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Section 1. Architecture

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THE CHARACTERISTICS OF ARCHITECTURAL AND PROJECT SOLUTIONS FOR THE PRESERVATION OF ECOLOGY AND THE CREATION OF A COMFORTABLE URBAN ENVIRONMENT IN HOT AND DRY CLIMATE CONDITIONS (ON THE EXAMPLE OF THE REPUBLIC OF KARAKALPAKSTAN)

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Abstract

The article is devoted to the study of architectural design solutions aimed at preserving the environment and creating a comfortable urban environment in hot and dry climates. Using the example of the Republic of Karakalpakstan, the author analyzes the influence of climatic factors on the design of residential and public buildings, as well as on the formation of urban infrastructure. Modern approaches to the use of environmentally friendly materials, energy-efficient technologies, and natural resources to ensure the sustainability of the urban environment are considered. Particular attention is paid to issues of landscaping, water conservation, and the creation of shade in public spaces, which helps improve the quality of life in extreme temperatures.

Keywords: *ecology, urban environment, climate, architectural design solutions, urbanization, waste*

The fact that the ecological problem is complex and has a threateningly increasing relevance is being perceived more and more all over the world. Not hunger and lack of food, as Malthus claimed at the time, and environmental pollution represents a real threat to the development of mankind.

One of the features of the modern stage of social and economic development of Uzbekistan is accelerated urbanization, which has led to the fact that the number of urban residents in the country has exceeded the number of rural residents and continues to grow. The reason for this is both demographic features (high population growth and a large share of children and adolescents in the 90s and at the beginning of the "zero" years), and factors of intensive economic development of the country.

Urbanization by itself is an objective and natural process, reflecting the level of development of society and the development of scientific and technological progress has a prevailing influence on it.

The process of urbanization has a direct impact on the environment. Moreover, these problems are much more acute for large cities. For example, to ensure the water supply of a large city, it is often necessary to deliver water through powerful pipelines over large distances. For the removal and utilization of household and industrial waste, large efforts are required for their collection, transportation and processing (utilization or disposal). In big cities, there are problems with the so-called smog: if in small and medium-sized cities emissions into the atmosphere can be carried by winds of insignificant intensity, then in big cities they have a tendency to accumulate. It is no accident that in such a metropolis as Moscow, where, according to the "wind rose", the western and south-western winds prevail and emissions into the atmosphere are carried to the eastern and northeastern parts of the city, fashionable areas of residential construction are spread over the western part of the city.

The high cost of land in large cities leads to the fact that often in central areas, areas under green spaces (parks, boulevards) are sharply reduced, which also negatively affects the living conditions of citizens.

In large cities, the number of journeys and their duration per 1 inhabitant is several times higher than in settlements with a small population. Therefore, the urban transport network in large cities is the "Achilles heel". The complexity of ensuring an effective organization leads to a decrease in local traffic speed, to traffic jams, to additional pollution of the city's air, and most importantly, it has a destructive effect on all aspects of the activities of citizens.

It should be noted that one of the important factors of increasing the urgency of the urban transport problem is the mass automobileization of the population.

That is why, at present, in many countries, there is an outflow of population from megalopolises to small towns and villages. Mainly, citizens-pensioners belong to this category.

Many studies are devoted to the reduction of negative consequences of environmental pollution in cities and the provision of comfortable urban conditions. Thus, Khinkis L. L. (Khinkis L. L., 2023) suggests using the capabilities of IT technologies and forming "smart cities", which should certainly give a tangible effect.

A number of measures on this problem are envisaged and reflected in (Denisov V. V., 2010). Aksenova L. L. (Aksenova L. L., 2014) for the same purposes outlined the utilization of construction waste to obtain effective green composites.

A number of studies suggest scaling up "green construction" (Is Russia ready for the era of "green construction" 2023). There is quite a wealth of experience in green construction: (Ecological Construction: 2023).

To solve the problem under study, Certification of buildings according to LEED (**Leadership in Energy and Environmental Design** (LEED) is a voluntary certification system for buildings related to green construction, developed in 1998 by the American Green Building Council to evaluate the energy efficiency and environmental friendliness of sustainable development projects) and BREEAM (The Building Environmental Performance Assessment Method is a voluntary green building rating system developed in 1990 by the British organization BRE Global to assess the environmental performance of buildings. Wikipedia) standards is proposed (Certification of Buildings According to LEED 2023).

It is certain that the studies presented will have a positive impact on the preservation of urban ecology and the creation of a favorable urban environment. The solution to emerging environmental problems and tasks in cities located in areas with dry and hot climates, which includes almost the entire territory of Uzbekistan, has its own specifics.

The analysis of the above studies and the study of the practice of architecture and construction in Uzbekistan and, in particular, in the Republic of Karakalpakstan allow us to substantiate and state the necessity of a number of the following measures and recommendations. It should be noted that the territory of the Republic of Karakalpakstan is the epicenter of a global environmental disaster associated with the shallowing and drying up of the Aral Sea. It is here that it is

necessary to treat the environment very carefully and carefully, since additional negative impacts can have a detrimental effect on the environmental situation.

The specified measures may include design and analytical measures during participation in the development and evaluation of investment and construction projects from the standpoint of environmental safety, based on the analysis of production and economic activities of enterprises and organizations engaged in environmental protection, including waste disposal enterprises, as well as the identification of reserves for increasing production efficiency during the development of design documentation for the organization of construction.

Of course, the expansion of the use of production waste and local raw materials for the production of building materials should be considered as a positive technogenic impact of the construction industry on the environment.

Preserving the environment in cities with a sharply continental climate, especially in arid and hot regions, requires taking into account many specific factors.

Here are some of them:

1. Water management: In arid regions, water is scarce. It is important to use efficient irrigation systems, install rainwater harvesting devices and implement wastewater recycling technologies.

2. Green spaces and landscaping: Increasing green areas, creating parks and landscaping city streets can significantly improve air quality, reduce temperatures and increase the attractiveness of the urban environment. Selecting local and drought-resistant plants will contribute to the sustainability of the ecosystem.

3. Energy efficiency: In cities with a sharply continental climate, it is necessary to develop projects that take into account both heat and cold. Modern buildings should be energy efficient, use insulation, solar panels and other environmentally friendly technologies.

4. Waste management: An effective waste disposal and recycling system will help reduce the burden on the environment. This includes sorting, recycling and reducing waste, as well as developing programs to reduce the use of plastic.

5. Climate Adaptation: Climate adaptation strategies are needed to protect cities from extreme temperatures. This may include installing shade structures, covering roofs with white materials to reduce the heat effect, and projects to improve the breathability of urban spaces.

6. Education and Community Engagement:

It is important to inform the population about environmental issues and involve citizens in environmental projects. This may include programs for volunteer assistance, organized greening or cleaning of the territory.

7. Transport Infrastructure: The development of public transport and cycling infrastructure can reduce the number of cars on the streets, improving air quality and reducing noise levels.

8. Air Quality Monitoring and Management: It is important to implement air pollution monitoring systems and develop measures to improve it, including increasing green spaces and monitoring industrial emissions.

These measures can significantly contribute to the preservation of the environment in cities with a sharply continental climate, maintaining a balance between urban development and environmental sustainability.

In addition, the creation of a comfortable urban environment in dry and hot climates with a high level of groundwater (this is the case in the lower reaches of the Amu Darya) requires careful planning and implementation of various infrastructure solutions. Among them:

1. Landscape design:

– Use of drought-resistant plants and trees that require minimal watering. This will help conserve resources and create a pleasant environment;

– Creation of green spaces and gardens on roofs and terraces, which not only improves the climate, but also helps to use rainwater.

2. Water management systems:

– Design of drainage systems to remove excess moisture and prevent flooding. It is important that the drainage is hidden and does not spoil the visual appearance of the city;

– Use of bioponds and reservoirs for natural filtration and storage of rain and groundwater.

3. Pavilions and Shade:

– Creating shaded areas using canopies, arches and pergolas for public spaces. This can significantly reduce temperatures during the summer months;

– Installing water features such as fountains or waterfalls which will also help cool the air.

4. Architectural Solutions:

– Designing buildings using thermally conductive materials and technologies to create natural air flows;

– Installing highly efficient systems for air conditioning and ventilation.

5. Industrial and Transport Infrastructure:

– Designing a transport network to help reduce car use and improve air quality.

– Implementing clean transport and electric vehicles.

6. Social Spaces:

– Design of public spaces such as parks and squares taking into account the comfort and safety of residents.

Such complex measures will allow to a certain extent to create a sustainable and comfortable urban environment, taking into account the peculiarities of the climate and the level of groundwater. The difficulty lies in the fact that these measures are combined with each other and do not create a counterproductive effect when added together. The task of architects is to ensure a "friendly" combination of the above measures in order to achieve their synergy.

References

Khinkis L. L. Paradigm of ecological architecture: aspects of implementation of the smart city concept // Language. Literature. Culture. 2023. – Vol. 13. – No. 3. – P. 9–14. DOI: 10.34670/AR.2023.80.87.006

Ecology of the city: a tutorial [Text] / Ed. by prof. V. V. Denisov. – Moscow, 2010. – 768 p.

Aksenova L. L. Processing and utilization of construction waste to obtain effective green composites [Text] / L. L. Aksenova, L. V. Khlebenskikh, S. N. Khlebenskikh. // Modern trends in technical sciences: materials of the III Int. scientific conf. (Kazan, October 2014). Kazan: Buk, 2014. – P. 63–65.

How Alternative Energy Sources Help Generate Heat and Electricity [Electronic resource]. URL: https://invlab.ru/texnologii/alternativnaya-energiya/ (accessed: 03/20/2021).

Certification of Buildings According to LEED and BREEAM Standards in Russia [Electronic resource]. URL: https://btfr.cc/gik (accessed: 05/20/2023).

Ecological Construction: Western and Russian Experience [Electronic resource]. URL: https://www.rmnt.ru/story/realty/ekologicheskoe-stroitelstvo-zapadnyy-i-rossiyskiy-opyt.367711/ (accessed: 05/20/2023).

Is Russia ready for the era of "green construction" [Electronic resource]. URL: https://pronovostroy.ru/news/6329274-gotova-li-rossiia-k-epokhe-zelenogo-stroitelstva/ (date of access: 20.05.2023).

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Section 2. Chemistry

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STUDY OF THE PROCESS OF HYDROXIDE ELECTROLYSIS POTASSIUM IN A MEMBRANE LABORATORY ELECTROLYSER

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Abstract

The article discusses the dependence of the product yield on temperature and current density in the process carried out in an electrolyzer with horizontally installed electrodes in a closed flow mode. In order to prevent side processes, oxide-ruthenium titanium anodes (ORTA) are used in the installation. The article also provides factors affecting the formation of potassium hydroxide. For the experiments, potassium chloride solutions prepared from purified potash fertilizer produced at JSC "Dekhkanabad Potash Plant" natural source materials were used.

Keywords: *potassium chloride, potassium hydroxide, mineral fertilizer, electrolysis unit, ion exchange membrane, ruthenium oxide titanium anodes, free active chlorine*

Introduction

During the electrolysis of aqueous solutions of alkaline earth metal chlorides, many substances are formed, of which the most important are gaseous hydrogen and free active chlorine, as well as hydroxides and hypochlorites, chlorates, and perchlorates of these metals. And during the electrolysis of sodium and potassium melts, metallic sodium and potassium can be obtained.

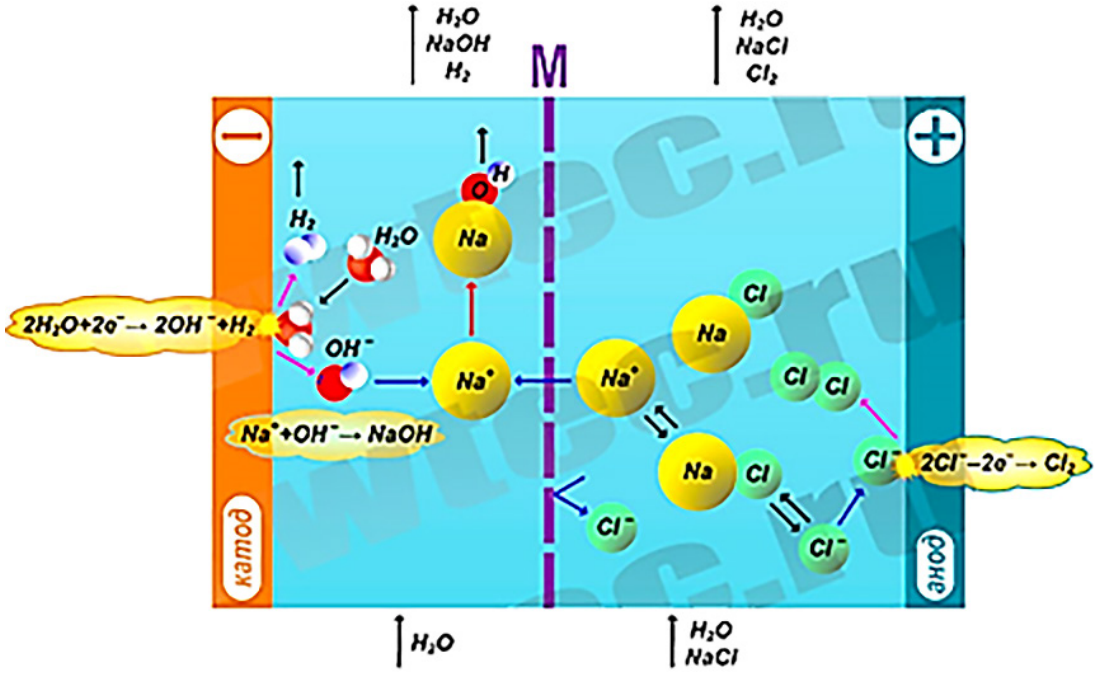
By organizing all the methods of electrolysis of these salts, it is possible to obtain the following types of chemical substances: gaseous chlorine and hydrogen, combining them and dissolving them in water – hydrochloric acid, metallic sodium and potassium, sodium and potassium hydroxides, hypochlorites, chlorates and perchlorates of both metals, a total of 13. This constitutes a significant part of the output of products of the entire chemical industry of Uzbekistan.

Uzbekistan is one of the countries where the subsoil is rich in minerals in the form of sylvinite. The mineral sylvinite mainly consists of sodium and potassium chlorides.

Caustic soda in Uzbekistan is obtained by electrolysis of an aqueous solution of table salt using a membrane method. Potassium hydroxide can be obtained from a purified aqueous solution of potassium chloride using the same method. In industrial conditions, potassium hydroxide is synthesized from an aqueous solution of potassium chloride using solid cathode, liquid mercury (mercury production method) and membrane methods in electrolysis units.

In membrane electrolysis, potassium cations, under the influence of an electric field, pass from the potassium chloride anode part of the electrolyzer through the ion-exchange membrane into the cathode hydroxide zone of the electrolyzer, where they combine with hydroxyl anions to form potassium hydroxide (Fig. 1). In this method, wastewater is returned back to the process, and a waste-free technology is created.

Figure 1. *Scheme of electrolysis of an aqueous solution of sodium chloride through a membrane*



Methods and materials

The mineral fertilizer of Dekhkanabad potash plant containing 90% potassium chloride (45% K and 45% Cl, see Table 1) and other substances was used for the study. The composition of the original mineral fertilizer was analyzed using the device "High-performance energy-dispersive X-ray fluorescence spectrometer – Japan, Rigaku NEX CG EDXRF Analyzer with Polarization in set – 9022 19000 0" (Fig. 2). The process temperature was measured using mercury glass laboratory thermometers manufactured according to GOST 215–73. The GUNT Geratebau GmbH CE – 105 unit of German manufacture was used as a DC power source. Hydrogen indicators of the obtained products were measured using a Bante 210 pH meter.

The concentration of solutions before and after the process was determined by density at 15°C and by a chemical method (Kodirov K. Y., Adilova M. Sh., Rakhmatov H. B., Erkaev A. U., 2014; Ibragimov G. I., Erkaev A. U., Yakubov R.Ya., Turobzhonov S. M., 2010; Chavlieva F. B., Kucharov B.Kh., Erkaev A. U., Turakulov B. B., Toirov Z. K., 2023; Chavlieva F. B., Turakulov B. B., Erkaev A. U., Kucharov B.Kh., Koshanova B. T., Dzhandullaeva M. S., Reimov A. M., 2023).

Results and discussion

The mineralogical composition of the raw material is given below.

Table 1. *Elemental composition of the original mineral fertilizer, %*

No.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Elements	Cl	Br	S	K	Ca	You	Fe	Cu
Result	45.0	0.058	0.34	45.0	0.5	0.0023	0.0257	0,0016
No.	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Elements	Rb	Sr	Y	Zr	Sn	Te	Fr	Dy
Result	0.009	0.0014	0.0005	0.175	0.003	0,0017	0.0074	0.0037

Figure 2. *Mineralogical composition of the raw material*

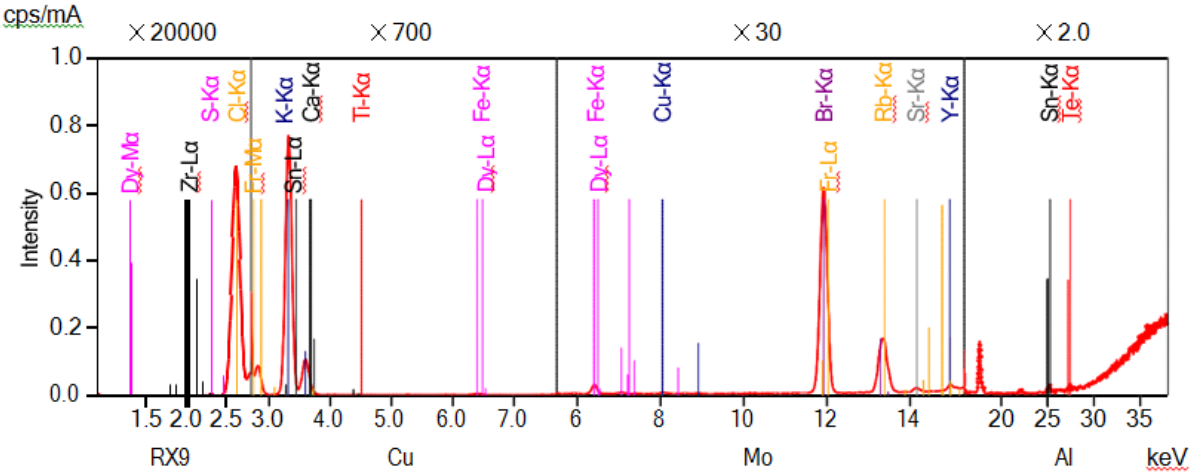
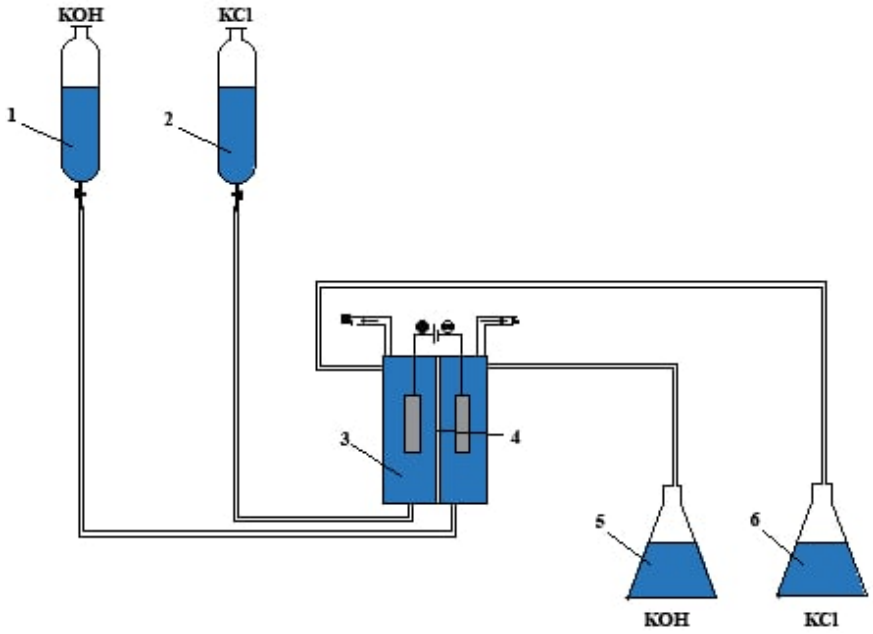


Figure 3. *Laboratory setup of the electrolyzer. 1, 2 – separatory funnels for feeding KOH and KCl respectively; 3 – electrolyzer; 4 – ion exchange membrane; 5, 6 – receiving flasks for KOH and KCl*



To conduct the research experiments, a laboratory electrolysis flow installation with an ion-exchange membrane was assembled. A sheet of stainless steel grade AISI304 (08X18H10) was used as the cathode, and a mesh ORTA anode with an area of 1 dm^2 was used for the anode. The distance between the electrodes was set at 0.16 dm. For the gravity feed of the initial solutions of potassium chloride and potassium hydroxide, two separatory

funnels with a volume of 1 liter were used and connected to the installation using a heat-resistant transparent hose and installed 50 sm above the installation. To receive the reaction products, the outlet of the installation was connected using hoses to two flasks, which were installed 50 sm below the installation.

In this paper, the influence of electrolyte temperature and operating current density on the yield of potassium hydroxide during the process in a membrane electrolyzer was studied (Fig. 3).

During electrolysis, the current density varied in the range of 1.0–5.5 A/dm^2. Electrolysis was carried out under the following conditions: at a temperature of 60˚C, a duration of 40 minutes and a potassium chloride concentration of 30%. The obtained data are presented in Table 1. The output parameter is the concentration of hydrogen ions in the anolyte and catholyte solutions. The initial concentration of the KOH solution entering the electrolyzer is 28.488%.

Table 2. *Dependence of product yield on current density with a process duration of 40 min. and a KOH concentration of 30%*

No.	Density of KOH at 15 ˚C, ρ, g/sm^3		Concentration of KOH after electrolysis, %	Current density, A/dm^2	Increase in concentration KOH, % KOH catalyte	pH of solutions after electrolysis	
	before electrolysis	after electrolysis				KOH catalyte	Anolyte KCl
1.	1.267	1.273	29.098	1	0.61	14.48	2.35
2.		1.275	29.258	2	0.77	14.43	2.35
3.		1.277	29.468	3	0.98	14.43	2.35
4.		1.278	29.588	4	1.10	14.43	2.75
5.		1.279	29.748	5	1.26	14.50	2.91
6.		1.280	29.828	5.5	1.34	14.41	3.75

To find the optimal temperature, the experiments were carried out by changing the temperature from 30 to 90˚C. The experiments were carried out for 40 minutes and with a potassium chloride concentration of 30%. The concentration of the initial KOH solution entering the electrolyzer was maintained at 28.488%. The current density during electrolysis was set at 5 A/dm^2.

Table 3. *Dependence of product yield on process temperature for a process duration of 40 minutes and a KOH concentration of 30%*

No.	Density of KOH at 15 ˚C, ρ, g/sm^3		Concentration of KOH after electrolysis, %	Process temperature ˚C	Increase in concentration KOH, % KOH catalyte	pH of solutions after electrolysis	
	before electrolysis	after electrolysis				KOH catalyte	Anolyte KCl
1.	1.267	1.273	29.488	30	1.10	14.48	2.35
2.		1.275	29.538	35	1.26	14.43	2.35
3.		1.277	29.628	40	1.34	14.43	2.35
4.		1.279	29.688	45	1.10	14.43	2.75
5.		1.280	29.748	50	1.26	14.50	2.91
6.		1.281	29.828	55	1.34	14.41	3.75
7.		1.282	29.958	60	1.44	14.45	2.85
8.		1.286	30.008	65	1.52	14.42	2.81

No.	Density of KOH at 15 °C, ρ, g/sm³		Concentration of KOH after electrolysis, %	Process temperature °C	Increase in concentration KOH, % KOH catalyte	pH of solutions after electrolysis	
	before electrolysis	after electrolysis				KOH catalyte	Anolyte KCl
9.		1.297	30.128	70	1.64	14.48	2.97
10.		1.308	30.218	75	1.73	14.45	2.87
11.		1.317	30.268	80	1.78	14.49	2.90
12.		1.328	30.348	90	1.86	14.48	2.88

Conclusion

According to the data obtained from Table No. 1, it is evident that with an increase in the process current density, the concentration of the resulting potassium hydroxide in the solution increases. The product increase is accordingly from 0.61 to 1.34% with a working current density range from 1 to 5.5 A/dm^2.

According to the data obtained from Table No. 2, it is evident that with an increase in the process temperature, the concentration of the obtained potassium hydroxide in the solution increases. The product increase is accordingly from 1.10 to 1.86% at a temperature range from 30 to 90°C.

References

Kodirov K. Y., Adilova M.Sh., Rakhmatov H. B., Erkaev A. U. Obtaining crystalline potassium chloride by the gallurgical method from the dust fraction of the flotation product of DZKU. Scientific, technical and production journal. 2014. – No. 4.

Ibragimov G. I., Erkaev A. U., Yakubov R.Ya., Turobzhonov S. M. Potassium chloride technology. 2010. – 200 p.

Chavlieva FB, Kucharov B.Kh., Erkaev AU, Turakulov BB, Toirov ZK Studying the Process of Purification of Solutions with Flotation and Hallurgical Potassium Chloride in Obtaining Potassium Hydroxide // International Journal of Advanced Research in Science, Engineering and Technology. – Vol. 10. – Issue 8, August, 2023.

Chavlieva F. B., Turakulov B. B., Erkaev A. U., Kucharov B.Kh., Koshanova B. T., Dzhandullaeva M. S., Reimov A. M. // Chemical and physicochemical characteristics of waste sulfuric acid formed during the production of caustic soda // Uzbek Chemical Journal Published since January 1957. – 6 issues per year 1. 2024. – Tashkent-2023.

Farog'at Chavliyeva*, Behzod Turakulov, Bakhrom Kucharov, Aktam Erkayev, Axmed Reyimov, Muzaffar Karshiboev, Maxamadadil Mamajonov // Study of Obtaining Potassium Hydroxide by Electrochemical Method on the Bases of Flotation and Hallurgic Potassium Chloride // Jomard Publishing New Materials, Compounds and Applications – Vol. 8. – No. 2. 2024. – P. 244–253. URL: https://doi.org/10.62476/nmca82244

Chavlieva F. B., Kucharov B.Kh., Erkaev A. U., Khamidov A. G., Turakulov B. B., Kushakov M. M. Study of the process of obtaining potassium hydroxide from potassium chloride in a membrane electrolyzer // Scientific week "Green chemistry and sustainable development". May 24–27, 2023 y. – Tashkent, Uzbekistan.

Chavlieva F. B., Turakulov B. B., Erkaev A. U., Kucharov B. Kh., Toirov Z. K., Karshiboev M. A., Mansurov T. A. Comparative analysis of electrolytic methods for producing potassium hydroxide // Collection of articles of the Republican scientific and practical conference "Prospects for the development of innovative technologies for the production of inorganic substances and materials in the context of globalization" (with the participation of foreign scientists). November, 9–10, 2023.

Chavlieva F. B., Turakulov B. B., Kucharov B. Kh., Erkaev A. U., Karshibaev M. A. Purification of initial potassium solutions for obtaining potassium hydroxide by electrochemical meth-

od // International scientific week “Sustainable Development and Green Economy”. May 20–25, 2024. – Tashkent, Uzbekistan.
Chlorine, Chlorum, Cl (17) (http://www.chem.msu.su/rus/history/element-/Cl.html). Discovery of elements and origin of their names. Chemical information network ChemNet. Date of access: January 27, 2010. Archived https://www.webcitation.org/615E8FsWx-?url=http://www.chem.m su.su/rus/history/element/Cl.html) August 20, 2011.
Myers RL the 100 Most Important Chemical Compounds: A Reference Guide. – Westport: Greenwood Press, 2007. – P. 260. – ISBN 978-0-313-33758-1.
Baldwin RT Uses of chlorine (http: //pubs. acs. org/ doi/ abs/ 10.1021/ ed00 4p 454) (English) // Journal of Chemical Education. 1927. – Vol. 4. – No. 4. – P. 454.
Sedneva T. A., Tikhomirova I. A. Electromembrane purification of potassium hydroxide solution from chloride ions // Series Critical technologies. Membranes, 2005. – No. 2 (26).
Watking I. M., McLoney D. E., Nation (R) membranes the choralkali industry // Symposium Chlorine Technology Venice. Oronzio de Nora, Milano, Italy. 1979. – 191 p.
Potassium hydroxide technical. TU GOST 9285–78. – M.: Publishing house of standards. 1984. – 23 p.
Mulder M. Introduction to membrane technology. – Moscow: Mir, 1999. – 518 p.

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FEATURES OF THE STRUCTURE OF MAGNETIC NANOPOWDERS OF IRON OXIDES IN VARIOUS METHODS OF THEIR SYNTHESIS

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Abstract

The article presents the results of obtaining iron oxide nanoparticles with magnetic properties – maghemite and magnetite, precipitated from solutions of ferrous and trivalent iron salts using various technological techniques. Depending on the deposition conditions, magnetic nanopowders corresponding to the composition of solid solutions of magnetite-maghemite were obtained. By methods of scanning electron microscopy and X-ray phase analysis, calculation of the parameters of the elementary cells of the crystal lattices of magnetite and maghemite, it is shown that the synthesis conditions affect the size and shape of nanoparticles and the degree of their aggregation. It was found that monophasic magnetite and maghemite do not form during chemical deposition, a solid solution of mixed composition precipitates.

Keywords: *iron oxides, maghemite, magnetite, chemical precipitation, nanoparticles, solid solution*

Magnetic nanoparticles of iron oxides (magnetite and maghemite) are increasingly being used in various branches of science and technology and especially in biomedical applications (Kurlandskaya, et.al, 2021; Marnautov, et.al, 2017; Wu, et.al, 2015; Corot, et.al, 2006). This is due to the unique magnetic properties of these materials, which largely depend on the phase composition, structure and morphology (size and shape) of the particles (Katz, 2019). These characteristics are significantly influenced by the conditions for obtaining nanoparticles (Chernova, et.al, 2022). To date, many methods for the synthesis of magnetic iron oxide nanoparticles are known, which are reflected in a number of scientific publications, including recent reviews (Tahir, et.al, 2021; Abilkosimova, et.al, 2024). The most technologically simple method is the joint precipitation of ferrous and trivalent iron salts from aqueous solutions (Taketomi, 1993). However, despite the apparent simplicity, the synthesis conditions by this method have a significant effect on the phase composition and morphology of particles, which ultimately affects their target properties. In

this regard, the interest in studying the factors determining the conditions for the synthesis of magnetic nanoparticles based on iron oxides is only increasing. It is known that magnetite, which has pronounced ferromagnetic properties, under oxidation passes into maghemite γ-Fe_2O_3, when heated to 230 ˚C, hematite is formed, as well as iron (III) oxide, but does not have magnetic properties (Nikiforov, et.al 2014). Since maghemite and magnetite are isostructural, the determination of the phase composition of nanoparticles is associated with the need to calculate the parameters of the crystal lattice, as well as with the involvement of a number of other physico-chemical research methods (Anthony, et.al 2018).

The aim of this work is to synthesize magnetic nanopowders of iron oxides by co-precipitation of trivalent and divalent iron salts from aqueous solutions by various methods and compare their structure and phase composition using modern analytical methods

Experimental

The salts $FeSO_4 \times 7H_2O$ and $FeCl_3 \times 6H_2O$ (pure for analysis, Sigma-Aldrich) and a 25% aqueous solution of ammonia were used in the work.

The deposition of magnetite was carried out by reaction

$$2FeCl_3 + FeSO_4 + 8NH_4OH = Fe_3O_4 + 6NH_4Cl + (NH_4)_2SO_4 + 4H_2O$$

To do this, 0.278 g. $FeSO_4 \times 7H_2O$ (1mmol) and 0.540 g. $FeCl_3 \times 6H_2O$ (2 mmol) were dissolved in 50 ml of bidistilled water at room temperature. 10 ml of 10% ammonia solution was injected into the resulting solution using a syringe. In the first variant, for the oxidation of magnetite into maghemite, precipitation was carried out under the influence of ultrasound (DSA50-SK1–1.8L. 50 W, 40 kHz) during the entire deposition process (30 min).

In the second variant, aqueous solutions of iron salts $FeSO_4$ and $FeCl_3$ were mixed, as in the first case, in the molar ratio $FeSO_4$: $FeCl_3$ = 1: 2, magnetite was precipitated with an aqueous solution of ammonia at an elevated temperature of 60 ˚C and bubbled with argon to remove dissolved oxygen and prevent oxidation and transition of magnetite to maghemite.

In the third variant, magnetite was obtained similarly to the previous variants, but neither ultrasound nor bubbling with an inert gas were used and the precipitate was kept for a day for complete maturation and partial oxidation of nanoparticles. The resulting precipitates were separated from the solution using a neodymium magnet, washed with distilled water and dried at 105 ˚C in a drying cabinet. Research methods. The phase composition and crystal structure of the powders were studied by powder radiography using the XRD-7000 MAXima diffractometer (Shimadzu). The lattice parameters were calculated using PDW in software. The particle size and degree of aggregation were evaluated using scanning electron microscopy (SEM).

As can be seen from (Fig. 1), in all three variants of synthesis (methods 1–3), nanoparticles are formed, the size of which does not exceed 20–30 nm. The resulting nanoparticles are prone to aggregation, which can be explained by residual magnetization. It can also be noted that the formation of spherical particles is observed under ultrasonic influence.

Figure 1. *SEM images of magnetic nanopowders obtained by chemical deposition using various techniques: method 1 – ultrasound, room temperature; method 2 – bubbling with inert gas, 60 °C; method 3 – room temperature, maturation during the day*

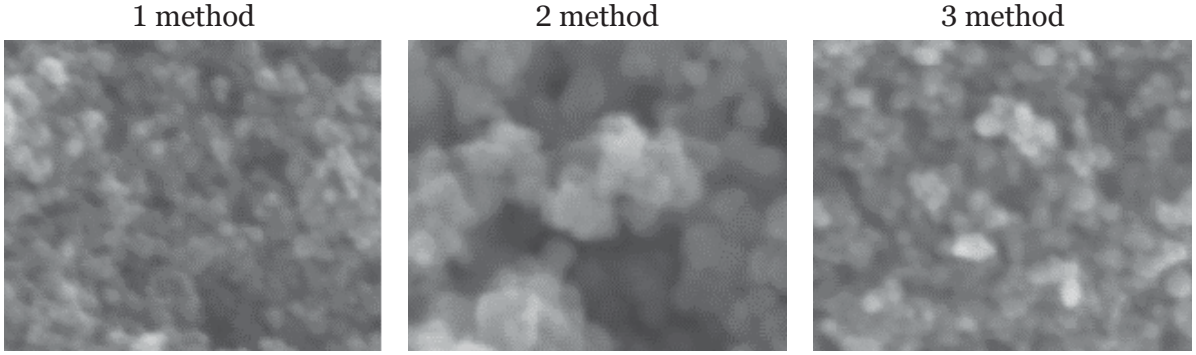
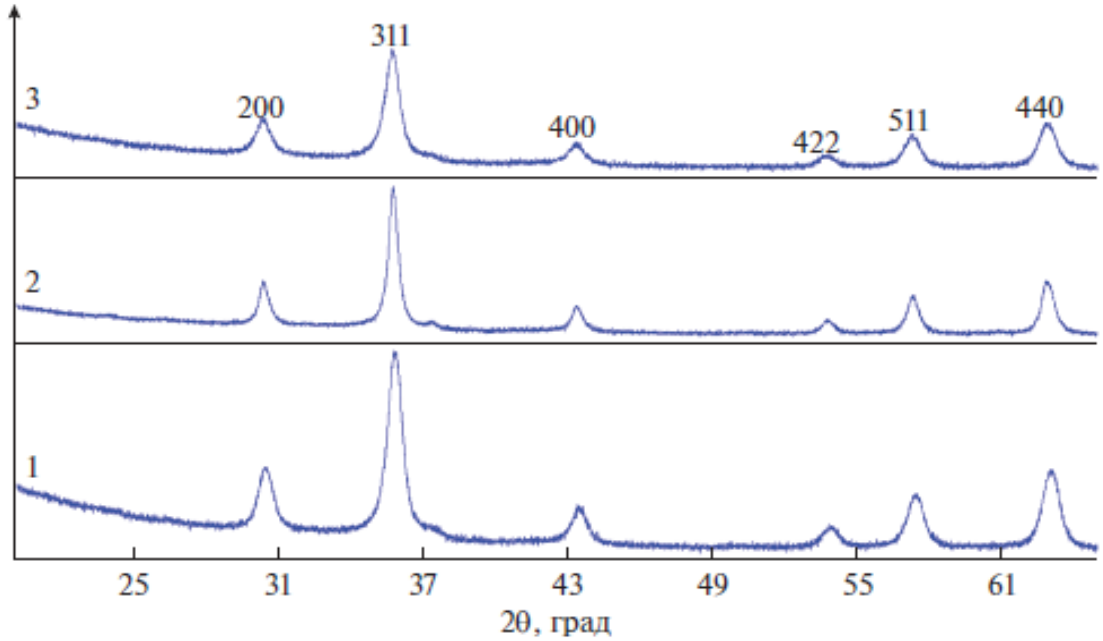


Figure 2. Shows X-ray images of the obtained iron oxide nanopowders

Figre 2. *X-ray images of magnetic nanopowders of iron oxides obtained by methods 1, 2and 3*



It follows from Figure 2 that all sediments correspond to the composition of magnetite-maghemite without significant impurities of any other phase. It is known that maghemite and magnetite have a common crystal lattice structure, which means that the positions of the diffraction peaks on their radiographs practically coincide. Therefore, based only on the analysis of the position of the peaks on the diffractograms of nanopowders, it is quite difficult to distinguish magnetite from maghemite. They can be distinguished by comparing the parameters of the unit cell.

Table 1 shows calculations of the parameters of the elementary cells of synthesized iron oxides, made on the basis of experimental and literary data.

Table 1. *Parameters of the elementary cells of the obtained nanopowders*

Title	*a*, A
Maghemite (Katz.2019)	8.336–8.339
Magnetite (Nasrazadani,1993)	8.396–8.397
Nanopowder synthesized	
by method 1	8.337
by method 2	8.350
by method 3	8.382

The results of the experiment and the calculations performed show that the nanopowder synthesized by method 1 under ultrasonic exposure, which possibly contributes to the oxidation of Fe(II) to Fe(III), is the closest in phase composition to maghemite (γ-Fe_2O_3). Elevated temperature and argon bubbling (method 2) contribute to the formation of trivalent iron oxide, while argon bubbling slowed down this process. The powder synthesized by method 3 is closer in size of the unit cell parameter to magnetite than the above samples. Obviously, exposure to mother liquor during the day has less effect on the oxidation of iron to a trivalent state.

The obtained results and conclusions are in good agreement with the results of the study by other authors (Shilova, et.al, 2020).

Conclusion

Nanopowders with a nanoparticle size in the range of ~10–25 nm were synthesized by chemical precipitation from aqueous solutions of iron (II, III) salts, corresponding to the compositions of magnetite-maghemite solid solutions, while the proximity of the resulting composition to the extreme members of a number of solid solutions depends on the synthesis conditions (ultrasound, bubbling, heating, duration of exposure in mother li-

quor). It is shown that the use of heating, bubbling with an inert gas, and especially ultrasonic exposure during the deposition of powders with an aqueous solution of ammonia promotes the formation of spherical nanoparticles and intensifies the oxidation of Fe(II) to Fe(III) and the formation of a solid solution, which is closer in composition to maghemite. It is noted that a longer maturation of the precipitate in the mother liquor increases the tendency of nanoparticles to aggregate, leading to the formation of nanoparticles that correspond to the composition of the solid solution, closer to magnetite.

References

Abilkosimova, G.M., Aronbaev, D.M., Aronbaev, S.D. (2024). Magnetic nanoparticles: production, stabilization, application. *Universum: Chemistry and Biology*: *electron. scientific Journal,* – 5(119) // doi – 10.32743/UniChem.2024.118.4.17194.

Anthony, J.W., Bideaux, R.A., Bladh, K.W. (2018). *Magnetite*. Handbook of Mineralogy. Chantilly, VA: Mineralogical Society of America, – 333 p.

Chernova, E., Botvin, V., Galstenkova, M., Mukhortova, M., Wagner, D., et.al. (2022). A Comprehensive Study of Synthesis and Analysis of Anisotropic Iron Oxide and Oxyhydroxide Nanoparticles. *Nanomaterials*. – 12. – 4321 p. URL: https:// doi.org/10.3390/nano12234321.

Corot, C., Robert, P., Idée, J.M., Port, M. (2006). Recent advances in iron oxide nanocrystal technology for medical imaging. *Adv. Drug Deliv. Rev*. – 58. – P. 1471–1504.

Katz, E. (2019). Synthesis, Properties and Applications of Magnetic Nanoparticles and Nanowires – A Brief Introduction. *Magnetochemistry* – 5: 61.

Kurlandskaya, G.V., Safronov, A.P., Shcherbinin, S.V., Beketov, I.V., et.al. (2021). Magnetic nanoparticles obtained by electrophysical methods: focus on biomedical applications. *Physics of the Solid State*. – 63, (9). – P. 1290–1305.

Marnautov, N.A., Komissarova, L.Kh., Tatikolov, A.S., Larkina, E.A., Elfimov, A.B., Vasilkov, O.O. (2017). Working out the optimal method to obtain chemical-and-size homogenous magnetite nanoparticles for biomedical purposes *Uspekhi sovremennogo estestvoznaniya*. – 6. – P. 23–27.

Nasrazadani, S., Raman, A. (1993). The application of infrared spectroscopy to the study of rust systems – II. Study of cation deficiency in magnetite (Fe_3O_4) produced during its transformation to maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3). *Corros. Sci.*, – 34. – 1355 p.

Nikiforov, V.N., Goldt, A.E., Gudilin, E.A., Sredin, V.G., Irkhin V.Yu. (2014). Magnetic properties of maghemite nanoparticles. *Izvestiya RAS. Physical Series*, – 78. – (10). – P. 1330–1335.

Pecharroman, C., Gonzalez-Carreno, T., Iglesias, J.E. (1995). The infrared dielectric properties of maghemite, γ-Fe_2O_3, from reflectance measurement on pressed powders. *Phys. Chem. Miner*. – 22: 21.

Shilova, O.A., Nikolaeva, A.M., Kovalenkoa, A.S., Sinelnikov, A.A., Kopitsa, G.P., Baranchikov, A.E. (2020). Synthesis of magnetic nanopowders of iron oxide – magnetite and maghemite. *Journal of Inorganic Chemistry*. – 65 (3). – P. 398–402.

Tahir, N., Yasmin, A., Noreen, S., Noor, T. (2021). Magnetic nanoparticles: synthesis, surface functionalization, and applications. *Journal of Nanoparticle Research*. – 23(2). – P. 1–25. URL: https://doi.org/10.1007/s11051-021-05297-9

Taketomi, S., Chikazumi, S. (1993). *Magnetic fluids*. – Moscow: Mir: – 272 p.

Wu, Z., Yu, T., Jiang, C., Kim, W.S. (2015). Recent progress on magnetic iron oxide nanoparticles: Synthesis, surface functional strategies and biomedical applications. *Sci. Technol. Adv. Mater*. – 16. – 23501 p.

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STUDY OF BIOLOGICAL ACTIVITY OF BIOMATERIAL BASED ON STRUCTURED FIBROIN

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Abstract

The article presents information on the significance, hemostatic and biological activity of fibroin-based drugs. The study examined samples of hemostatic biomaterial obtained on the basis of carboxymethylinulin and fibroin, depending on the amount of polymer components of carboxymethylinulin and fibroin. It was found that the carboxymethylinulin/fibroin sample at a mass ratio of 1:0.5 exhibits high hemostatic activity and complete resorption occurs within 21 days.

Keywords: *carboxymethylinulin, fibroin, biomaterial, biological activity, hemostatic, resorption*

Introduction

In recent years, the attention of researchers has been drawn to the creation of medical products based on silk fibroin, the determination of their physical and chemical properties and biological activity. This is due to the convenience of developing a biomaterial based on it and the possibility of obtaining various forms of the drug. Research is mainly aimed at creating wound healing and hemostatic agents. The reason for this is that the hemostatic stage is the first stage of wound treatment, and rapid hemostasis prevents major blood loss and potential death. The manifestation of the hemostatic activity of fibroin occurs through two main mechanisms:

– firstly, in the bleeding zone, as a result of its swelling, fibroins surround the surface layer and hemostasis is observed with the formation of a septum. For example, a sponge was obtained by freeze-drying from a composition of silk fibroin and polyethylene glycol (PEG, 1500 Da). In an experiment conducted on a rabbit liver injury model, it was found that in the process of interaction with blood, the sponge turns into a gel and is mechanically blocked in the areas of bleeding (Wei W., Liu J., Peng Z., et al., 2020).

– secondly, silk fibroin directly affects the blood clotting process by activating clotting factors or platelets, thereby stimulating platelet adhesion and aggregation, facilitating the

interaction between platelets and fibrinogen (Chouhan D., Mandal B. B., 2020).

Studies to determine the effect of fibroin on coagulation time were conducted in comparison with platelet-free plasma and platelet-rich plasma. Based on the results of in-depth analysis, it was noted that fibroin activates the platelet-mediated coagulation cascade (Kundu B., Schlimp C. J., Nurnberger S., Redl H., Kundu S. C., 2014). In addition, the ability of fibroin to quickly bind to fibrinogen and platelets was revealed, which stimulates the coagulation cascade and facilitates the hemostasis process (Dahlke H., Dociu N., Thurau K., 1980).

Kukun shaklidagi biomaterial yopishqoq xususiyatga ega bo'lsa va suyuqlik ta'sirida bo'kuvchanligi yuqori bo'lsa, o'ziga suv molekulalarini singdirishi orqali hajmining oshishiga olib keladi. Natijada qon oqayotga sohada to'siq hosil qilib, qon ivish omillarini to'playdi. Ushbu xususiyat ayniqsa tolasimon tuzilishli gemostatik kukunlarda yaqqol kuzatiladi (Babiuc R. D., Purcarea M., Sadagurschi R., Negreanu L., 2013; Wang X. X., Liu Q., Sui J. X., Ramakrishna S., Yu M., Zhou Y., Jiang X. Y., Long Y. Z. 2019; Barkun A. N., Moosavi S., Martel M., 2013).

If the biomaterial in the form of a powder has viscous properties and has a high swelling under the influence of liquid, it increases its volume by absorbing water molecules. As a result, this creates an obstacle in the area of blood flow and accumulates factors of blood coagulation. This feature is particularly pronounced in the fibrous structure of hemostatic powders (Babiuc R. D., Purcarea M., Sadagurschi R., Negreanu L., 2013; Wang X. X., Liu Q., Sui J. X., Ramakrishna S., Yu M., Zhou Y., Jiang X. Y., Long Y. Z., 2019; Barkun A. N., Moosavi S., Martel M., 2013).

In our study, we set the task of determining the degree of swelling of biomaterial samples in the form of powder obtained from polymer compositions of fiproin and carboxymethylinulin (CMI), as well as studying the activity in stopping blood and the dependence of the absorption time in the body on the mass ratio of the polymer components.

The object and methods of research. In the study, biomaterial samples in the form of a powder obtained on the basis of CMI/fibroin compositions in mass ratios of 1:0.25; 1:0.5; 1:0.75 and 1:1 were used.

Determining the degree of swelling. The swelling degree of the samples was determined using the following formula:

$$A = (m - m_0)100/m_0$$

Here: A – swelling degree, %;

m – the mass of the powder soaked in water, g.

m_0 – the mass of the original dry powder, g.

Microscopic analysis. Microscopic examination was performed using the LEICA ICC50 optical microscope (Germany). For this purpose, a small amount of test powders (at least 5 mg) was placed on a microscope bottle. The microscope was then mounted on a stand, adjusted the focus of the microscope until a clear image was obtained, and photographed using a digital camera.

Determining hemostatic activity. The studies were conducted on non-pedigreed white rats weighing 200–210 grams. The rats were anesthetized by introducing etaminal sodium into the abdominal cavity at a dose of 50 mg/kg. The abdominal cavity was opened using a surgical instrument (scalpel). The abdominal cavity is incised longitudinally along the white line of the abdomen and opened with a wide incision using special instruments. The intestines are pushed out and bounded with a special napkin or paper. The anterior surface of the liver was also removed. The liver protrusion was resected with a knife using a special device – a limiter (plastic material with a round hole in the center). A segment cut in a vertical projection looks like a circle or ellipsis, its dimensions are constant. The formation of an evenly bleeding wound with soft edges and uniform curvature has a total area of about 1–1.5 cm^2 and a depth of about 0.3 cm. The aforementioned experiment was conducted simultaneously to conduct a comparative assessment of the tested powder and the control (using gauze). The time of hemostasis was determined using a stopwatch.

Determining biosolvability. The biosolvability of biomaterial samples in powder form was studied in white non-pedigreed rats weighing 180±10 g. In the experiments, 24 rats were divided into 4 groups. In the experiments, a «pocket» was formed in the lumbar region of the rats and placed in an amount of 0.2 g (with an accuracy of 0.001 g) of the test-

ed powder samples. After the operation was completed, the skin was closed, 1–2 sutures were sutured and cleaned in a 5% alcohol iodine solution. To determine the biosolvability of the samples under the skin, the amount of powder was taken from the skin and monitored for 7, 14, 21, and 28 days.

Results and their discussion

When obtaining all types of hemostatic agents, it is important to study the degree of swelling under the influence of liquid. Especially for hemostatic agents in powder form. The high fluid retention capacity of the biomaterial not only increases its hemostatic properties, but also ensures faster absorption by the body. Taking this into account, in our experiments: 1:0.25; 1:0.5; We determined the swelling degree in water of powdered biomaterial samples obtained based on compositions of CMI/fibroin in a mass ratio of 1:0.75 and 1:1 (Fig. 1). The experiments were conducted in room conditions and until the samples swelled in water and became a thick gel.

Figure 1. *The degree of swelling of biomaterial samples in powder form*

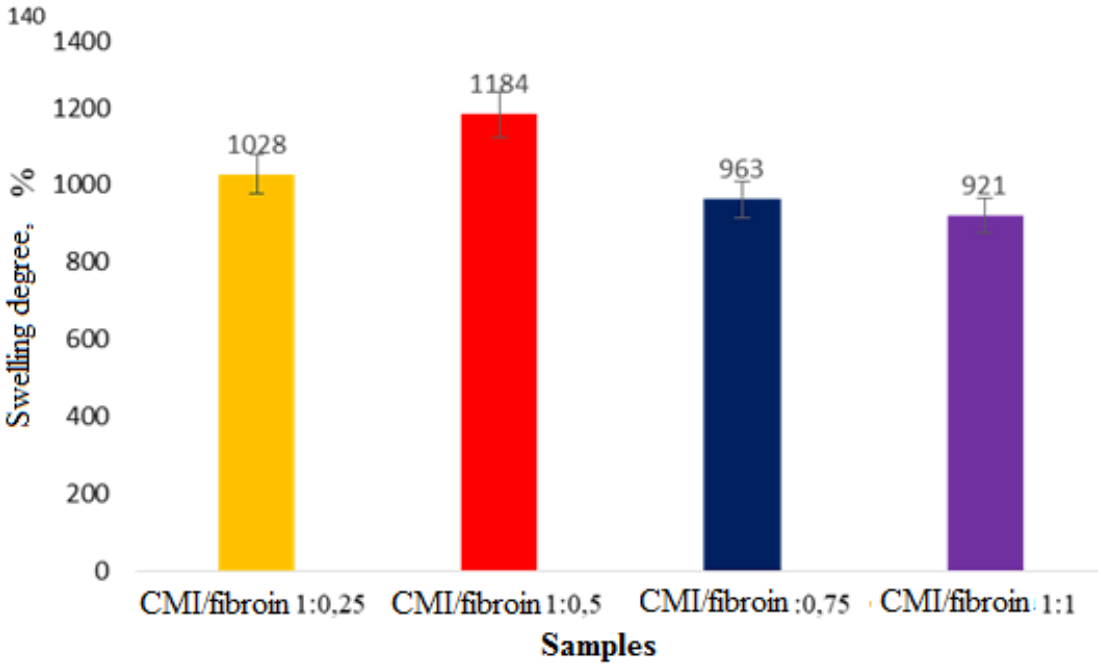


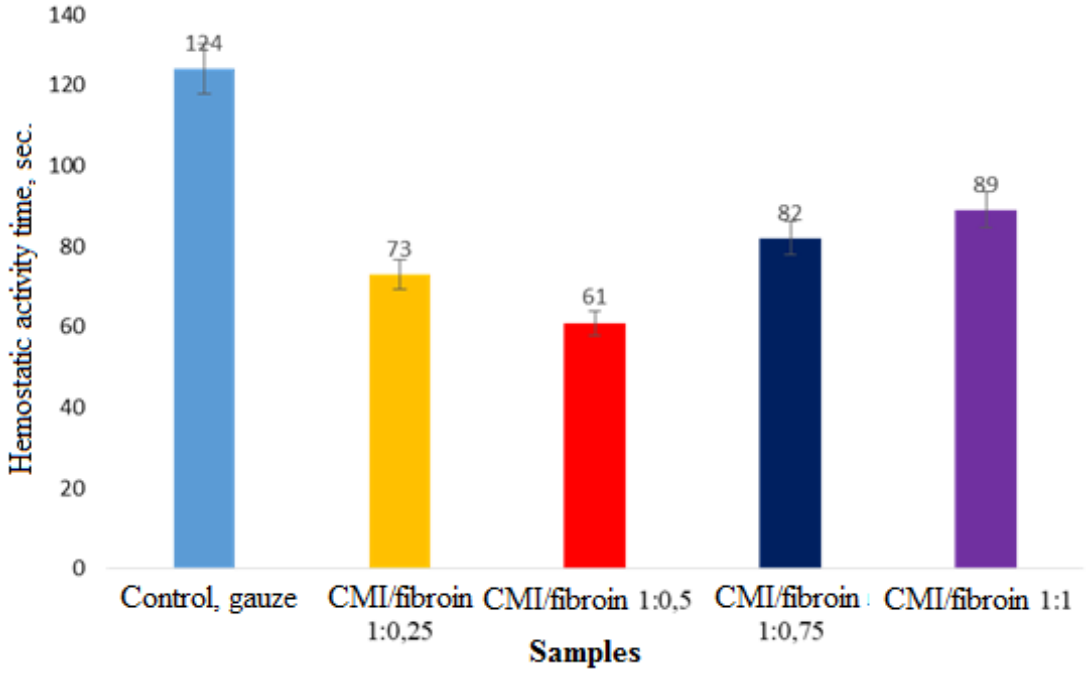
Figure 2. Biomaterial in a mass ratio of CMI/fibroin 1:0.5:
a) powder form; b) magnified x100 times

According to the results of the study of the swelling degree of powdered biomaterials based on compositions of CMI/fibroin in different mass ratios, at mass ratios of 1:0.75 and 1:1, the swelling of biomaterials based on compositions of CMI/fibroin was relatively low (963% and 921%), and at a mass ratio of CMI/fibroin of 1:0.25, the swelling was 1028%. The best indicator was found in a sample with a CMI/fibroin ratio of 1:0.5

(1184%). The main reason for this is that the powdered biomaterial in this mass ratio not only retains the same particle size, but also retains a fibrous structure (Fig. 2).

In our subsequent experiments, the hemostatic activity of biomaterials based on CMI/fibroin in various mass ratios was studied for bleeding in the liver of the parenchymal organ of rats (Fig. 3).

Figure 3. *Hemostatic activity of biomaterial samples*



As a result, compared to the control (control, gauze), the KIM/fibroin was 1:0.25; Experimental samples with mass ratios of 1:0.75 and 1:1 were respectively 1.7; 1.51 and 1.39 times faster. The highest hemostatic activity was observed in the experimental sample with a CMI/fibroin ratio of 1:0.5 mass, which is 2.03 times faster than in the control group.

The absorption rate of powdered biomaterial samples in the body was also determined by implantation under the skin of experimental animals. The results of the experiments are presented in Table 1.

Table 1. *Determining the absorption time of biomaterials implanted under the skin into the body (M±c; n=6)*

Samples	Duration of absorption, a day				
	Initial mass, g.	Mass on the 7 th day, g (%)	Mass on the 14 th day, g (%)	Mass on the 21 st day, g (%)	Mass on the 28 th day, g (%)
CMI/ fibroin 1:0.25	0.2±0.001	0.124± ±0.001(62%)	0.053±0.001(26.5%)	100% absorbed	–
CMI/fibroin 1:0.5	0.2±0.001	0.127± ±0.001(63.5%)	0.058±0.001(29%)	100% absorbed	–
CMI/ fibroin 1:0.75	0.2±0.001	0.143± ±0.001(71.5%)	0.096±0.001(48%)	0.048±0.001(24%)	100% absorbed
CMI/fibroin 1:1	0.2±0.001	0.158± ±0.031(79%)	0.104±0.031(52%)	0.054±0.031(27%)	100% absorbed

As can be seen from the results presented in Table 1, all samples were completely absorbed in the body. The total absorption of powder samples based on CMI/fibroin in mass ratios of 1:0.25 and 1:0.5 in the body was 21 days. Samples based on CMI/fibroin in a mass ratio of 1:0.75 and 1:1 absorbed 76 and 73% respectively on day 21, with a full absorption time of 28 days in the body. Based on the obtained results, it can be concluded that with a low amount of fibroin, the rate of biomaterial absorption in the body is high, and in these samples, fibroin is relatively well structured using CMI.

Conclusion

It has been determined that biomaterials with a CMI/fibroin ratio of 1:0.75 and 1:1 exhibit relatively low swelling (963% and 921%), a biomaterial with a 1:0.25 mass ratio of 1028%, and a sample with a 1:0.5 mass ratio of 1184% exhibit high swelling. A study of the hemostatic activity of biomaterials revealed that a BMI/fibroin sample with a mass ratio of 1:0.5 stops twice as quickly and exhibits high hemostatic activity and is completely absorbed by the body after 21 days compared to the control.

References

Wei W., Liu J., Peng Z., et al. Gellable silk fibroin-polyethylene sponge for hemostasis // Artif Cell Nanomed B, 2020. – 48(1). – P. 28–36.

Chouhan D., Mandal B. B. Silk biomaterials in wound healing and skin regeneration therapeutics: From bench to bedside // Acta Biomater, 2020. – 103. – P. 24–51.

Kundu B., Schlimp C. J., Nurnberger S., Redl H., Kundu S. C. Thromboelastometric and platelet responses to silk biomaterials. Sci. Rep. 2014. – 4. – P. 4945. Doi: 10.1038/srep04945.

Dahlke H., Dociu N., Thurau K. Thrombogenicity of Different Suture Materials as Revealed by Scanning Electron-Microscopy // J. Biomed Mater Res, 1980. – 14(3). – P. 251–268.

Babiuc R. D., Purcarea M., Sadagurschi R., Negreanu L. Use of Hemospray in the treatment of patients with acute UGIB-short review // J. Med. Life 2013. – 6. – P. 117–119.

Wang X. X., Liu Q., Sui J. X., Ramakrishna S., Yu M., Zhou Y., Jiang X. Y., Long Y. Z. Recent Advances in Hemostasis at the Nanoscale // Adv. Healthc. Mater. 2019; 8: e1900823. Doi: 10.1002/adhm.201900823.

Barkun A. N., Moosavi S., Martel M. Topical hemostatic agents: A systematic review with particular emphasis on endoscopic application in GI bleeding. Gastrointest. Endosc. 2013. – 77. P. 692–700. Doi: 10.1016/j.gie.2013.01.020.

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STUDIES OF IMMOBILIZATION OF SOME DIAMINES TO DIALDEHYDINULIN MACROMOLECULES

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Abstract

Modified derivatives of polysaccharides containing aldehyde groups in their structure are unique intermediate materials for the production of new polymeric compounds. In the present study, periodate oxidation of inulin was carried out. The physicochemical properties of the resulting dialdehyde inulin with varying degrees of oxidation were investigated. Due to the presence of aldehyde groups in the structure of oxidized inulin, immobilization of hydrazine, ethylenediamine, and propylenediamine was performed via covalent azomethine bonds. The presence of diamines in the dialdehyde inulin structure was confirmed by elemental analysis (by nitrogen content) and FTIR-spectroscopy.

Keywords: *polymers, inulin, periodate oxidation, dialdehyde inulin, hydrazine, ethylenediamine, propylenediamine*

Introduction

The application area of macromolecular compounds covers a wide range of polymer materials intended for use in various fields of practical activity. The results achieved to date demonstrate the possibility of producing polymer products with specified physicochemical, mechanical, operational, and medical-biological properties (Bhatt Sh., Pathak A., Grover P., Kaurav M., 1985; Andrews G. P., Laverty T. P., Jones D. S., 2009; Peponi L., Lopez D., 2018). Among the different classes of polymers, special importance is given to macromolecular compounds that contain specific functional groups in their structure, which later determine a number of key properties of the synthesized polymers. One such class of polymer compounds is macromolecular systems containing amine groups in their structure (Xuan M., Gu X., Li J., Huang D., Xue Ch., He Yu., 2023; Kuksa V., 2000; Pegg A. E., McCann P. P., 1982; Abdulhussein A. A., Wallace H. M., 2014). It is well known that many polymeric amines exhibit antimicrobial, hemostatic, wound-healing, and antitumor properties.

Inulin is a heteropolysaccharide that has been increasingly used in medicine in recent years as a hypoglycemic agent, sorbent, and biologically active supplement. Unlike many polysaccharides, inulin has its own biological activity and a low molecular weight, which eliminates the need for hydrolysis to impart new physicochemical and pharmacological properties to the macromolecular chain. To date, only a limited number of chemical transformations of inulin have been explored, mainly involving the immobilization of low-molecular fragments into the structural units of inulin. Among these studies, the synthesis of amino-containing derivatives of inulin is a particularly interesting area of research. The aim of our study was to investigate the chemical immobilization of amino-containing compounds into the monomeric units of inulin to obtain new derivatives.

Materials and method

The following reagents were used for the synthesis of amino-containing derivatives of inulin: inulin, extracted from Jerusalem artichoke (variety «Mujiza») with an average molecular weight of 5600 Da; hydrazine sulfate – CAS 10034–93–2; ethylenediamine – CAS 107–15–3; propylenediamine – CAS 109–76–2.

Synthesis of dialdehydeinulin. 1–2 g of thoroughly dried inulin were placed in a heat-resistant dark glass flask with a volume of 300 mL, and 100 mL of acetate buffer (pH = 5) and 0.2 N freshly prepared sodium periodate solution were added, maintaining a molar ratio of inulin: $NaIO_4$ = 1 : 1. The reaction mixture was left to stir in the dark for 1–5 hours at 20–25 °C. To complete the reaction, 30 mL of ethylene glycol was added. After the reaction, the mixture was dialyzed against distilled water to remove any residual IO_4^- and IO_3^- ions (monitored using silver nitrate solution). The final products were isolated by sublimation drying. The degree of oxidation of inulin was determined by iodometric titration (Rhee, K. C., 2001).

Modification of Hydrazine, Ethylenediamine, and Propylenediamine with Dialdehyde Inulin Samples. 0.5–1.0 g of dialdehyde inulin with varying degrees of oxidation was dissolved in 50 mL of water at room temperature to form a clear solution. Then, hydrazine, ethylenediamine, or propylenediamine was added with stirring at a molar ratio of DAI: H_2N-R = 1 : 2.5. The resulting solution was stirred for 1 hour at 20–25 °C. After the reaction, the clear solution was placed in dialysis membranes and purified against distilled water for 24 hours. The final reaction products were isolated by sublimation drying.

FTIR-spectra of the synthesized compounds were recorded on a Vector-22 IR spectrometer in the wavelength range of 400–4000 cm^{-1} using KBr pellets (3–5 mg of sample/300 mg of KBr). The nitrogen content by weight in the synthesized compounds was determined using the Kjeldahl method (Tunik T. V., Nemchenko U. M., Ganenko T. V., Yurinova G. V., Dzhioev Yu.P., Sukhov B. G., Zlobin V. I., Trofimov B. A., 2019). ζ-potential of the samples was measured on a Zetasizer Nano ZS instrument (Malvern, UK) in plastic cuvettes using the immersion cell ZEN1002.

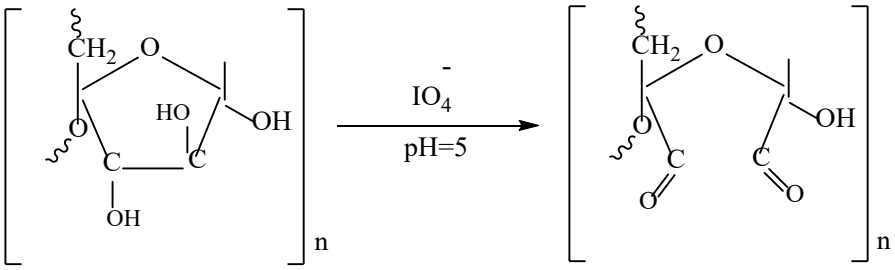
The molecular weight of the synthesized samples was determined by size-exclusion liquid chromatography on Yedrogel 100, 500, and 1000 columns from Waters (USA), at a temperature of 20±1 °C, equipped with a refractive index detector. The eluent used was a 0.1 N NaCl solution, with a flow rate of 0.1 mL/min. The calibration curve was standardized using dextran with a narrow molecular weight distribution.

Determination of pKa values of amino-containing derivatives of inulin. 100–150 mg of the dried sample was dissolved in water, and then 0.1 N sodium hydroxide solution was added to the solution. Titration was started while stirring continuously, adding aliquots of 0.1 N hydrochloric acid solution. The pKa values of the samples were calculated based on the pH value at which the midpoint of the plateau appeared on the resulting titration curve (Rawlinson L. B., Ryan S. M., Mantovani G., Syrett J.A., Haddleton D. M., Brayden D. J., 2010).

Result and discussions

It is known that oxidized polysaccharides containing electrophilic aldehyde groups in their structure exhibit high reactivity and can interact with molecules containing primary amine groups. These characteristics are typical for dialdehyde derivatives of polysaccharides, which are widely used for the chemical immobilization

of low-molecular-weight biologically active substances. When aldehyde groups react with primary amines, Schiff bases (–C = N-) are formed, which can decompose in acidic or alkaline environments. Based on this, we have developed methods for the fixation of amine groups into the structure of dialdehyde inulin with varying degrees of oxidation. The periodate oxidation of inulin was carried out according to the following scheme:



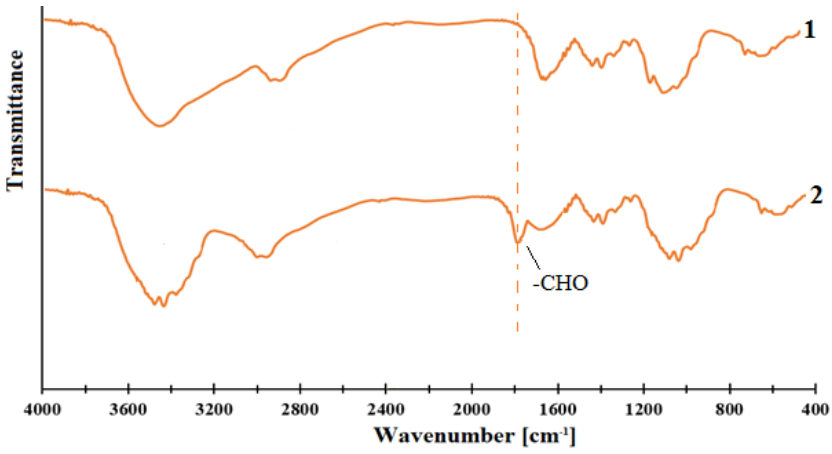
The table 1 presents the physicochemical characteristics of dialdehyde inulin with varying degrees of oxidation, which were obtained by altering the reaction time.

Table 1. *Physicochemical characteristics of dialdehyde inulin with varying degrees of oxidation*

№	Degree of oxidation of DAI, mol%	[η], dL/g	M×10⁻⁴, Da	ζ- potential, mV	Color of the sample
1.	13	0.64	5.4	–12.0±1.5	White
2.	20	0.58	5.1	–19.0±1.6	White
3.	28	0.52	4.8	–21.5±1.0	White
4.	35	0.45	3.7	–23.7±2.1	Cream
5.	37	0.41	3.0	–25.4±1.0	Cream

Experimental data presented in Table 1 show that the periodate oxidation of inulin proceeds with partial destruction of the original macromolecular chain, resulting in a decrease in molecular weight and the yield of reaction products. The data also reveal that the intensity of the molecular weight decrease of inulin occurs in two stages: the first stage is characterized by a slight reduction in the average molecular weight of inulin (from 5600 to 4800 Da) over the first 2.5 hours, while the second stage involves a more significant drop in the molecular weight of dialdehyde inulin (DAI) to 3000 Da. This indicates that as the number of aldehyde groups increases, the stability of DAI in acidic media decreases. Furthermore, with an increase in the degree of oxidation of inulin, there is a consistent shift in the ζ-potential of the investigated samples into the negative region.

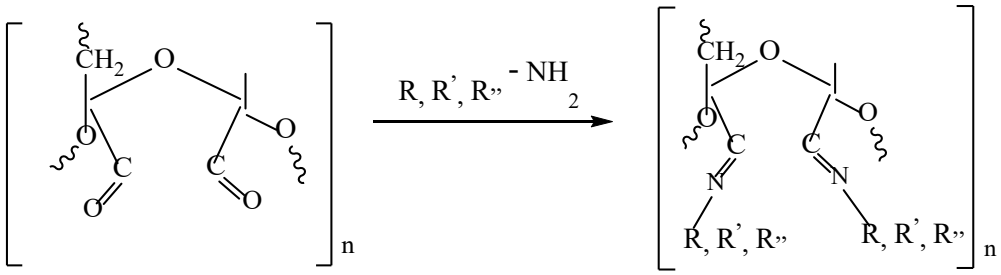
Figure 1. *FTIR-spectra of inulin (1) and dialdehyde inulin (2) with an oxidation degree of 37 mol%*



The reason for the decrease in the ζ-potential with increasing degree of oxidation of DAI is explained by the fact that aldehyde groups carry a partial negative charge due to the polarization of the π-bond, imparting polymeric acid properties to the main macromolecular chain of oxidized inulin.

In the FTIR-spectrum of inulin (Fig. 1), absorption bands are observed at 3429 cm^{-1} (–OH), associated with the formation of hydrogen bonds, 2924 cm^{-1} ($–CH_2–$), 1133 cm^{-1} (C-O-C bonds), and 1032 cm^{-1}, corresponding to the vibration of primary -OH groups. In the FTIR-spectra of DAI, a new absorption band appears at 1730 cm^{-1}, corresponding to the vibration of the aldehyde group, the intensity of which increases with the degree of oxidation of inulin.

Since the oxidized derivatives of inulin contain electrophilic aldehyde groups, we carried out the immobilization of diamines (hydrazine, ethylenediamine, and propylenediamine) based on a nucleophilic addition reaction according to the following scheme:



R = $-NH_2$
R' = $-CH_2-CH_2-NH_2$
R" = $-CH_2-CH_2-CH_2-NH_2$

The research results illustrating the effect of the degree of oxidation of inulin on the composition and substitution degree of the reaction products are presented in tables 2–4.

Table 2. *Effect of the degree of oxidation of inulin on the composition of the reaction products (t = 20 °C; DAI: hydrazine=1:2.5; τ=1 hour)*

№	Degree of oxidation of DAI, mol%	$\gamma_{ок}$ DAI	Nitrogen content, %	Degree of substitution, mol%	pKα value
1.	13	26	4.2	25	7.2
2.	20	40	6.5	38	7.4
3.	28	56	8.8	54	7.6
4.	35	70	10.9	70	7.8
5.	37	74	11.5	72	7.8

Note: $\gamma_{ок}$ DAI – The content of aldehyde groups in 100 elementary units of inulin

Table 3. *Effect of the degree of oxidation of inulin on the composition of the reaction products (t = 20 °C; DAI: ethylenediamine=1:2.5; τ=1 hour)*

№	Degree of oxidation of DAI, mol%	$\gamma_{ок}$ DAI	Nitrogen content, %	Degree of substitution, mol%	pKα value
1.	13	26	4.5	26	7.8
2.	20	40	6.8	36	8.0
3.	28	56	9.1	55	8.2
4.	35	70	11.6	68	8.4
5.	37	74	12.0	74	8.5

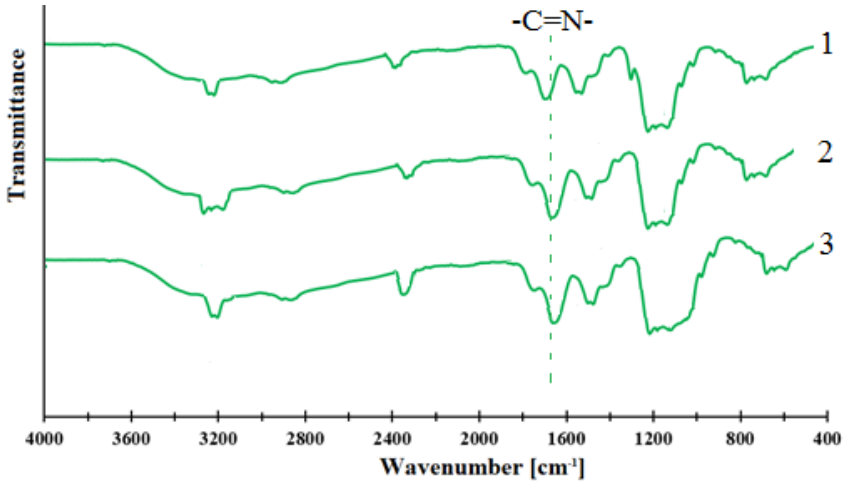
Table 4. *Effect of the degree of oxidation of inulin on the composition of the reaction products (t = 20 °C; DAI: propylenediamine =1:2.5; τ=1 hour)*

№	Degree of oxidation of DAI, mol%	$\gamma_{ок}$ DAI	Nitrogen content, %	Degree of substitution, mol%	pKα value
1.	13	26	4.7	23	7.5
2.	20	40	7.0	36	7.9
3.	28	56	9.5	54	8.1
4.	35	70	11.8	68	8.3
5.	37	74	12.3	72	8.3

The results presented in Tables 2–4 show that with an increase in the degree of oxidation of inulin, the nitrogen content and the degree of substitution of the reaction products increase. By comparing the degree of oxidation with the degrees of substitution of the synthesized compounds, it can be concluded that each aldehyde group corresponds to one molecule of hydrazine, ethylenediamine or propylenediamine. After the immobilization of hydrazine, ethylenediamine, and propylene diamine onto the macromolecules of dialdehyde inulin, the resulting samples begin to exhibit properties characteristic of polymeric bases. The data presented in Tables 2––4 show that the pKa value ranges from 7.2 to 8.5. As the degree of substitution of the samples increases, the pKa value also increases.

The presence of Schiff bases (–C=N-) in the synthesized azomethine derivatives of inulin, which contain fragments of hydrazine, ethylenediamine, and propylenediamine in their structure, was confirmed by FTIR-spectroscopy (Fig. 2). A common absorption band in the range of 1634–1652 cm^{-1} indicates the presence of covalent -C=N- Schiff base linkages.

Figure 2. *FTIR-spectra of the azomethine derivatives of inulin containing hydrazine (1), ethylenediamine (2), and propylenediamine (3) fragments in their structure*



Conclusion

Thus, in the present research work, dialdehyde inulins with varying degrees of oxidation were obtained. The presence of aldehyde groups in oxidized inulin was confirmed by iodometric titration and IR spectroscopy. The molecular weight characteristics of dialdehyde inulin were studied. In the next stage, hydrazine, ethylenediamine, and propylenediamine were immobilized onto the monomeric units of oxidized inulin. It was established that as the content of aldehyde groups in oxidized inulin increases, the degree of substitution of the reaction products also increases. IR spectroscopy confirmed that the chemical binding of hydrazine, ethylenediamine, and propylenediamine to the aldehyde groups of dialdehyde inulin occurs through covalent azomethine (–C=N-) linkages.

References:

Bhatt Sh., Pathak A., Grover P., Kaurav M. Different aspects of polymers // Journal of Pharmaceutical Sciences. 1985. – V. 74. – P. 399–405.

Andrews G. P., Laverty T. P., Jones D. S. Mucoadhesive polymeric platforms for controlled drug delivery // European Journal of Pharmaceutics and Biopharmaceutics. 2009. – V. 71(3). – P. 505–518.

Peponi L., Lopez D. Smart Polymers // Modification of Polymer Properties. 2018. – P. 131–154.

Xuan M., Gu X., Li J., Huang D., Xue Ch., He Yu. Polyamines: their significance for maintaining health and contributing to diseases // Cell Communication and Signaling. 2023. – V. 21. – P. 1–23.

Kuksa V. Synthesis of Polyamines, Their Derivatives, Analogues, and Conjugates // ChemInform. 2000. – V. 9. P. – 1189–1207.

Pegg A. E., McCann P. P. Polyamine metabolism and function // Am. J. Physiol. 1982. – V. 243. – P. 212–221.

Abdulhussein A. A., Wallace H. M. Polyamines and membrane transporters // Amino Acids. 2014. – V. 46. – P. 655–660.

Rhee, K. C. Determination of Total Nitrogen // Curr. Protoc. Food Anal. Chem. 2001. – B1. 2.1-B1.2.9.

Tunik T. V., Nemchenko U. M., Ganenko T. V., Yurinova G. V., Dzhioev Yu.P., Sukhov B. G., Zlobin V. I., Trofimov B. A. Synthesis and Spectral Characterization of New Biodegradable Arabinogalactan Derivatives for Diagnosis and Therapy // Bulletin of the Russian Academy of Sciences: Physics. 2019. – V. 83. – P. 343–349.

Rawlinson L. B., Ryan S. M., Mantovani G., Syrett J.A, Haddleton D. M., Brayden D. J. Antibacterial Effects of Poly(2-(dimethylamino ethyl)methacrylate) against Selected Gram-Positive and Gram-Negative Bacteria // Biomacromolecules. 2010. – V. 11(2). – P. 443–453.

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SYNTHESIS OF NANOCOMPOSITE MATERIALS AND THEIR PROPERTIES BASED ON POLYMETHYLENE NAPHTHYLENESULFONATE AND TiO2 NANOTUBES

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Abstract

In this article, the optimal conditions for the formation of nanotubes based on titanium oxide were determined and the synthesis of nanotubes was carried out. The obtained material was studied using scanning electron microscope (SEM) and IR-spectroscopy methods. Naphthalene-based copolymer products were obtained, their formation mechanisms,^{1}H and^{13}C spectra were studied. Nanocomposite products based on titanium oxide were synthesized and volt-amperometric properties of obtained nanocomposite materials were determined.

Keywords: *anodization, pore formation kinetics, volt-amperometric properties*

Introduction

In the last decade, electrochemical synthesis and anodization process have attracted more attention (Yu, C., et al., 2019; Sun, X., et al., 2019; Zhang, K., et al., 2019). Porous anodic oxides, such as porous aluminum and titanium nanotubes, have attracted great scientific interest because their nanomaterials are used in many fields, especially anodic titanium oxide nanotubes (ATO) in solar energy conversion, supercapacitor, sensor, photocatalytic decomposition and is also of great importance in the fields of converting solar energy into hydrogen fuel (Lee, W., et al., 2014; Cheng, Y., et al., 2015; Li, Z., et al., 2018). The formation of pores and formation of nanotubes depends on such parameters as concentration of the electrolyte composition, anode voltage, current density, temperature of the electrolyte.For example, the height of nanotubes differs from each other in different literature (Feng, C., et al., 2019; Wang, K., et al., 2014; Lee, K., et al., 2014). At the same concentration of ammonium fluoride (0.3% NH_4F) and ethylene glycol electrolytes, it was reported that the height of the obtained nanotubes was significantly different from each other (Zhang, Y., et al., 2015). Zhang et al. 4.7 μm long nanotubes were obtained at a current density of 7.5 mA·cm-2, Sui et

al. reported that the height of the nanotubes obtained as a result of anodizing at a current density of 10 mA·cm-2 for 45 minutes was 15.3 μm (Cui, H., et al., 2017). Liu et al. reported that the height of the nanotubes was 8.5 μm obtained by anodizing at a constant voltage of 50 V for 60 minutes (Li, W., et al., 2019). .Masak et al. They studied the effect of Ti substrate on nanotube growth and size in 0.3% NH_4F electrolyte, nanotubes with a height of 32 ~ 50 μm were obtained by anodizing at 60 V for 360 minutes (Sopha, H., et al., 2016). It can be seen that the anodizing voltage, anodizing current, Ti substrate, and anodizing time are different in the electrolyte with the same concentration of NH_4F, resulting in a large difference in the height of the nanotubes. This means that the electrochemical dissolution reaction in the presence of fluoride ions ($TiO_2+6F^-+4H^+\rightarrow[TiF_6]_2^-+$ $+2H_2O$) is not a factor determining the nanotube height (Zhang, J., et al., 2018) synthesized nanotubes with a height of 29.8 μm in an ethylene glycol electrolyte containing 0.30% NH_4F and 2% water at 60 V for 180 minutes. Zhao et al. height of nanotubes reported that the height of nanotubes obtained by anodizing at 60 V for 10 minutes in an ethylene glycol electrolyte consisting of 0.50% NH_4F and 2% water was 9.0 μm (Zhao, S., et al., 2018). However, Liu et al. also reported that the height of nanotubes obtained by constant voltage anodization at 60V for 360 minutes in an ethylene glycol electrolyte consisting of 0.83% NH_4F and 8% water was 10 μm (Wang, L., et al., 2024).This is due to the fact that the fluoride ion participates in the melting reaction and the water content affects the height of the nanotubes.

Experimental part

A 0.1 mm thick titanium foil (99.8% purity, Sigma Aldrich) was cut into strips (10 mm × 40 mm) and polished. To clean the surface of the foil from various roughnesses and inclusions, it was cleaned in a solution consisting of HF: HNO_3: H_2O = 1:1:2) for 15 minutes (GT Sonic-D 6, AC-220–240V). Then it was washed in distilled water for another 15 minutes and air-dried for one hour. After that, an electrolyte containing 2% water, 98% ethylene glycol solution with 0.1 and 0.2% NH_4F was prepared. Titanium foil was used as the anode and graphite electrode was used as the counter electrode. A titanium foil immersed in an electrolyte has an area of 4 cm2 (2cm×1cm×2 sides). The voltages were applied in different sequence from 30V to 70 V (Potentiostat: (Model-SS-350M, S/N 21121062). Anodizing time was 2, 3, 4 and 6 hours and two electrodes were kept constant in two different electrolytes. anodizing voltages were applied and each process was repeated three times.The anodizing process was 20 °C, 50 V and The nanotubes obtained at 20 °C, 60 V showed the formation of highly ordered nanotubes with a flat surface.

Results and its discussion

Figure 1 shows the variation of electric current and formation of TiO_2 nanotubes at 20 °C 50 B, 0.1% NH_4F.

Figure 1. *20 °C 50 B, 0.1% NH_4F, electric current change and TiO_2 nanotube formation diagram (I), (II), (III)*

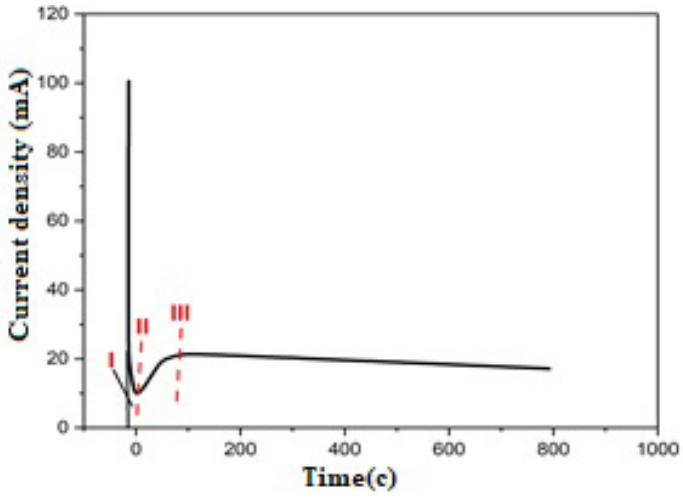
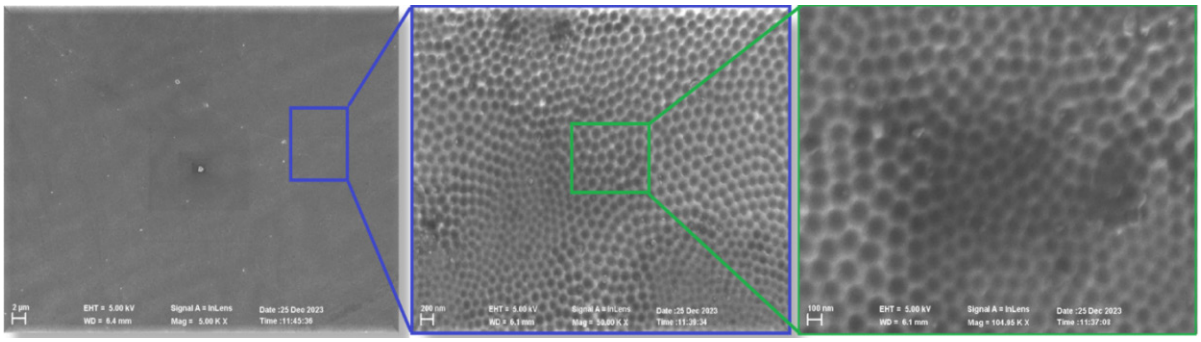


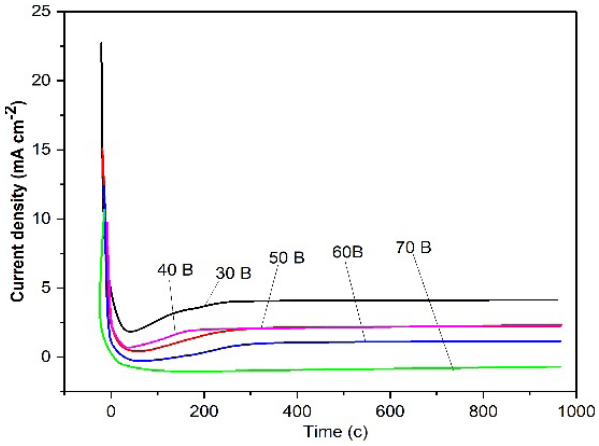
Figure 1 (20 °C 50 B, 0.1% NH_4F) shows the formation of pores in stage I initially at 100 mA, in stage II at 101 mA and 10 s, and in stage III, the nanotubes are fully formed. It can be seen that t, the time and the current are in the same state, i.e. at 20 mA, it continued in the range of 10–800. The formation of nanotubes at this anodic voltage resulted in the formation of double-walled nanotubes with a uniform flat surface and highly ordered (Figures 2a, b).

Figure 2. *SEM-EDS (a-b) of nanotubes obtained in 0.1% NH_4F at 20 °C, 50V and the resulting formation time (c)*

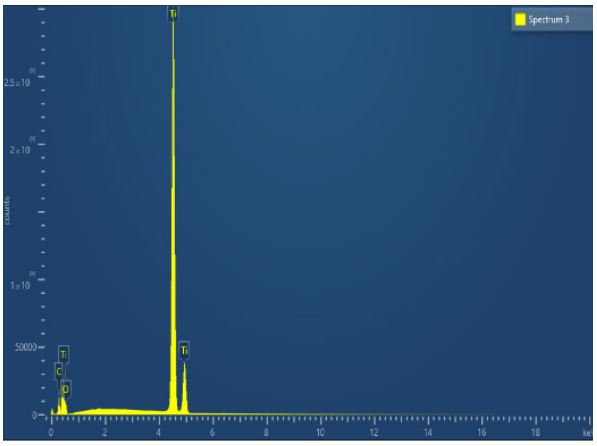
a)



b)



c)

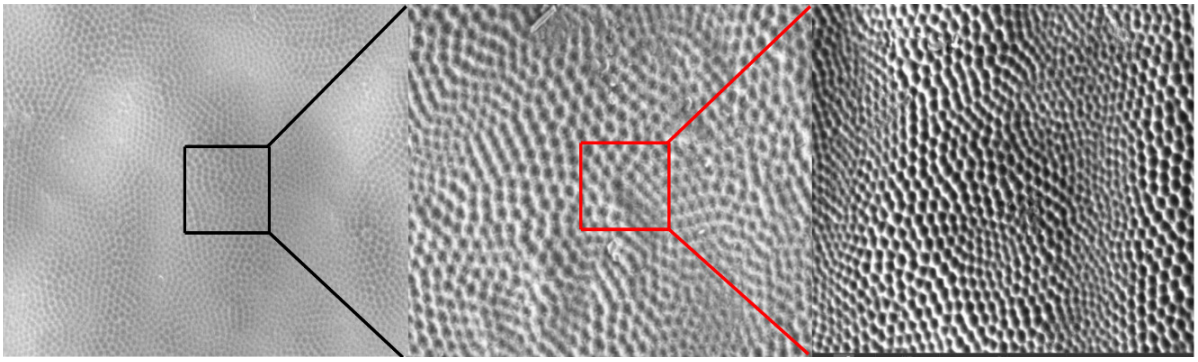


The element composition is 67.55% Ti, 30.45% O and 2% C. Looking at the time curves of the formed current at 20 °C, (30––70 V) in the presence of 0.1% NH_4F, it can be seen that initially at 30 V 22.5 mA 10 s pore formation begins, but they are not uniform. can be seen. At 40V, 9.9 mA started to form pores at 9 s, 50 V at 15mA at 8.5s, at 60 V 12.5 mA at 8 s and continued to form pores, and at 70 V at 10.8 mA starting at 7.5 s, irregular and flat it can be seen that the nanotubes formed without,

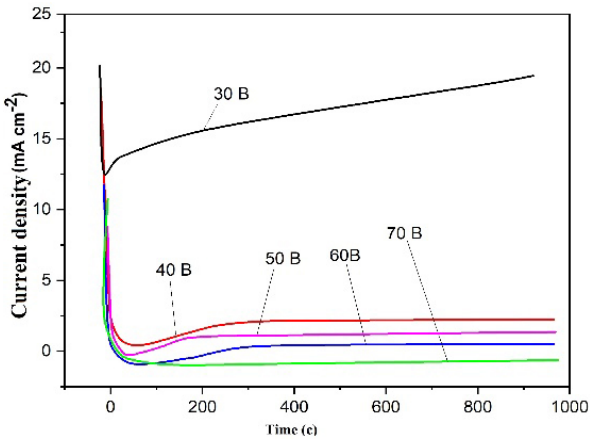
It can be concluded that the nanotubes formed at 50 V, 8.5 seconds and 60 V, 8 seconds have a flat surface and higher order than the nanotubes formed at other voltages. Formation of nanotubes As can be seen from Figures 3 a, b, double-walled nanotubes with uniform flat surface and high order were formed. The element composition is 65.55% Ti, 31.45% O and 3% C. Looking at the time curves of nanotube formation (Fig. 3 c), 30 V, 20 mA showed that disordered pores started to form in 10 s, 40 V, 7 mA showed highly disordered pores in 9.5 s, 50 V, 12 mA 9 seconds and 60V, 11mA in 8 seconds high-order flat surface, 70 V 10 mA At 7.5 seconds, you can see that nanotubes with irregular but smooth surface are formed. It can be concluded that the nanotubes formed at 50 V, 12 mA 9 seconds and 60 V, 11 mA 8 seconds, while the nanotubes formed at other voltages are known to have a smooth surface and higher order.

Figure 3. *Of nanotubes obtained in 0.2% NH_4F at 20 °C, 60 V. SEM-EDS (a-b) and formation time results (c)*

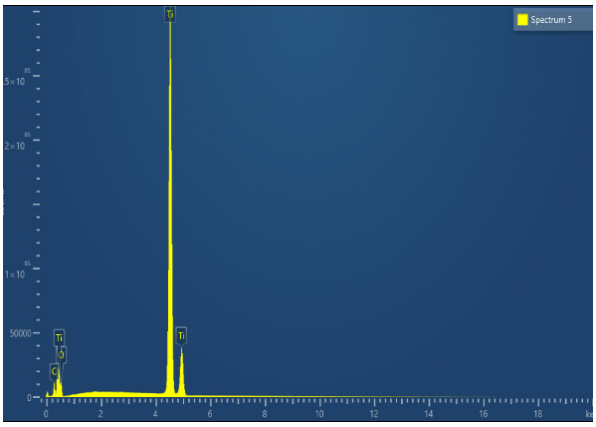
a)



b)



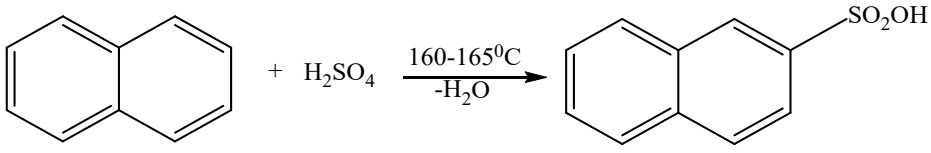
c)



2. Synthesis of polymethylene naphthalene sulfonate (PMNS)

The process of obtaining a copolymer product consists of the following stages:

1. Sulfolation of the naphthalene fraction. 64 g of naphthalene-based fraction (210–250 °C) was placed in a three-necked flask equipped with a mechanical stirrer, a dropping funnel and a reflux condenser, heated to 140 °C and liquefied, and 3 ml/ml of 60 g of sulfuric acid solution of 98% was added using a funnel. min dripped. Since the process was exothermic, the temperature rose to 160–165 °C. In this case, the process was continued for 4 hours. The reaction equation is:



process mechanism:

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

$$H_3SO_4^+ \rightleftharpoons SO_3H^+ + H_2O$$

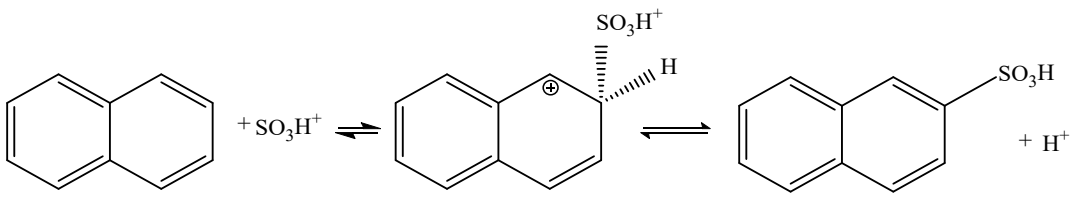
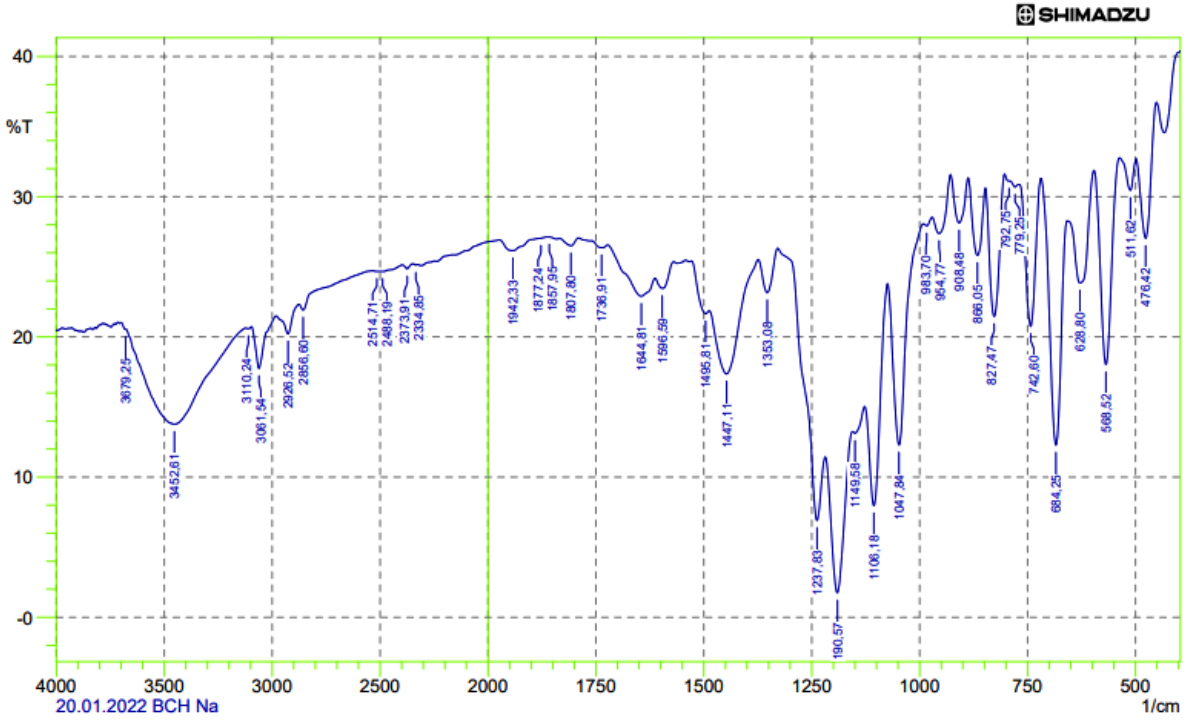


Table 1. *Conditions for the synthesis of 2-naphthalenesulfoacid*

Substance name	Mole ratio of naphthalene and H_2SO_4 (98% li).	Tempera-ture, °C	Duration of the reaction, hours	Reaction product (%)
1-Naphthalene sulfonic acid	1:1.2	60	4	48
			6	56
			8	54
	1:1.2	70	4	58
			6	69
			8	61
	1:1.2	80	4	83
			6	**91**
			8	85
	1:1.2	90	4	79
			6	84
			8	76
2-Naphthalene sulfonic acid	1:1.08	140	4	54
			6	59
			8	55
	1:1.08	150	4	67
			6	82
			8	78
	1:1.08	160	4	81
			6	**89**
			8	90
	1:1.08	170	4	71
			6	86
			8	76

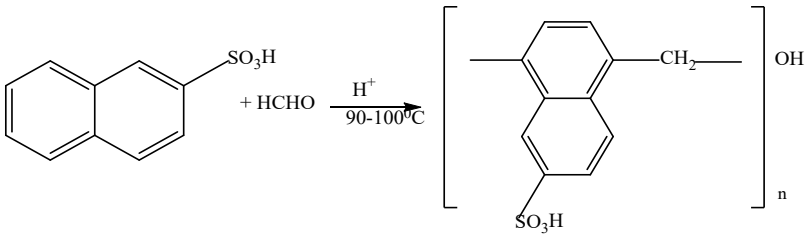
Figure 4. *IR spectrum of 2-sulfonaphthalene*



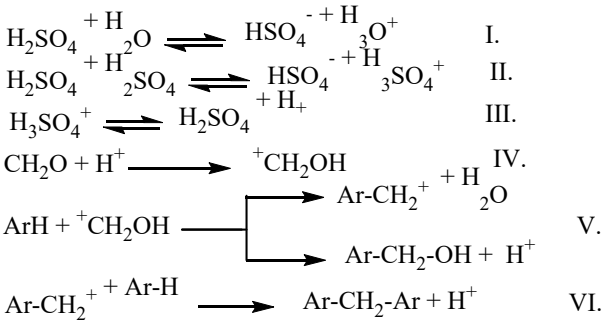
The optimal conditions for the synthesis of 2-naphthalene sulfoacid were naphthalene and sulfuric acid in the ratio of 1:1.08 mol, at a temperature of 160 °C and a process duration of 6 hours, with an efficiency of 89%. During the synthesis of 1 and 2 naphthalene sulfoacids, increasing the duration of the reaction leads to a decrease in yield. Because, as a result of additional reactions (oxidation, 1.1 and 2.2-sulfonyldinaphthalene), the yield of naphthalene sulfoacids decreases.

The vibrational frequency is the valence vibration of the -C-H group in the aromatic nucleus in the 3061.54 cm^{-1} area, the valence vibration of the C=C bond in the aromatic nucleus in the 1596.59 cm^{-1} area, the valence vibration of the aromatic nucleus in the 742.6 cm^{-1} area, the valence vibration of the -SO_3H group in the 1106.18 cm^{-1} area vibration, the valence vibration of the C=O bond can be observed in the region of 1190.57 cm^{-1}.

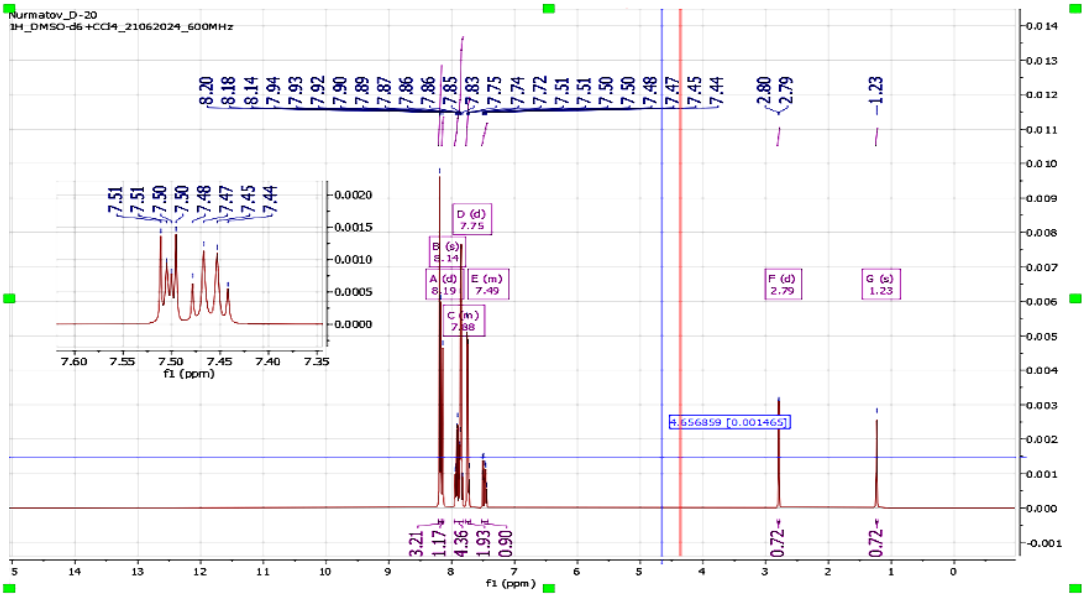
2. Polycondensation of β-naphthalene sulfoacid with formalin (35%). The process was carried out in a hermetic reactor equipped with a mechanical stirrer. For the reaction, *β*-naphthalene sulfonic acid and formaldehyde were taken in a ratio of 1:0.8 mol, and the process was carried out at 90–100 °C for 5 hours. As a result, polymethylenenaphthalene sulfonic acid was synthesized with a yield of 82.4% (Cheng, Y., Peng, Z., Wu, X., Cao, J., Skeldon, P., & Thompson, G. E., 2015). The polycondensation reaction scheme is as follows:



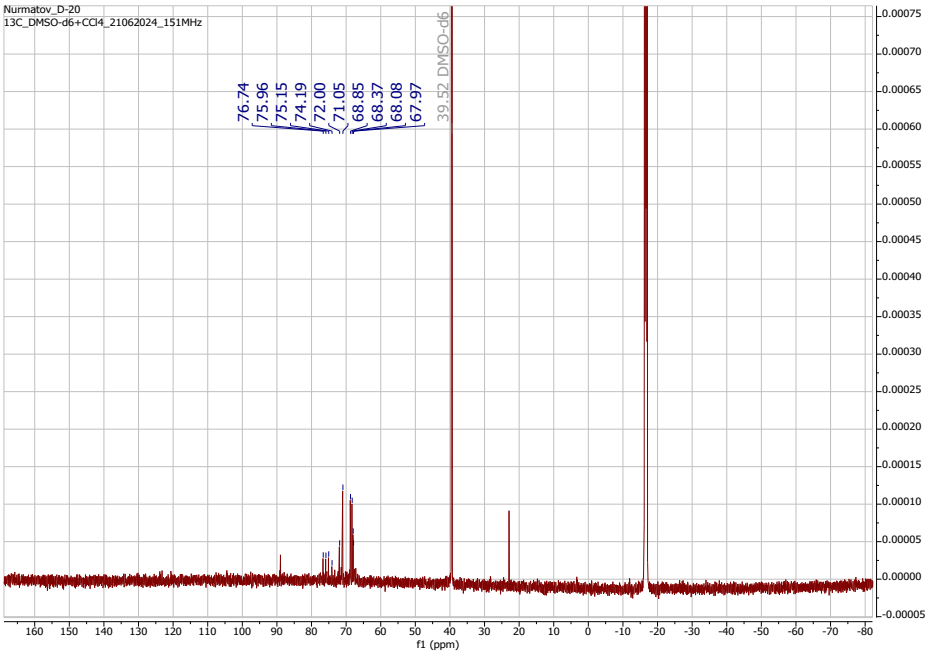
Mechanism of action:



1 H and 13 C NMR spectra of the resulting polymer



(Polymethylenenaphthalene sulfonate acid1H) YaMR (600 MHz, DMSO-D_6) δ 8.19 (d, J = 11.8 Hz, 3H), 8.14 (s, 1H), 7.95–7.81 (m, 4H), 7.75 (d, J = 0.0 Hz, 2H), 7.53–7.43 (m, 1H), 2.79 (d, J = 5.0 Hz, 1H), 1.23 (s, 1H).



(Polymethylenenaphthalene sulfonate acid13C) YaMR (151 M Hz, DMSO-D_6) δ 76.74, 75.96, 75.15, 74.19, 72.00, 71.05, 68.85, 68.37, 68.08, 67.97.

SEM was used to determine the morphology and surface structure and elemental composition of spatially structured polymethylenenaphthalene sulfoacids (Fig. 5). The results of the SEM analysis of polymethylenenaphthalene sulfoacid are presented in pictures (c, d). The SEM result shows that it contains macropores from 114 μm to 613 μm. The composition of the element consists of 68.3% C, 18.1% O.

3. Preparation of nanocomposite materials and their physical and hemical characteristics. To carry out this experiment, the following processes were carried out: an electrochemical polymerization process, using titanium oxide nanotubes as anode and graphite as counter electrode and polymer dissolved in DMSO (15g polymer dissolved in 100 g DMSO) as electrolyte. The titanium oxide nanotubes immersed in the electrolyte have an area of 4 cm^2 (2 cm × × 1 cm × 2 sides). Voltages were made at 50 V, 60 V, respectively. Anodizing voltages were continuously applied to two electrodes in five different electrolytes for 4 hours. Each step of anodization was repeated three times.

Figure 5. *SEM-EDS analysis of polymethylene sulfonate naphthalene*

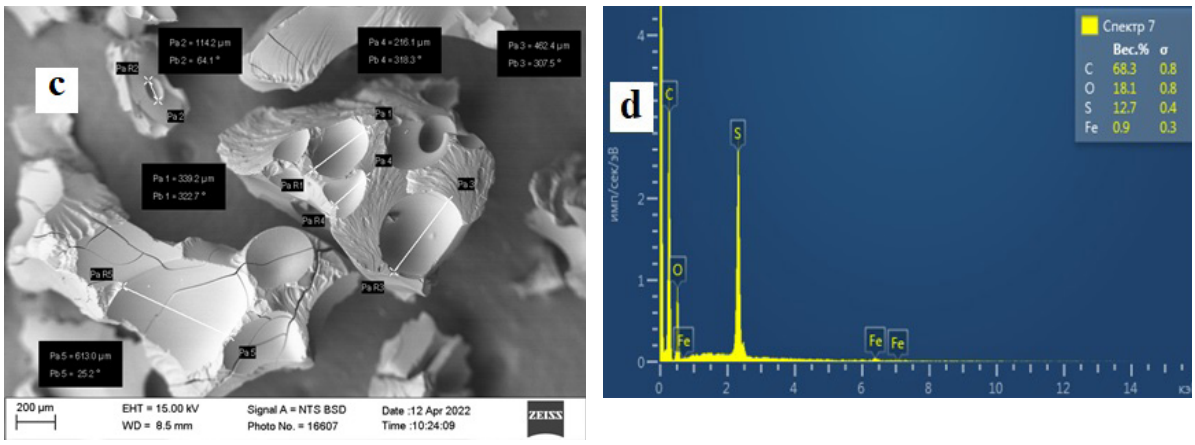


Figure 6. *SEM micrographs of nanocomposites formed on the basis of nanotubes containing 2, 10 and 45% water*

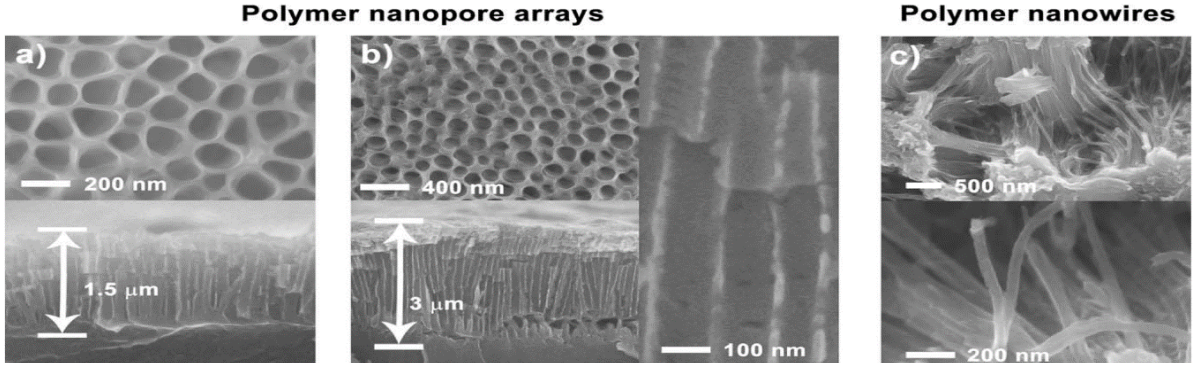
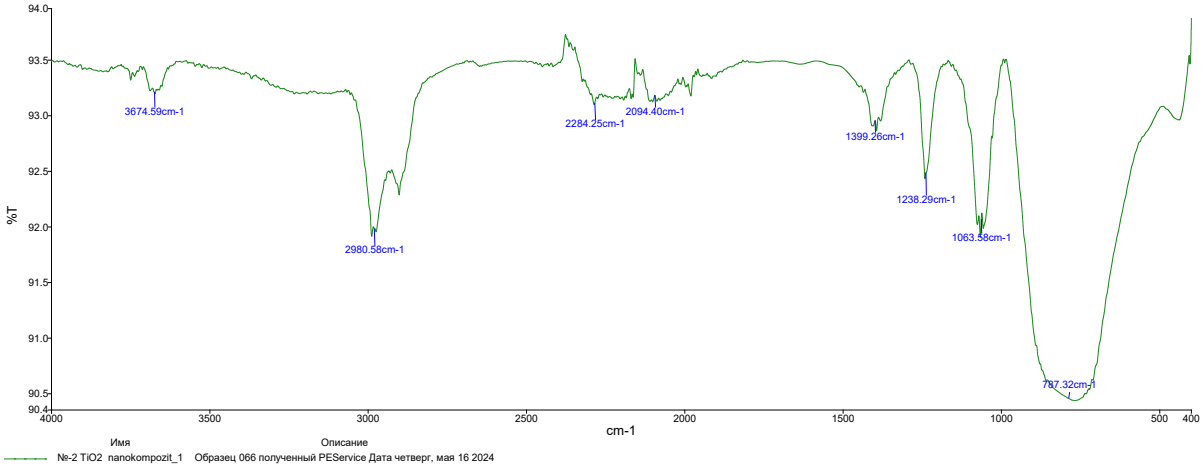


Figure 6a shows that the nanotubes with 2% water have a flat surface and are ordered with a side length of 1.5 microns, (b) the pores formed at 10% water are irregular but with a side length of 3 microns, (c) At 45% water, we can see that nanotubes are formed randomly.

Figure 7. *IR spectrum of the obtained nanocomposite*



The vibrational frequency is the valence vibration of the -Ti-O bond in the aromatic nucleus in the 787.3 cm^{-1} region, the valence vibration of the C=C bond in the aromatic nucleus in the 2980.58 cm^{-1} region, the valence vibration of the -SO_3H group in the 1063.58 cm^{-1} region, and the 1238.29 cm^{-1} region In the –1 region, the valence vibration of the C=O bond can be observed.

The volt-ampere characteristics of the obtained nanocomposites (0–1.5 V) were studied:

Figure 8. *Volt-ampere characteristic of nanocomposite containing 2% H_2O*

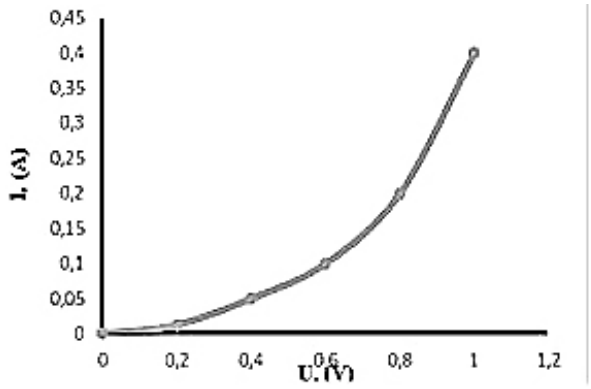
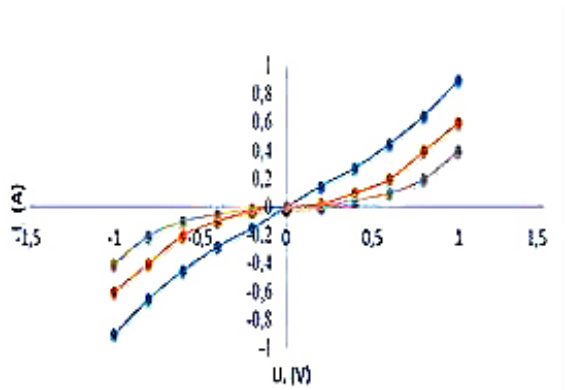


Figure 9. *Volt-ampere characteristics of forward and reverse conductivity of nanocomposite samples*



The volt-amperometric characteristics of nanocomposite materials in the range (0–1.5V) were studied. In Figure 8, the sample in 2% water in the electrolyte is initially in the ranges from 0 to 1V, that is (0.2 V–0.0125 A, 0.4 V-0.025 A, 0.6V–0.05 A, 0.8 V–0.09 A, and at 1V 0.15 A) it can be seen that the electrical conductivity of nanotubes increases. Figure 9 shows the diagram of the volt-amperometric characteristics of the samples in forward and reverse quenching (2%, 10% and 45% water in the electrolyte) it can be seen that the conductivity is good.

This table shows the relative electrical conductivity of nanocomposites obtained at different voltages (from 30 V to 70 V). We can see that the highest values are 14.500 at 50 V and 22.100 at 60 V. It is known from the table that these values are low in the remaining voltages.

Activation energies and specific electrical conductivity values of polymer composites based on TiO2 (U= 0.5 V)

№	Voltage (V)	TiO_2 E, ev	Relative electrical conductivity, Sm/sm
1.	30	0.210	13.200
2.	40	0.092	2.400
3.	50	0.090	14.500
4.	60	0.120	22.100
5.	70	0.070	0.005

Summary

The volt-ampere characteristics of the polymer obtained on the basis of naphthalene and its nanocompositions with metal oxides (TiO2), the activation energies of electrical current conductivity were determined. It was found that the electrical conductivity of polymethylene naphthalene sulfonate acid is “p” type, and its nanocompositions with metal oxides are “n” type conductive materials.

Technical conditions of storage, use and other indicators of composite materials based on polymethylenenaphthalene sulfonate have been developed. The practical importance of polymer nanocomposites can be explained by the fact that they can be used as components of electrode materials for rechargeable batteries and supercapacitors, as additives in the preparation of various antistatic composites, as contact and current-carrying elements in control and measurement equipment.

References

Yu, C., Zhang, W., Guo, S., Hu, B., Zheng, Z., Ye, J., Zhu, J. (2019). A safe and efficient liquid-solid synthesis for copper azide films with excellent electrostatic stability. Nano energy, – 66. – 104135 p.

Sun, X., Mo, X., Liu, L., Sun, H., & Pan, C. (2019). Voltage-driven room-temperature resistance and magnetization switching in ceramic TiO_2/PAA nanoporous composite films. ACS appl. mater&inter., – 11(24). – P. 21661–21667.

Zhang, K., Cao, S., Li, C., Qi, J., Jiang, L., Zhang, J., & Zhu, X. (2019). Rapid growth of TiO_2 nanotubes under the compact oxide layer: Evidence against the digging manner of dissolution reaction. Electrochem. Comm, – 103. – P. 88–93.

Lee, W., & Park, S. J. (2014). Porous anodic aluminum oxide: anodization and templated synthesis of functional nanostructures. Chem. Rev., – 114(15). – 7487 p.

Cheng, Y., Peng, Z., Wu, X., Cao, J., Skeldon, P., & Thompson, G. E. (2015). A comparison of plasma electrolytic oxidation of Ti-6Al-4V and Zircaloy-2 alloys in a silicate-hexametaphosphate electrolyte. Electroch. Acta, – 165, – 301 p.

Li, Z., Li, Y., Li, S., Wu, J., Hu, X., Ling, Z., & Jin, L. (2018). A modified quantitative method for regularity evaluation of porous AAO and related intrinsic mechanisms. Journal of The Electrochemical Society, – 165(5). – E214.

Feng, C., Zhang, Z., Li, J., Qu, Y., Xing, D., Gao, X., ... & Sun, R. (2019). A bioinspired, highly transparent surface with dry style antifogging, antifrosting, antifouling, and moisture self-cleaning properties. Macromolecular rapid communications, – 40(6). – 1800708 p.

Wang, K., Liu, G., Hoivik, N., Johannessen, E., & Jakobsen, H. (2014). Electrochemical engineering of hollow nanoarchitectures: pulse/step anodization (Si, Al, Ti) and their applications. Chem. Soc. Rev., – 43(5). – 1476 p.

Lee, K., Mazare, A., & Schmuki, P. (2014). One-dimensional titanium dioxide nanomaterials: nanotubes. Chemical reviews, – 114(19). – P. 9385–9454.

Zhang, Y., Cheng, W., Du, F., Zhang, S., Ma, W., Li, D., Zhu, X. (2015). Quantitative relationship between nanotube length and anodizing current during constant current anodization. Electrochimica Acta, – 180. – P. 147–154.

Cui, H., Chen, Y., Lu, S., Zhang, S., Zhu, X., & Song, Y. (2017). TiO_2 nanotube arrays treated with $(NH_4)_2TiF_6$ dilute solution for better supercapacitive performances. Electrochimica Acta, – 253. – P. 455–462.

Li, W., Zhang, W., Li, T., Wei, A., Liu, Y., & Wang, H. (2019). An Important Factor Affecting the Supercapacitive Properties of Hydrogenated TiO_2 Nanotube Arrays: Crystal Structure. Nanoscale Research Letters, – 14. – P. 1–14.

Sopha, H., Jäger, A., Knotek, P., Tesař, K., Jarosova, M., & Macak, J. M. (2016). Self-organized anodic TiO_2 nanotube layers: Influence of the Ti substrate on nanotube growth and dimensions. Electrochimica Acta, – 190. – 744 p.

Zhang, J., Li, Y., Zhang, Y., Qian, X., Niu, R., Hu, R., Zhu, J. (2018). The enhanced adhesion between overlong TiNxOy/MnO_2 nanoarrays and Ti substrate: Towards flexible supercapacitors with high energy density and long service life. Nano Energy, – 43. – P. 91–102.

Zhao, S., Chen, Y., Zhao, Z., Jiang, L., Zhang, C., Kong, J., & Zhu, X. (2018). Enhanced capacitance of TiO_2 nanotubes topped with nanograss by H_3PO_4 soaking and hydrogenation doping. Electrochimica Acta, – 266. – P. 233–241.

Wang, L., Wei, Z., Sun, Z., Zhu, L., Gao, Y., Chen, Z., Chen, W. (2024). Carbon-based double-metal-site catalysts: advances in synthesis and energy applications. J. Mater. Chem A, – 12(20). – P. 11749–11770.

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DRILLING SOLUTIONS BASED ON HOVDAK BENTONITE AND THEIR APPLICATION TECHNOLOGY

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Abstract

Chemical reagents are added to drilling fluids to improve their properties. Clay rocks are primarily used in the preparation of drilling fluids. These clays, depending on their mineral composition, are divided into 4 types. Montmorillonite, kaolin, hydro-micaceous and palygorskite minerals. Drilling fluids have specific functions, such as: cleaning the wellbore wall, removing rock from the bottom of the well, cooling the drill bit, blocking (weighing) the movement of gas and oil in the reservoir. Instead of drilling muds, water was also widely used. Drilling fluids are prepared based on the liquid phase, clay particles, and chemical reagents. Bentonite-based drilling fluids, currently used as the main raw material, yield high efficiency.

Keywords: *Paligorskite, bentonite, clays, weighting, barite, rocks, weighting, flotation, reagent, solution, drilling, lightening, well, liquid, montmorillonite, oil, gas*

Introduction

There is very little information about the drilling fluids created in the early stages. A solution in the form of liquid clay formed during drilling in wells drilled by the first rotor method was used. Undoubtedly, liquid clay was used at that time because there were no impressions of drilling fluids. The control of the physical properties of drilling fluids and changes in their properties were not recorded, as these questions were not controlled and practically created at that time. It can only be assumed that in cases where the drilling mud was very thick, it was diluted by vomiting water. The properties of drilling fluids show that when drilling at high speeds, work must be completed to ensure safety and maximize well productivity. The use of drilling fluids with controlled properties leads to significant costs, which must be economically justified. To do this, the drilling fluid must behave during the drilling process and be given the qualities required by the drilling conditions using the available chemical reagents (Aminov A. M., Makhamatkhojaev D. R.).

Chemical reagents are added to drilling fluids to improve their properties. Clay rocks are primarily used in the preparation of drilling fluids. These clays, depending on their mineral composition, are divided into 4 types. These. Montmorillonite (bentonite), kaolin, hydro-micaceous and palygorskite minerals.

Montmorillonite is a bentonite clay mineral. Bentonite clays are more effective than other types of clays. For example, if 16–24 m^3 of a mixture is obtained from bentonite, then 4–6 m^3 of a mixture is obtained from hydromica. Therefore, it is advisable to use a bentonite mixture. Hydro slurry is ubiquitous in terms of quantity, it is used only where there is no bentonite. However, when using hydromica, a sharp increase in the content of the solid phase is observed, and chemical reagents are often used to soften this solid phase. Kaolinite is practically not used in drilling.

Since the minerals of palygorskite are primarily linearly fibrous, salt-tolerant and high-quality mixtures are prepared. Paligorskite mixtures yield very good results in the process of drilling salt deposits (Yuldashev T. R., kat, o'q. Shonazarov E. B., 2019).

Purpose of the research: According to the requirements for mixtures, the water release of the mixtures within 12 hours should not exceed 2.5%. The Paligorskite mixture is in a salty environment, it is saturated with salt and does not excrete water at all. Clay is primarily used as a powder in mixtures. Currently, bentonite clays are extracted from the Navbakhor deposit (Yuldashev T. R., kat, o'q. Shonazarov E. B., 2019). Bentonite reserves are also found in large quantities in Hovdak, where the resulting samples are used to produce drilling fluids.

Table 1. *Chemical characteristics of bentonite*

Indicators	Flow rate (with SPV-5), S	Mixture density, g/cm³	Mixture yield, m³/t	Water retention, cm³ 30 min	Crust thickness, mm
Navbakhor bentonite	25	1.04	15	16	2
Kasantau Bentonite	25	1.06	10	18	2
Saltwort	25	1.30	2	30	3
Constantine bentonite	25	1.06	10	12	2
Hovdak Bentonite	25	1.05	15	17	2

Main technological features. Hydromica and bentonite are primarily used to obtain drilling fluids. The density of solutions prepared from hydromica is 1.15–1.25 g/cm³, while bentonite has a lower density of 1.05–1.08 g/cm³. Until relatively recent years, weighing solutions, i.e., high density, were used, which mainly served to accelerate the drilling process and assist the drill bit (drilling head). Barite ($BaSO_4$) is primarily used as a weighting agent ($\rho > 1.26$ g/cm³). Barite has a specific gravity of 4.48 g/cm³, and its granularity is very low. Barite is widespread in rocks, its extraction is mainly carried out in two ways (Yuldashev T. R., kat, o'q. Shonazarov E. B., 2019). These are the methods of gravitation and flotation.

Barite obtained by gravitation is of higher quality than barite obtained by flotation.

Table 2. *Indicators of different varieties of weighting barite*

№	Indicators	I type	II type
1.	$BaSO_4$ content, %	92	87
2.	Density, g/cm³	4.25	4.15
3.	Moisture content, %	1.5	1.5
4.	The content of water-soluble salts, %	0.30	0.35
5.	No. 009K sieve residue, %	4	4
6.	The number of particles measuring 5 microns, %	5	10

Drilling fluids have specific functions, such as: cleaning the wellbore wall, removing rock from the bottom of the well, cooling the drill bit, blocking (weighing) the movement of gas and oil in the reservoir. Instead of drilling muds, water was also widely used. Drilling fluids are prepared based on liquid phase, clay particles, and chemical reagents

(Yuldashev T. R., kat, o'q. Kholbazarov I. R., Kurbanov A. T., 2015).

The gas phase is also used in the cleaning of wells, and the role of air is also of great importance. The gas phase is pumped into the well using a compressor. The gas or air phase pumped into the well is supplied with PAV (a substance that activates the elastic surface) (Yuldashev T. R., kat, o'q. Kholbazarov I. R., Kurbanov A. T., 2015).

Table 3. *Types and quantity of PAV*

№	Types of PAV	PAV content, %	Crushed rock: water coming out of the layer
1.	Sulfanol, NP-1	0.23	1:2
2.	"Progress", OP-10	0.10	1:2
3.	KAUFE-14	0.12	4:1
4.	"Azolyat-A"	0.10	1:2

Drilling mode: The parameters of the drilling mode depend on the speed of the drill bit's rotation, its load value, the amount of fluid supplied for pipe flushing, and its properties. High efficiency is achieved when all these parameters work. The cutting speed of the cutter is adopted, which is called the mechanical cutting speed and the cutting speed of the cutter (Yuldashev T. R., kat, o'q. Kholbazarov I. R., Kurbanov A. T., 2015).

It is calculated using the following formula:

$$V_m = h/t_{dril} \quad (1)$$

$$V_r = h/t_{dril}+t_{sub} \quad (2)$$

Here, Vm, Vr are the mechanical transition and flight speed of the drill bit; h is the depth of the drill bit; tbur + talm is the time spent on drilling and changing the drill bit.

The following important factors influence this indicator.

1. Natural factors, including the composition of rocks, mechanical properties, and their depth layers.

2. Technical and technological factors, the design of the drill bit, methods of rock crushing, strength and power of drilling rigs.

3. Experience and skills of workers, the process of organizing work.

Research results: This research was conducted at the Termez State University of Engineering and Agrotechnology. Drilling fluids were obtained in laboratory conditions using Hovdak bentonite by scientists at the University. These solutions were tested during drilling.

Currently, the main task is to correctly select these mitigators. Its primary function is to facilitate the uplift of the resulting rock and clay solution by lightening the drilling mud. This is due to the fact that if the clay emulsion formed during drilling remains at the bottom for a long time, the liquid in it will separate and solidify, which has a significant impact on the work. This research paper attaches great importance to this. Table 4 presents a number of types of reagents used to improve drilling properties. These reagents were used during the research, and positive results were obtained.

Table 4. *Reagents used to improve drilling properties*

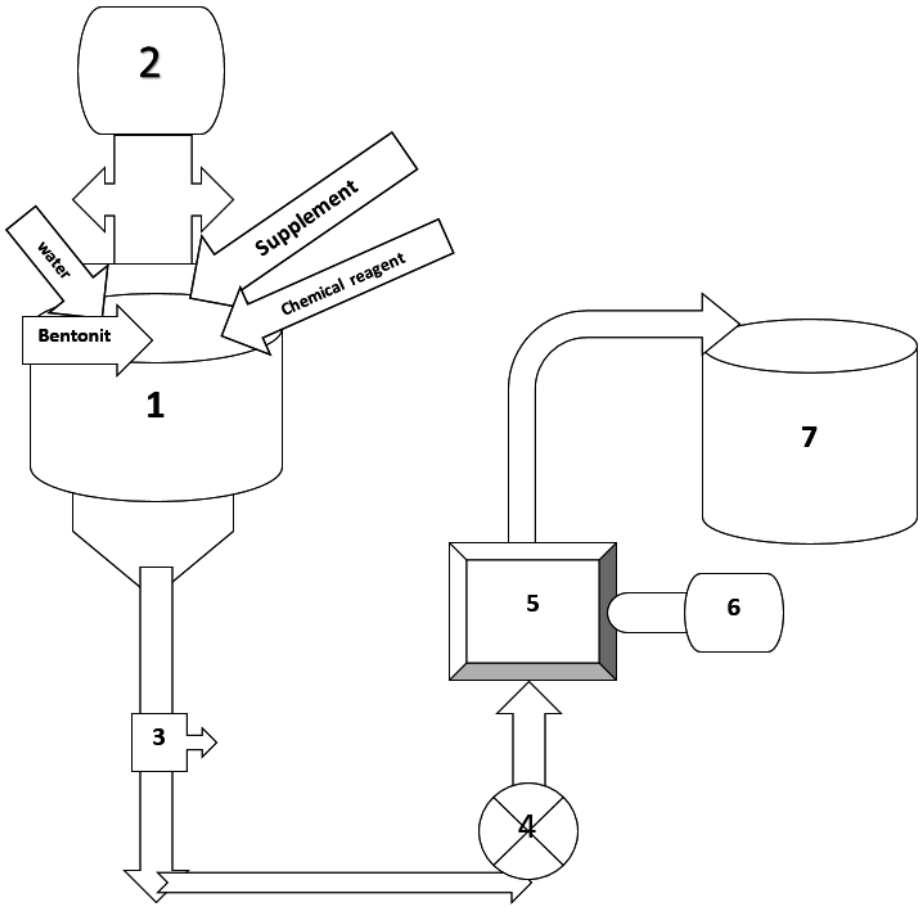
№	Function to perform	Reagents
1.	Dehydration-reducing reagents	UHR (coal-alkaline reagent), KSSB
2.	Reagents that reduce fluidity and viscosity	(In a sulphite-alcohol bar). CMC (carboxymethylcellulose), hypan, K-4, starch
3.	Inhibitors	Nitrolignin, sunide,
4.	Fatty substances	Hetane, FXLS, phosphates, etc.
5.	Emulsifier	Potassium chloride, magnesium chloride, lime, table salt, etc.
6.	Foam removers	SMAD-1, graphite, oil, suapstock, and other oils.

№	Function to perform	Reagents
7.	Reagents that change hydrogen parameters	OP-7, OP-10, sulfonate.

These reagents are used in an amount of 3–4% of the total volume of the drilling fluid.

This figure shows the technological scheme for obtaining a drilling fluid.

Figure 1. *Drilling fluid preparation scheme*



1-reactor-mixer, 2-engine, 3-fluid feed valve,
4-pump, 5-mechanical-chemical disperser (MCD),
6-engine, 7-ready drilling fluid

According to this scheme, the study of the developed technology for producing heat-and salt-resistant drilling fluids based on Hovdak clays using MCD at a speed of 2100 rpm shows high efficiency compared to the traditional method.

Conclusion: Based on the results presented above, samples obtained from bentonite clays are widely used in drilling fluids. The main indicators of Khoddak bentonite also correspond to the drilling fluids obtained from Navbakhor bentonite and other regions. Based on these indicators, we consider the use of bentonite from the new deposit to be a solution to several problems in obtaining and using drilling fluids. During the drilling process, the tasks of drilling muds are to prevent the destruction, breakage, and decrease in the speed of the process of the drill bit (drilling head). Laboratory experiments have proven the possibility of using this bentonite as a drilling fluid, as it possesses the aforementioned properties and possesses a very good adhesion process with water and rocks.

References:

Aminov A. M., Makhamatkhojaev D. R. Text of lectures. “Drilling Fluids.” – Tashkent, Tashkent State University.

Prof. Yuldashev T. R., kat, o’q. Shonazarov E. B. Associated Press A. Kh. Samadov, methodological instructions for practical exercises in the subject “Drilling of Oil and Gas Wells.” Karshi-2019.

Prof. Yuldashev T. R., kat, o’q. Kholbazarov I. R., associate professor. A. T. Kurbanov. Methodological guide for practical exercises in the subject “Drilling of Oil and Gas Wells.” Karshi-2015.

Rakhimov A. Kh., Eshkurbonov F. B., Bobokulova M. Sh., Ashurova A. A. Study of the chemical mineralogical composition of bentonite from the Khovdak deposit // Universum: Chemistry and Biology. – Moscow, – № 7 (109). 2023. – C. 41–47.

Eshkurbonov F. B., Abduraimov Zh. B. Development of new technologies for drilling mud modifiers based on ethylene and propylene oxides // “DIGITAL TECHNOLOGIES IN INDUSTRY” Journal (E) ISSN: 3030–3214. – Vol. 2. – No. 2. June, 2024. URL: http://www.srt-journal.uz

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SYNTHESIS AND STUDY OF BIOLOGICAL ACTIVITY OF COORDINATION COMPOUNDS BASED ON COPPER (II) NITRATE AND QUINAZOLIN-4-ONE

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Abstract

In this work, quinazolin-4-one and copper (II) nitrate are used as ligands to investigate the synthesis of coordination compounds. The complexes were created by a controlled reaction and examined using a range of spectroscopic methods, such as XRD, UV-Vis, and infrared. The effective coordination of copper(II) ions with quinazolin-4-one was validated by the structural analysis. The produced compounds' antibacterial and antioxidant properties were assessed using biological tests. Significant biological activity was shown in the results, indicating possible uses in the agricultural and medicinal sectors. This study advances our knowledge of metal-ligand interactions and how they can improve biological efficacy.

Keywords: *Copper(II) nitrate, quinazolin-4-one, coordination chemistry, antimicrobial activity, antioxidant properties, spectroscopic characterization, pharmaceutical applications*

Introduction

In order to create novel molecules with improved chemical and biological characteristics, coordination chemistry is essential. Transition metals have been extensively investigated for the synthesis of physiologically active complexes because of their varied oxidation states and coordination capabilities. Among them, Copper (II) has garnered significant attention due to its role in biological systems, acting as a cofactor in enzymes and displaying intrinsic antimicrobial and antioxidant properties. Copper (II)-based coordination compounds have shown potential applications in pharmaceutical, agricultural, and environmental fields.

Quinazolin-4-one, a heterocyclic compound, is another noteworthy ligand in coordination chemistry. It serves as a versatile scaffold for synthesizing bioactive molecules,

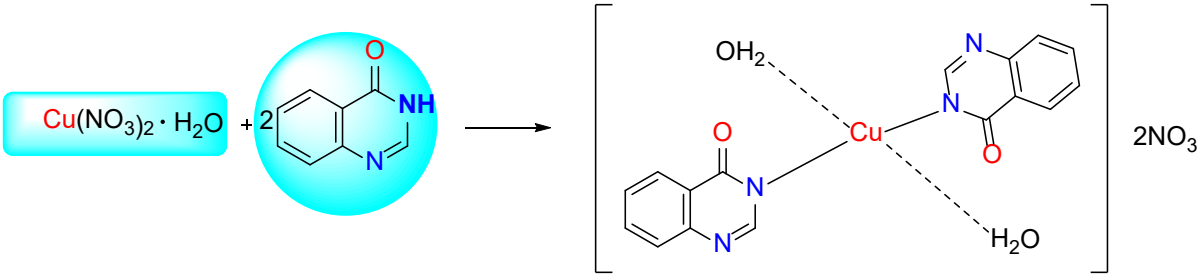
exhibiting a wide range of pharmacological activities such as antimicrobial, anti-inflammatory, and anticancer effects. A possible route to creating new coordination compounds with enhanced biological characteristics is provided by the coupling of quinazolin-4-one with copper (II) ions (Sapaev, B., Saitkulov, F. E., Tashniyazov, A. A., & Normurodov, O. U. 2021; Sapaev, B., Sapaev, I. B., Saitkulov, F. E., Tashniyazov, A. A., & Nazaraliev, D. 2022; Saitkulov, F., Ahmatov, I., Meliboyeva, F., Saydaxmatova, D., & Turopova, S. 2022; Boymuratova, G. O., Saitkulov, F. E., Nasimov, K. M., & Tugalov, M., 2022; Saitkulov, F., Abdusattorova, D., Ismoilova, U., Xasanova, D., & Xusanova, M. 2022; Saitkulov, F. E., Giyasov, K., & Elmuradov, B. J., 2022; Sapayev, B., Saitkulov, F. E., Normurodov, O. U., Haydarov, G., & Ergashyev, B. 2023; Saitkulov, F., Abdukadirov, S., Ashurova, N., Turapov, J., & Zoxidjonova, A. 2022; Saitkulov, F., Begimqulov, I., O ʻralova, N., Gulimmatova, R., & Rahmonqulova, D. 2022; Saitkulov, F., Uralova, B., Ermonova, O., Mamurova, M., & Karimova, K. (2022). Saitkulov, F. E., & Elmuradov, B.J. 2022; Saitkulov, F., Eshqobilov, J., Turgunova, N., & Xamidov, A., 2022.

The purpose of this work is to manufacture and investigate coordination compounds made from quinazolin-4-one and copper(II) nitrate. Because of its high reactivity and capacity to generate stable complexes, copper(II) nitrate is selected as the metal precursor. It is anticipated that quinazolin-4-one will combine with copper (II) ions to produce new compounds with improved biological activity, which could make them suitable for use in medicine and agriculture.

Spectroscopic methods like IR, UV–Vis, and XRD were used in this study to describe the produced complexes and verify their composition and structure. Standard test organisms were used to assess the biological activities, which included antioxidant and antibacterial qualities. By clarifying the connection between the synthetic compounds' structure and activity, these studies hope to advance knowledge of metal-ligand interactions and how they improve biological processes.

Method and results

Under carefully monitored laboratory settings, quinazolin-4-one and copper(II) nitrate were used to synthesize coordination compounds. After dissolving copper (II) nitrate in distilled water, quinazolin-4-one dissolved in ethanol was gradually added to complete the reaction. To make sure the metal and ligand were completely interacting, the mixture was agitated for a few hours at room temperature. After letting the resultant solution crystallize, the solid was filtered, cleaned with ethanol, and vacuum-dried. The reaction equation can be written as follows.



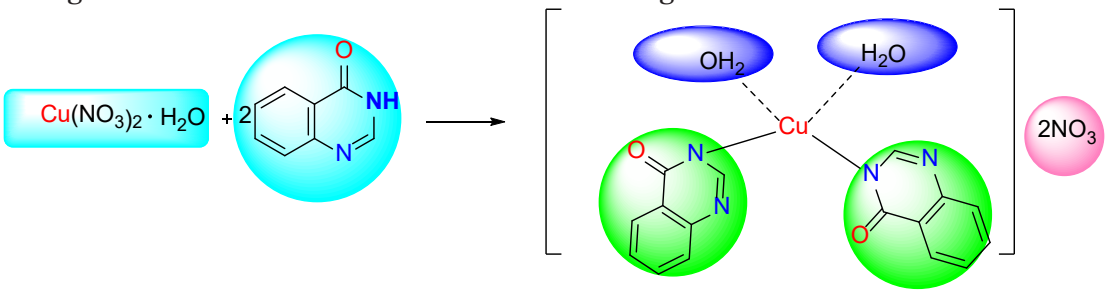
Several spectroscopic and analytical methods were used to characterize the produced molecules. Functional group interactions were detected using infrared (IR) spectroscopy, and electronic changes within the complexes were revealed using UV–Vis spectroscopy. To ascertain the crystal structure and validate the coordination geometry, X-ray diffraction (XRD) research was performed.

X-ray diffraction analysis results confirm that a trans coordination compound is formed when the central atom and ligands are mixed at room temperature.

The reaction is heated to 78–80 °C, resulting in the formation of the cis isomer along with the trans isomer. The structure is expressed as follows.

High yield and stability were achieved by obtaining the synthesised coordination compounds as crystalline solids. Copper(II) ion coordination to quinazolin-4-one was verified by IR spectroscopy by means of distinctive shifts in ligand vibration bands. The

coordination environment surrounding the metal core was indicated by d-d transitions and charge transfer bands found in UV–Vis spectra. The complexes formed in a monoclinic system with distinct geometries, according to XRD measurements.



The produced compounds showed strong antibacterial action against both Gram-positive and Gram-negative bacteria, as well as several fungus strains, in biological testing. Their potential as antimicrobial agents was demonstrated by the zones of inhibition, which were similar to those of conventional antibiotics. Strong free radical scavenging capabilities demonstrated by the antioxidant assays point to their potential use in reducing diseases linked to oxidative stress.

Discussion

The adaptability of these ligands and the metal ion in creating stable complexes has been proven by the synthesis of coordination compounds utilizing quinazolin-4-one and copper(II) nitrate. Optimizing the yield and purity of the products was largely dependent on the reaction parameters, which included temperature, reaction duration, and solvent selection. The effective coordination of copper(II) ions with quinazolin-4-one was validated by the results of spectroscopic and structural studies, which also shed light on the electronic environment and bonding within the complexes.

Significant changes in the distinctive stretching vibrations of functional groups, especially in the carbonyl and amine regions, were visible in the IR spectra, suggesting that these groups were involved in coordination.

The biological active

The biological analysis of these complexes produced encouraging findings. The antibacterial activity against different strains of bacteria and fungi indicates that quinazolin-4-one's biological efficiency is increased by copper II coordination. This could be explained by the metal ion's capacity to interfere with enzyme processes and damage microbial membranes. Furthermore, the DPPH assay's antioxidant activity shows a potent capacity to scavenge free radicals, most likely as a result of Copper II's redox-active properties and the ligand's electronic structure. The findings also demonstrate how crucial metal-ligand synergy is for enhancing the biological characteristics of particular constituents. In addition to stabilizing the ligand, the coordination improves its ability to interact with biological targets. In pharmaceutical applications, where these complexes may function as possible therapeutic candidates, this is very pertinent. Although the results are promising, more research is required to fully understand the molecular mechanism of action of these coordination molecules. A thorough grasp of their therapeutic potential would be possible by looking at their toxicity profiles, stability in physiological settings, and interactions with biomolecules.

Conclusion

The synthesis and characterization of coordination compounds derived from Copper(II) nitrate and quinazolin-4-one have yielded promising results, demonstrating the versatility and biological potential of these complexes. Spectroscopic and structural analyses confirmed the successful coordination of the metal ion to the ligand, highlighting the stability and defined geometry of the synthesized compounds.

The biological activity studies revealed significant antimicrobial and antioxidant properties, suggesting the potential of these complexes as candidates for pharmaceutical and agricultural applications. The coordination of Copper(II) ions not only enhanced the bioactivity of quinazolin-4-one but also provided a framework for understanding the

role of metal-ligand interactions in biological systems.

These findings open avenues for further exploration of Copper(II)-based coordination compounds, particularly in drug development and bioactive material design. Future work should focus on detailed mechanisms of action, in vivo studies, and exploring the potential of modifying the ligand structure to enhance activity and specificity. The study underscores the importance of coordination chemistry in advancing materials with multifunctional properties.

References

Sapaev, B., Saitkulov, F. E., Tashniyazov, A. A., & Normurodov, O. U. (2021). Study of methylation reactions of 2-phenylquinazoline-4-tion with “soft” and “hard” methylation agents and determination of its biological activity. In *E3S Web of Conferences* (Vol. 258. – P. 04023). EDP Sciences.

Sapaev, B., Sapaev, I. B., Saitkulov, F. E., Tashniyazov, A. A., & Nazaraliev, D. (2022, June). Synthesis of 2-methylquinazoline-4-thione with the purpose of alkylation of 3-propyl 2-methylquinazoline-4-thione with alkylating agents. In *AIP Conference Proceedings* (Vol. 2432, No. 1). AIP Publishing.

Saitkulov, F., Ahmatov, I., Meliboyeva, F., Saydaxmatova, D., & Turopova, S. (2022). Titrimetric analysis of calcium cation in” obi navvot” variety of melon. *Academic research in modern science*, – 1(19). – P. 302–304.

Boymuratova, G. O., Saitkulov, F. E., Nasimov, K. M., & Tugalov, M. (2022). To Examine the Processes of Biochemical Action of 6-Benzylaminopurine with Cobalt-II Nitrate Dihydrate on the “Morus Alba” Variety of Moraceae Plant. *Eurasian Journal of Physics, Chemistry and Mathematics*, – 3. – P. 39–42.

Saitkulov, F., Abdusattorova, D., Ismoilova, U., Xasanova, D., & Xusanova, M. (2022). Study of the effect of fertilizing on grain productivity. *Development and innovations in science*, – 1(17). – P. 32–35.

Saitkulov, F. E., Giyasov, K., & Elmuradov, B. J. (2022). Methylation of 2-methylchiazoline-4-one by "soft" and "hard" methylating agents.. *Universum: Chemistry and biology*, (11–2 (101)), – 49 c.

Sapayev, B., Saitkulov, F. E., Normurodov, O. U., Haydarov, G., & Ergashyev, B. (2023). Studying Complex Compounds of Cobalt (II)-Chlooride Gecsacrystolohydrate with Acetamide and Making Refractory Fabrics from Them.

Saitkulov, F., Abdukadirov, S., Ashurova, N., Turapov, J., & Zoxidjonova, A. (2022). Recommendations for the use of fats. *Theoretical aspects in the formation of pedagogical sciences*, – 1(7). – P. 175–177.

Saitkulov, F., Begimqulov, I., O‘ralova, N., Gulimmatova, R., & Rahmonqulova, D. (2022). Biochemical effects of the coordination compound of cobalt-ii nitrate quinazolin-4-one with 3-indolyl acetic acid in the “amber” plants grades phaseolus aureus. *Academic research in modern science*, – 1(17). – P. 263–267.

Saitkulov, F., Uralova, B., Ermonova, O., Mamurova, M., & Karimova, K. (2022). Biochemical nutrition family plant rute-lemon leaved. *Academic research in modern science*, – 1(17). – P. 268–273.

Saitkulov, F. E., & Elmuradov, B. J. (2022). UV spectral characteristics of quinazoline-4-one and–thions. In *Innovative developments and research in education international scientific-online conference*. – P. 10–12.

Saitkulov, F., Eshqobilov, J., Turgunova, N., & Xamidov, A. (2022). Plant nutrition, the process of absorption. *Current approaches and new research in modern sciences*, – 1(7). – P. 25–29.

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DETERMINATION OF CERTAIN HEAVY METALS IN FOOD COMPOSITION BY VOLTAMMETRIC METHOD

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Abstract

This study uses the voltammetric method, a very sensitive and trustworthy electrochemical measurement technique, to determine the presence of heavy metals in dietary samples. Food samples are prepared through digestive procedures as part of the research, and then metals like lead (Pb) and cadmium (Cd) are measured. To accurately detect and measure the concentration of these metals, differential pulse voltammetry (DPV) was used. The findings raise questions regarding food safety and possible health hazards because they show that some food samples contain heavy metals in excess of allowable limits. This study highlights how well the voltammetric approach works as a tool for controlling heavy metal contamination and monitoring food safety.

Keywords: *Heavy metals, food analysis, voltammetric method, electrochemical detection, food safety, lead, cadmium*

Introduction

Heavy metals' harmful effects on human health, even at low doses, have raised concerns about their presence in food. Particularly dangerous metals include lead (Pb), cadmium (Cd), which build up in the body over time and can result in long-term health problems like cancer, kidney failure, and neurological damage. Polluted soil, water, and air, as well as industrial and agricultural processes, can all introduce these toxins into the food chain. Therefore, detecting and measuring heavy metals in food is essential to guaranteeing both public health safety and adherence to food safety laws. Heavy metals are detected using a variety of analytical techniques, but voltammetry stands out as a potent tool because of its high sensitivity, selectivity, and affordability. By measuring current as a function of applied potential, voltammetry makes it possible to find traces of metal ions in complex matrices like food. Among the several voltammetric methods, Differential Pulse Voltammetry (DPV) has shown itself to be very useful for accurately identifying tiny quantities of heavy metals. This study's goal is to create a trust-

worthy voltammetric technique for identifying specific heavy metals in food samples, with an emphasis on Pb, Cd. By using DPV, this technique seeks to offer a quick and effective tool for food safety monitoring, making it possible to identify heavy metal contamination in a variety of food items. In order to identify potential health hazards, this study also aims to measure the concentrations of these metals in food samples and compare the findings with set regulatory limits (Sapaev, B., Saitkulov, F. E., Tashniyazov, A. A., & Normurodov, O. U. 2021; Sapaev, B., Sapaev, I. B., Saitkulov, F. E., Tashniyazov, A. A., & Nazaraliev, D. 2022; Saitkulov, F., Ahmatov, I., Meliboyeva, F., Saydaxmatova, D., & Turopova, S. 2022; Boymuratova, G. O., Saitkulov, F. E., Nasimov, K. M., & Tugalov, M., 2022; Saitkulov, F., Abdusattorova, D., Ismoilova, U., Xasanova, D., & Xusanova, M. 2022; Saitkulov, F. E., Giyasov, K., & Elmuradov, B. J., 2022; Sapayev, B., Saitkulov, F. E., Normurodov, O. U., Haydarov, G., & Ergashyev, B. 2023; Saitkulov, F., Abdukadirov, S., Ashurova, N., Turapov, J., & Zoxidjonova, A. 2022; Saitkulov, F., Begimqulov, I., O'ralova, N., Gulimmatova, R., & Rahmonqulova, D. 2022; Saitkulov, F., Uralova, B., Ermonova, O., Mamurova, M., & Karimova, K. (2022). Saitkulov, F. E., & Elmuradov, B. J. 2022; Saitkulov, F., Eshqobilov, J., Turgunova, N., & Xamidov, A., 2022).

Method and results

The voltammetric approach was used in multiple steps to determine the presence of heavy metals in food samples. In order to break down the organic matrix and release metal ions into the solution, food samples were first prepared through a digestion process that involved treating them with powerful acids (such as hydrochloric acid and nitric acid). To enable the analysis, the digested samples were subsequently filtered and diluted to the proper volume. Metals including lead (Pb), cadmium (Cd) were electrochemically determined using Differential Pulse Voltammetry (DPV). A potential scan was applied to the sample solution in order to perform the voltammetric measurements, and the current that resulted was noted. Standard solutions with known concentrations were prepared in order to create calibration curves for each metal. The amounts of heavy metals in the food samples were ascertained by measuring the peak currents derived from the standards' voltammograms. The standard deviation of the blank readings was used to determine the detection limits for each metal. The voltammetric analysis of food samples for **lead (Pb)** and **cadmium (Cd)** was conducted using Differential Pulse Voltammetry (DPV) with the following findings.

Table 1.

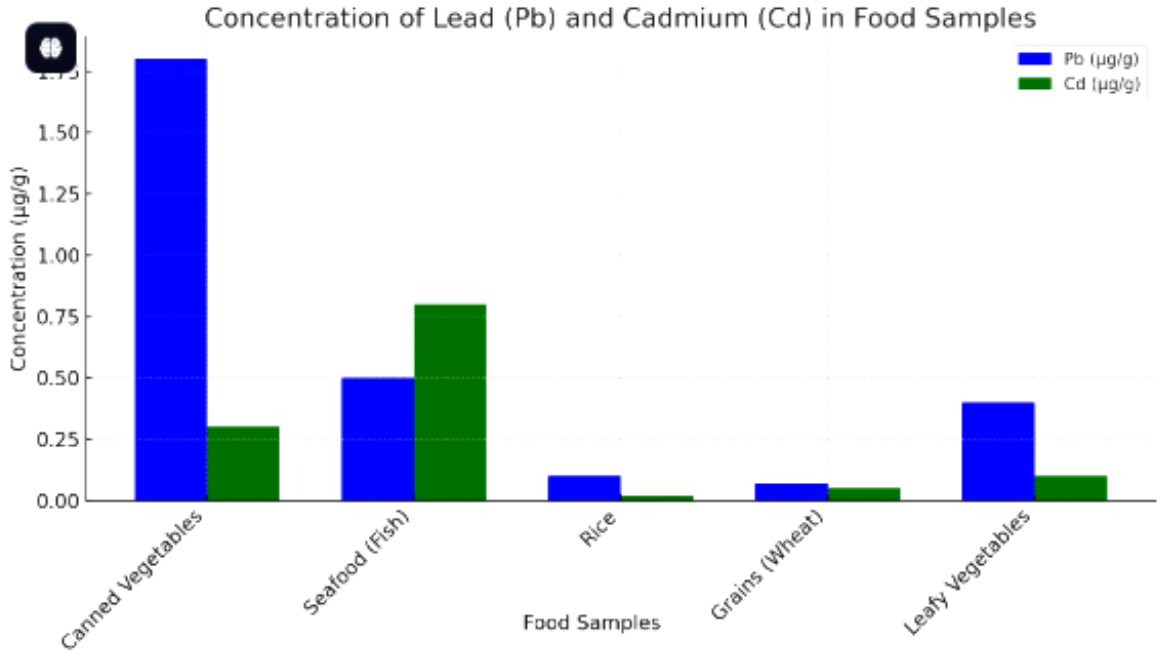
Sample Type	Lead (Pb) Concentration (µg/g)	Cadmium (Cd) Concentration (µg/g)
Canned Vegetables	1.8	0.3
Seafood (Fish)	0.5	0.8
Rice	0.1	0.02
Grains (Wheat)	0.07	0.05
Leafy Vegetables	0.4	0.1

For **lead (Pb)**, the concentrations in canned vegetables and seafood were the highest, with canned vegetables showing levels of 1.8µg/g. These concentrations are well above the regulatory limit of 0.2µg/g for lead in food, suggesting potential contamination during processing. The lowest concentration of Pb was found in grains (0.07 µg/g), which is within the acceptable limits.

For **cadmium (Cd)**, the highest levels were detected in seafood, with concentrations up to 0.8 µg/g, which exceeds the permissible limit of 0.05 µg/g. Other samples, including canned vegetables and rice, showed relatively lower concentrations, but still, canned vegetables had higher cadmium content (0.3 µg/g), indicating a potential risk for contamination, especially from the environmental sources of Cd. These results emphasize the need for continuous monitoring of heavy metal levels in food products, especially processed foods and seafood, to ensure they meet the safety

standards and protect consumers from potential health risks. The voltammetric method proved to be an efficient and reliable tool for the determination of Pb and Cd in food, with high sensitivity and precision.

Diagram 1. *Representing the concentrations of Lead (Pb) and Cadmium (Cd)*



Here is the diagram representing the concentrations of Lead (Pb) and Cadmium (Cd) in various food samples, based on the data provided. The blue bars represent the Pb concentrations, while the green bars represent the Cd concentrations.

Experimental part

Food samples (approximately 10 g) were weighed and subjected to a digestion process. A mixture of concentrated nitric acid and hydrochloric acid (1:3 ratio) was added to the samples in a digestion chamber. The samples were digested under controlled temperature and pressure to break down the food matrix. After digestion, the excess acid was evaporated, and the sample was filtered. The filtrate was diluted with deionized water to a final volume of 100 mL, depending on the concentration of the heavy metals in the samples.

Voltammetric measurements were performed using a potentiostat/galvanostat with a three-electrode system. The working electrode was a glassy carbon electrode (GCE), which was polished with alumina slurry and rinsed with deionized water before each measurement. The reference electrode used was silver/silver chloride (Ag/AgCl), and the counter electrode was a platinum wire. The sample solution (2 mL) was placed into the electrochemical cell, and 0.1 M KCl was added as the supporting electrolyte to ensure proper conductivity.

Differential Pulse Voltammetry (DPV) was employed, with a potential scan range selected for each metal: Pb (–0.3 to 0.1 V) and Cd (–0.8 to –0.4 V). DPV was performed under optimized experimental conditions, with a pulse amplitude of 50 mV and a scan rate of 10 mV/s. The peak current was measured to determine the concentration of each metal.

Standard solutions of Pb and Cd were prepared by diluting known concentrations of stock solutions. Calibration curves were constructed by plotting the peak current against the concentration of each metal. The concentration of Pb and Cd in the food samples was determined by comparing the voltammetric peak currents obtained from the sample solutions with the calibration curves.

The detection limits (LOD) for each metal were calculated based on the standard deviation of the blank and the slope of the calibration curve. The measured concentrations were compared with regulatory limits for Pb and Cd in food, which are 0.2 µg/g for

Pb and 0.05 μg/g for Cd. Recovery tests were performed by spiking food samples with known amounts of Pb and Cd to validate the accuracy and reliability of the method.

Conclusion

The voltammetric method has proven to be an effective and reliable technique for the determination of heavy metals, specifically lead (Pb) and cadmium (Cd), in food samples. The method demonstrated high sensitivity, accuracy, and precision for the analysis of these toxic metals in a variety of food types, including canned vegetables, seafood, rice, grains, and leafy vegetables.

The results of the analysis indicated that certain food samples, particularly canned vegetables and seafood, exhibited higher concentrations of lead and cadmium, surpassing the permissible limits set by food safety regulations. This highlights the potential risks associated with heavy metal contamination in food, which can pose serious health threats if consumed over extended periods.

The use of Differential Pulse Voltammetry (DPV) facilitated the precise quantification of these metals, with calibration curves ensuring the accurate determination of concentrations. Additionally, recovery tests confirmed the reliability of the voltammetric method in real-world applications, with satisfactory results for the detection and quantification of Pb and Cd.

Overall, the findings emphasize the importance of continuous monitoring and regulation of heavy metal levels in food products. Voltammetric techniques offer a valuable tool for food safety assessments, ensuring that consumers are protected from the harmful effects of heavy metal contamination.

References:

Sapaev, B., Saitkulov, F. E., Tashniyazov, A. A., & Normurodov, O. U. (2021). Study of methylation reactions of 2-phenylquinazoline-4-tion with “soft” and “hard” methylation agents and determination of its biological activity. In *E3S Web of Conferences* (Vol. 258. p. 04023). EDP Sciences.

Sapaev, B., Sapaev, I. B., Saitkulov, F. E., Tashniyazov, A. A., & Nazaraliev, D. (2022, June). Synthesis of 2-methylquinazoline-4-thione with the purpose of alkylation of 3-propyl 2-methylquinazoline-4-thione with alkylating agents. In *AIP Conference Proceedings* (Vol. 2432, No. 1). AIP Publishing.

Saitkulov, F., Ahmatov, I., Meliboyeva, F., Saydaxmatova, D., & Turopova, S. (2022). Titrimetric analysis of calcium cation in” obi navvot” variety of melon. *Academic research in modern science,* – 1(19). – P. 302–304.

Boymuratova, G. O., Saitkulov, F. E., Nasimov, K. M., & Tugalov, M. (2022). To Examine the Processes of Biochemical Action Of 6-Benzylaminopurine with Cobalt-II Nitrate Dihydrate on the “Morus Alba” Variety of Moraceae Plant. *Eurasian Journal of Physics, Chemistry and Mathematics*, – 3. – P. 39–42.

Saitkulov, F., Abdusattorova, D., Ismoilova, U., Xasanova, D., & Xusanova, M. (2022). Study of the effect of fertilizing on grain productivity. *Development and innovations in science*, – *1*(17). – P. 32–35.

Saitkulov, F. E., Giyasov, K., & Elmuradov, B. J. (2022). Methylation of 2-methylchiazoline-4-one by "soft" and "hard" methylating agents. Universum: Chemistry and Biology, (11–2 (101)), – 49 c.

Sapayev, B., Saitkulov, F. E., Normurodov, O. U., Haydarov, G., & Ergashyev, B. (2023). Studying Complex Compounds of Cobalt (II)-Chlooride Gecsacrystolohydrate with Acetamide and Making Refractory Fabrics from Them.

Saitkulov, F., Abdukadirov, S., Ashurova, N., Turapov, J., & Zoxidjonova, A. (2022). Recommendations for the use of fats. *Theoretical aspects in the formation of pedagogical sciences*, – 1(7). – P. 175–177.

Saitkulov, F., Begimqulov, I., O‘ralova, N., Gulimmatova, R., & Rahmonqulova, D. (2022). Biochemical effects of the coordination compound of cobalt-ii nitrate quinazolin-4-one

with 3-indolyl acetic acid in the “amber” plants grades phaseolus aureus. *Academic research in modern science*, – 1(17). – P. 263–267.

Saitkulov, F., Uralova, B., Ermonova, O., Mamurova, M., & Karimova, K. (2022). Biochemical nutrition family plant rute-lemon leaved. *Academic research in modern science*, – 1(17). – P. 268–273.

Saitkulov, F. E., & Elmuradov, B. J. (2022). UV spectral characteristics of quinazoline-4-one and thions. In *Innovative developments and research in education international scientific-online conference*. – P. 10–12.

Saitkulov, F., Eshqobilov, J., Turgunova, N., & Xamidov, A. (2022). Plant nutrition, the process of absorption. *Current approaches and new research in modern sciences*, – 1(7). – P. 25–29.

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STUDY OF BENZYLATION REACTIONS OF QUINAZOLIN-4-ONE IN THE PRESENCE OF VARIOUS SOLVENTS

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Abstract

In order to improve reaction conditions and product yields, this study examines quinazolin-4-one's benzylation reactions using different solvents. An essential scaffold for the production of bioactive compounds is quinazolin-4-one, a substance with notable pharmacological activity such as anti-inflammatory, anticancer, and antibacterial qualities. Quinazolin-4-one's biological potential can be enhanced and structural variety introduced via benzylation. The effects of several solvents on reaction kinetics, selectivity, and overall efficiency were investigated. The results show how different solvents affect the reaction's process, providing important information for choosing the best solvents to increase yields and regulate product production. This work advances the creation of more effective synthesis processes for quinazolin-4-one derivatives with specific characteristics.

Keywords: *benzylation, quinazolin-4-one, solvent effects, organic synthesis, pharmacological properties, structural diversity, reaction optimization, bioactive compounds*

Introduction

The study of benzylation reactions of quinazolin-4-one is of considerable importance in the field of organic chemistry due to its potential to synthesize biologically active compounds with a wide range of pharmacological activities. Heterocyclic quinazolin-4-one has been identified as having important biological qualities, such as antioxidant, antibacterial, anti-inflammatory, and anticancer activities. These attributes make quinazolin-4-one derivatives valuable in the design and development of novel therapeutic agents. The ability to modify the quinazolin-4-one structure through various functionalization reactions allows for the en-

hancement of its biological activity and physicochemical properties, which are crucial for drug development.

Benzylation, a process in which a benzyl group is added to the chemical, is one of the best ways to change quinazolin-4-one. The structural complexity and variety of quinazolin-4-one derivatives can be easily increased by this functionalization. Because they can increase a compound's solubility, stability, and reactivity — all of which are critical for the end product's biological activity — benzylation reactions have drawn a lot of interest. Quinazolin-4-one's medicinal potential can be increased by adding a benzyl group, which can also affect how it interacts with biological targets (Sapaev, B., Saitkulov, F. E., Tashniyazov, A. A., & Normurodov, O. U., 2021; Sapaev, B., Sapaev, I. B., Saitkulov, F. E., Tashniyazov, A. A., & Nazaraliev, D., 2022; Saitkulov, F., Ahmatov, I., Meliboyeva, F., Saydaxmatova, D., & Turopova, S., 2022; Boymuratova, G.O., Saitkulov, F. E., Nasimov, K. M., & Tugalov, M., 2022; Saitkulov, F., Abdusattorova, D., Ismoilova, U., Xasanova, D., & Xusanova, M., 2022; Saitkulov, F. E., Giyasov, K., & Elmuradov, B. J., 2022; Sapayev, B., Saitkulov, F. E., Normurodov, O. U., Haydarov, G., & Ergashyev, B., 2023; Saitkulov, F., Abdukadirov, S., Ashurova, N., Turapov, J., & Zoxidjonova, A., 2022; Saitkulov, F., Begimqulov, I., O'ralova, N., Gulimmatova, R., & Rahmonqulova, D. 2022; Saitkulov, F., Uralova, B., Ermonova, O., Mamurova, M., & Karimova, K., 2022; Saitkulov, F. E., & Elmuradov, B. J., 2022; Saitkulov, F., Eshqobilov, J., Turgunova, N., & Xamidov, A., 2022).

The choice of solvent, however, is very important for the performance of benzylation reactions since it affects the reaction's efficiency, pace, and selectivity. By stabilizing or destabilizing intermediates, regulating the reactants' nucleophilicity, and modifying the reaction temperature, the solvent not only modifies the solubility of the reactants but also has an impact on the reaction process. Therefore, regulating product formation and attaining high yields depend on optimizing solvent conditions.

Materials and Methods

Spectroscopic Analysis: The infrared (IR) spectra of the compounds were recorded using a Perkin-Elmer IR-Furye System 200 spectrometer in KBr pellets. The ^1H NMR spectra were obtained on a UNITY-400+ spectrometer with a working frequency of 400 MHz, using deuterated solvents (CD3Cl, DMSO-d6 + CCl4, Pyridine-d5) and an internal standard (GMDS, δ scale).

Thin Layer Chromatography (TLC): Thin-layer chromatography was performed using "Sorbfil" (Russia) and "Whatman® UV-254" (Germany) plates. The eluents used for separation were benzene: acetone (3:1) and chloroform: methanol (8:1).

Melting Point Determination: The melting points of the synthesized compounds were determined using a "Boetius" (Germany) and "MEL-TEMP" (USA) apparatus.

Results

The benzylation reaction in the presence of different solvents exhibited significant variations in reaction rates and product yields. In polar protic solvents, such as ethanol and water, the reactions proceeded relatively smoothly but required longer reaction times compared to non-polar solvents. Ethanol provided moderate yields, while water yielded a lower product yield, likely due to the solubility issues and possible hydrolysis of the reactants.

In polar aprotic solvents like acetone and dimethyl sulfoxide (DMSO), the reactions showed faster rates and higher yields, suggesting that these solvents effectively solvate both quinazolin-4-one and benzyl bromide, enhancing their reactivity. DMSO, being a highly polar aprotic solvent, facilitated the reaction more efficiently, leading to higher yields of the benzylated product compared to acetone.

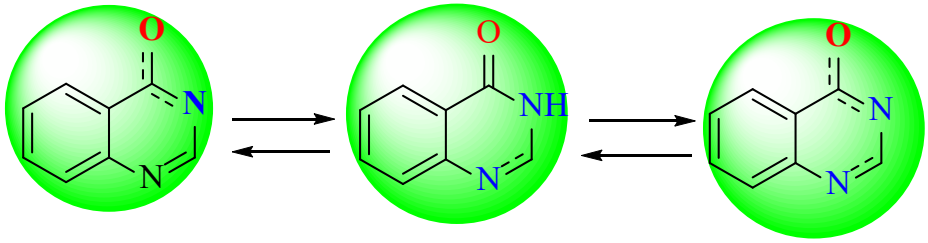
The non-polar solvents, such as toluene and dichloromethane, provided the highest selectivity for the benzylation reaction, although the overall reaction rate was slower compared to polar solvents. The benzylation reaction in toluene gave a high yield with minimal side reactions, suggesting that the non-polar environment might promote a cleaner reaction with fewer competing side reactions. Dichloromethane, although less efficient than toluene, also resulted in high selectivity but required longer reaction times to achieve comparable yields.

The base played a crucial role in enhancing the reaction rate and yield. Potassium carbonate and sodium hydroxide were both effective in promoting the nucleophilic substitution, though potassium carbonate gave slightly better results in polar solvents. The mechanism appears to involve the deprotonation of quinazolin-4-one to generate a nucleophilic intermediate, which then attacks the electrophilic benzyl bromide.

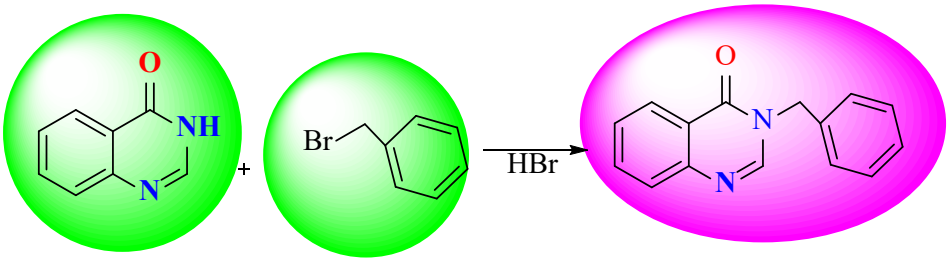
Overall, the study showed that solvent choice significantly impacted both the rate and yield of the benzylation reaction of quinazolin-4-one. The best results were achieved in polar aprotic solvents, with DMSO offering the highest efficiency, followed by acetone. Non-polar solvents like toluene provided high selectivity but required longer reaction times. These findings indicate that solvent optimization is crucial for achieving high yields and selectivity in the benzylation of quinazolin-4-one.

Discussions

The benzylation reactions of quinazolin-4-one were carried out under different solvent conditions to examine the influence of solvent polarity, protic or aprotic nature, and solubility on reaction efficiency and product formation. Quinazolin-4-one (1 mmol) was reacted with benzyl bromide (1.2 mmol) in the presence of a base (such as potassium carbonate or sodium hydroxide) to promote the nucleophilic substitution of the benzyl group onto the quinazolin-4-one scaffold. The reactions were conducted in a variety of solvents, including polar protic solvents (e.g., ethanol, water), polar aprotic solvents (e.g., acetone, dimethyl sulfoxide), and non-polar solvents (e.g., toluene, dichloromethane). The reaction mixtures were stirred at room temperature or heated, depending on the solvent's boiling point, and monitored via thin-layer chromatography (TLC) to track the progress of the reaction. After completion, the products were isolated by filtration or extraction, followed by purification using column chromatography.



Quinazolin-4-one is an ambident compound, meaning it possesses two or more reactive sites that can undergo substitution or addition reactions, leading to different types of products. This ambident nature is due to the presence of functional groups on the quinazolin-4-one structure that allow it to participate in various types of chemical reactions.



In quinazolin-4-one, the most notable ambident behavior is seen at the position of the nitrogen atom in the 1- and 3-positions of the quinazoline ring. The nitrogen atom in the 1-position is nucleophilic and can react with electrophilic reagents, while the nitrogen atom in the 3-position, with its lone pair of electrons, can also participate in nucleophilic reactions. These two reactive sites create a situation where the molecule can react in different ways, depending on the conditions of the reaction, such as the choice of reagents or solvents.

Experimental part

In a 100 mL round-bottom flask, 1.37 g (0.01 mol) of quinazolin-4-one, 30 mL of ethanol (C2H5OH), and 0.672 g (0.012 mol) of KOH are added. The mixture is slightly heat-

ed and stirred to dissolve the components. After cooling the reaction mixture, 2.16 mL (2.74 g, density = 1.27 g/mL) (0.02 mol) of benzyl bromide is added. The reaction is then heated at 102 °C for 4 hours in DMFA (Dimethylformamide). Once the reaction is complete and the mixture has cooled, 30 ml of a 5% aqueous NaOH solution is added, followed by 60 mL of chloroform. The mixture is stirred to extract the product. The chloroform layer is separated, and the chloroform is evaporated. The crude product obtained is then recrystallized to purify the synthesized compound.^{1}H NMR spectrum (400 MHz, CD_3OD, δ, ppm, *J*/Hz): 8.35 (1H, s, H-2), 8.17 (1H, dd, *J*=8.0, 1.6, H-5), 7.76 (1H, ddd, *J*=8.3, 7.2, 1.6, H-7), 7.62 (1H, ddd, *J*=8.2, 1.1, H-8), 7.49 (1H, ddd, *J*=8.2, 7.1, 1.2, H-6), 7.32 (2H, m, H-2`,6`), 7.28 (2H, m, H-3`,5`), 7.22 (1H, m, H-4`), 5.19 (2H, br. s, H-7`).^{13}C NMR spectrum (100 MHz, CD_3OD, δ, ppm): 148.99 (C-2), 162.58 (C-4), 123.02 (C-4a), 129.17 (C-5), 127.98 (C-6), 135.87 (C-7), 128.74 (C-8), 148.99 (C-8a), 137.63 (C-1`), 129.93 (C-2`), 128.94 (C-3`), 127.53 (C-4`), 128.94 (C-5`), 129.93 (C-6`), 50.68 (C-7`).

Consulsion

In conclusion, quinazolin-4-one's ambident nature — which includes two reactive sites that may take part in a variety of chemical reactions — makes it a very reactive and versatile molecule. The quinazoline ring's 1- and 3-position nitrogen atoms provide unique nucleophilic sites that allow the molecule to react with electrophilic or nucleophilic reagents in addition or replacement, respectively. The synthesis of several derivatives with specific characteristics is made possible by this ambident reactivity.

Quinazolin-4-one is a useful intermediate in organic synthesis because it may selectively target one reactive site over the other, depending on the reaction circumstances. The biological activity and molecular variety of quinazolin-4-one derivatives can be improved by regulating the reaction environment.

References

Sapaev, B., Saitkulov, F. E., Tashniyazov, A. A., & Normurodov, O. U. (2021). Study of methylation reactions of 2-phenylquinazoline-4-tion with "soft" and "hard" methylation agents and determination of its biological activity. In *E3S Web of Conferences* (Vol. 258, – P. 04023). EDP Sciences.

Sapaev, B., Sapaev, I. B., Saitkulov, F. E., Tashniyazov, A. A., & Nazaraliev, D. (2022, June). Synthesis of 2-methylquinazoline-4-thione with the purpose of alkylation of 3-propyl 2-methylquinazoline-4-thione with alkylating agents. In *AIP Conference Proceedings* (Vol. 2432, No. 1). AIP Publishing.

Saitkulov, F., Ahmatov, I., Meliboyeva, F., Saydaxmatova, D., & Turopova, S. (2022). Titrimetric analysis of calcium cation in" obi navvot" variety of melon. *Academic research in modern science,* – 1(19). – P. 302–304.

Boymuratova, G. O., Saitkulov, F. E., Nasimov, K. M., & Tugalov, M. (2022). To Examine the Processes of Biochemical Action Of 6-Benzylaminopurine with Cobalt-II Nitrate Dihydrate on the "Morus Alba" Variety of Moraceae Plant. *Eurasian Journal of Physics, Chemistry and Mathematics*, – 3. – P. 39–42.

Saitkulov, F., Abdusattorova, D., Ismoilova, U., Xasanova, D., & Xusanova, M. (2022). Study of the effect of fertilizing on grain productivity. *Development and innovations in science*, – 1(17). – P. 32–35.

Saitkulov, F. E., Giyasov, K., & Elmuradov, B. J. (2022). Methylation of 2-methylchiazoline-4-one by "soft" and "hard" methylating agents. Universum: Chemistry and Biology, (11–2 (101)), – 49 c.

Sapayev, B., Saitkulov, F. E., Normurodov, O. U., Haydarov, G., & Ergashyev, B. (2023). Studying Complex Compounds of Cobalt (II)-Chlooride Gecsacrystolohydrate with Acetamide and Making Refractory Fabrics from Them.

Saitkulov, F., Abdukadirov, S., Ashurova, N., Turapov, J., & Zoxidjonova, A. (2022). Recommendations for the use of fats. *Theoretical aspects in the formation of pedagogical sciences*, – 1(7). – P. 175–177.

Saitkulov, F., Begimqulov, I., Oʻralova, N., Gulimmatova, R., & Rahmonqulova, D. (2022). Biochemical effects of the coordination compound of cobalt-ii nitrate quinazolin-4-one with 3-indolyl acetic acid in the “amber” plants grades phaseolus aureus. *Academic research in modern science,* – 1(17). – P. 263–267.

Saitkulov, F., Uralova, B., Ermonova, O., Mamurova, M., & Karimova, K. (2022). Biochemical nutrition family plant rute-lemon leaved. *Academic research in modern science*, – 1(17). – P. 268–273.

Saitkulov, F. E., & Elmuradov, B. J. (2022). UV spectral characteristics of quinazoline-4-one and thions. In *Innovative developments and research in education international scientific-online conference*. – P. 10–12.

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SYNTHESIS, ANTIBACTERIAL, AND ANTIOXIDANT ACTIVITY OF NOVEL 1,3,4-THIADIAZOLE DERIVATIVES

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Abstract

The antibacterial and antioxidant activities of six novel 1,3,4-thiadiazole derivatives were evaluated. The compounds exhibited significant antibacterial effects against Listeria monocytogenes, Proteus mirabilis, and Pseudomonas aeruginosa and moderate antifungal activity against Candida albicans. Antiradical activity was determined using a DPPH assay, with compound 3 demonstrating the highest effectiveness (59.9%). The lipid peroxidation inhibition assay revealed compound 3 as the most potent antioxidant, reducing malondialdehyde (MDA) levels by 49.9%. These results highlight the potential of 1,3,4-thiadiazole derivatives for therapeutic applications.

Keywords: *1,3,4-thiadiazole derivatives, Antibacterial activity, Antioxidant activity*

Introduction

The exploration of heterocyclic compounds as potential therapeutic agents has gained significant momentum in medicinal chemistry. Among these, **1,3,4-thiadiazole derivatives** have emerged as promising candidates due to their unique structural properties and broad spectrum of biological activities, including antibacterial, antifungal, antiviral, anticancer, and antioxidant effects. The presence of a thiadiazole moiety in their structure facilitates interactions with biomolecular targets, contributing to their pharmacological relevance.

The increasing prevalence of **antibiotic-resistant bacteria** and the global threat posed by **free radical-induced oxidative stress** underscore the urgent need for novel compounds with dual antibacterial and antioxidant activities. Antibiotic resistance has rendered many conventional drugs ineffective, necessitating the development of innovative molecules to combat resistant strains. Concurrently, oxidative stress is implicated in the pathogenesis of numerous chronic diseases, including cancer, diabetes, and cardiovascular disorders. Compounds capable of mitigating these effects are of significant interest for both therapeutic and preventive applications.

This study focuses on the synthesis and biological evaluation of six novel **1,3,4-thiadiazole derivatives**, aiming to investigate their **antibacterial properties** against both Gram-positive and Gram-negative

bacterial strains, as well as their antifungal activity against *Candida albicans*. Additionally, the **antioxidant potential** of these compounds was assessed using the DPPH radical scavenging assay and lipid peroxidation inhibition in mitochondrial systems. Previous research has demonstrated effective termite management strategies using bait formulations (Togaev U., Turaev A. S., Mathur V., Tilyabaev Z., Zhaloliddinov F., Turageldiyev S., Shakirzyanova G., Khashimova M., Rustamov K., Matchanov A., 2024; Tilyabaev Z., Khaitbaev Kh., Shakirzyanova G. S., Togaev U. R., Prokofyeva O. B., Abdullaeva L. K., Babaev B. N., Abdukakharov V. S., Abduvakhabov A. A., 2024; Togaev U., Khaitbaev K., Tilyabaev Z., Toshov K., Khaitbaev A., 2021; Tilyabaev Z., Babaev B. N., Khaytbaev H., Togaev U. R.).

The results reveal a structure-activity relationship that highlights the potential of these derivatives as candidates for further development in the treatment of bacterial infections and oxidative stress-related conditions. The study provides valuable insights into their mechanisms of action and sets the stage for future research into their therapeutic applications.

The problem of free radicals has revolutionized the understanding of many processes occurring in the human body in the last decade. Today, free radicals are considered as a source of numerous disorders leading to the development of a number of diseases.

Materials and Methods

Chemicals and Reagents

All reagents and solvents used in the synthesis and biological evaluation of the compounds were of analytical grade. The synthesized **1,3,4-thiadiazole derivatives (1–6)** 1. 5-ethyl-1,3,4-thiadiazol-2-amine; 2. N- (5-ethyl-1,3,4-thiadiazol-2-yl)benzamide; 3. N-(5-ethyl-[1,3,4]thiadiazol-2-yl)-toluenesulfonamide; 4. N-(5-ethyl-1,3,4-thiadiazol-2-yl) monochloroacetamide; 5. N-(5-ethyl-1,3,4-thiadiazol-2-yl)acetamide6. N-(5-ethyl-1,3,4-thiadiazol-2-yl)propionamide were prepared using standard synthetic procedures, and their purity was confirmed by chromatographic and spectroscopic methods. DPPH (2,2-diphenyl-1-picrylhydrazyl) was purchased from Sigma-Aldrich, and other reagents, including Mueller-Hinton agar (MHA), thiobarbituric acid (TBA), and trichloroacetic acid (TCA), were obtained from reliable suppliers.

Synthesis of 5-ethyl-1,3,4-thiadiazole Derivatives.

The six compounds were synthesized through [insert synthetic procedure, e.g., cyclization or condensation reactions]. Detailed protocols, reaction conditions, and yields are provided in the supplementary section. The structural confirmation was achieved using mass spectrometry.

Antibacterial Activity

The antibacterial activity of the compounds was evaluated in vitro using the **agar diffusion method (glass cylinder technique)** as per the guidelines outlined in "MUK 4.2.1890–04."

- **Microorganisms Tested:**
- **Gram-positive bacteria:** *Listeria monocytogenes 2*, *Staphylococcus aureus* ATCC, *Staphylococcus aureus* D-8, *Staphylococcus aureus* D-5, *Enterococcus faecalis*, *Bacillus subtilis*;
- **Gram-negative bacteria:** *Klebsiella pneumoniae*, *Escherichia coli*, *Pseudomonas aeruginosa* UM 477, *Proteus mirabilis*;
- **Fungi:** *Candida albicans*;
- **Preparation of Microbial Suspensions:** The inoculum was prepared by suspending colonies from 18–24-hour cultures in sterile isotonic solution and adjusting turbidity to 0.5 McFarland standard (approximately $1–2 \times 10^8$ CFU/mL);
- **Agar Plate Preparation:** Mueller-Hinton agar was poured into Petri dishes and inoculated with microbial suspensions;
- **Test Procedure:** Glass cylinders (10 mm outer diameter, 8.5 mm inner diameter) were placed on the agar surface, and 0.1 mL of test solutions (concentrations: 0.5%, 1.0%, 2.0%, and 5.0%) were added. Ethyl alcohol (96%) served as the solvent control, and antibiotic discs were included as a reference.
- **Incubation:** Plates were incubated at 37 ± 1 °C for 18–24 hours. The diameter of growth inhibition zones

was measured using a micro ruler to the nearest millimeter.

Antiradical Activity

The antiradical activity of the substances was measured using a modified method by Zhang et al., based on their interaction with the stable free radical DPPH (diphenylpicrylhydrazyl, Sigma-Aldrich). The DPPH molecule is a stable radical characterized by stability in various media and over a wide temperature range. This is due to the maximum delocalization of the free electron throughout the molecule, spatial screening of atoms with the highest spin density, and the absence of hydrogen atoms in positions where isomerization or disproportionation can occur. It is delocalization that is the cause of the intense violet color of this radical in aqueous-alcoholic media (λmax = 520 nm, ε520 = 6.5 × 10^3 cm^2/mol). When interacting with an antioxidant capable of donating a proton, the radical is reduced, which leads to decolorization of the DPPH solution.

Preparation of DPPH Solution: A 0.2 mM DPPH solution was prepared in 96% ethanol.

Reaction Setup: The reaction mixture contained 1 mL of DPPH solution and test compounds at a final concentration of 0.5 mg/mL.

Incubation: Samples were incubated in the dark at room temperature for 60 minutes, followed by centrifugation at 3000 rpm for 10 minutes.

Spectrophotometric Analysis: Absorbance was measured at 517 nm. The antiradical activity (ARA) was calculated.

Lipid Peroxidation Inhibition Assay

Induction of non-enzymatic Fe^{2+}/ascorbate-dependent lipid peroxidation was performed by adding a mitochondrial suspension at a rate of 0.5 mg protein per 1 ml of MI, 10^{-5} M $FeSO_4$ and 2 × 10^{-4} M ascorbate to an incubation medium (IM) containing 125 mM KCl, 10 mM Tris-HCl (pH 7.4) (Zhang L., Liu C., Li D., Zhao Y., Zhang X., Zeng X., Yang Z., Li S., 2013). The substances were dissolved in 50% ethyl alcohol and stored in a dark place. Samples were added after adding the mitochondrial suspension to the reaction mixture. Incubation was performed at 37 °C in a water bath with constant stirring for 30 minutes. The reaction was stopped by adding 200 μl of 70% trichloroacetic acid (TCA). The precipitated protein was removed by centrifugation at 3000 rpm for 15 minutes.

For analysis, 2 ml of supernatant were collected, 1 ml of warm thiobarbituric acid (TBA) solution was added and the tubes were boiled for 15 minutes. After cooling, the volume was brought to 3 ml and the color intensity was measured on a spectrophotometer (Cary-60) at a wavelength of 535 nm.

The amount of formed MDA was determined using the molar extinction coefficient equal to 1.56 × 10^5 M^{-1} cm^{-1}. The concentration of MDA was expressed as nmol MDA/mg protein.

The ability of the compounds to inhibit lipid peroxidation (LPO) was evaluated in a mitochondrial suspension model.

Isolation of Mitochondria: Mitochondria were isolated from the liver of rats (150–200 g) using differential centrifugation. The liver was homogenized in isolation medium (125 mM KCl, 10 mM Tris-HCl, pH 7.4), and centrifugation steps were performed at 600 g (7 minutes) and 6000 g (15 minutes).

Induction of LPO: Lipid peroxidation was induced using Fe^{2+}/ascorbate-dependent systems. The reaction mixture contained mitochondrial suspension (0.5 mg protein/mL), 10^{-5} M $FeSO_4$, and 2 × 10^{-4} M ascorbate.

Measurement of Malondialdehyde (MDA): After 30 minutes of incubation at 37 °C, the reaction was stopped with 70% TCA, and the supernatant was reacted with TBA at 535 nm. MDA levels were calculated using the molar extinction coefficient of 1.56 × × 10^5 M^{-1} cm^{-1}.

Results and Discussions:

Table 1. *Antimicrobial activity of the compounds*

Microorganisms	1	2	3	4	5	6
Gram-positive bacteria						
Listeria monocytogenes 2	+	+	+	+	–	–

Microorganisms	1	2	3	4	5	6
Staphylococcus aureus ATCC	+	–	–	–	–	–
Staphylacoccus aureus D-8	–	–	–	–	–	–
Staphylacoccus aureus D-5	–	–	–	–	–	–
Enterococcus faecalis	–	–	–	–	–	–
Bacillus subtilis	–	–	–	–	–	–
Gram-negative bacteria						
Klebsiella pneumoniae	–	–	–	–	–	–
Eshericha coli 477						
Pseudomonas aeruginosa UM	+	+	+	+	+	+
Proteus mirabilis	+	+	+	–	–	–
Fungi's						
Candida albicans	+	–	+	–	–	–

As can be seen from Table 1, the synthesized thiadiazole derivatives have a bactericidal effect on both bacteria (gram-positive and gram-negative) and fungi. For example, all synthesized thiadiazole derivatives have a negative effect on the growth of the bacterium Pseudomonas aeruginosa UM. Substances 1, 2, and 3 effectively suppressed the growth of the food pathogen Listeria monocytogenes 2 and the bacterial strain Proteus mirabilis. However, none of the studied substances affected the growth of the microorganism strains Klebsiella pneumoniae, Bacillus subtilis, Enterococcus faecalis, Staphylococcus aureus D-5, Staphylococcus aureus D-8, and their isolates. Antiradical activity results obtained indicate the presence of antiradical properties in all of the studied compounds, which is confirmed by a decrease in the absorption level of the reaction solutions in the following order: DPPH: 1: 2: 3: 4: 5: 6: 1.1. In percentage terms, this looks like:100: 64.7: 70.0: 59.9: 67.9: 66.9: 92.4: 68.5: 70.8, respectively.

• Thus, it was shown that all of the studied substances have antiradical activity (ARA) with varying degrees of effectiveness. The highest ARA was found in substance 3, whose antiradical effect was 40.5% of the control level. Compounds 1, 5, 4, 1.1 and 2 also showed antiradical activity, and their efficiency was distributed in the following descending order: 35.29%; 33.05%; 32.07%; 31.5% and 29.97%, respectively.

Table 2.

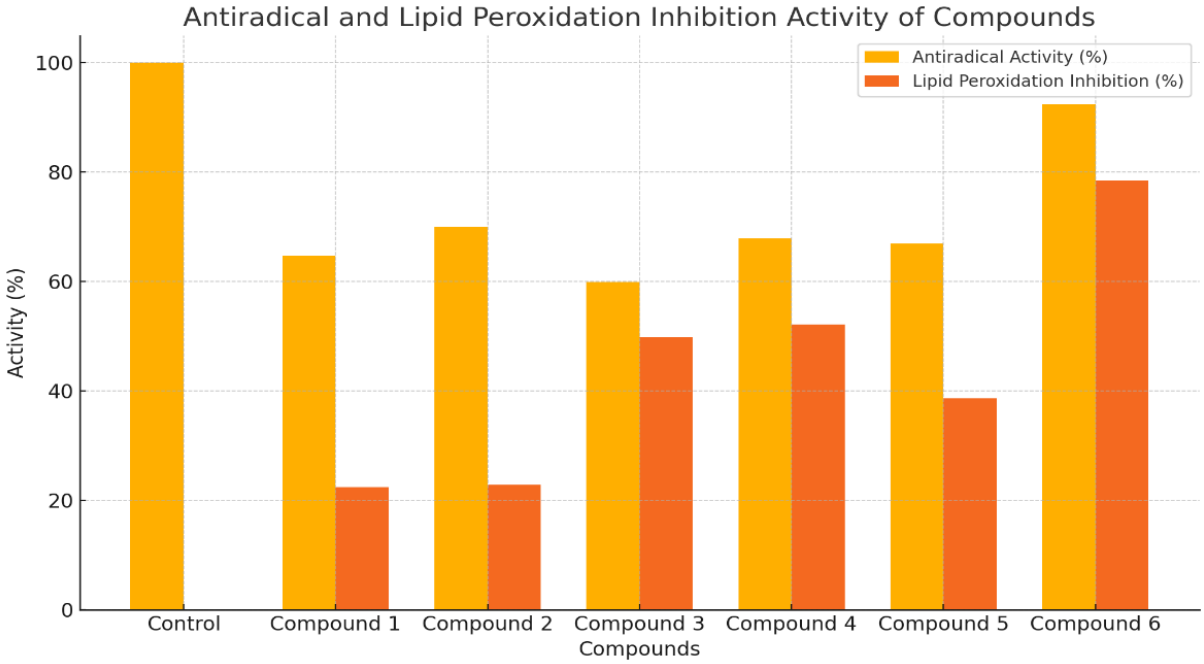
№	APA (DPPH (diphenylpicrylhydrazyl), %	LPO (malondialdehyde -MDA) nmol/mg protein
Control	100%	77.09
1.	64.7	59.79
2.	70.0	59.52
3.	59.9	38.48
4.	67.9	36.81
5.	66.9	47.23
6.	92.4	16.59

MDA accumulation under Fe/ascorbate-induced LPO in the control sample was 77.09 nmol/mg mitochondrial protein and was taken as 100% of the conventional units of the maximum level of MDA production under our experimental conditions.

Analysis of the obtained data showed that substances 3 and 4 possessed the highest antioxidant activity. In percentage terms, the decrease in the level of MDA accumulation in the presence of these substances was 49.9% and 47.7%, respectively. Substances 5 and 1.1 had a less pronounced antioxidant activity, the antioxidant effect of which was 61.2% and 55.3%, respectively. Substances 1 and 2 also showed an antioxidant effect, but among the studied compounds, their activity was the least pronounced and was about 77% relative to the control level.

Thus, all the studied substances demonstrated antioxidant activity. The obtained data correlate with the results previously obtained in the study of their antiradical effects. It should be noted that the most promising compound for further detailed study of its effect on oxidative processes in living systems is substance 3.

Figure 1. *Antiradical and Lipid Peroxidation Inhibition Activity of Compounds*



Conclusion

In this study, six novel **1,3,4-thiadiazole derivatives** were synthesized and evaluated for their **antibacterial** and **antioxidant activities**. The results demonstrate that these compounds exhibit promising biological activities, with potential applications in combating bacterial infections and oxidative stress-related disorders.

Key findings include:

1. Antibacterial Activity:

- Compounds 1, 2, 3, and 4 effectively inhibited *Listeria monocytogenes 2*, while all six compounds showed notable activity against *Pseudomonas aeruginosa*.
- The compounds displayed selective antibacterial properties, particularly against Gram-negative strains like *Proteus mirabilis*, indicating their potential as targeted antimicrobial agents.

2. Antioxidant Activity:

- The antiradical activity, assessed through the DPPH assay, revealed that all compounds exhibited free radical scavenging potential, with compound 3 showing the highest efficacy.
- The lipid peroxidation inhibition assay further confirmed the antioxidant capabilities, with compounds 3 and 4

significantly reducing malondialdehyde (MDA) levels.

These findings underscore the importance of 1,3,4-thiadiazole derivatives as a versatile scaffold for developing multifunctional therapeutic agents. Among the tested compounds, **compound 3** emerged as the most promising candidate, demonstrating both potent antibacterial and antioxidant activities.

Future research should focus on:

- Elucidating the mechanisms of action underlying the observed biological activities;
- Exploring structural modifications to enhance efficacy and selectivity;
- Investigating in vivo effects and potential applications in clinical settings.

The promising results reported here provide a solid foundation for further studies aimed at the development of **1,3,4-thiadiazole derivatives** as effective agents for addressing global challenges in infectious diseases and oxidative stress management.

References:

Schneider W. C., Hogeboom G. H. Cytochemical studies of mammalian tissues: the isolation of cell components by differential centrifugation // Cancer.Res. 1951. — V. 11. — P. 1–22.

Gornal A. G. Bardawill C. J., David M. Determination of serum protein by means of biuret reaction // J.Biol. Chem. 1949. — V. 177. — P. 751–766.

Ohkawa H., Ohaahi N., Jadi K. Assay for lipid peroxides in animal tissues by thiobarbituric acid reaction // Anal. Biochem. 1979. — Vol. 95. — № 2. — P. 351–358.

Zhang L., Liu C., Li D., Zhao Y., Zhang X., Zeng X., Yang Z., Li S., Int.J.Biol. Macromol. — 54. (2013). — P. 210–275.

Togaev U., Turaev A. S., Mathur V., Tilyabaev Z., Zhaloliddinov F., Turageldiyev S., Shakirzyanova G., Khashimova M., Rustamov K., Matchanov A. Innovative Strategies for Termite Management: Development and Evaluation of Effective Baits against Anacanthotermes turkestanicus. Biotech Res Asia 2024. — 21(4).

Tilyabaev Z., Khaitbaev Kh., Shakirzyanova G. S., Togaev U. R., Prokofyeva O. B., Abdullaeva L. K., Babaev B. N., Abdukakharov V. S., Abduvakhabov A. A. Results of research on some pheromones from insect pests in Uzbekistan. Uzbekistan Journal of Biology. 2017; 3: 27–31.

Togaev U., Khaitbaev K., Tilyabaev Z., Toshov K., Khaitbaev A. Investigation of the attractive properties of compounds in Anacanthotermes turkestanicus. Nat. Volatiles & Essent. Oils, 2021; 8(7): 12564–12573.

Tilyabaev Z., Babaev B. N., Khaytbaev H., Togaev U. R. Application of the chemicals against termites. Scientific Discussions, 2017; 1(7): 6–13.

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Section 3. Food processing industry

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PROSPECTS FOR THE USE OF WHEAT GERM PRODUCT IN THE PRODUCTION OF GRAIN BREAD FOR SPECIAL PURPOSES

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Abstract

The article considers the feasibility of using the germ product as an alternative substitute for wheat grain in the production of grain bread for special purposes. A comparative analysis of the fractional and chemical composition, biological value of the studied raw materials was carried out. The main quality indicators and therapeutic-prophylactic properties of wheat germ product are described. The expediency of using this product in the production of grain types of bread is substantiated.

Keywords: *wheat, grain, germ product, quality, medicinal properties, nutritional value, biological value*

In recent years, the problem of providing the population with high-quality and nutritious food products has become particularly acute, in the range of which grain types of wheat bread are of no small importance. However, as is well known, neither wheat grain, nor wheat flour of the highest and first grades, in terms of the content and balance of the most important macro- and micronutrients and structural components, is able to provide the necessary, according to the requirements of modern dietetics and nutritionology, a complete composition of the finished product.

One of the most promising ways to solve this problem is to include multifunctional natural raw materials in the formulation, in particular wheat germ product as an alternative to grain in the production of grain bread with a predicted health-improving effect, especially for dietary nutrition in senile asthenia and its main geriatric syndromes (malnourishment, sarcopenia).

The wheat germ product is obtained both in the grain cleaning and grinding department. The principle of embryo selection in the grain cleaning department is based on the separation of some part of the embryo during dry peeling of grain on paper or brush machines, followed by pneumatic separation of feed products (Juraeva N. R. 2017. P. 81–84; Babaev S. D., 2012. p. 16; Alekseeva T. V., P. 30–33).

The research used samples of wheat germ product (hereinafter referred to as WGP) obtained at JSC Dunyo-M (Uzbekistan). The comparison sample was wheat grain (hereinafter referred to as WG), which, according to GOST 9353–2016, belonged to type III wheat – soft spring white grain, subtype 4, class 3 (Fig. 1).

Figure 1. *Appearance of grain (a) and wheat germ product (b)*

a) b)

In terms of organoleptic (sensory) and physico–chemical quality parameters, the studied WGP met the requirements of TU 9295–010–00932732–08 "Wheat germ flakes, edible" for this raw material (Table.1), which determines the possibility of using this product as an alternative to wheat grain (wheat grits) in the production of grain bread, which will also improve the taste and aromatic properties of this product, which are particularly important for consumers (Table 1).

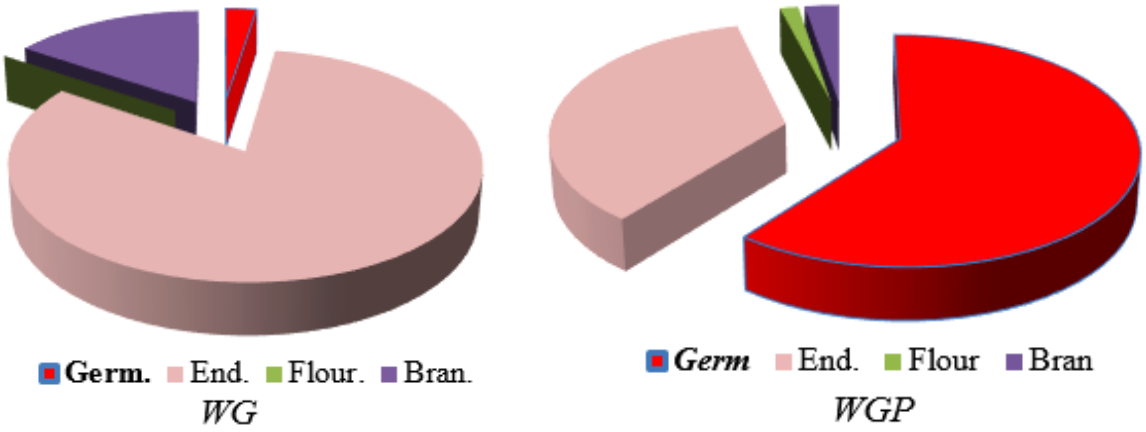
Next, the fractional composition of WP and WGP was studied (Fig. 2).

Table 1. *Organoleptic and physico– chemical quality indicators of wheat germ product*

Indicator	Characteristic
Appearance	Heterogeneous, loose mass
Colour	Heterogeneous, from light brown to brown
Smell	Characteristic, slightly pronounced, without musty, malty and moldy odors
Taste	Characteristic, with a nutty taste, without extraneous flavors
The presence of mineral impurities	Not detected
Humidity, %	12.50 ± 0.20
Volume weight, g/dm ^{3}	645 ±15
Weight of 1000 pieces, g	0.45 ± 0.50
Peroxide number, mM/kg	0. 90 ± 0.10
Acid number, mg KOH/g	5. 30 ± 0.20

The fractional composition of WG and WGP was studied (fig. 2)

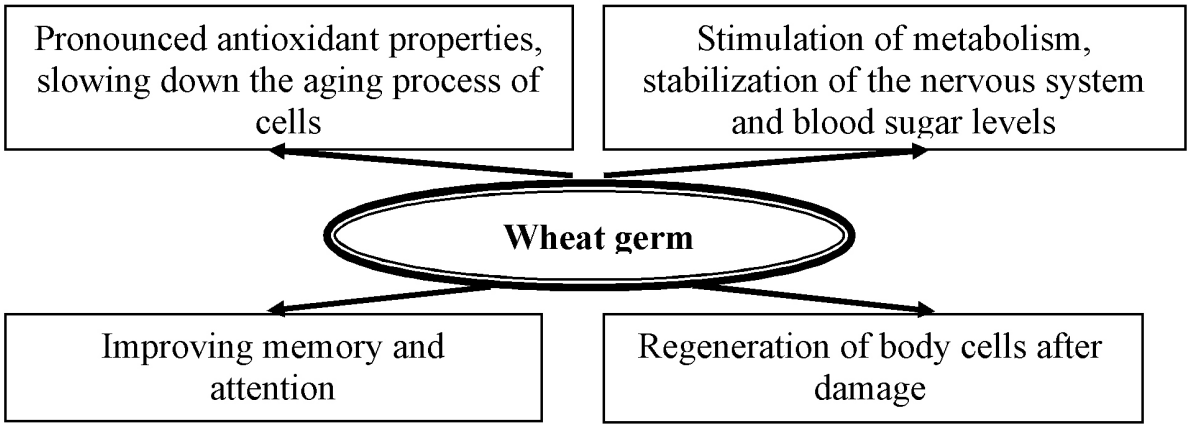
Figure 2. *The average fractional composition of wheat grain (WG) and germ product (WGP):* Ger. – germ, End. – endosperm, Flour. – flour-like feed, bran. –bran, shells, aleurone layer



As follows from the data obtained (Fig. 2), WGP contains on average 24...30 times more germ (~ 60.0...65.0% of the total weight of the product) and almost 2.4 times less than other parts of the grain (endosperm, flour, bran, amounting to about 35.0...40.0% of the total weight of the product), than the WG.

Particularly valuable components of this potential grain substitute are the high content of germs, which are the most nutritious part of it, which determines the prospects of its use for fortification of the functional properties of bread intended for the prevention and treatment of alimentary-dependent diseases (Fig. 3).

Figure 3. *Characteristics of the therapeutic and prophylactic properties of the wheat germ product as a raw material for the production of grain bread for special purposes*



WGP is characterized by an increased content of proteins, minerals, vitamins, and one of the most deficient and significant fatty acids, omega – 3, is found in its oil (Sergeev V. N., P. 143–152).

The uniqueness of this raw material also lies in the presence of polycosanol (germ oil, saturated with vitamin E), which has a beneficial effect on physical fitness, energy, and the cardiovascular system. Especially important for solving the main goal of the work, namely the development of a grain bread recipe for the prevention and treatment of the main symptoms of senile asthenia, is the proven effectiveness of germ oil in pain caused by muscular dystrophy and other neuromuscular diseases (Alekseeva T. V., P. 30–33; Sergeev V. N., P. 143–152).

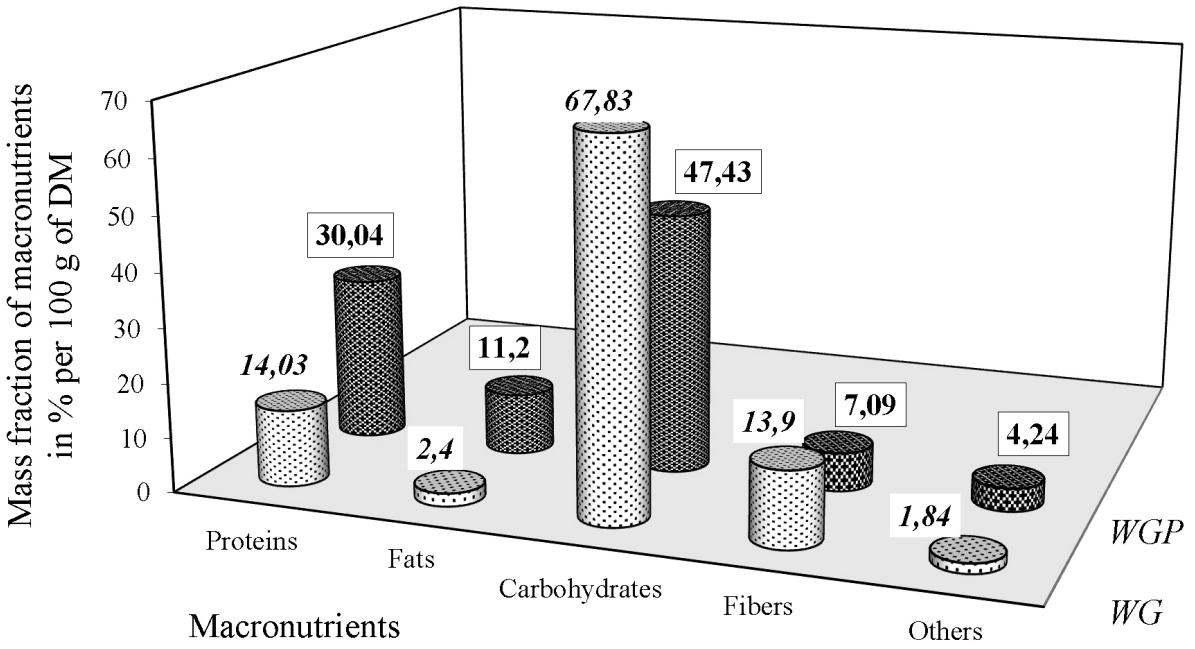
However, there are certain risks and limitations when using this product, as, in other respects, for almost all cereals. Thus, wheat germ contains gluten, which makes

it unsuitable for people with celiac disease or gluten intolerance. This product is subject to rapid oxidation due to its high fat content, which leads to its rapid rancidity and loss of useful properties, and phytic acid is found in it. The latter circumstance is not significant, since this problem is successfully solved by soaking or heat treatment of the product. In the case of bread production, in particular grain, these two stages of the technological process are envisaged (soaking and heat treatment – baking), therefore, the negative impact of phytic acid is practically canceled, that is, minimized. For food purposes, it is recommended to use a large and medium undisturbed germ, and a small destroyed one for forage purposes.

The results of a comparative analysis of the chemical composition that determines the nutritional value of raw materials, WGP, positioned as an alternative (substitute) for WG in the formulation of grain bread for special purposes, are shown in Figure 4 and in Table 2. For greater clarity and an objective assessment of the comparison of the studied raw materials with different humidity, the mass fraction of the main macronutrients was recalculated for dry substances (Fig. 4).

It was found that the content of proteins and fats in the WGP is quantitatively higher than similar indicators in the WG by an average of 2.1 and 4.7 times, respectively. At the same time, carbohydrates and dietary fiber in the study object are 1.6 and 2.0 times less than in the comparison sample, respectively.

Figure 4. *Composition of the main macronutrients in wheat grain and germ product, in % of dry matter (DM)*



It should be noted that the ratio of proteins and fats in the WGP has been slightly improved – 1.0:0.4, with this ratio in the WG – 1.0:0.2; the ratio of proteins: carbohydrates – 1.0:3.3 with optimal – 1.0;4.0.

It has been established that in terms of the content of certain, in this case important, minerals, namely calcium, magnesium, phosphorus and iron, WGP is inferior, and in terms of vitamins it surpasses WG, especially in terms of the mass fraction of tocopherols (vitamin E) (Table 2). At the same time, the mineral composition of these nutrients as in the control, and the experimental samples are not balanced in accordance with the requirements of modern nutritionology.

Table 2. *Mineral and vitamin composition of the studied raw materials*

Nutrients	The amount of nutrients in mg per 100 g of product/ grade	
	WG	WGP
Calcium (Ca)	51.00 / 1	26.80 / 2
Magnesium (Mg)	107.10 / 1	32.05 / 2
Phosphorus (P)	347.16 / 1	132.00 / 2
Iron (Fe)	5.28 / 1	9.12 / 1
Thiamine (B1)	0.39 / 2	2.20 / 1
Riboflavin (B2)	0.16 / 2	1.48 / 1
Niacin (PP)	6.82 / 2	7.32 / 1
Tocopherols (E)	2.20 / 2	34.05 / 1
Total points (rank)	12 / 2	11 / 1

The biological value of wheat germ is estimated very highly, especially in comparison with ordinary wheat flour. This makes them a useful addition to the diet, especially for those who seek to improve the quality of their protein intake and increase the intake of micronutrients. The biological value of WGP proteins was investigated (Amanov, B. N., & Nurmatov, J. J., 2023; Amanov, B. N., & Baqoyeva, S. S., 2023). The comparison sample was the WG and the reference protein according to FAO/WHO. The results of the study are shown in Figure 5 and in Table 3. It has been established that the protein in the PSA is almost 2.0 times more than in the WG. Accordingly, the content of essential amino acids (EAA) in the study object increased by an average of 3.0 times, since the mass fraction of the main sources of protein in the germ is almost 5.0 times higher than in the grain, in which up to 82.0% of the grain weight is accounted for by the endosperm (Fig. 5).

Figure 5. *Mass fraction of essential amino acids (EAA) in 100 g of grain and wheat germ product (in mg)*

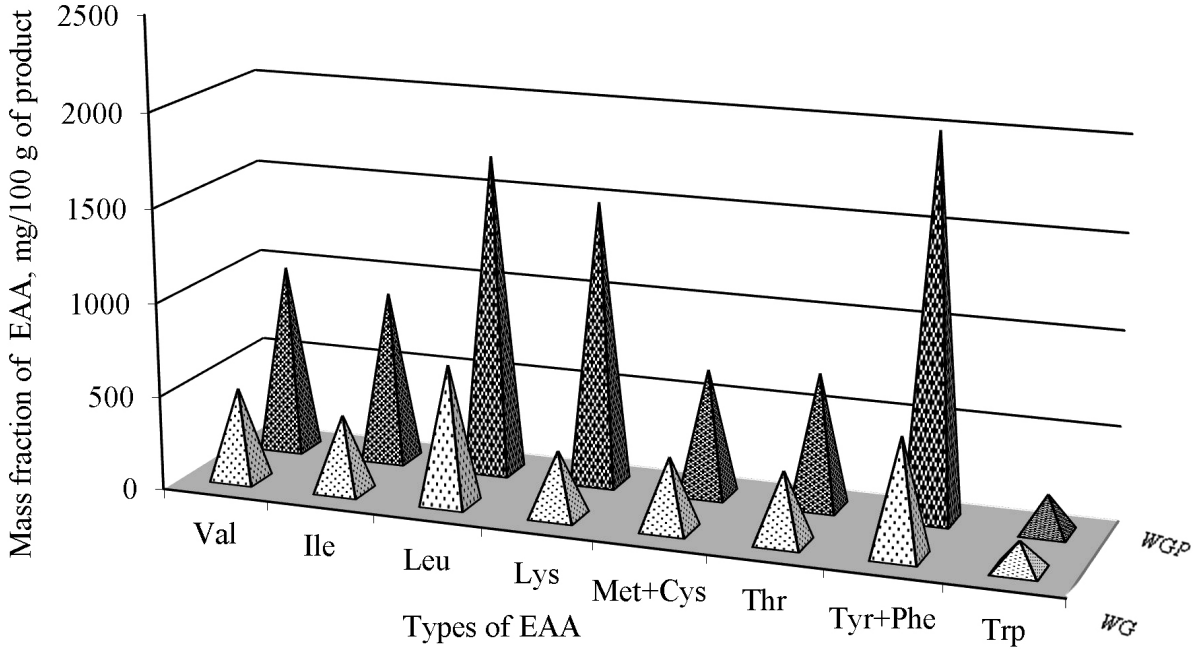


Table 3. *The matrix of ranking of the studied raw materials according to indicators of biological value*

Indicators of biological value	The value of indicators / Rank, score	
	WG	WGP
Mass fraction of protein, %	12.53/2	26.20/1
The total amount of EAA in the product, g/100 g of the product	3.330/2	9.814/1
EAA content in protein, g/100 g of protein	28.06/2	37.97/1
BCAA content, g/100 g of product	1.64/2	3.71/1
The minimum score for the 1st limiting amino acid (amino acid)	50 (Lysine)	73 (met. + cys.)
Total AKS (at NSR' = 0.93), %	67/2	95/1
Coefficient of imbalance of amino acid composition (CIA), %	32.5	29.0
Biological value of protein, %	67.5/2	71.0/1
Total rank, score / place	12 / 2	6 / 1

Of particular importance in this context, namely for the production of bread intended for preventive and curative nutrition in sarcopenia, is the increased content of lysine and BCAA amino acids (English branched-chain amino acids, BCAA), these include valine (maintains nitrogen balance, participates in regenerative processes), leucine (stimulates synthesis protein, regulates blood sugar levels) and isoleucine (participates in energy metabolism, provides muscle recovery), recommended for a number of diseases associated with depletion of muscle mass and their corresponding weakness (sarcopenia) (BCAA/ The material is from Wikipedia 2024; BCAA – its role in the body and effectiveness in sports. 2024).

It was found that the biological value of the WGP is almost 3.5% (abs.) higher than that of the WG (Table.3), and the value of the total Amino acods score (at SSD = 0.93) is approaching the "ideal" value (100%) and is 95% with a control value in the comparison sample of 67%.

Thus, the technological effectiveness of the use of WGP in the composition of grain bread for special purposes as a full-fledged substitute (substitute) for wheat grain (wheat grits) is substantiated. This replacement is also advisable in the sense that no pretreatment is required to use the WGP, the raw materials from the mill come ready for use, while the whole grain must be ground to medium size.

References

Juraeva N. R. The use of wheat germ flour as part of a fat-flour composition for the production of flour confectionery such as biscuits / N. R. Juraeva, I. B. Isabaev // Universum: Technical Sciences: electron. scientific journal. 2017. – № 2(35). URL: http://7universum.com/ru/tech/archive/item/4371/ (date of application 03.12.2019).

Vishnyakov A. B. Wheat germ as a component of compound feed/A. B. Vishnyakov, V. N. Vlasov // Compound feed. 2011. – № 2. – P. 81–84.

Babaev S. D. Determination of the germ content in wheat milling products and rational technology of their stabilization / S. D. Babaev // Bread products. 2012. – № 5. – P. 16.

Alekseeva T. V. Quality management of food systems based on wheat germ cake/ T. V. Alekseeva, A. A. Rodionov// Economy. Innovation. Quality management. 2013. – № 5. – P. 30–33.

Sergeev V. N. The use of functional wheat germ products in the nutritional support of patients with chronic gastroduodenitis and duodenal ulcer at the sanatorium stage of treatment

(literature review) / V. N. Sergeev, O. M. Musayeva, A. S. Dydykin// Bulletin of Restorative Medicine. 2020. – № 97 (3). – P. 143–152. – URL: https://doi.org/10.38025/2078-1962-2020-97-3-143-152

BCAA/ The material is from Wikipedia, the free encyclopedia. – URL: https://ru.wikipedia.org/wiki/BCAA (date of application: 10/22/2024).

BCAA – its role in the body and effectiveness in sports. – URL: https://geneticlab.ru/blog/bcaa-rol-v-organizme-i-effektivnost-pri-zanyatiyakh-sportom/(date of application: 22.10.2024).

Muzafarova Kh. M. Organization of nutrition for the elderly/ Kh. M. Muzafarova, M. T. Kurbanov, D. M. Muzafarova//Results of National Scientific Research. scientific journal. 2022. – Volume 1| Issue 9. URL: https://academicsresearch.com/index.php/rnsr/index.

Akabirov, L., Research of impact of discharge parameters of electric impulse on the damage of tissue cells of the fig and the drying process and determination of its parameters // Narziyev, M., Khujakulova, N.//Journal of Physics: Conference Series, 2022. – 2388(1). – 012180 p.

Ismatova S. N. Determining the optimal modes of the technological process of obtaining dietary flour from oat grain // Ismatova S. N. Yuldasheva S. J., Khujakulova N. F.// In E3S Web of Conferences (Vol. 390), 2023. EDP Sciences.

Amanov, B. N., & Nurmatov, J. J. (2023). Nutritional Value of Bakery Products Increasing It. Vital Annex: International Journal of Novel Research in Advanced Sciences, – 2(1). – P. 165–169.

Amanov, B. N., & Baqoyeva, S. S. (2023). Evaluation of the Biological Value of Pumpkin Powder When Used in Production. Vital Annex: International Journal of Novel Research in Advanced Sciences, – 2(1). – P. 18–22.

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SELECTION AND OPTIMIZATION OF THE MAIN PARAMETERS OF THE TECHNOLOGY OF "COLD PRESSING" OF SUNFLOWER SEEDS IN A HYDRAULIC PRESS

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Abstract

The paper studies the influence of the main process parameters (pressing pressure and particle size of oilseed material) during cold hydraulic pressing on the residual oil content of the cake and the acid number of oil from local varieties of sunflower seeds. Using the nonlinear programming optimization method, it was found that, at a pressing pressure of 50 MPa and a petal thickness of oilseed material of 0.3 mm, the residual oil content of the cake will be within 6.5%; and the acid number of the resulting oil will be within 1.4 mg KOH/g.

Keywords: *sunflower seeds, oil, pressing, hydraulics, pressure, thickness of the petal sunflower seeds, residual oil content of the cake, acid number*

Introduction

Cold pressing of oilseeds in a hydraulic press is a process in which oil is extracted from the seeds of various oilseed crops (such as sunflower, flax, sesame, and others) without the use of heat. This method allows preserving the maximum amount of nutrients and vitamins in the oil, since in the absence of high temperatures, the beneficial substances are not destroyed (Kopylov, M.V., 2013; Proctor, A., 2013).

The main stages of the cold pressing process: seed cleaning; seed preparation for pressing; pressing; oil purification.

Advantages of cold pressing: preservation of natural antioxidants, vitamins (especially E) and fatty acids (e.g. omega-3, omega-6). The oil has a more pronounced taste and aroma, characteristic of the original raw material. No chemical additives or solvents (Çakaloğlu, B., Özyurt, V. & Ötleş, S., 2018).

Disadvantages: lower oil yield compared to hot pressing or solvent extraction. The process may be slower and less cost-effective (Çakaloğlu, B., Özyurt, V. & Ötleş, S., 2018).

The main factors affecting the oil yield during hydraulic pressing include (Gafurov, K. Kh., Safarova, D. N., 2022; Mustafaev, S. K., Kalienko, E. A., Sonina, D. V., & Efi-

menko, S. G., 2014; Çakaloğlu, B., Özyurt, V. & Ötleş, S., 2018):

1. Raw material moisture: the moisture content and maturity of the raw material also play a role. Raw materials with the right moisture content will maximize oil yield, while those that are too dry or too wet may reduce efficiency.

2. Size and shape of raw material particles: finer grinding of raw material is easier to press, as oil is released more easily from small particles. However, excessive grinding can lead to the formation of too dense a mass, which complicates the extraction of oil.

3. Temperature and pre-treatment of raw materials: heating the raw material before pressing reduces the viscosity of the oil and increases its flowability, which helps increase the yield. Too high a temperature can lead to oxidation of the oil, deterioration of quality and losses. Methods such as heating, wet-heat treatment or fermentation can increase the yield of oil by breaking down the cell walls and facilitating pressing.

4. Pressing pressure: The higher the pressure, the more oil can be extracted. However, excessive pressure can lead to the destruction of the cellular structure of the raw material and a decrease in oil yield.

5. Duration of pressing: The longer the pressing, the more oil can be extracted, but at a certain point, additional effort does not significantly increase the yield, since most of the oil has already been extracted.

The correct combination of these factors allows for the most efficient extraction of oil during hydraulic pressing.

The purpose of this stage of the work is to study the influence of the main factors during hydraulic pressing on the residual oil content of the cake and the acid number of sunflower oil, with the subsequent determination of the optimal values of the influencing factors.

Object and methods of research. The object of the study was the seeds of the sunflower hybrid Dushko, included in the State Register of Agricultural Crops Recommended for Sowing in the Republic of Uzbekistan. Before pressing, the sunflower seed meal was treated with IR rays with a heat flux density of 7.2 kW/m^2 andan irradiation duration of 60 s in the mode:

+60–120+35–120+35–120+35–120+30 (the "+" sign indicates the duration of IR irradiation; the "-" sign indicates the duration of exposure without irradiation) (Gafurov, K.Kh., Safarova, D.N., 2022; Gafurov, K. Kh., 2020).

The temperature of the raw material under this heat treatment regime does not reach 60 °C, and the humidity of the raw material is 6%, which is optimal for cold pressing (Cai, Z., et al., 2021).

6YZ –230 hydraulic press was used to extract the oil by pressing. Hydraulic presses for cold pressing are distinguished by the fact that they create high pressure using hydraulics, which allows for the oil to be extracted carefully without a significant increase in temperature.

The residual oil content of the cake was determined according to the state standard *O'z DSt 2438:2012* Oil seeds. Methods for determination of oil content.

The acid number of the oil was determined according to the state standard *O'z DSt 1203:2015* Vegetable oils. Methods for determination of acid number.

The study used the compositional design of experiments method (Murray P. M., et al. 2016; Georgakis C., 2013).

Analysis of results. For the study, we select the pressing pressure and the particle size of the raw material as influencing factors. The pressure of the hydraulic press plays an important role in obtaining vegetable oil, since it helps to extract oil from seeds or fruits. The pressure required for pressing oil varies depending on the type of process and the purpose of production, but it is usually from 20 to 70 MPa. We select the limiting pressure values $z_1^- = 40$ MPa; $z_1^+ = 60$ MPa.

The particle size of the raw material during hydraulic pressing plays a key role in the efficiency of the oil extraction process. The correct particle size during hydraulic pressing must be carefully selected for each type of seed. The optimal size ensures both efficient oil extraction and minimal oil loss in the cake. To achieve maximum oil yield, it is important that the seed particles are small enough to break down the cellular structures, but not too small to form a dense, poorly permeable mass. Typically, for sunflower pressing, the particle size after grinding is about 0.2–0.5 mm.

We select the boundary dimensions of sunflower seed meal (petal seeds): $z_2^- = 0.2\ mm\ z_2^+ = 0.4\ mm.$

The output parameters are the residual oil content of the cake, y_1, %, and the acid number of the oil, y_2, mg KOH/g.

The results of the experiments were processed using mathematical and statistical methods. To assess the homogeneity of variances with an equal number of repetitions of each experiment, the Cochran criterion was used, the significance of the coefficients of the empirical model was determined using the Student criterion, and the adequacy of the equations was proven using the Fisher criterion (Murray P. M. et al., 2016; Georgakis C., 2013).

Empirical models in coded values of influencing factors were obtained in the following form.

For residual oil content of oil cake:

$$y_1 = 3.91 - 3.40x_1 - 0.26x_2 - \\ -0.18x_1x_2 + 2.03x_1^2 - 0.29x_2^2 \quad (1)$$

For acid number of oil:

$$y_2 = 1.96 + 0.15x_3 + 0.4x_4 - 0.3x_3^2 + 0.191x_4^2 \quad (2)$$

We write out mathematical models in natural values of variables, substituting their expressions through z_i instead of x_i. After performing arithmetic operations, we obtain an equation in natural values of influencing factors:

For residual oil content of oilcake:

$$Y_1 = 67.13 - 2.316z_1 + 23.8z_2 + \\ +0.0203z_1^2 - 29.0z_2^2 - 0.18z_1z_2 \quad (3)$$

For acid number of oil:

$$Y_2 = -5.771 + 0.315z_1 - \\ -7.46z_2 - 0.003z_1^2 + 19.1z_2^2 \quad (4)$$

We designate the optimality criteria.

Optimality criterion for residual oil content of oilcake: $Y_1 = f(z_1, \ z_2) \to Y_{1\min}$.

Optimality criterion for the acid number of the oil: $Y_2 = f(z_1, \ z_2) \to Y_{2\min}$.

Corresponding problem is to study the possibilities of using different optimization methods (Pen, R.Z., Pen V. R., 2022; Kashtaeva, S.V., 2020).

Nonlinear programming methods are used to solve optimal problems with nonlinear objective functions. The nonlinear programming method combines a large group of numerical methods, many of which are adapted to solve optimal problems of the corresponding class. A number of nonlinear programming methods are almost always used in combination with other optimization methods (for example, with the scanning method in dynamic programming).

The scanning method consists of sequentially viewing the optimality criterion in a number of points belonging to the range of variation of independent variables, and finding among these points the one in which the optimality criterion has a maximum (minimum) value. The accuracy of the method is naturally determined by how "densely" the selected points are located in the permissible range of variation of independent variables (Pen R. Z., Pen V. R., 2022; Kashtaeva S. V., 2020).

The quality of the final oil is inextricably linked to the condition of the sunflower seeds used. Proper preparation is paramount to maximizing oil yield and minimizing the presence of undesirable compounds in the finished product. Key aspects of raw material preparation include:

- **Seed Cleaning:** Removal of foreign materials (e.g., dust, stones, weeds) is crucial. This prevents damage to the press, contamination of the oil, and uneven pressing. Effective cleaning methods might involve sieving, aspiration, and magnetic separation;
- **Seed Dehusking (Optional):** While not always necessary, dehusking (removing the seed hull) can improve oil yield. The hull absorbs some oil, and its removal reduces the overall pressure required during pressing, potentially increasing the efficiency of the process. Dehusking can be achieved mechanically, using dehulling machines;
- **Seed Crushing/Flaking:** This step significantly increases the surface area of the seeds, allowing for better oil extraction. Crushing or flaking should be done to a degree that maximizes surface area without creating excessive fines (small particles) which can clog the press. The desired size and consistency of the flakes will de-

pend on the specific press and seed characteristics. Roller mills and hammer mills are commonly used for this purpose;

- **Seed Moisture Content:** Optimal moisture content is vital. Too much moisture can lead to lower oil yield and potential microbial growth, while excessively dry seeds can be difficult to press and may result in higher energy consumption. The ideal moisture content typically ranges from 6–8%, though this can vary slightly depending on seed variety and press characteristics.

Cold pressing of sunflower seeds is a popular method for producing high-quality sunflower oil, prized for its retention of beneficial nutrients and its characteristic flavor profile. This process, unlike hot pressing or solvent extraction, avoids high temperatures that can degrade the oil's quality. However, achieving optimal oil yield and quality in cold pressing requires careful selection and optimization of several key parameters within the hydraulic pressing process.

To determine the optimal values of factors influencing the yield and acid number of sunflower oil, a calculation program was compiled in the *Delphi* algorithmic language.

Conclusion

Thus, under appropriate conditions, the minimum values of residual oil content of the cake after cold hydraulic pressing and the acid number of the oil will be obtained at a pressing pressure of z_1 = 50 MPa and a seed meal (petal seeds) thickness of z_2 = 0.3 mm. In this case, the residual oil content of the cake is 6.5%, the acid number of the oil is 1.4 mg KOH/g. The obtained data on the optimal operating parameters of the pressing process are necessary for the implementation of this process under production conditions.

References

Kopylov, M. V. (2013). *Improving the process of cold pressing of vegetable oil crops with subsequent blending*. Abstract of dissertation, Voronezh, Russia.

Proctor, A. (2013). Green Vegetable Oil Processing. Retrieved from: URL: https://ru.everand.com/book/282669726/Green-Vegetable-Oil-Processing-Revsied-First-Edition

Çakaloğlu, B., Özyurt, V. H. & Ötleş, S. (2018). *Cold press in oil extraction. A review*. Ukrainian Food Journal.;7(4): 640–654. Retrieved from URL: http://dx.doi.org/10.24263/2304–974X-2018-7-4-9

Gafurov, K.Kh., Safarova, D.N. (2022). *Development of Technology for Oil Extraction from Local Sunflower Seeds at Moderate Temperature*. Global Scientific Review, – 8, – P. 33–37. Retrieved from URL: https://www.scienticreview.com/index.php/gsr/article/view/56

Mustafaev, S. K., Kalienko, E. A., Sonina, D. V., & Efimenko, S. G. (2014). *The influence of flax seed pressing conditions on the yield and quality of oil*. Scientific journal of KubSAU, 100(06). Retrieved from URL: http:// ej. kubagro. ru /2014/06/ pdf /103. pdf

Gafurov, K. Kh. (2020). *Change of physiological and biochemical properties of plant raw materials during thermal preparation before extraction*. The American Journal of Engineering and Technology, – 11(2). – P. 197–205. URL: https://doi.org/10.37547/tajet/Volume 02I ssue 11–31

Cai, Z., Li, K., Lee, W. J., Reaney, M., Zhang, N., & Wang, Y. (2021). *Recent progress in the thermal treatment of oilseeds and oil oxidative stability: A review*. Fundamental Research, – 6(1). – P. 767–784. Retrieved from https://doi.org/10.1016/j.fmre.2021.06.022

Murray, P.M. et al. (2016). *The application of design of experiments (DoE) reaction optimization and solvent selection in the development of new synthetic chemistry*, Org. Biomol. Chem., – 14, – P. 2373–2384.

Georgakis, C. (2013). *Design of Dynamic Experiments: A Data-Driven Methodology for the Optimization of Time-Varying Processes*. Industrial & Engineering Chemistry Research, – 52, – P. 12369–12382.

Pen, R. Z., Pen V. R. (2022). *Statistical methods of mathematical modeling, analysis and optimization of technological processes*. – St. Petersburg, Russia: Lan https:// e. lanbook. com / book /264239
Kashtaeva, S. V. (2020). *Optimization methods*. Perm. Russia: Prokrost.

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INFLUENCE OF REFINING PROCESSES ON OXIDATIVE STABILITY OF COTTONSEED OIL

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Abstract

Phospholipids and metals ions such as iron (III) often produce deleterious effect when present in vegetable oils. The trace quantities of iron (III) and phospholipids reduce the oxidative stability of vegetable oils. The present study reports show the influence of refining processes on the oxidative stability of cottonseed oils. The process of water degumming effectively reduces phosphorus and iron (III) content in cottonseed oil. The oxidative stability of water degummed oil is reduced by nearly half compared to crude oil. Consequently, neutralized and bleached oils exhibit compromised oxidative stability, with an induction period of 3.18 h for extracted oil and 2.97 h for pressed oil. Tocopherol losses of approximately 30% occur during deodorization process, significantly impacting oxidative stability. Deodorized cottonseed oils demonstrate the lowest oxidative stability, with induction periods of 2.47–2.55 h.

Keywords: *cottonseed oil; refining; gossypol; oxidative stability; iron*

Introduction

Edible oils assume a central role in human dietary practices, constituting a primary reservoir of essential fatty acids and vital nutrients. Within this spectrum of oils, cottonseed oil has ascended to eminence, attributable to its versatility, nutritional significance and prospective applications in various industrial sectors.

The susceptibility of edible oils to oxidative instability presents a notable challenge, resulting in the onset of rancidity and a consequent decline in their nutritional quality. Cottonseed oil, derived from the seeds of the Gossypium plant, has garnered broad utility across culinary, food processing, and industrial domains owing to its substantial presence of saturated fatty acids and advantageous bioactive constituents (Manoj, K.·Bbaohong, Z.·Jayashree, P.·Kanika, S. Radha, C. H.·Vijay, S. Deepak, C.·Sangram, D., Abhijit, D.·Nadeem, R.·Marisennayya, S. Suman, N. Sabareeshwari, V. Pran, M. José. M.L., 2023). The oxidative stability

of cottonseed oil is inherently influenced by its fatty acid composition. Cottonseed oil is characterized by the predominance of C16 and C18 fatty acids, resulting in the presence of no more than two double bonds. Approximately 50% of the fatty acid composition of cottonseed oil comprises polyunsaturated fatty acids, with linoleic acid being the primary constituent. Consequently, the crude cottonseed oil exhibits comparatively lower oxidative stability comparing with oils such as olive oil, palm oil, peanut oil. The presence of tocopherols in cottonseed oil acts as an effective inhibitor of rancidity development, thereby enhancing the stability of the resulting product and extending its shelf life. Cottonseed oil is inherently hydrogenated and possesses a favorable fatty acid composition, including significant quantities of palmitic, stearic, oleic, linoleic, and linolenic acids, rendering it suitable for cardiovascular health. Cottonseed oil has gained prominence in culinary applications due to its high smoke point, which reaches 232 °C. This characteristic sets it apart from other cooking oils, making it well-suited for the process of frying various food items. The distinctive strong yellow coloration of cottonseed oil is attributed to the presence of gossypol (Ziaa, M. A. Shahc, S. H. Shoukata, S., Hussaind, Z., Khane, S. U., Shafqatf N. 2022; O'Brien, R.D., 2002; O'Brien, R.D. et al. 2005). Oxidative stability, denoting an oil's capacity to withstand oxidation, stands as a fundamental factor influencing its storage longevity, flavor preservation, and overall quality. The oxidative stability of cottonseed oil is subject to the influence of multiple factors, encompassing its fatty acid composition, the presence of gossypol and tocopherols, the constituents acting as antioxidants, and the employed processing techniques. Gossypol, akin to numerous other aromatic phenolic compounds, exerts a robust and efficacious role as a natural antioxidant (Laughton, M. J. Halliwell, B. Evans, P. J. Hoult, J.R. 1989). As an illustration, gossypol has demonstrated its capacity to safeguard carotene from pre-existing lipid peroxides in vitro and exhibits carotene-preserving antioxidant properties in vivo. Furthermore, natural antioxidants like tocopherols and gossypol have exhibited their effectiveness in enhancing the oxidative stability of biodiesel (Hove E. L., 1944; Moser, B., 2012).

The process of oil refining plays a pivotal role in the oil processing industry, with its primary objectives being the removal of impurities and the enhancement of oil stability. These refining procedures typically encompass degumming, neutralization, bleaching, and deodorization, each exerting distinct influences on the composition and stability of the oil (Gharby, S., 2022). Throughout the refining process, impurities such as phospholipids, free fatty acids, and trace metals function as prooxidants and are eliminated from the crude oil. However, it's noteworthy that natural antioxidant constituents present in crude oils, including tocopherols, squalene, and phytosterols, are also removed during the refining process (Ghazani, S. M. Marangoni, G.A. 2013; Kreps, F. Vrbiková, L. Schmidt, Š., 2014). In the refining process, compounds like gossypol and related molecules are eliminated. However, crude cottonseed oil still retains phospholipids and tocopherols. Notably, the levels of tocopherols are diminished through the high-temperature physical refining process (Gunstone, F.D., 2007). Phospholipids and trace metals are eliminated from the oil through processes involving water treatment, "Totaal Ontslijmings Process," total degumming process, acid treatment, and other related techniques. However, it's noteworthy that water-degummed oil may still retain elevated levels of iron (III). Consequently, addressing the challenge of iron removal can be addressed by developing a method that effectively breaks down these iron/phosphatide complexes, ultimately converting the resulting iron into a form that can be readily removed from the oil (Albert, J. D., Martin, V. O., 1989). The pro-oxidative properties of phospholipids stem from their anionic structural characteristics, which enable them to attract pro-oxidative metal ions. Conversely, their antioxidative effect against lipid oxidation arises from their capacity to enhance the binding affinity of antioxidants to the interfacial region, facilitate the breakdown of hydroperoxides, and form complexes with metal ions. (Chen, B. McClements, D. J. Decker, E.A., 2013). The oxidative stability of vegetable oils, as assessed by the Rancimat method, exhibited a notable

decline during the neutralization stage (Zacchi, P. Eggers, R. 2008; Suliman, T.E.M.A. Jiang, J., Liu, Y.F., 2013). This phenomenon arises from the elimination of bioactive compounds, including phenolic compounds, tocopherols, and phytosterols, through their absorption by the soapstock during the neutralization stage. The most sensitive stage within the refining process is the bleaching phase. During this step, undesirable components, including pigments, trace metals, phospholipids, and specific degradation products, are eliminated. However, it's important to note that certain valuable compounds like tocopherols and sterols may also be unintentionally removed. This can lead to a substantial reduction in oxidative stability of the oil (Dubravka, K. Tomislav, D. Klara, K. Jasenka, G. Sandra, N. Marko, O. 2012). The most substantial reduction in oxidative indices was observed during the deodorization phase (Ardakani, M.S., Mohajeri, F.A., Askari, E. Javdan, G., Pourramezani, F., Fallahzadeh, H., Sadrabad, E.K., 2023). Elevated temperatures during the deodorization process are accountable for the degradation of tocopherols, which hold significance for maintaining the oxidative stability of edible oils (Jawad, I. M., Kochhar, S. P. Hudson, B.J.F. 1983). Among these variables, the employed refining techniques exert a substantial influence on the degree of oxidative stability alteration. To comprehensively assess the impact of refining approaches on oxidative stability, it is crucial to possess a profound comprehension of the underlying mechanisms involved. Cottonseed oil, characterized by its valuable nutritional characteristics and multifarious applications, necessitates careful consideration to safeguard its oxidative stability and extend its shelf life. The refining methodologies applied during processing substantially modify the oxidative stability of the oil by impacting its chemical constitution and antioxidant content. The aim of this article is the study influence of refining methods on oxidative stability of cottonseed oil.

Materials and methods

Materials

Cottonseed oil samples were collected from local oil factory situated at the "Kattakurgan Oil Plant" (Kattakurgan, Uzbekistan). Subsequently, the collected samples were carefully transported to the laboratory, ensuring light protection and an inert nitrogen atmosphere, and were then stored at the low temperature (8 °C) until further analytical procedures were conducted.

Refining process

Apparatus

Magnetic stirrer (IKA Werk, Staufen im Breisgau, Germany), centrifuge (MPW-340, CHEMARGO, Blachownia, Poland) at 1,3 $m.s^{-2}$, spectrophotometer (UV/VIS-1601, Shimadzu, Tokyo, Japan), inductively coupled plasma optical emission spectroscopy (V Liberty 200, Victoria, Australia) and Rancimat (743, Metrohnm, Herisau, Switzerland) were used during the experiments.

Water degumming. Crude cottonseed oils were degummed by heating the oils to 70 °C, adding water (5% by volume) and stirring for 20 min by magnetic stirrer. Then, the mixture was centrifuged for 20 min.

Neutralization. Water-degummed cottonseed oils were heated to 80 °C, and a water solution including NaOH (20% weight) in a portion of 5% by volume of the oil was added and the mixture was stirred for 30 min. The mixture was kept at 80 °C up to 30 min. and transferred to a holding vessel. After settling for 60 min the mixture was centrifuged for 20 min.

Bleaching. Neutralized oils were heated to 80 °C and were initially mixed intensively with bleaching clay in a portion of 0.5% by weight of the oil. The total reaction times are only 30 min. The mixture was filtered to obtain bleached oil.

Deodorization. The deodorization process was conducted in laboratory equipment at a temperature of 230 °C and under a vacuum of 0.2 kPa for 30 min, utilizing 0.2% steam.

Determination of phosphorus, iron, gossypol, tocopherols and fatty acid composition of vegetable oils

The content of phospholipids was determined as the total phosphorus on a vegetable oil according to AOCS Official Method Ca 12–55 (AOCS. Official Method Ca 12–55. 1994). Iron was also determined following AOAC Official Method 990.08 (AOAC. Of-

ficial method 990.08. 2003). The gossypol content in cottonseed oil was determined by AOCS Official Method Ca 13–56 (AOCS. Official Method Ca 13–56. 1993). The total tocopherol content in cottonseed oil was determined be AOCS Official Method Ce 8–89 1993). The fatty acid composition of cottonseed oil was determined by a capillary gas chromatography (Niklová, I., Schmidt, Š., Habalová, K., Sekretár, S., 2001; Christopherson, S. W., Glass, R., 1969).

Determination of oxidative stability

To monitor the oxidation of cottonseed oils, Rancimat (743, Metrohnm, Herisau, Switzerland) apparatus was used. Oxidation progression was tracked by measuring the increase in conductivity within a constant volume under isothermal conditions set at 110 °C. The oxidative environment was maintained with air at a flow rate of 20 $l.h^{-1}$. Each sample weighed 3 grams, and we conducted three parallel measurements for every sample.

Results and discusion

The oxidative stability of vegetable oil is significantly influenced by its fatty acid composition. The impact of the fatty acid composition of cottonseed oil, characterized by the presence of fatty acids containing no more than 2 double bonds, cottonseed oil contain 54.9% linoleic acid and 17.2% oleic acid (Tab.1), has a substantial effect on the oil's ability to resist oxidative decomposition. For cottonseed oil, characterized by a low content of 3 double bonds, specifically no more than 0.5% in its fatty acids, higher oxidative stability can be expected compared to oils containing a greater amount of polyunsaturated fatty acids, such as sunflower oil. This is because the double bonds in fatty acids are vulnerable points where oxidative reactions begin. Therefore, cottonseed oil with a low content of double bonds in its fatty acid composition has the potential to provide high oxidative stability. Crude cottonseed oil exhibits an induction period of 7.6–8.7 h, indicating a higher oxidative stability of the oil (Tab.4).

Tab1. *Fatty acid composition (% of area) of cottonseed oil*

Fatty acids		%
Myristonic acid	(14:0)	0. 8
Palmitic acid	(16:0)	23.1
Stearic acid	(18:0)	2.3
Oleic acid	(18:1)	17.2
Linoleic acid	(18:2)	54.9
a-linolenic acid	(18:3–9,12,15)	0.3
y-linolenic acid	(18:3–6,9,12)	0.2
Arachic acid	(20:0)	0.1
Behenic acid	(22:0)	–
Other fatty acids		1.1

Water degumming reduces the phosphorus content to 15.5–22.9% in cottonseed oil (Tab. 2 and Tab. 3), mainly removing easily hydratable phospholipids during water degumming. Phospholipids can be a cause of oxidative processes in the oil, leading to a loss of its stability. Additionally, water degumming also has a positive effect on reducing the iron content in the oil. The water degumming process promotes the formation of complexes between iron and phospholipids, increasing the efficiency of their removal from the oil during refining. As a result, the iron content is reduced to 42.1% in extracted and 30.1% in pressed oil (Tab. 2 and Tab. 3), which contributes to improving the quality of the oil and its long-term stability. During water degumming, some tocopherols can transfer to the aqueous phase and be removed along with phospholipids and other impurities. A reduction in tocopherol content by 3–4% can weaken the oil's antioxidant capacity and make it more vulnerable to oxidative processes. Also, during water de-

gumming, the content of gossypol decreases by 15–18%, which has a positive effect on its quality but also reduces its oxidative stability. The oxidative stability of water degummed oil decreased by almost 2 times comparing with crude oil, with induction periods of 4.06 h for extracted oil and 4.24 h for pressed oil (Tab. 4).

Table 2. *Influence of water degumming, neutralization, bleaching and deodorization processes on phosphorus, iron, tocopherols and gossypol removal from cottonseed extracted oil*

Vegetable oils	Cottonseed extracted oil							
	Phosphorus		Iron		Tocopherols		Gossypol	
	[mg.kg^{-1}]	[%]	[mg.kg^{-1}]	[%]	[mg.kg^{-1}]	[%]	[mg.kg^{-1}]	[%]
Crude oil	713.4	100	7.6	100	776.7	100	2364.1	100
Water degummed	110.4	15.5	3.2	42.1	752.1	96.8	1938.5	82.1
Neutralized	19.5	2.7	0.9	11.8	691.3	89.0	312.1	13.2
Bleached	12.1	1.7	0.4	5.3	663.2	85.3	120.6	5.1
Deodorazed	11.1	1.5	0.3	3.9	432.1	55.6	119.1	5.0

Table 3. *Influence of water degumming, neutralization, bleaching and deodorization processes on phosphorus, iron, tocopherols and gossypol removal from cottonseed pressed oil*

Vegetable oils	Cottonseed pressed oil							
	Phosphorus		Iron		Tocopherols		Gossypol	
	[mg.kg^{-1}]	[%]	[mg.kg^{-1}]	[%]	[mg.kg^{-1}]	[%]	[mg.kg^{-1}]	[%]
Crude oil	312.4	100	5.3	100	530.7	100	1891.2	100
Water degummed	71.5	22.9	1.6	30.1	514.3	96.9	1607.5	85.1
Neutralized	14.1	4.5	0.6	11.3	477.1	89.9	270.4	14.3
Bleached	9.1	2.9	0.3	5.6	453.4	85.4	115.4	6.1
Deodorized	8.6	2.7	0.2	3.7	294.7	55.5	114.1	6.0

Neutralization. The process of neutralization in cottonseed oil plays a pivotal role in reducing the content of various components, such as phospholipids, iron, tocopherols, and gossypol. Typically carried out using NaOH, the neutralization process aids in the removal of phospholipids from the oil. Caustic soda breaks down phospholipids into insoluble precipitates that can be easily separated from the oil. During the neutralization of extracted cottonseed oil, the phosphorus content decreases to 19.5 mg.kg^{-1}, while in pressed oil, it reduces to 14.1 mg.kg^{-1}. Additionally, the neutralization process contributes to the removal of iron. Caustic soda used in neutralization can form insoluble complexes with iron, making it more suitable for removal from the oil. The iron content in extracted oil decreases to 0.9 mg.kg^{-1}, and in pressed oil, it drops to 0.6 mg.kg^{-1}. However, the neutralization process also reduces the content of tocopherols by 10–11% compared to crude oil since they are removed along with other impurities such as phospholipids.

During neutralization process of cottonseed oils, gossypol is removed by 86–87% (Tab. 2 and Tab. 3). The reduction in tocopherol content, along with the presence of gossypol and high temperatures during oil neutralization, decreases the induction period of extracted oil to 3.61 h and pressed oil to 3.37 h (Tab. 4).

Table 4. *Influence of refining processes on oxidative stability of cottonseed oils*

Cottonseed oils	Oxidative stability of cottonseed oils	
	Extracted oil IP (h)	Pressed oil IP (h)
Crude oil	8.27	7.67
Water degummed	4.24	4.06
Neutralized	3.61	3.37
Bleached	3.18	2.97
Deodorized	2.55	2.47

Bleaching. Bleaching of cottonseed oil involves the use of adsorbents, such as bleaching clay. These materials are capable of adsorbing and removing phospholipids from the oil. After the bleaching process, the phosphorus content in the oils decreased by less than 12.1 mg.kg^{-1}. The bleaching process using adsorbents also contributes to the removal of iron and reduces the iron content to less than 0.4 mg.kg^{-1}. However, the bleaching process reduces the content of tocopherols in the oil by 4–5%. This is because bleaching involves the extraction of oil using adsorbents, and during this extraction, some bioactive components, including tocopherols, may be removed. The bleaching process partially removes gossypol from the oil, which can affect its color and oxidative stability. Bleached oils contain no more than 5–6% gossypol based on crude oil (Tab. 2 and Tab. 3). The removal of gossypol and tocopherols during the bleaching process reduces the oxidative stability of cottonseed oil. The induction period of extracted cottonseed oil was 3.18 h, while that of pressed oil was 2.97 h (Tab. 4).

Deodorization. The deodorization process typically results in the slight removal of iron from the oil, around 0.1 mg.kg^{-1}, which contributes to improved oxidative stability. However, during the deodorization process, which involves heating the oil at high temperatures and steam treatment, tocopherols can undergo decomposition. High temperatures and steam exposure can lead to the thermal degradation of tocopherols, resulting in their loss in the oil. Tocopherol losses are significant, accounting for approximately 30% of the total tocopherol content in crude oil. The substantial loss of tocopherols leads to a reduction in the oxidative stability of the oils. Deodorized cottonseed oils have the lowest oxidative stability, with an induction period of 2.47–2.55 h (Tab. 4).

Conclusion

The goal of this paper is analyse the effects of refining processes on the cottonseed oil oxidative stability with the Rancimat device. At each stage of refining process, undesirable components such as iron, phospholipids and gossypol are removed, but natural antioxidants like tocopherol are also eliminated. According to the results, we have found that crude cottonseed oil exhibits three times greater oxidative stability compared to deodorized cottonseed oils. The degumming process reduces the oxidative stability of oils by nearly half. Neutralization and subsequent oil bleaching have a minor impact on the oxidative stability of oils. During the deodorization process, the most significant loss occurs in tocopherols, resulting in the lowest oxidative stability of the oils. The oxidative stability of cottonseed oil is profoundly affected by its fatty acid composition and various refining stages. Understanding these factors is crucial for optimizing the quality and shelf life of cottonseed oil-based products.

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References:

Manoj, K.·Bbaohong, Z.·Jayashree, P.·Kanika, S. Radha,·C. H.·Vijay, S. Deepak, C.·Sangram, D, Abhijit, D.·Nadeem, R.·Marisennayya, S. Suman, N. Sabareeshwari, V. Pran, M. José. M. L. Cottonseed Oil: Extraction, Characterization, Health Benefits, Safety Profile, and Application. Food Analytical Methods, – 16, 2023. – P. 266–280. DOI: https://doi.org/10.1007/s12161-022-02410-3.

Ziaa, M. A. Shahc, S. H. Shoukata, S., Hussaind, Z., Khane, S. U., Shafqatf N. Physicochemical features, functional characteristics, and health benefits of cottonseed oil: a review. Brazilian Journal of Biology, – 82. 2022. – P. 1–16. DOI: https://doi.org/10.1590/1519-6984.243511.

O'Brien, R. D. Cottonseed oil. In: Gunstone, F.D., Ed.: Vegetable Oils in Food Technology – Composition, Properties and Uses, Blackwell Publishing, Oxford, 2002. – P. 203–230.

O'Brien, R. D. et al., Cottonseed oil. In: Shahidi, F., Ed.: Bailey's Industrial Oil and Fat Products, 6th ed., – Vol. 2. Wiley Inter science, – New York, 2005. – P. 173–280.

Laughton, M. J. Halliwell, B. Evans, P. J. Hoult, J. R. Antioxidant and prooxidant actions of the phenolics quercetin, gossypol, and myricetin. Biochemical Pharmacology, – 38, 17, 1989. – P. 2859–2865. DOI: https://doi.org/10.1016/0006-2952(89)90442-5.

Hove EL. Gossypol as a carotene-protecting antioxidant, in vivo and in vitro. Journal of Biological Chemistry. – 156. 1944. – P. 633–642. DOI: https://doi.org/10.1016/S0021-9258(18)51146-7.

Moser, B. Efficacy of Gossypol as an Antioxidant Additive in Biodiesel. *Renewable Energy.* – 40. 2012. – P. 65–70. DOI: https://doi.org/10.1016/j.renene.2011.09.022.

Gharby, S. Refining Vegetable Oils: Chemical and Physical Refining. Scientific World Journal, 2022, – P. 1–10. DOI: https://doi.org/10.1155/2022/6627013.

Ghazani, S. M. Marangoni, G. A. Minor Components in Canola Oil and Effects of Refining. on These Constituents. Journal American Oil Chemistry Society, – 90. 2013. – P. 923–932. DOI: 10.1007/s11746-013-2254-8.

Kreps, F. Vrbiková, L. Schmidt, Š. Influence of industrial physical refining on tocopherol, chlorophyll and beta-carotene content in sunflower and rapeseed oil. European Journal of Lipid Science and Technology – 116(11). 2014. – P. 1572–1582. DOI: https://doi.org/10.1002/ejlt.201300460.

Gunstone, F. D. Harwood, J.L- Dijcstra, A. J. Cottonseed oil. The Lipid Handbook, third edition, Taylor & Francis Group, 2007. – 44 p.

Albert, J. D. Martin, V. O. The total degumming process. Journal of the American Oil Chemists' Society, – 66. 1989. – P. 1002–1009.

Chen, B. McClements, D. J. Decker, E. A. References. In: Logan, A.- Nienaber, A.- Pan, X. Lipid Oxidation: Challenge in Food System. AOCS Press; Urbana, IL, USA: 2013. – P. 129–154.

Zacchi, P. Eggers, R. High-temperature pre-conditioning of rapeseed: A polyphenol-enriched oil and the effect of refining. European Journal of lipid science and technology. – 110. – 2. 2008. –P. 111–119. DOI: https://doi.org/10.1002/ejlt.200700135.

Suliman, T.E.M.A. Jiang, J. Liu, Y. F. Chemical refining of sunflower oil: Effect on oil stability, total tocopherol, free fatty acids and colour. International Journal of Engineering Science and Technology – 5(2). 2013. – P. 449–454.

Dubravka, K., Tomislav, D., Klara, K., Jasenka, G., Sandra, N., Marko, O. Optimization of Bleaching Parameters for Soybean Oil. Food Technology and Biotechnology. – 50 (2). 2012. – P. 199–207.

Ardakani, M.S., Mohajeri, F.A., Askari, E. Javdan, G., Pourramezani, F., Fallahzadeh, H., Sadrabad, E. K. Efficacy of Different Sesame Oil Refining Stages in Reduction of Heavy Metals, Antioxidant Activity, and Oxidative Parameters. Journal of Food Processing and Preservation, 2023. – P. 1–8. DOI: https://doi.org/10.1155/2023/1197398.

Jawad, I. M., Kochhar, S. P. Hudson, B. J. F. Quality characteristics of physically refined soyabean oil: effects of pre-treatment and processing time and temperature. Journal Food

technology. – 18. 1983. – P. 4353–4360. DOI: https://doi.org/10.1111/j.1365-2621.1983.tb00278.x.
AOCS. Official Method Ca 12–55. Phosphorus. In: Official Methods and Recommended Practices of AOCS. 4th ed. Champaign: American Oil Chemists' Society Press, 1994.
AOAC. Official method 990.08. Metals in solid wastes by inductively coupled plasma atomic emission method. In: Official Methods of Analysis of AOAC International. 17 th ed. Gaithersburg: AOAC International, 2003.
AOCS. Official Method Ca 13–56. Total gossypol in oils. In: Official Methods and Recommended Practices of AOCS. 3 th ed. Champaign: American Oil Chemists' Society Press, 1993.
AOCS. Official Method Ce 8–89. Tocopherols and Tocotrienols in Vegetable Oils and Fats by HPLC. In: Official Methods and Recommended Practices of AOCS. Champaign: American Oil Chemists' Society Press, 1993.
Niklová, I., Schmidt, Š., Habalová, K., Sekretár, S. Effect of evening primrose extracts on oxidative stability of sunflower and rapeseed oils. European Journal of Lipid Science and Technology, – 103. 2001. – P. 299–306.
Christopherson, S. W., Glass, R. Preparation of milk fat methyl esters by alcoholysis in an essentially non-alcoholic solution. Journal of Dairy Science, – 52. 1. 1969. – P. 1289–1290. DOI: https://doi.org/10.3168/jds.S0022-0302(69)86739-1.

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Section 4. Mechanical engineering

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CALCULATION OF A THIN PLATE BY NUMERICAL METHOD IN THE LIRA CAD SOFTWARE PACKAGE

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Abstract

The method of calculating a thin plate using the LIRA CAD software package is an important aspect of modern engineering analysis. In this study, a thin rectangular plate is considered, and finite element analysis is used, which allows us to study in detail the behavior of materials under the influence of various loads. The LIRA CAD software package allows not only to model such structures, but also to conduct a comparative analysis using analytical methods, which makes it possible to evaluate the accuracy and effectiveness of various approaches. The analytical calculation method based on finite integral transformations provides a closed solution for plates of various sizes and shapes. This solution has been found to be the most accurate and versatile, which allows it to be used in various software packages.

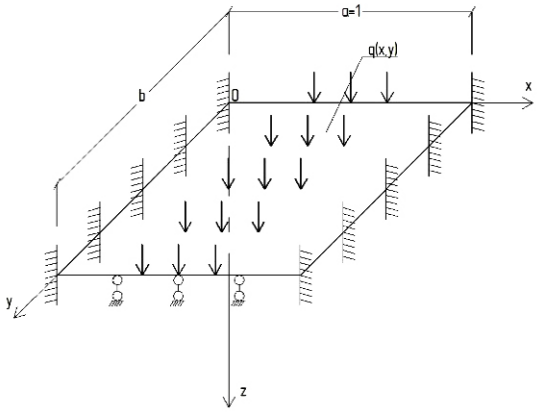
Keywords: *thin rectangular plate, CAD LIRA, differential equation*

The use of analytical methods is especially relevant in cases where high accuracy is required, for example, in the aerospace or shipbuilding industries, where structures are subjected to significant loads and impacts. Structures made of flexible shells and plates are widely used in various fields such as mechanical engineering, aviation and construction. In construction, thin slabs are used for floors, coverings and canopies, which makes them an integral part of modern buildings and structures. However, despite its widespread use, the calculation of such structures can be a complex and time-consuming process. Approximate methods such as the grid method are also used to solve problems related to the analysis of thin plates. These methods can only provide point information and require special conditions for approximating functions. Unlike analytical methods, approximate approaches, such as the finite element method (FEM) (Reddy, J., 2006; Senitsky Yu.E., 2011), allow you to split complex areas into simpler elements, which greatly simplifies the modeling process. There are also new directions in the development of methods

for solving differential equations, which are aimed at reducing the time it takes to find a solution. These methods make it possible to process large amounts of data more efficiently and get results faster, which is critically important in the context of modern design and calculation requirements. Modern technologies, including machine learning algorithms, are also beginning to find applications in the field of engineering analysis (Ratmanova O. V., Kalmova M. A., 2022). These algorithms, with proper selection and training, can significantly improve traditional calculation methods, allowing you to quickly find optimal solutions for complex problems. The LIRA CAD software package actively uses such technologies, which makes it one of the most advanced tools in the field of design and analysis of structures. Thus, the method of calculating a thin plate using the LIRA CAD software package in combination with analytical and approximate methods, as well as new approaches based on machine learning, opens up new horizons in the field of engineering analysis. This allows not only to increase the accuracy of calculations, but also to reduce the time required for the development and design of complex structures, which is an important aspect in today's competitive environment.

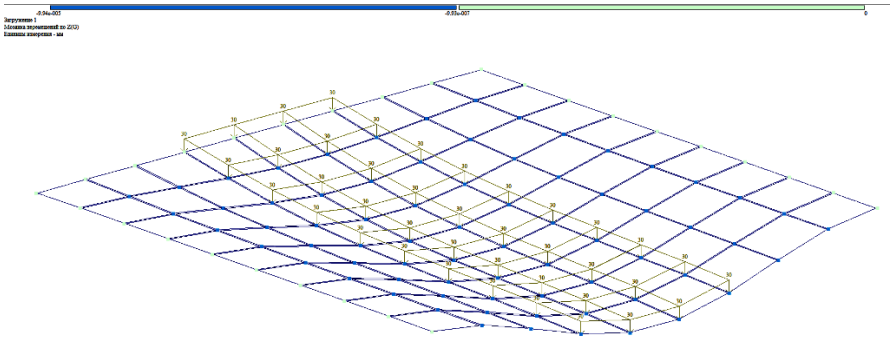
Let's analyze the calculation scheme shown in Figure 1, the dimensions of the plate are 1 ×1, the fixation along the ordinate axis is rigid on both sides, hinged and free along the abscissa axis, the load is applied to 1/3 of the plate in the center.

Figure 1. *Design scheme of the plate*



The advantage of the CAD LIRA is the rapid variability in the characteristics of the plate, including stiffness and fastening, as well as the type and distribution of the load. Calculating the design in the LIRA CAD software package, the following deformation pattern is obtained:

Figure 2. *Plate movements under load*



Considering the problem by an analytical calculation method, the differential equation and boundary conditions are presented in a dimensionless form:

$$\frac{\partial^4 W}{\partial \tilde{x}^4} + 2\frac{\partial^4 W}{\partial \tilde{x}^2 \partial \tilde{y}^2} + \frac{\partial^4 W}{\partial \tilde{y}^4} = q^*. \qquad (1)$$

$$\tilde{x} = 0,1 \;\; W = 0, \; \frac{\partial^2 W}{\partial \tilde{x}^2} = 0 \; (M_x = 0), \qquad (2)$$

$$\tilde{y}=0 \qquad \frac{\partial^2 W}{\partial \tilde{y}^2}+\mu\frac{\partial^2 W}{\partial \tilde{x}^2}=0 \quad M_y=0, \qquad (3)$$

$$\frac{\partial^3 W}{\partial \tilde{y}^3}+(2-\mu)\frac{\partial^3 W}{\partial \tilde{x}^2\partial \tilde{y}}=0 \quad (Q^*_{yz}=0),$$

$$\tilde{y}=p \qquad W=0, \ \frac{\partial^2 W}{\partial \tilde{y}^2}=0 \qquad (4)$$

where $\{W,\tilde{x},\tilde{y},p\}=\{w,x,y,b\}/a$, $q^*=\frac{q}{D}a^3$, $D=\frac{Eh^3}{12(1-\mu^2)}$

The solution of the problem is carried out using the sine Fourier transform with finite limits on the variable, using the following transform

$$W_s(n,\tilde{y})=\int_0^1 W(\tilde{x},\tilde{y})\sin(j_n\tilde{x})\,d\tilde{x},$$

and the conversion formula

$$W(\tilde{x},\tilde{y})=2\sum_{n=1}^{\infty}W_s(n,\tilde{y})\sin j_n\tilde{x}, \ (j_n=n\pi).$$

A structural calculation algorithm has been developed, according to which a solution is subsequently carried out, namely equations (1) and (3), (4) are multiplied by $\sin(j_n\tilde{x})$ and integrated in parts in the interval [0,1]. Thus, we get a new boundary value problem:

$$\frac{d^4W_s}{d\tilde{y}^4}-2j_n^2\frac{d^2W_s}{d\tilde{y}^2}+j_n^4W_s=q_s, \qquad (5)$$

$$\tilde{y}=0,p \qquad \frac{d^2W_s}{d\tilde{y}^2}-\mu j_n^2W_s=0,$$

$$\frac{d^3W_s}{d\tilde{y}^3}-j_n^2(2-\mu)\frac{dW_s}{d\tilde{y}}=0, \qquad (6)$$

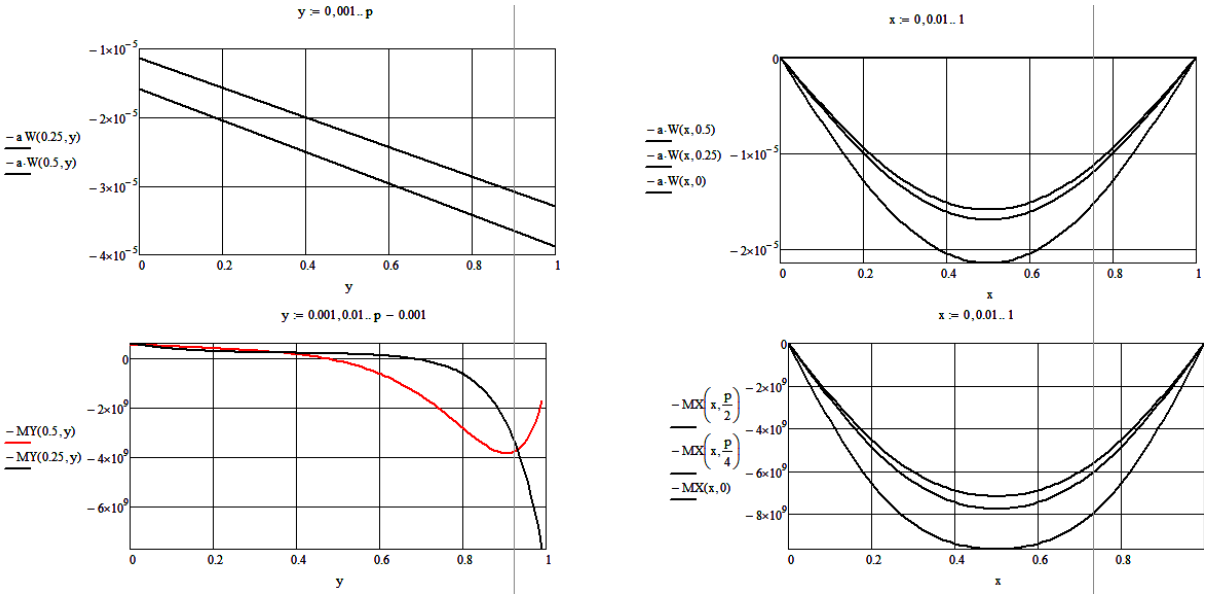
where $q_s(n,\tilde{y})=\int_0^1 q^*\sin(j_n\tilde{x})\,d\tilde{x}$.

The general integral of the differential equation (5) has the form:

$$W_s(n,\tilde{y})=C_{1n}\,\mathrm{ch}(j_n\tilde{y})+C_{2n}\,\mathrm{sh}(j_n\tilde{y})+C_{3n}\tilde{y}\,\mathrm{ch}(j_n\tilde{y})+C_{4n}\tilde{y}\,\mathrm{sh}(j_n\tilde{y})+$$
$$+\frac{1}{2j_n^3}\int_0^{\tilde{y}}q_s(n,\tau)\left[j_n(\tilde{y}-\tau)\mathrm{ch}(j_n(\tilde{y}-\tau))-\mathrm{sh}(j_n(\tilde{y}-\tau))\right]d\tau, \qquad (7)$$

As a result of substituting (7) into (5), a system of algebraic inhomogeneous equations is formed, which makes it possible to determine the integration constants $C_{1n}...C_{4n}>$. Having calculated this problem using Mathcad, we get:

Figure 3. *Graphs of plate movement*



A comparison of the results of calculating the bending of the plate obtained using the LIRA-CAD software package (Fig. 2) and the analytical method (Fig. 3) demonstrates

the advantage of the analytical approach in achieving high accuracy. The analytical method based on the solution of differential equations of the theory of elasticity allows us to obtain an accurate solution for the linear elastic problem of plate bending under given boundary conditions and load distribution. Graphs (presumably showing deflections or stresses) clearly illustrate this difference. The deviations observed when comparing the results may be due to a number of factors inherent in finite element modeling (CAM) used in LIRA-CAD. LIRA-CAD, as a typical representative of CAM programs, discretizes a plate into a set of finite elements, approximating its geometry and physico-mechanical properties. The accuracy of the result directly depends on the size and type of elements used, as well as on the approximation scheme used. A finer finite element grid increases accuracy, but at the same time increases computational costs. In addition, the accuracy is influenced by the accepted simplifying assumptions in modeling, such as the idealization of the material (linear elastic behavior, lack of plasticity, creep, etc.), the idealization of boundary conditions (rigid pinches, hinge supports, etc.) and the method of accounting for distributed load. In real designs, these assumptions can lead to significant discrepancies with the results of the analytical method. While LIRA-CAD provides a convenient tool for quickly analyzing various design options by changing geometric parameters, material, types of supports and loads, the analytical method remains the standard of accuracy, especially in cases where a high degree of reliability of the results is required. For example, when designing critical structures such as aerospace engineering elements or high-precision instruments, the use of an analytical solution is critical to ensure safety and reliability. However, the analytical method is often limited to solving only relatively simple bending problems, whereas LIRA-CAD allows modeling complex structures with nonlinear material properties and geometric nonlinearity. The optimal approach is to combine these methods: using an analytical method to verify and calibrate the model in LIRA-CAD, as well as to evaluate the accuracy of the obtained CAM results. Depending on the complexity of the task and the required accuracy, the choice between the analytical method and the use of a software package such as LIRA-CAD should be reasonable and balanced.

References:

Reddy, J. Theory and Analysis of Elastic Plates and Shells / J. Reddy – CRC Press, 2006. – 2nd Edition. – 568.

Ratmanova O. V., Kalmova M. A. Dynamicactions of a two-layer freely supported beam / O. V. Ratmanova, M. A. Kalmova // LNCE, 2022. – T. 189. – P. 3–9.

Senitsky Yu. E. The method of finite integral transformations – a generalization of the classical decomposition procedure by eigenvector functions // Izv. Saratov University. A new series. Math., mechanics., computer science, 2011. – № 3(1). – P. 61–89.

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Section 5. Technical sciences in general

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OBTAINING AND STUDYING THE PROPERTIES OF MODIFIED THREE-COMPONENT PHOSPHOGYPSUM INTERPOLYMER COMPLEXES AND COMPOSITES

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Abstract

The article is based on the preparation of a three-component composite mixture based on phosphogypsum, an interpolymer complex and humus and its study. It is known that phosphogypsum is a waste product of the chemical industry. The results of scientific research and practical experience have convincingly proved the technical feasibility and expediency of using phosphogypsum in the national economy instead of traditional types of natural raw materials. A brief description of phosphogypsum, promising areas of its processing and some statistical data are presented. The article deals with the use of a chemical meliorant based on phosphogypsum for effective fertilization in various soil and climatic zones for cereals, vegetables, industrial and other agricultural crops, to improve the soil structure. That the use of phosphogypsum as a chemical meliorant improves the chemical, physical and water-physical properties of saline soils.

Keywords: *interpolymer complex, phosphogypsum, humus, soil structure, chemical reclamation, salinization, gypsum, calcium dihydrate, calcium semi-hydrate, composite complex*

Introduction

The rapid pace of development of industry, energy, metallurgy, metalworking, chemical, petrochemical and other industries, as well as areas of engineering, construction and household activities entail the inevitable formation and accumulation of industrial waste on a global scale. And one of the mass types of waste is waste from the chemical industry (Ivanitsky V. V., Klassen P. V., Novikov A. A. et al., 1990).

The Decree of the President of the Republic of Uzbekistan dated February 13, 2021 No. PP-4992 "On measures for further reform and financial recovery of chemical industry enterprises, development of production of

chemical products with high added value" also mentioned the use of chemical industry waste as secondary raw materials (Decree of the President of the Republic of Uzbekistan 02/13/2021).

Analysis of literature on the topic. During the production of mineral fertilizers, various types of waste are generated, among which phosphogypsum is a waste product from the production of phosphate fertilizers (Kamilov K. U., 2005).

It should be noted that at present, in general, there is a significant layer of problems of a geo-ecological nature, associated, first of all, with extensive forms of environmental management, deterioration of the environmental situation for various reasons (Meshcheryakov Yu.G., Fedorov S. V. 2007; Best Available Techniques for Pollution Prevention), including the irrational management of many sectors of environmental management (Tayibi H., Choura M., López F. A., Alguacil J. A., López-Delgado A., 2009).

Currently, the dumps of "Samarkand-kimyo" OJSC contain more than 80 million tons of phosphogypsum and its amount continues to increase annually (in terms of calcium dihydrate) (Tayibi H., Choura M., López F. A., Alguacil J. A., López-Delgado A., 2009; Hilton, Julian, Phosphogypsum (PG): 2010). Monitoring studies of a phosphogypsum dump located on the territory of the Almalyk chemical mineral fertilizer plant of "Samarkand-kimyo" OJSC showed that old phosphogypsum has an identical chemical and phase composition (Fuleihan, Nadim F., 2011; Gennari R. F., Garcia I., Medina N. H., Silveira M. A.G., 2011).

Phosphogypsum in its chemical composition contains mainly oxides of calcium, sulfur and silicon with an admixture of oxides of iron, aluminum, magnesium, phosphorus, sodium and others. As can be seen from the table, the mass fraction of the main substance ($CaSO_4 \cdot 2H_2O$) in terms of dry dihydrate is 97%, the mass fraction of hygroscopic moisture is 16.4%, the content of water-soluble fluoride compounds in terms of fluorine is 0.12%. No toxic compounds of cadmium, arsenic, mercury, or lead were found in phosphogypsum (Larionov M. V., 2015; Kurbanova A. J. 2021; Kendivan O. D.-S., 2021).

Table 1. *Results of chemical analysis of phosphogypsum samples from Ammophos-Maxam OJSC*

Name of indicators	Phosphogypsum (stale). waste of OJSC	
	density g/cm³	density g/cm³
1. P_2O_5 general	2.00	1.39
2. SO_3	44.33	44.95
3. CaO	29.81	31.33
4. Fe_2O_3	0.29	0.64
5. F general	0.42	0.39
6. SiO_2	13.75	12.44
7. Al_2O_3.	0.31	0.58
8. Fe_2O_3	0.29	0.64
9. MgO	traces	0.5
Insoluble residue	9.09	7.78

For samples of old phosphogypsum (waste from "Samarkand-kimyo" OJSC), the specific effective activity of natural radionuclides was determined, on the basis of which a sanitary and epidemiological conclusion was given that the phosphogypsum samples comply with SP No. 202 dated 02/03/2012. "Sanitary and epidemiological requirements for ensuring radiation safety" and phosphogypsum can be used in economic activities without restrictions. Toxicological indicators were determined for phosphogypsum samples, which showed that the toxicity value of phosphogypsum aqueous filtrate in an experiment on laboratory animals (white mice) corresponds to the 4th hazard class. The total toxicity index of a phospho-

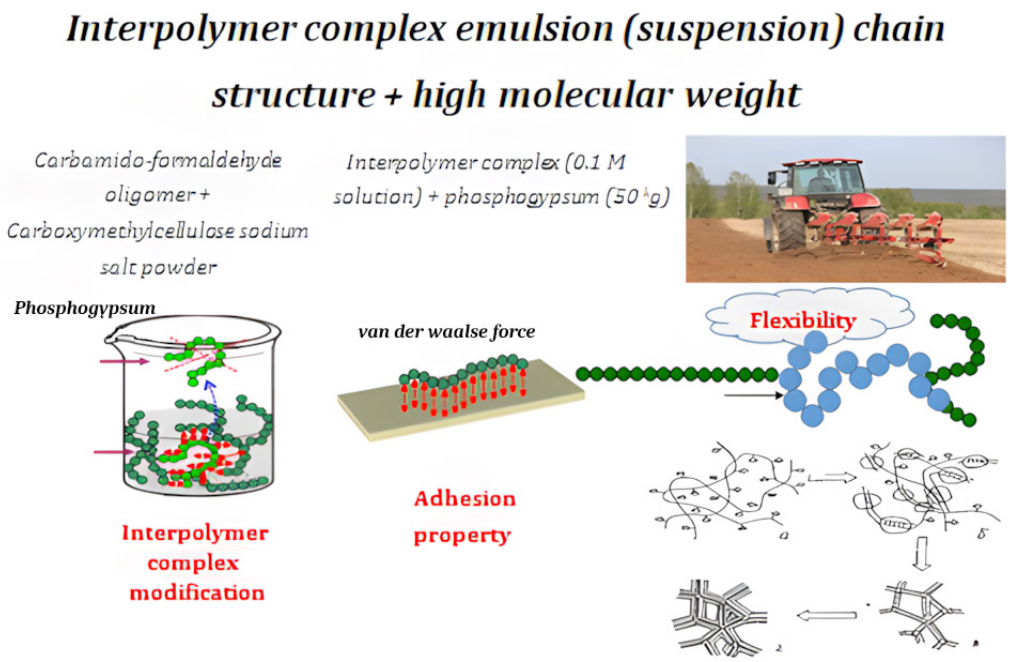
gypsum sample is 7.53 units, which, according to GOST 30774–2001, classifies this waste as hazard class 5 (not hazardous).

Research methodology. The total area of solonetzic soils in the Republic of Uzbekistan is more than 2 million hectares, of which about 50% of the irrigated lands of Khorezm and the Republic of Karakalpakstan have been subject to salinization and loss of nutrient reserves. For this reason, agricultural yields on these lands have decreased by almost 2 times.

To increase the yield of agricultural crops on alkaline and saline soils, it is necessary to increase calcium reserves in them by adding calcium-containing chemical mixtures (gypsum, phosphogypsum). Under the conditions in the above areas, the most effective chemical mixture is phosphogypsum, obtained as an industrial waste from phosphorus production. Today, the "Samarkand-kimyo" OJSC plant (Samarkand, Uzbekistan) has accumulated a huge amount (more than 60 million tons) of phosphogypsum, which consists mainly of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$), phosphogypsum also includes phosphates (1.3–2.9%) (Kurbanova A.Dj., 2021; Allaev Zh., 2021).

It should be noted that our country traditionally occupies one of the leading places in the Central Asian market of phosphate raw materials (Temirov G. B., Alimov U. K., Seitnazarov A. R., Namazov Sh. S., Kaimakova D. A., 2021). In Uzbekistan, the largest enterprise in the mineral fertilizer industry is "Samarkand-kimyo" OJSC.

Figure 1. *Preparation of modified three-component phosphogypsum-interpolymer complexes and composites*



The problem of using phosphogypsum as a secondary raw material for the production of liquid products has been relevant since the 60 s. XX century. The results of numerous studies and practice have convincingly proven the technical feasibility and feasibility of using phosphogypsum in the national economy instead of traditional types of natural raw materials (Eshmatov A. M., 2021). This is due to the content of phosphogypsum from 80 to 98% gypsum, which allows it to be classified as gypsum raw material. Here we should note the most promising areas for using phosphogypsum as a valuable large-scale secondary resource:

- in agriculture for chemical reclamation of acidic and saline soils and composting with organic fertilizers;
- in the cement industry as a mineralizer – an additive to the raw material mixture and as a setting rate regulator – instead of natural gypsum;

- for the production of gypsum binders and products, filler in the production of plastics and glass;
- in the construction of highways, construction of buildings and structures;
- in the development of marine and coastal zones;
- for the production of sulfuric acid, etc.

Analysis and results. Thermal analysis. Phosphogypsum, one of the components of the three-component mixture, was heated to 300 degrees Celsius and subjected to heat treatment.

Quantitative analysis. A 0.1 m/L solution of the interpolymer complex (derived from (1.1;1.2;1.3;1.4;1.5):1 oligomeric urea-formaldehyde and carboxylmethylcellulose) was prepared and mixed with spraying to obtain phosphogypsum masses.

Humus (phosphogypsum-humus 5:1) was added to the resulting phosphogypsum mass and a three-component composite mixture was formed.

To improve the structure of the soil, it is desirable to include various structural formers in its composition. For this purpose, we developed and carried out laboratory processing of a three-component composite mixture that positively changes the structure of the soil.

Phosphogypsum is used for alkalization, desalinization of soil and reclamation of solonetzes. Phosphogypsum is effectively used on soils with a high sodium content as fertilizing ameliorants (1 ton of Phosphogypsum contains about 10 kg of phosphorite), for composting with biological products and organic fertilizers.

We have obtained a three-component composite mixture taking into account some of the above-mentioned features.

The effectiveness of using phosphogypsum in heat treatment will be relatively higher compared to using it only by itself as a soil stricture improver, which we have concluded based on our research.

Results and discussion. In connection with the above, laboratory and field studies were carried out using a three-component composite mixture (TCMC) as soil structure-formers. TCCC is introduced into the soil along with plowing, during which microelements, Ca, S, are introduced into the soil, a water-saving process with an interpolymer complex occurs, and the supply of humus leads to an increase in soil fertility.

Conclusions and suggestions. According to forecasts, by 2040 the amount of waste could double. The issue of bringing phosphogypsum to a state in which it would be possible to use it entirely or assimilate waste into the natural environment without damaging its natural state is more relevant than ever. Thus, modern problems of environmental management and waste generation are interconnected, which requires a phased and at the same time comprehensive solution.

References

Ivanitsky V. V., Klassen P. V., Novikov A. A. et al. Phosphogypsum and its use / V. V. Ivanitsky, P. V. Klassen, A. A. Novikov et al. – M.: Chemistry, 1990. – 224 p.

Decree of the President of the Republic of Uzbekistan 02/13/2021 n pp-4992. “On measures for further reform and financial recovery of chemical industry enterprises, development of production of chemical products with high added value. Information retrieval and expert systems all legislation of Uzbekistan.

Kamilov K. U. Nonstoichiometric interpolymer complexes based on urea-formaldehyde resin and dispersed fillers: Diss. ...cand. tech. Sci. – Tashkent: 2005.

Meshcheryakov Yu. G., Fedorov S. V. Industrial processing of phosphogypsum. – St. Petersburg: Stroyizdat St. Petersburg, 2007. – 104 p.

Best Available Techniques for Pollution Prevention and Control in the European Fertilizer Industry, Booklet – No. 4 of 8: Production of phosphoric acid, European Fertilizer Manufacturers’ Association, EFMA B-1160, Brussels, Belgium.

Tayibi H., Choura M., López F. A., Alguacil J. A., López-Delgado A. (2009). Environmental impact and management of phosphogypsum (Review). J. Environ. Manage. – 90. – P. 2377–2386.

Tayibi H., Choura M., López F. A., Alguacil J. A., López-Delgado A. (2009). Environmental impact and management of phosphogypsum (Review). J. Environ. Manage. – 90. – P. 2377–2386.

Hilton, Julian, Phosphogypsum (PG): Uses and Current Handling Practices Worldwide, Proceedings of the 25th Annual Lakeland Regional Phosphate Conference. October 13–14, 2010. – London UK.
Fuleihan, Nadim F., Phosphogypsum disposal – The pros & cons of wet versus dry stacking // Florida, 2011. – 11 p.
Gennari R. F., Garcia I., Medina N. H., Silveira M. A. G. Phosphogypsum analysis: total content and extractable element concentrations, International Nuclear Atlantic Conference. 2011. – Brazil.
Larionov M. V. Scheme technogenic stress of natural and artificial landscapes of the Saratov and Volgograd regions // Theoretical and applied issues of science and education: at 16 hours. Part 15. – Tambov, 2015. – P. 8–9.
Kurbanova A. J. Preparation and application of porous composite materials // Journal of Economics and Society. 2021. – No. 2 (81). – 59 p.
Kendivan O. D.-S. Application of gypsum when using phosphogypsum compositions // "Economy and Society". 2021. – No. 3(82).
Kurbanova A. Dj. New Technology of Cotton Sowing // Psychology and Education. 2021. – 58(2). – P. 296–303.
Allaev Zh. Preparation and application of composite materials based on polymer-polymer complexes and phosphogypsum // Society and Innovation. 2021. – P. 113–122.
Temirov G. B., Alimov U. K., Seitnazarov A. R., Namazov Sh. S., Kaimakova D. A. Utilization of phosphogypsum by the method of ammonia conversion with potassium chloride // Universum: technical sciences. 2021. – Issue: 5(86). – P. 44–47.
Eshmatov A. M. Application of interpolymer complexes to improve the agrophysical properties of soils // Universum: technical sciences. 2021. – Issue: 5(86). – P. 44–47.

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