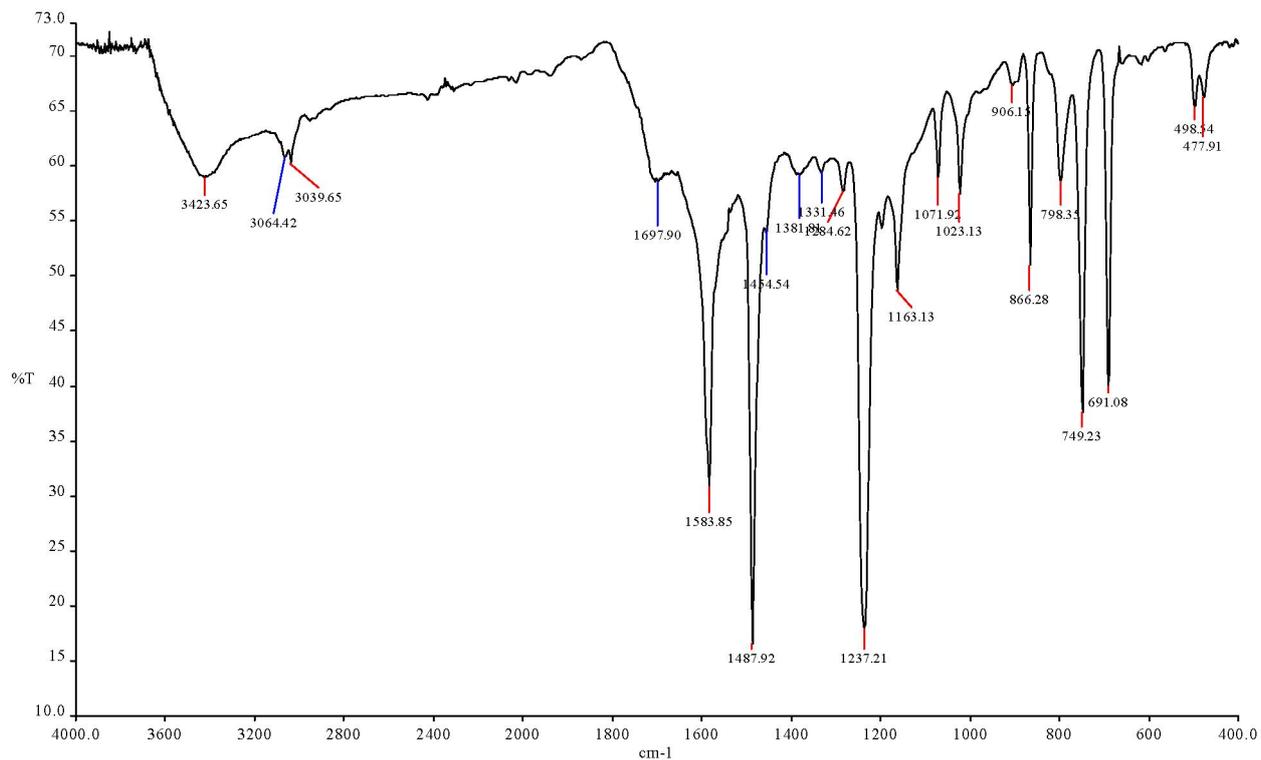
a
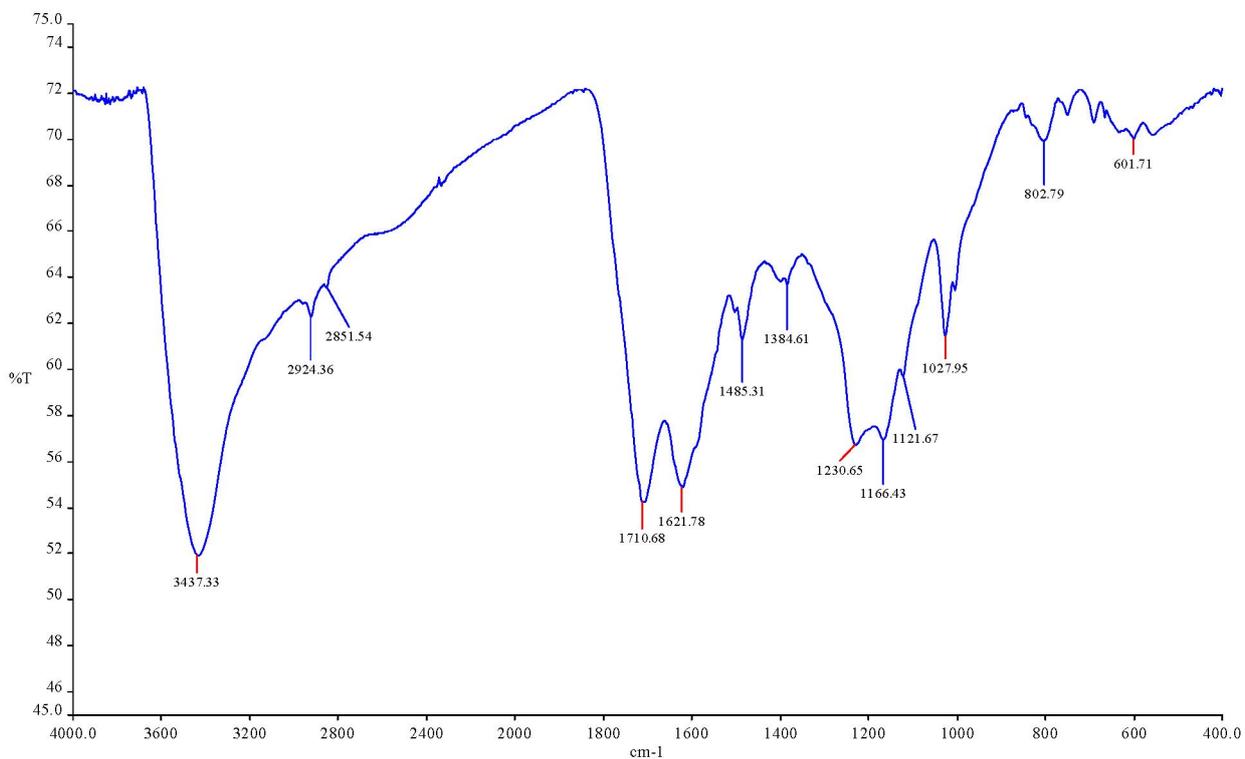
b

Figure 1 – IR spectroscopy of the obtained polymer and sulphocathionite:
a – polymer; b – sulfocathionite

soda to 3.0 mg-eq/g. In addition, the sulphonation of the ion exchanger requires saponification of the sulfochloride groups, this process is carried out with the release of hydrogen chloride as a by-product that causes corrosion of the equipment. Using 5% oleum leads to a deterioration in the mechanical strength of the ion exchanger. 92% sulfuric acid is the most acceptable as a sulphurizing agent [18].
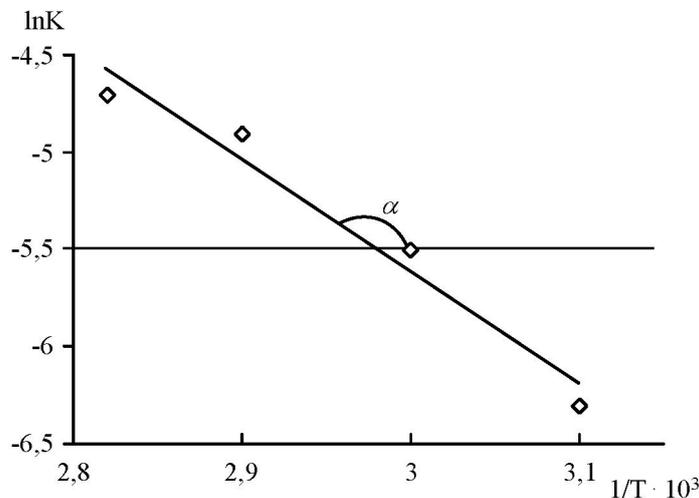

Figure 2 – Dependence of lnK from $1/T \cdot 10^3$ on the sulfonation of a polymer based on diphenyloxide and furfural

From the graphical dependence shown in figure 2 with the use of the Arrhenius equation with respect to the slope angle *tgα*, the activation energy of the chemical reaction is found:

$$k = k_0 e^{-\frac{E}{RT}}$$

where T is the absolute temperature, K; k_0 is the pre-exponential factor (pre-exponential); R is the gas constant; E is the activation energy of the reaction

$$E = tg\alpha \cdot R,$$

where R is the gas constant is 8.314. The activation energy of the cation exchanger sulfonation reaction is calculated to be $E_a = 4.306 \cdot 104$ J/mol or 19.35 kcal/mol.

The value of the activation energy indicates that the process of sulfonation of the polymer proceeds fairly easily. Thus, it can be judged that in the initial period of sulfonation (τ = 90 minutes), the polymer sulfonation reaction is characterized by a chemical reaction. As the duration of the reaction increases and the degree of conversion increases (F≥0.6), the influence of the intra-diffusion process, which is characterized by the penetration of -SO_3H groups, into the grain depth of the polymer, increases, on the sulfonation rate. The limiting stage of the sulfonation process is the diffusion of ionogenic groups in the polymer granule. On the basis of the experimental data obtained, it can be concluded that the sulfonation reaction of the resulting diphenyl-oxide furfural polymer proceeds with a sufficiently high conversion degree. The speed of the sulfonation process in the initial stage is determined by the kinetics of a purely chemical reaction, and in the final diffusion into the depth of the polymer grain. The data obtained by us agree with the literature data [19].

Until now, considering in general terms the chemical structure of polymers of different classes, we essentially talked about the structural formula of the repeating unit of the macromolecule. However, the presence of many such links in the macromolecule immediately complicates the picture. Let us start with the fact that each link in the process of an elementary act of growth of a macromolecule can join the neighboring link in different ways. In this case, chemists talk about joining "head to head", "tail to tail" or "head to tail" [20]. The chemistry of the polycondensation reaction is based on the electrophilic substitution of a hydrogen atom in para or ortho positions.
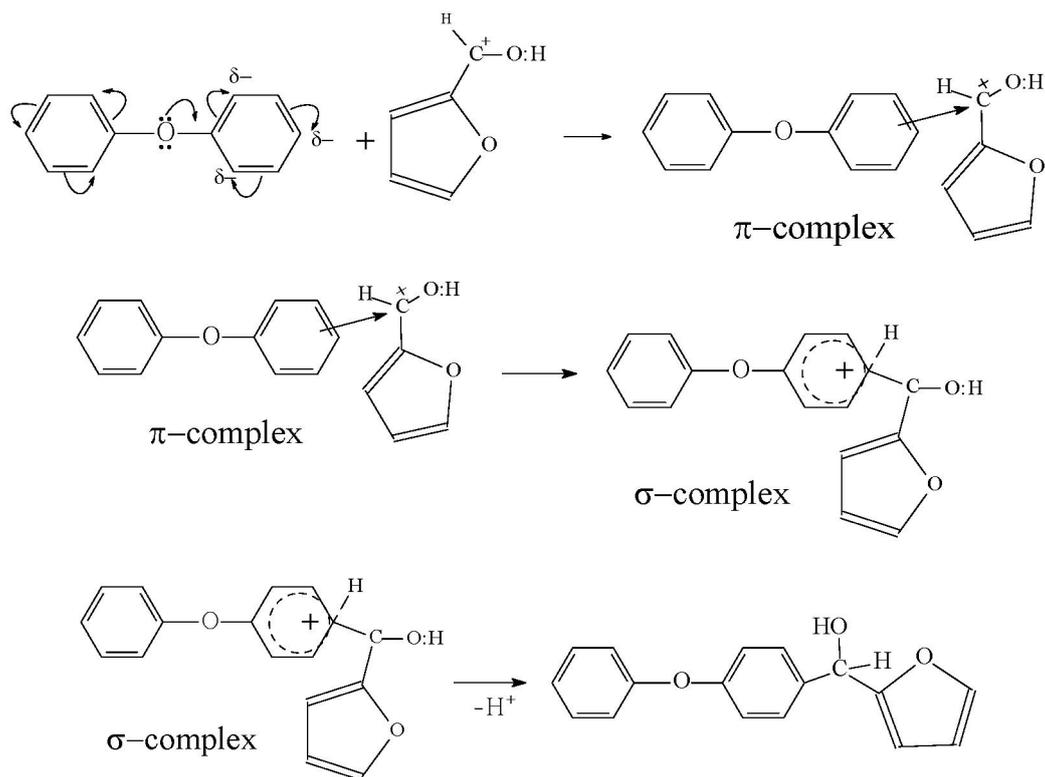
Scheme 1 – Interaction of diphenyloxide with a catalyst of sulfuric acid

As we can see from scheme 1 that when the concentrated sulfuric acid acts on diphenyloxide, the hydrogen atoms in the benzene nucleus are replaced by the sulfo group, the furfural molecules form an active center. Carbocation attacks the benzene rings of diphenyloxide, thereby forming a π-complex, which in turn turns into a σ-complex, which in its turn is transformed into σ-complex by the reduced scheme 1.

Cleavage of the proton from the σ-complex produces intermediate compounds according to scheme 2. Intermediates bind the protons of the catalyst and transform into electrophilic particles that initiate chain growth:
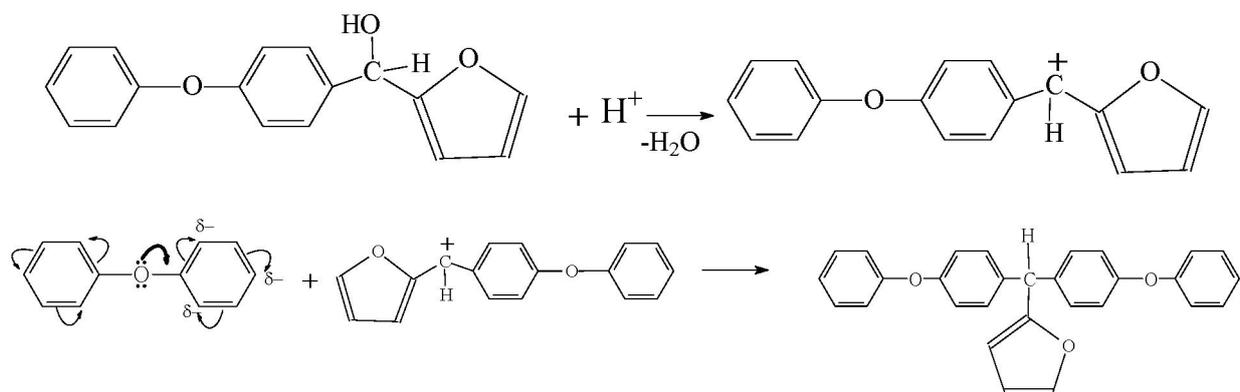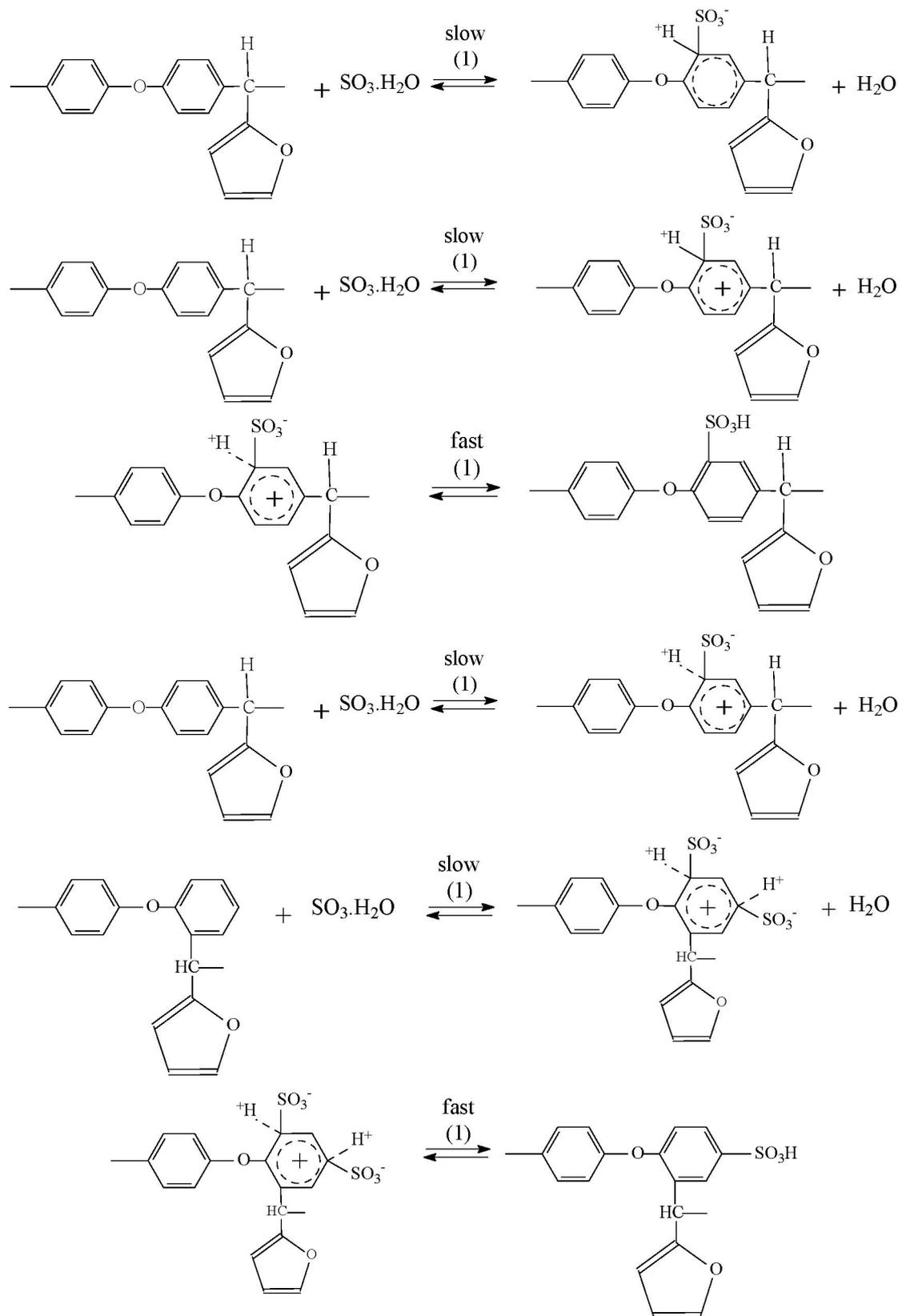
Scheme 2 – Intermediates in the polycondensation reaction

The growth of the chain occurs gradually as a result of the interaction of the molecules of monomers with the polymer formed [21]. At certain stages of production, the molecules have a branched structure, and only in the final stage of the preparation of finished products reactions can occur, resulting in the formation of a three-dimensional structure. The main factors affecting the speed and direction of the polycondensation reaction; the structure of the monomers, in particular the number of functional groups, their properties and ratio in the reaction mixture, the type of catalyst and its activity, the presence of impurities in the monomer, as well as strict adherence to the reaction technological regime (temperature, pressure, mixing degree, duration, etc.).

The process proceeds stepwise, i.e. the growth of chains occurs due to the consecutive addition of molecules to each other. Therefore, polycondensations proceed slowly than they differ from polymerization that passes quickly through the chain mechanism at low temperatures. Often during polycondensations, the primary reaction is the migration of a hydrogen atom from one molecule to another, as in the case of aldol condensations, the Perkin reaction and similar processes [22].

To determine the expected chemical structure, the ion exchange polymer obtained was subjected to elemental analysis. The results of the experiment are shown in electronic images (figure 3).
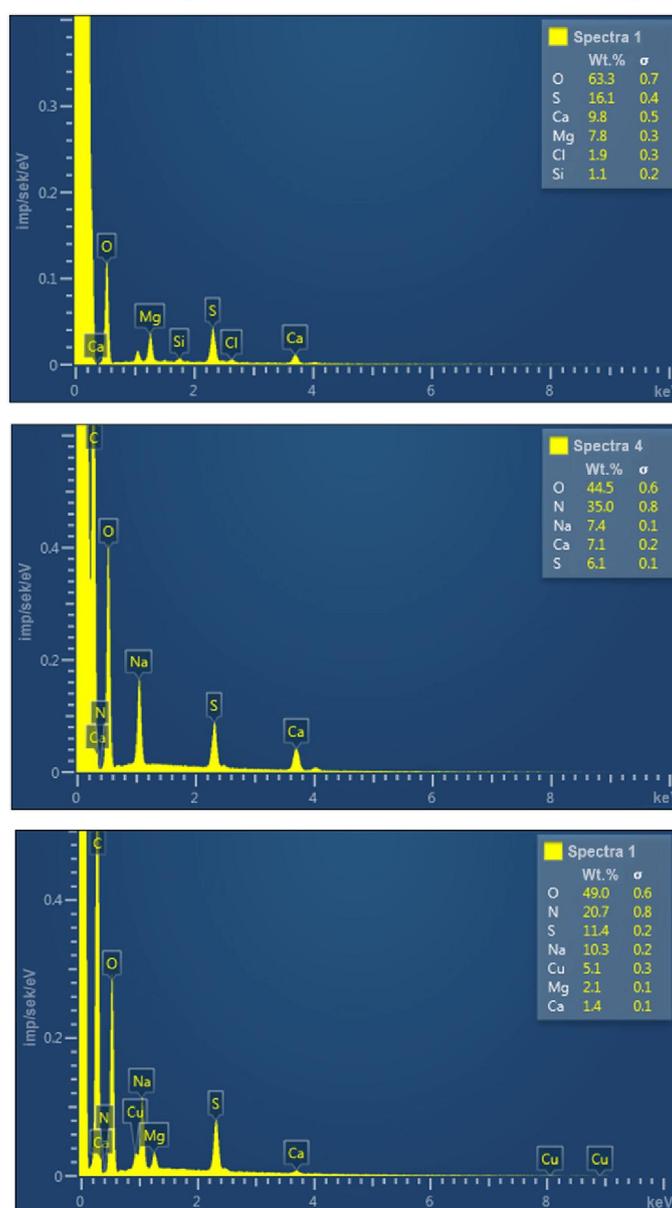

Figure 3 – Results of elemental analysis of obtained sulfocathionite

It can be seen from figure 3 that the obtained ion exchangers basically contain oxygen atoms of 63.3, 44.5, 49% by weight. This is due to the fact that in the formation of a polymer matrix, diphenyloxide molecules retain oxygen atoms that play the role of a bridgehead between benzene rings, and oxygen atoms are also retained in the heterocyclic furan nucleus. In the sulfonation process, to introduce sulfo groups, sulfur atoms penetrate the interior of the polymer (in our case, 16.1, 6.1, 11.4 wt.%). The finished products also contain sorbed atoms of sodium, calcium, magnesium and copper, indicating selective, as well as selective properties of the resulting ion exchanger [23-25]. Adverse atoms such as silicon, nitrogen, chlorine appear due to poor washing of the resulting ion exchangers or untreated starting reagents.

The high-molecular basis of ion-exchange resins, the so-called ion-exchange matrix, can differ substantially not only in chemical but also in physical structure, depending on the synthesis method [26]. Three-dimensional polycondensation leads to the production of non-porous resins, which are shown in the electronic images in figure 4.

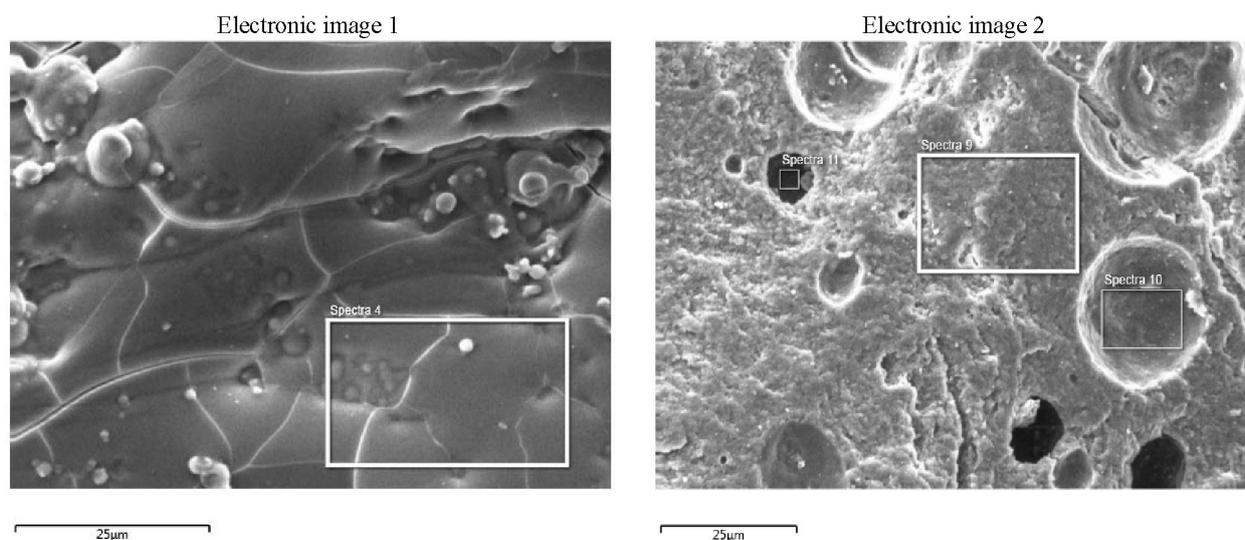Electronic image 1   Electronic image 2

Figure 4 – Electronic images of the obtained ion exchanger

It can be seen from the data in figure 4 that the obtained ion-exchange polymer is a gel structure and has micropores. Thanks to these pores, the cation exchanger sorbs ions of certain metals. The results of sorption properties and the main physicochemical parameters are given in the table.

Physico-chemical characteristics of cation exchanger based on diphenyloxide and furfural

Indicators	H-form	Na-form
Humidity, %	15	18
Bulk weight, g/ml	0.18	0.2
Specific volume, ml/g	6.3	8.2
SVC according to 0.1N solutions, mg-eqv/g		
NaCl	1.85-2.0	–
NaOH	5.7-6.0	–
CaCl$_2$	1.6-1.8	3.2-3.8
MgCl$_2$	1.4	2.2-2.4
CuSO$_4$	0.8-0.9	2.0-2.2

The granules of the obtained cation exchanger have a black color and an irregular shape. The specific volume of the swollen cation exchanger is higher in the sodium form than in the hydrate form, this causes the penetration of metal ions into the grain of the ion exchanger, which indicates the sorption properties given in the table. Our further research is aimed at a more detailed study of the sorption and physico-chemical properties of the obtained cation exchanger, with the aim of finding specific objects and their practical application for wastewater treatment from ions of heavy metals.

Conclusion. Co-polycondensation of diphenyloxide with furfural gave a new polymer that was used as a polymer matrix for introducing ionogenic groups. The data of the study, depending on the reaction temperature on the duration of the polycondensation reaction, show that the polycondensation reaction at 80°C proceeds for 65-70 minutes. Under these conditions, the reaction proceeds violently, as a result of which the synthesized cation exchanger has a low exchange capacity and swelling. Carrying out the reaction at 60°C leads to the formation of sulfocathionite with a reduced value of the exchange capacity in comparison with the cation exchanger obtained at 70°C. This, apparently, is explained by the incompleteness of the interaction of diphenyloxide with furfural. The chemistry of polycondensation reaction is based on the electrophilic substitution of a hydrogen atom in para- or ortho-positions.

The main regularities of the process of sulfonation of the polymer obtained, i.e. sulfonating agent, temperature and duration of sulfonation. It was found that the cation exchanger obtained in its structure has functional groups, which are represented in electronic images, as well as IR-spectroscopy. Using mathematical data, the rate constant of the sulfonation process and the activation energy were calculated on the basis of the data obtained. The results of modern studies have shown that the polymer matrixes obtained have a three-dimensional structure and possess sorption properties due to the presence of functional groups in the polymer.

С. М. Турабджанов[1], Б. Ш. Кеделбаев[2], П. И. Кушназаров[1], Ф. М. Бадритдинова[1], Т. В. Понамарёва[1], Л. С. Рахимова[1]

[1]Ислам Каримов атындағы Ташкент мемлекеттік техникалық университеті, Ташкент, Өзбекстан,
[2]М. О. Әуезов атындағы Оңтүстік Қазақстан мемлекеттік университеті, Шымкент, Қазақстан

ТАЗАЛАНҒАН ҚАЛДЫҚТАРДЫ ТАЗАЛАУҒА АРНАЛҒАН ПОЛЬКОНЕНЦЕНЦИЯЛЫҚ ИННОСТИЦИЯЛЫҚ ПОЛИМЕРЛЕР СИНТЕСІНЕ ҚАЛПЫНДАҒЫ ЖАҢА ОПЕРАЦИЯ

Аннотация. Жұмыста фурфурлы және дифенилоксид негізіндегі жаңа ион алмастырғыш полимерлер синтезделді, содан кейін функционалдық топтарды енгізу үшін сульфонат болды. Поликонденсация реакциясының механизмі, катализаторлар мен сульфонирленген агенттердің табиғаты зерттелді. Алынған ион алмастырғыш полимерлердің үлгілері сканерден өткізілген электрондық микроскопта зерттелді. Негізгі элементті талдау жүргізілді. Ұстағыштың бетіне орнатылған үлгілер. Содан кейін беті қалыңдығы 5-20 нм болатын көміртекті қабатымен шашылды. Элементтік талдау төмендегідей орындалды: іріктелген бетінің жалпы аумағы қабылданды және элементтік талдау жасалды, таңдалған аймақтың элементтік анализі таңдалған жалпы аймақта қайталанды. Идентификациялау үшін полимердің құрамын анықтау ИК-Фурье спектрометрінде ішкі көріністі қосу арқылы жоғары жылдамдықты жедел талдау жүргізілді. Заманауи зерттеулердің нәтижелері алынған полимерлік матрица үш өлшемді құрылымға ие және полимердегі функционалдық топтардың болуына байланысты сорбциялық қасиеттерге ие екендігін көрсетті. Синтезделген ион алмастырғыш полимерлер ауыр металл иондарынан ағынды суларды өңдеуге жарамды деп анықталған.

Түйін сөздер: сорбент, селективтілік, механизм, кеуекті құрылым, элементтік талдау, сульфонирленген агент, катализатор, поликонденсация, сорбция, айырбастау қабілеті.

С. М. Турабджанов[1], Б. Ш. Кеделбаев[2], П. И. Кушназаров[1], Ф. М. Бадритдинова[1], Т. В. Понамарёва[1], Л. С. Рахимова[1]

[1]Ташкентский государственный технический университет им. Ислама Каримова, Ташкент, Узбекистан,
[2]Южно-Казахстанский государственный университет им. М. Ауезова, Шымкент, Казахстан

НОВЫЙ ПОДХОД К СИНТЕЗУ ПОЛИКОНДЕНСАЦИОННЫХ ИОНООБМЕННЫХ ПОЛИМЕРОВ ДЛЯ ОЧИСТКИ СТОЧНЫХ ВОД

Аннотация. В работе синтезированы новые ионообменные полимеры на основе фурфурола и дифенил-оксида с последующим сульфированием для введения функциональных групп. Изучены механизм реакции поликонденсации, природы катализаторов и сульфирующих агентов. Образцы полученных ионообменных полимеров исследованы на сканирующем электронном микроскопе. Проведён элементный анализ. Образцы установлены на поверхность держателя. Затем поверхность напыляли слоем углерода толщиной 5-20 нм. Элементный анализ осуществляли следующим образом: был взят общий участок поверхности образца и проведён элементный анализ, в выбранном общем участке повторно проведён элементный анализ выделенного участка. Определение состава полимера для идентификации также был проведён высокопроизводительный экспресс-анализ в приборе ИК-Фурье спектрометр с приставкой внутреннего отражения. Результаты современных исследований показали, что полученная полимерная матрица имеет трехмерную структуру и обладает сорбционными свойствами благодаря наличию функциональных групп в полимере. Выявлено, что синтезированные ионообменные полимеры пригодны для применения очистки сточных вод от ионов тяжелых металлов.

Ключевые слова: сорбент, селективность, механизм, пористая структура, элементный анализ, сульфирующий агент, катализатор, поликонденсация, сорбция, обменная емкость.

Information about authors:

Turabdzhanov Sadritdin Maxamatdinovich, Doctor of Technical Sciences, professor, rector of Tashkent State Technical University; tur_sad@mail.ru; https://orcid.org/0000-0001-8963-5763

Kedelbayev Bakhitjan Shilmirzaevich, doct. chem. sciences, professor of the department "Chemistry" of M. Auezov South Kazakhstan State University, Shymkent, Kazakhstan; kedelbaev@yandex.kz; https://orcid.org/0000-0001-7158-1488

Kushnazarov Pulat Islamovich, PhD student, Tashkent State Technical University; polat.komol@mail.ru; https://orcid.org/0000-0002-9039-4044

Badritdinova Farida Maxamatdinovna, Candidate of technical sciences, professor-assistant of Tashkent Chemical Technological Institute; badritdinova_f@mail.ru

Ponamaryova Tatyana Vladimirovna, PhD student, Tashkent State Technical University; tatyana111183@mail.ru; https://orcid.org/0000-0002-1688-9073

Rakhimova Latofat Sobirjonovna, Doctor of Technical Sciences, assistant-professor, Tashkent State Technical University; latofat.2011@mail.ru; https://orcid.org/0000-0002-4257-0496

REFERENCES

[1] Dueck Johann, Tatayeva R., Baymanova A., Bakeshova Zh., Kapsalyamov B. (**2018**). Biological treatment of waste water: theoretical background and experimental research // News of the National Academy of Science of the Republic of Kazakhstan. Series geology and technical sciences.Vol. 6, N 432(2018). P. 16-22. https://doi.org/10.32014/2018.2518-1491.21. ISSN 2518-1491 (Online). ISSN 2224-5286 (Print) (in Eng.).

[2] Rahimova L.S., Turobzhonov S.M. (**2016**) // Chemistry and Chemical Technology [Himija i himicheskaja tehnologija]. 2:40-44 (in Rus.).

[3] Rahimova L.S., Turobzhonov S.M. (**2015**) // Uzbek Chemical Journal [Uzbekskij himicheskij zhurnal]. 2:28-31 (in Rus.)

[4] Turabdzhanov S.M., Rakhimova L.S. (**2016**). Synthesis of phosphoric acid cation-exchange polymer of polycondensation type // Austrian Journal of Technical and Natural Sciences. Issue 1-2/2016. P. 111-113. https://doi.org/10.20534/ajt-16-1.2-111-113 (in Eng.).

[5] Rakhimova L.S., Abdutalipova N.M., Nazirova R.A (**2014**). Study of «SKDF» sulphocationite thermal stability // VI International Conference of Young Scientists "Organic chemistry today". Saint Petersburg, Russia. P. 115.

[6] Rahimova L.S. (**2014**). Composite materials [Kompozicionnye materialy]. 4:28-31.

[7] Kedelbaev B.Sh., Turabdzhanov S.M. and co-authors (**2018**). Continuous hydrogenation of benzene on promoted skeletary nickel catalysts // News of the National Academy of Science of the Republic of Kazakhstan. Series geology and technical sciences. Vol. 3, N 429(2018). P. 84-87. ISSN 2518-170X (Online), ISSN 2224-5278 (Print) (in Eng.).
http://nauka-nanrk.kz/ru/assets/%D0%B6%D1%83%D1%80%D0%BD%D0%B0%D0%BB%202018%203/%D0%93%D0%B5%D0%BE%D0%BB%D0%BE%D0%B3%D0%B8%D1%8F__03_2018__%D0%93%D0%9E%D0%A2%D0%9E%D0%92.pdf

[8] Harland C.E., Franks Felix, Tyson Julian, Everett D.H., Coultate T.P., Nicholson J.W. (**1994**). Ion exchange: theory and practice, second edition // Royal Society of Chemistry, United Kingdom. ISBN 0851864848.

[9] Hradil J. (**2008**). Adsorption Properties of Polymer Adsorbents // In: Mota J.P., Lyubchik S. (eds). Recent Advances in Adsorption Processes for Environmental Protection and Security // NATO Science for Peace and Security Series C: Environmental Security. Springer, Dordrecht. ISBN 978-1-4020-6803-4.

[10] Ergozhin E.E. , Nikitina A.I. , Kabulova G.K. , Bektenov N.A. (**2012**). Crude oil and its products as feedstock for producing ion-exchange materials // Journal Petroleum Chemistry. January 2012. Vol. 52, Issue 1. P. 49 -54. https://doi.org/10.1134/s09655441111050070 (in Eng.).

[11] Jyo A., Matsufune S., Ono H., Egawa H. (**1997**). Preparation of phosphoric acid resins with large cation exchange capacities from macroreticular poly(glycidyl methacrylate-codivinylbenzene) beads and their behavior in uptake of metal ions // Appl. Polym. Sci. 1997. 63:1327-34. https://doi.org/10.1002/(sici)1097-4628(19970307)63:10%3C1327::aid-app12%3E3.0.co;2-1 (in Eng.).

[12] Rakhimova L.S., Abdutalipova N.M., Nazirova R.A., Tursunov T.T., Berdieva M. I., Mutalov Sh. A. (**2014**). Synthesis and property of new polycondensation type of ion exchanging polimer // The Advanced Science Journal Vol. 2014. Issue 7. P. 91-96. ISSN 2219–746x (Print). 2219-7478 (Online). https://doi.org/10.15550/asj.2014.07.091 (in Eng.).

[13] Dospaev M.M., Bayeshov A., Zhurinov M.Z., Zhumakanova A.S., Bayeshova A.K., Syzdykova B.B., Dospaev D.M., Kakenov K.S. (**2018**). Physical-and-chemical regularities of forming chrysocolla mineral in metasilicate solutions // News of the National Academy of Science of the Republic of Kazakhstan. Series geology and technical sciences. Vol. 5, N 431(2018). P. 84-87. ISSN 2518-170X (Online). ISSN 2224-5278 (Print). https://doi.org/10.32014/2018.2518-170X.15 (in Eng.).

[14] Rakhimova L.S., Abdutalipova N.M., Nazirova R.A., Tursunov T.T. (**2015**). Method for producing phosphorus-containing cation exchanger [Sposob poluchenija fosforsoderzhashhego kationita]. Patent of the Republic of Uzbekistan [Patent respubliki Uzbekistan] (in Rus.).

[15] Rahimova L.S., Abdutalipova N.M., Tursunov T.T., Mutalov Sh.A., Nazirova R.A. (**2012**). Composite materials [Kompozicionnye materialy]. 3:54-58 (in Rus.).

[16] Dzhandosova K.D. (**1970**). Polycondensation cationexchangers based on dyphenyloxide. Cand. Chem. sci. diss. abstr. [Polikondensacionnye kationoobmenniki na osnove difeniloksida: Avtoref. dis. ... kand. khim. nauk]. Alma-Ata, 1970. 27 p. (in Rus.).

[17] Nakanishi K. Infrared Spectra and the Structure of Organic Compounds [Russian translation]. M., 1965.

[18] Rakhimova L.S., Abdutalipova N.M., Tursunov T.T., Nazirova R.A. (**2014**). Chemistry and chemical technology [Himija i himicheskaja tehnologija]. 4:45-49.

[19] Boyd G.E., Adamson A.W., Myers L.S. (**1947**). The Exchange Adsorption of Ions from Aqueous Solutions by Organic Zeolites. III. Performance of Deep Adsorbent Beds under Non-equilibrium Conditions // J. Am. Chem. Soc. 1947. 69(11). P. 2849-2859. DOI 10.1021/ja01203a067.

[20] Tager A.A. (**2007**). The Physical Chemistry of Polymers. M.: Nauchnyi Mir. 573 p.

[21] Mukhlenov I.P., et al. (**1984**). General Chemical Technology. Vol. 2. Most Important Chemical Production. Vysshaya Shkola Publisher, Moscow. 263 p.

[22] Dolgov B.N. (**1959**). Catalysis in organic chemistry. M.: Goskhimizdat. 810 p.

[23] Turabdzhanov S.M., Tashkaraev R.A., Kedel'Baev B.Sh. (**2013**). Hydrogenation of benzene on nickel catalysts promoted by ferroalloys // Theoretical Foundations of Chemical Engineering. 2013. Vol. 47, Issue 5. P. 633-636. ISSN 0040-5795 (Print). ISSN1608-3431(Online). https://doi.org/10.1134/s0040579513050102 (in Eng.).

[24] Rahimova L.S., Abdutalipova N.M. (**2014**). Uzbek Chemical Journal [Uzbekskij himicheskij zhurnal]. 3:22-26 (in Rus.).

[25] Rahimova L.S., Mutalov Sh.A., Abdutalipova N.M., Tursunov T.T., Nazirova R.A. (**2012**). Composite materials [Kompozicionnye materialy]. 4: 4-7.

[26] Koganovskiy A.M. (**1983**). Cleaning and use of sewage in industrial water supply. M.: Chemistry. 288 p.