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EFFECT OF POLYMER COMPOSITION AND TEMPERATURE ON THE RHEOLOGICAL PROPERTIES OF CHITOSAN-CARBOXYMETHYL CELLULOSE HYDROGELS

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Abstract. *Introduction.* Over the past decade, superabsorbent hydrogels based on natural polymers (cellulose, chitosan) have been widely applied in biomedicine. Despite their high stability and biocompatibility, these hydrogels exhibit several drawbacks associated with insufficient pseudoplasticity and thixotropy. Consequently, the development of hydrogel systems with tailored rheological properties has acquired critical medical relevance. *The objective of this study* was to develop and comprehensively investigate the rheological properties of hydrogels based on chitosan (CS) and carboxymethylcellulose (CMC) with different component ratios, as well as to evaluate the effects of shear rate and temperature on their rheological characteristics in order to identify promising formulations for topical application. *Results and Discussion.* Chitosan/carboxymethylcellulose (CS/CMC) hydrogels with different polymer ratios were investigated by rheometry at temperatures of 20, 25, and 35°C over a shear-rate range of 3-120 s⁻¹. The highest apparent viscosity under all investigated conditions was observed for the CS2.0/CMC0.5 formulation, whereas increasing temperature resulted in a consistent decrease in viscosity. To quantitatively evaluate the rheological behavior, the experimental data were fitted using the Power-law, Herschel-Bulkley, and Casson models. *Conclusion.* CS/CMC hydrogels exhibited pronounced shear-thinning behavior at 20-35°C and shear rates of 3-120 s⁻¹, facilitating their application to the skin. The CS2.0/CMC0.5 formulation showed the highest viscosity and stable rheological behavior ($K = 16.90 \text{ Pa}\cdot\text{s}^n$, $n = 0.389$, $R^2 = 0.987$ at 25°C), making it a promising matrix for topical hydrogel systems.

Keywords: chitosan, carboxymethylcellulose, hydrogel, rheological characteristics, pseudoplasticity, topical application

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1. Introduction

Hydrogels' capacity to hold water and their structural resemblance to the natural extracellular matrix have made them popular as prospective scaffolds for tissue engineering in recent years. Owing to these properties, hydrogels have found broad applications in biomedicine, including wound and burn dressings, due to their excellent biocompatibility, low toxicity, elasticity, and high swelling capacity in aqueous media [1-3].

For topical applications, not only the biological properties of hydrogels but also their rheological characteristics are of particular importance, as these properties determine the application, spreading, and retention of the material on the skin surface. Specifically, system stability and uniform spreading during application may be facilitated by a combination of sufficiently high viscosity at low shear rates and a reduction in viscosity with increasing shear rate. Therefore, investigation of the dependence of viscosity on shear rate is an important step in the development of hydrogel systems for topical application [4,5].

Hydrogels based on chitosan (CS) and carboxymethylcellulose (CMC) are of particular interest in this field due to their high hydrophilicity, biocompatibility, and water-retention capacity. Chitosan is a natural cationic polysaccharide [6,7], whereas CMC is a water-soluble cellulose derivative with pronounced thickening and water-retention properties [8-11]. Varying the ratio of these polymers makes it possible to modify the structural and rheological characteristics of the hydrogel system and thereby select formulations with the desired flow behavior [12,13].

The rheological properties of polymeric hydrogels depend not only on their composition but also on temperature, as changes in temperature may affect molecular mobility and intermolecular interactions within the polymer system [14,15]. Quantitative characterization of rheological behavior can be performed using the Power-law, Herschel-Bulkley, and Casson models, which allow flow parameters to be determined and different formulations to be compared [16-18].

2. Materials and Experimental Methods

2.1. Materials

Chitosan (CS, Cat. No. C804729) was obtained from Shanghai Macklin Biochemical Technology Co., Ltd. (China). The manufacturer's specs state that chitosan has a viscosity of 200-400 mPa·s in 1% acetic acid and a degree of deacetylation (DDA) of 88-92%. The polymer was recovered as an off-white to yellow powder.

Carboxymethyl cellulose (CMC, Cat. No. C889437) was obtained from Shanghai Macklin Biochemical Technology Co., Ltd. (China) and employed as the second polymer component for the manufacture of CS/CMC hydrogel systems.

Acetic acid was utilized as a solvent for the dissolving of chitosan in aqueous medium. Polymer solutions and hydrogel compositions were prepared using purified water. All materials and reagents were used as received without any further purification.

2.2. Chitosan-Carboxymethyl Cellulose Hydrogels Preparation

Chitosan-carboxymethyl cellulose (CS/CMC) hydrogels were synthesized with polymer concentration from 0.5 to 2.0%. Table 1 shows the results of six formulations with different polymer ratios.

Table 1 - Composition of the investigated CS/CMC hydrogel formulations

№	Sample	Chitosan (CS), %	Carboxymethyl cellulose (CMC), %
1	CS0.5/CMC1.0	0.5	1.0
2	CS0.5/CMC1.5	0.5	1.5
3	CS0.5/CMC2.0	0.5	2.0
4	CS1.0/CMC0.5	1.0	0.5
5	CS1.5/CMC0.5	1.5	0.5
6	CS2.0/CMC0.5	2.0	0.5

For the preparation of the hydrogel formulations, CS was dissolved in an aqueous acetic acid solution at the minimum concentration required for complete polymer dissolution. CMC was separately dissolved in purified water. The CS and CMC solutions so obtained were combined in prescribed ratios and the volume was made up to the final volume with filtered water. The solutions were well homogenized to generate homogenous hydrogel compositions.

2.3. Rheological Measurements

The rheological properties of the prepared CS/CMC hydrogel formulations were investigated using a Rheotest II rotational viscometer equipped with a cylindrical measuring system. Measurements were performed at 20, 25, and 35°C over a shear rate range of 3-120 s⁻¹ to evaluate the effects of polymer composition and temperature on the rheological behavior of the hydrogels. The apparent viscosity was recorded at each shear rate, and viscosity-shear rate curves were subsequently plotted. The measuring system was selected according to the viscosity range of the samples, taking into account the corresponding instrument constants. The mean ± standard deviation (SD) was used to express the findings of all measurements, which were done in triplicate (n=3).

2.4. Data Analysis and Rheological Modeling

The experimental rheological data were fitted using the power-law, Herschel-Bulkley and Casson models to characterize the rheological behavior of the CS/CMC hydrogel compositions. Consistency index (K) and flow behavior index (n) were estimated using power-law model. The flow behavior index (n) reflects how the viscosity of the hydrogel depends on the shear rate: n<1 means shear-thinning, n=1 means Newtonian behavior, and n>1 means shear-thickening. Yield stress and other rheological parameters were obtained by using the Herschel-Bulkley and Casson models.

The model parameters were determined by fitting the matching models to the experimental data for each formulation and temperature. The coefficient of determination, R², was used to evaluate the goodness of fit and to compare the adequacy of the models studied to represent the rheological behavior of the

hydrogel formulations. The results are shown as mean $\pm$ SD based on three replicate measurements (n=3).

3. Results and discussion

3.1. Effect of Polymer Composition on Apparent Viscosity

Rheological behavior of CS/CMC hydrogel compositions relied on polymer mix, shear rate and temperature. All formulations showed a progressive decrease in the apparent viscosity with the increase of the shear rate and the level of viscosity depended on the polymer content.

At 25°C and 3s⁻¹, increasing the CMC concentration from 1.0 to 2.0% at a constant CS concentration of 0.5% increased the apparent viscosity from 1.43 $\pm$ 0.04 to 5.21 $\pm$ 0.15 Pa·s. Similarly, at a constant CMC concentration of 0.5%, increasing the CS concentration from 1.0 to 2.0% increased the viscosity from 2.79 $\pm$ 0.12 to 8.09 $\pm$ 0.20 Pa·s. The highest apparent viscosity was therefore observed for CS2.0/CMC0.5. The viscosity–shear rate profiles of the six formulations at 25°C are presented in Figure 1.

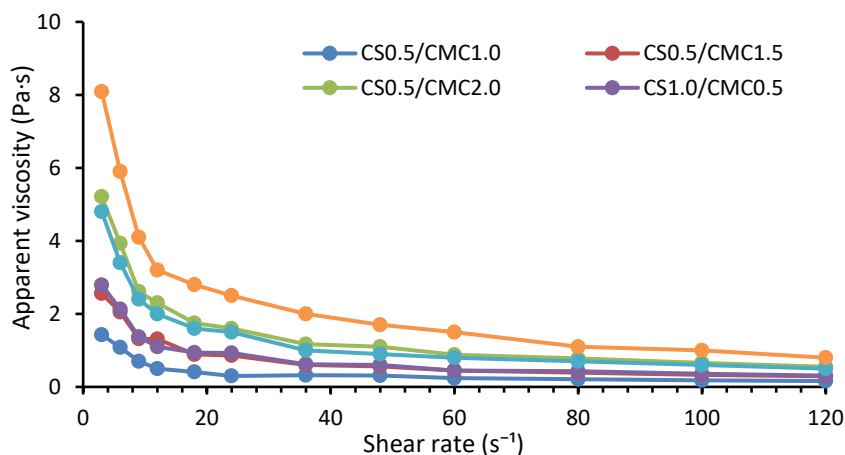


Figure 1 – Apparent viscosity as a function of shear rate for CS/CMC hydrogel formulations with different polymer compositions at 25°C. Data are presented as the mean $\pm$ SD.

The increase of the polymer concentration leads to a rise of the apparent viscosity due to the lower mobility of the polymer chains and the higher intermolecular interactions between CS and CMC that favor the creation of a more interconnected polymeric structure and increase the resistance to flow.

3.2. Shear rate effect on flow behavior

Figure 1 demonstrates that all CS/CMC formulations displayed a significant reduction in apparent viscosity with increasing shear rate from 3 to 120 s⁻¹, confirming the characteristic non-Newtonian shear-thinning behavior. At 25°C, the apparent viscosity of CS2.0/CMC0.5 declined from 8.09 $\pm$ 0.20 Pa·s at 3 s⁻¹ to 0.89 $\pm$ 0.02 Pa·s at 120 s⁻¹, which was approximately 89% reduction, while

CS0.5/CMC1.0 decreased from 1.43 ± 0.04 to 0.15 ± 0.01 Pa·s. The decrease could be linked with orientation and restructuring of polymer chains under shear, resulting in reduced flow resistance [17]. The substantial shear thinning tendency seen in all the formulations should be beneficial for topical administration since the increased viscosity at low shear could increase the retention, whilst the decrease of the viscosity under shear facilitates the spreading over the skin surface [19].

3.3 Influence of Temperature on Rheological Properties

The rheological behavior of the CS/CMC formulations was significantly affected by temperature. The overall apparent viscosity decreased with increasing temperature from 20 to 35 °C in the studied shear-rate range. For CS2.0/CMC0.5 at 3 s^{-1} , the apparent viscosity decreased from 10.14 ± 0.60 Pa·s at 20°C to 8.09 ± 0.20 Pa·s at 25°C and 7.42 ± 0.19 Pa·s at 35°C; the corresponding viscosity–shear rate curves are presented in Figure 2.

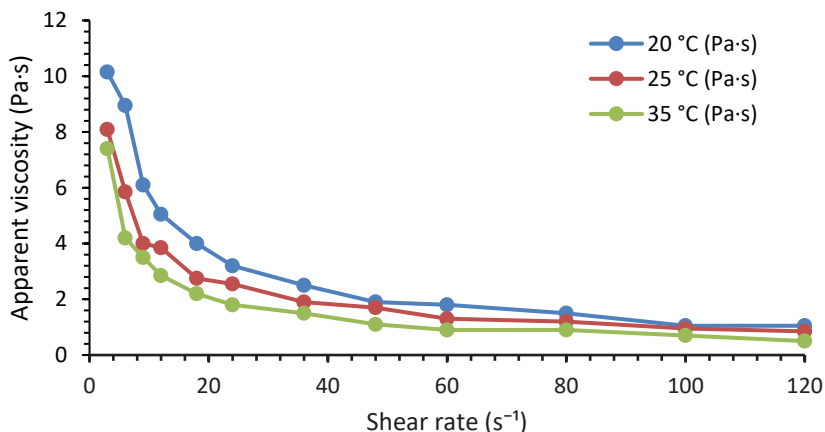


Figure 2 – Effect of temperature on the apparent viscosity of the CS2.0/CMC0.5 hydrogel formulation as a function of shear rate at 20, 25, and 35°C. Data are presented as the mean $\pm$ SD.

The decrease in apparent viscosity with increasing temperature may be attributed to increased molecular mobility and reduced resistance to polymer-chain rearrangement, while the characteristic shear-thinning behavior was maintained at all investigated temperatures. Therefore, throughout the temperature range of 20–35 °C, the overall flow behavior of the hydrogels, which is relevant to the consistency and spreading in topical application, was not altered by the temperature except for to the magnitude of viscosity.

3.4 Power-Law Analysis of the CS/CMC Formulations

The experimental rheological data were fitted to the power-law model to characterize the shear-dependent behavior of the CS/CMC formulations. The flow behavior index (n) was below unity for all formulations and temperatures, confirming their pseudoplastic (shear-thinning) character. The calculated power-law parameters are summarized in Table 2.

Table 2 – Power-law parameters of CS/CMC hydrogel formulations at various temperatures

Formulation	Temperature, °C	K, Pa·s ⁿ	n	R ²
CS0.5/CMC1.0	20	3.384	0.389	0.981
	25	3.126	0.378	0.987
	35	2.436	0.392	0.985
CS0.5/CMC1.5	20	6.400	0.384	0.982
	25	5.711	0.382	0.988
	35	4.603	0.388	0.984
CS0.5/CMC2.0	20	12.440	0.387	0.981
	25	11.253	0.381	0.987
	35	9.168	0.386	0.984
CS1.0/CMC0.5	20	6.580	0.395	0.980
	25	5.890	0.391	0.983
	35	4.881	0.391	0.981
CS1.5/CMC0.5	20	11.464	0.386	0.981
	25	9.958	0.390	0.984
	35	8.388	0.381	0.986
CS2.0/CMC0.5	20	18.533	0.396	0.988
	25	16.899	0.389	0.987
	35	14.102	0.385	0.985

The flow behavior index (*n*) ranged from 0.378 to 0.396 and remained well below unity for all formulations, confirming consistent shear-thinning behavior. In contrast, the consistency index (*K*) strongly depended on polymer composition and temperature. CS2.0/CMC0.5 exhibited the greatest *K* values, which declined from 18.53 Pa·sⁿ at 20 °C to 16.90 Pa·sⁿ at 25 °C and 14.10 Pa·sⁿ at 35 °C. The decrease in *K* with increasing temperature was in agreement with the observed decrease of apparent viscosity. Figure 3 shows a representative power-law fit for CS2.0/CMC0.5 at 25 °C.

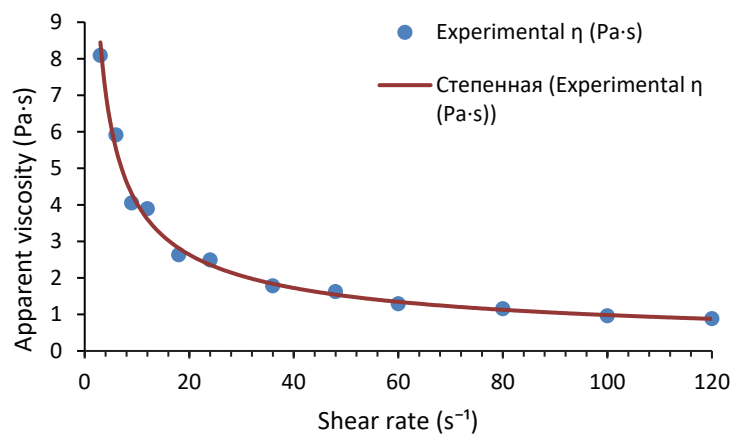


Figure 3 – Power-law fitting of the experimental rheological data for the CS2.0/CMC0.5 hydrogel formulation at 25°C. Experimental values are presented as the mean ± SD (*n* = 3).

For this formulation, the power-law model yielded *K* = 16.90 Pa·sⁿ, *n* =

0.389, and $R^2 = 0.987$. The low n value quantitatively confirmed the pronounced shear-thinning behavior observed experimentally.

3.5. Comparison of Rheological Models

The experimental data were additionally fitted using the Herschel-Bulkley and Casson models, and a representative comparison of these models for CS2.0/CMC0.5 at 25°C is presented in Figure 4.

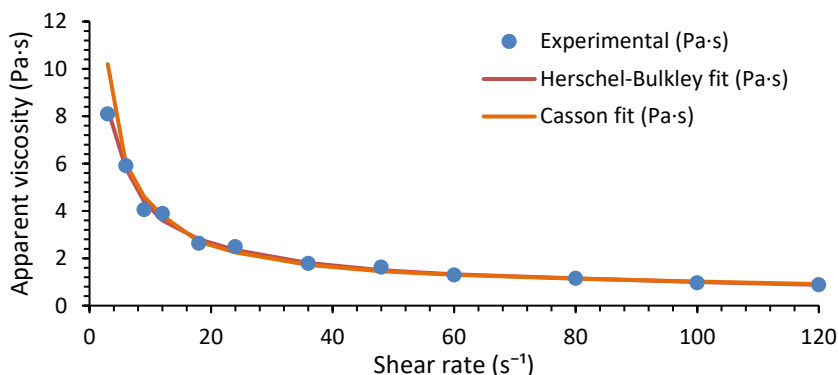


Figure 4 – Comparison of Herschel-Bulkley and Casson model fits for the CS2.0/CMC0.5 hydrogel formulation at 25°C. Experimental points represent mean values from three independent measurements ($n = 3$).

For the representative CS2.0/CMC0.5 formulation at 25 °C, the power-law model provided a satisfactory fit to the experimental data ($R^2 = 0.987$), comparable to that obtained with the Herschel–Bulkley model ($R^2 = 0.987$). The Casson model showed a lower goodness of fit ($R^2 = 0.961$), indicating a less adequate description of the experimental flow behavior. These results support the predominantly pseudoplastic nature of the formulation. Therefore, the power-law model was selected as the principal model for the quantitative comparison of the investigated formulations.

Overall, increasing the concentration of either polymer increased the apparent viscosity and consistency index, whereas increasing temperature reduced these parameters. All formulations retained pronounced shear-thinning behavior. CS2.0/CMC0.5 exhibited the highest apparent viscosity and consistency index together with substantial shear-dependent viscosity reduction, supporting its potential as a topical hydrogel formulation for further investigation [20,21].

4. Conclusion

The rheological properties of CS/CMC hydrogels were strongly influenced by polymer composition and temperature. Increasing the concentration of either polymer increased the apparent viscosity, whereas increasing temperature reduced it. All investigated formulations exhibited pronounced non-Newtonian shear-thinning behavior, confirming the pseudoplastic nature of the developed hydrogel

systems. Among the investigated formulations, CS2.0/CMC0.5 demonstrated the highest apparent viscosity and consistency, making it a promising formulation for topical applications.

The experimental data were adequately described by the applied rheological models, supporting the quantitative characterization of the flow behavior of the CS/CMC systems. Overall, the findings demonstrate that adjustment of the CS/CMC ratio and temperature provides an effective approach for controlling hydrogel rheology. These results provide a basis for the further development and optimization of CS/CMC hydrogel systems for topical and biomedical applications.

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ПОЛИМЕР ҚҰРАМЫ МЕН ТЕМПЕРАТУРАНЫҢ ХИТОЗАН- КАРБОКСИМЕТИЛЦЕЛЛЮЛОЗА ГИДРОГЕЛЬДЕРІНІҢ РЕОЛОГИЯЛЫҚ ҚАСИЕТТЕРІНЕ ӘСЕРІ

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Түйіндеме. *Kіріспе.* Соңғы онжылдықта биомедицинада табиғи полимерлер (целлюлоза, хитозан) негізіндегі аса жоғары сіңіргіш гидрогельдер кеңінен қолданылуда. Жоғары тұрақтылығы мен биосәйкестігіне қарамастан, бұл гелидер псевдопластикалық және тиксотропиялық қасиеттерінің жеткіліксіз болуына байланысты бірқатар кемшіліктерге ие. Осыған байланысты берілген реологиялық қасиеттері бар гидрогельдік жүйелерді әзірлеу медициналық тұрғыдан өзекті міндет болып табылады. *Зерттеудің мақсаты* – хитозан (CS) мен карбоксиметилцеллюлоза (CMC) негізіндегі гидрогельдерді әртүрлі компоненттік қатынаста алу және олардың реологиялық қасиеттерін кешенді зерттеу, сондай-ақ перспективалы сыртқа қолдануға арналған құрамдарды анықтау мақсатында ығысу жылдамдығы мен температураның олардың құрылымдық-тұтқырлық сипаттамаларына әсерін бағалау. *Нәтижелер және талқылау.* Әртүрлі полимерлік қатынастағы хитозан және карбоксиметилцеллюлоза (CS/CMC) негізіндегі гидрогельдер 20, 25 және 35°C температураларда, 3-120 с⁻¹ ығысу жылдамдығы диапазонында реометрия әдісімен зерттелді. Зерттелген барлық жағдайларда ең жоғары көрінерлік тұтқырлық мәндері CS2.0/CMC0.5 құрамында байқалды, ал температураның жоғарылауы тұтқырлықтың заңды түрде төмендеуіне әкелді. реологиялық қасиеттерін сандық бағалау үшін эксперименттік деректер Power-law, Herschel-Bulkley және Casson модельдерімен аппроксимацияланды. *Қорытынды.* 20-35°C температура аралығында және 3-120 с⁻¹ ығысу жағдайында CS/CMC гидрогельдері теріге жағуды жеңілдететін айқын сұйылу қасиетін көрсетті. CS2.0/CMC0.5 құрамы ең жоғары тұтқырлықты және тұрақты реологиялық қасиеттерін көрсетті (25°C температурада $K=16,90 \text{ Па} \cdot \text{с}^n$, $n=0,389$, $R^2=0,987$). Алынған нәтижелер CS2.0/CMC0.5 құрамын тері сыртына қолдануға арналған топикалық гидрогельдік жүйелерді әзірлеу үшін перспективалы негіз ретінде қарастыруға мүмкіндік береді.

Түйінді сөздер: хитозан, карбоксиметилцеллюлоза, гидрогель, реологиялық сипаттамалар, псевдопластикалық, топикалық қолданыс

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ВЛИЯНИЕ СОСТАВА ПОЛИМЕРОВ И ТЕМПЕРАТУРЫ НА РЕОЛОГИЧЕСКИЕ СВОЙСТВА ХИТОЗАН-КАРБОКСИМЕТИЛЦЕЛЛЮЛОЗНЫХ ГИДРОГЕЛЕЙ

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Резюме. Введение. В последнее десятилетие в биомедицине широко применяются сверхпоглощающие гидрогели на основе природных полимеров (целлюлоза, хитозан). Несмотря на высокую стабильность и биосовместимость, данные гели обладают рядом недостатков, связанных с недостаточной псевдопластичностью и тиксотропностью. В связи с этим критическую медицинскую актуальность приобретает разработка гидрогелевых систем с заданными реологическими свойствами. Целью исследования является получение и комплексное реологическое исследование гидрогелей на основе хитозана (CS) и карбоксиметилцеллюлозы (CMC) с различным соотношением компонентов, а также оценка влияния скорости сдвига и температуры на их структурно-вязкостные характеристики для определения перспективных составов для наружного применения. Результаты и обсуждение. Гидрогели на основе хитозана и карбоксиметилцеллюлозы (CS/CMC) с различным соотношением полимеров были исследованы методом реометрии при температурах 20, 25 и 35°C в диапазоне скоростей сдвига 3-120 с⁻¹. Наибольшие значения кажущейся вязкости во всех исследованных условиях наблюдались для состава CS2.0/CMC0.5, тогда как повышение температуры приводило к закономерному снижению вязкости. Для количественной оценки реологического поведения экспериментальные данные были аппроксимированы моделями Power-law, Herschel-Bulkley и Casson. Заключение. Гидрогели CS/CMC при 20-35 °C и сдвиге 3-120 с⁻¹ проявили выраженное разжижение, облегчающее их нанесение на кожу. Состав CS2.0/CMC0.5 показал максимальную вязкость и устойчивое реологическое поведение ($K=16,90$ Па·сⁿ, $n=0,389$, $R^2=0,987$ при 25°C), что делает его перспективной основой для топических гидрогелевых систем.

Ключевые слова: хитозан, карбоксиметилцеллюлоза, гидрогель, реологические характеристики, псевдопластичность, топическое применение

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SILICA FOULING OF ANION-EXCHANGE RESINS IN URANIUM IN-SITU RECOVERY: CURRENT UNDERSTANDING AND REGENERATION APPROACHES

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Abstract. The growing share of in-situ leaching (ISL) in global uranium mining is increasing the demands on the efficiency of ion-exchange processing of pregnant solutions. Strongly basic anion exchange resins that sorb uranyl sulfate or uranyl carbonate complexes are typically used for uranium extraction. Over long periods of operation, their properties deteriorate due to the accumulation of silicon compounds released into the solution during the leaching of silicate rocks. This review examines the mechanisms of silicon fouling of anion exchange resins used in ISL, as well as existing methods for desilication and regeneration. An analysis of scientific publications and technical materials shows that fouling is primarily due to the penetration of silicic acid into the resin pores and its subsequent polymerization. With localized increases in pH, silicate anions can also interact with exchange sites. The formation of oligomeric and polymeric siloxane structures hinders mass transfer, blocks active sites, and reduces the uranium sorption capacity. Alkaline treatment with NaOH and fluoride-containing reagents are used for regeneration. Alkaline solutions are technologically simpler, but less effective against highly polymerized silica phases and, under harsh conditions, can damage the resin. Fluoride systems provide deeper silicon removal but place increased demands on the corrosion resistance of equipment and wastewater treatment. Therefore, the regeneration process must ensure silicon removal without significantly reducing the mechanical strength and sorption properties of the resin.

Keywords: uranium, in-situ recovery, sorption, silicon, desilication

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1. Introduction

Uranium retains a significant role in the global energy sector as the primary fuel for nuclear reactors generating electricity with low carbon emissions. According to the World Nuclear Association (WNA), global uranium demand is estimated at approximately 68,920 tU in 2025. In the baseline scenario, it could exceed 150,000 tU by 2040, driven by a projected increase in installed nuclear power capacity to 746 GW [1].

This demand growth is driven by the transition to sustainable energy systems and the goal of achieving carbon neutrality by 2050, as well as the need to diversify supplies in the face of geopolitical risks and a structural deficit in primary uranium production. In 2024, production covered only approximately 90% of global demand, with the remainder supplied by stockpiles and secondary sources [2]. Additional confirmation of the strategic role of nuclear energy is reflected in projections of the International Atomic Energy Agency (IAEA), according to which, under the high-growth scenario, global nuclear capacity may increase 2.6-fold, from 377 GW in 2024 to 992 GW by 2050 [3].

Uranium mining is one of the technologically complex areas of mining production, and the choice of method for developing a deposit is determined primarily by its lithological structure and hydrogeological conditions. In 2024, global uranium production amounted to about 60,000 tons. Underground in-situ leaching accounted for approximately 52% of this volume, or about 31,000 tons of uranium. With this method, the leaching solution is pumped into permeable, water-saturated ore-bearing horizons, where uranium is converted into a soluble form and then extracted through extraction wells. This makes it possible to significantly reduce the volume of overburden and underground mining operations. About 30 % of the world's uranium was extracted using the underground method, 14 % using the open-pit method, and about another 4 % was obtained as a by-product during the processing of other mineral raw materials. Kazakhstan maintains the world's leading position in terms of uranium production volume - about 39%, or 22,000 tons, with the bulk of production based on in-situ leaching. In Canada, which accounts for about 24% of global production, mainly the rich in-situ deposits of the Athabasca Basin are being developed. In Namibia and Australia, mainly open-pit and combined schemes are used; in Australia, uranium is also obtained as a by-product at the Olympic Dam deposit [4]. It is expected that the share of in-situ leaching may continue to grow as deposits suitable for this method are brought into development [5].

In in-situ leaching, the solution is injected through a system of injection wells into a mineralized aquifer. In the formation, uranium transitions from the solid phase into the solution, after which the productive solution is pumped to the surface through production wells. Depending on the composition of the ore, two main leaching systems are used - acidic and carbonate. In acid-based schemes, solutions of sulfuric acid are primarily used; in carbonate-based schemes, solutions of sodium carbonate and sodium bicarbonate, or ammonium-containing reagents, are used. The choice of medium depends on the mineralogical

composition of the ore-bearing rocks and, especially, on the content of carbonates, which consume the acid for neutralization [6, 7]. In some studies, a CaCO_3 content of up to 4 % is indicated as an approximate limit for applying an acid-based scheme. With a higher carbonate content, the acid consumption increases, so a carbonate-based scheme may turn out to be more technologically feasible [8].

To maintain oxidizing conditions in acidic systems, H_2O_2 , O_2 , Fe^{3+} , or hypochlorite are used. These reagents promote the conversion of uranium into the mobile hexavalent form U(VI) [9]. In carbonate systems, uranium recovery is based on the combination of oxidation and complex formation of uranyl with carbonate ions, resulting in the formation of the soluble complex $\text{UO}_2(\text{CO}_3)_3^{4-}$, which is widely applied in ISR operations in the United States. The World Nuclear Association also emphasizes the widespread use of the alkaline ISR variant in the United States due to the presence of acid-consuming minerals in host formations [10].

After the PLS is lifted to the surface, uranium is recovered by hydrometallurgical methods. For solutions with low and moderate mineralization, ion exchange is the most widely used method, whereas at high mineralization levels (approximately TDS above ~8000 mg/L) solvent extraction is preferred due to the decrease in resin efficiency [11]. In ion exchange schemes, the solution is sent to the sorption stage, where uranium is selectively fixed on anion exchange resins with high affinity for uranyl anionic complexes. The contact of the solution with the resin in the columns ensures the concentration of uranium in the sorbent granules, after which the purified solution is returned to the circulation circuit or sent for disposal [6, 12].

As the resin is saturated, an elution stage is carried out, during which uranium is displaced from the active centers by solutions of sodium or ammonium salts (chlorides or nitrates), which leads to the formation of concentrated uranium eluate, which is then sent to the precipitation stage [13]. In industrial practice, precipitation of ammonium diuranate with the addition of NH_3 , as well as precipitation of uranium peroxide using H_2O_2 , are widely used; the final product is usually obtained in the form of U_3O_8 (yellowcake) [14].

A significant operational limitation of ion exchange systems is the contamination and degradation of sorbents during repeated use. In addition to uranium, resins inevitably interact with the accompanying components of solutions, including iron, organic substances and silicon compounds. This leads to a decrease in exchange capacity, deterioration of sorption kinetics and an increase in reagent consumption at the desorption stage. In this regard, regular flushing, chemical cleaning and resin regeneration are considered as necessary elements of the technological scheme that ensure the stability of the sorption cycle [12].

Silicon compounds occupy a special place among pollutants. Silicic acid enters the solution during sulfuric acid leaching of aluminosilicate rocks and can accumulate in anion exchange resins to levels of about 12–17%, which is accompanied by a decrease in the sorption capacity of uranium and a deterioration

in the mechanical strength of resin granules [15]. The physico-chemical nature of this phenomenon is associated with the polymerization of SiO_2 and the formation of hard-to-remove deposits on the surface and inside the porous structure of the resin, which leads to blocking of active centers and slowing down the processes of mass transfer. Industrial practice shows that critical contamination can form after 15-20 sorption-desorption cycles, while the mass fraction of silicon impurities in the resin can reach tens of percent, which leads to a noticeable decrease in the efficiency of uranium extraction.

Thus, the purification and regeneration of sorbents in the uranium industry is not an auxiliary operation, but a system tool for maintaining the stability of the technological process. Alkaline desilication using NaOH solutions remains the most common approach; however, strongly basic anion-exchange resins have limited stability in alkaline environments, requiring strict control of process conditions and the use of protective technological measures. Increasing the NaOH concentration promotes increased silicon desorption but also increases the risk of degradation of the resin's polymer matrix [16].

In this context, analyzing the mechanisms of silicon contamination of ion-exchange resins and systematizing their purification methods used in industrial practice is particularly relevant, as silicon accumulation is considered one of the factors limiting the efficiency of uranium sorption extraction in ISR processes. However, an analysis of the literature shows that information on the influence of silicon compounds on the sorption properties of resins and the effectiveness of regeneration measures remains limited and fragmented, and the number of publications devoted to this issue in the context of uranium sorption extraction remains relatively small.

2. Modern Uranium Mining Methods and Their Influence on Market Structure

Modern uranium mining is a system in which the geology of deposits and the selected mining technology directly determine the stability of supply and, through contracting, shape the market cycle. In-situ leaching/in-situ recovery (ISL/ISR) dominates the current structure of global uranium mining: according to the World Nuclear Association, in 2024 approximately 52% of uranium was mined by ISL, approximately 44% by conventional methods (open-pit and underground mining), and approximately 4% is recovered as a by-product. This ratio should not be considered as a purely statistical characteristic; it reflects the technological shift of the market towards production schemes with lower capital intensity and higher scalability, which allows manufacturers to respond more quickly to changes in contract demand. A later WNA estimate places the ISL share above 55%, consistent with the forecast of 55–60% by 2026 cited above and indicates the continued strengthening of the role of ISR technologies in the global uranium industry [4].

Classical uranium mining includes open-pit and underground methods, the choice of which is determined by the depth of occurrence, geometry of the ore

body, and mining-geological conditions. In a fundamental review by the International Atomic Energy Agency (IAEA), it is emphasized that uranium extraction, depending on the depth of occurrence, may be carried out either by open-pit mining (with drilling-and-blasting preparation, bench systems, and radiometric grade control) or by underground mining [12]. From a practical perspective, this corresponds to the scheme shown in Figure 1, which illustrates three basic classes of uranium extraction: open-pit mining, underground mining, and ISL/ISR.

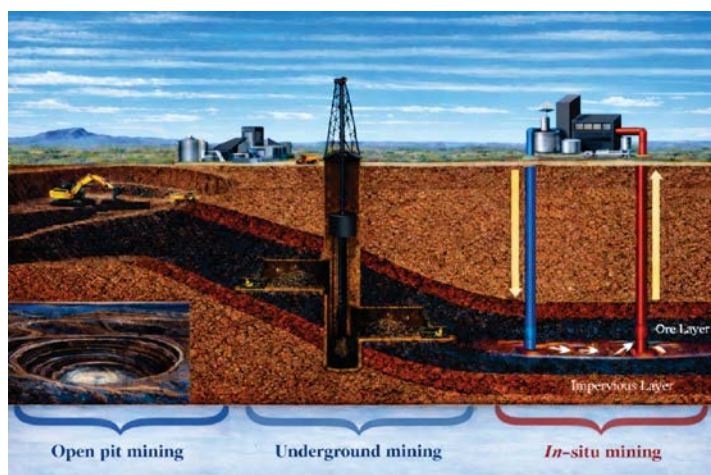


Figure 1 – Schematic representation of the main uranium mining methods (open-pit, underground, ISR).

Due to the high concentration of global uranium production within a limited number of supplier countries, not only the geographical distribution of mining but also the technological approaches used for deposit development acquire considerable importance. Leading producing countries employ fundamentally different mining methods – from in-situ recovery (ISR) to open-pit and underground mining of hard ores – which results in different sensitivities of their production systems to geotechnological, reagent-related, and infrastructural constraints. The systematization of countries according to dominant mining methods, based on national production profiles presented in the report OECD-NEA/IAEA Uranium 2024: Resources, Production and Demand [5], is presented in Table 1.

Table 1 – Distribution of Major Uranium-Producing Countries by Dominant Mining Methods (2024)

Country	Dominant mining method	Deposit type	Notes
Kazakhstan	ISR	Sandstone	Almost all production via ISR
Uzbekistan			ISR is the principal method
USA			ISR is the main operating method
Canada	Underground	High-grade	Underground mining

		unconsolidated ores	
Namibia	Open-pit	Granites, calcretes	Conventional mining
Australia	Underground / open-pit	Hard rock ores	Olympic Dam, Ranger, etc.
Russia	Underground / ISR	Sedimentary and hard rock	Mixed model
China		Various	ISR is being implemented
Niger	Underground / open-pit	Sedimentary	Conventional mining
Ukraine	Underground	Metasomatites	Underground mining
India	Underground / open-pit	Hard rock ores	Conventional mining
South Africa	Underground (as by-product)	Gold-bearing conglomerates	By-product uranium recovery

The transition toward ISR dominance is explained by a combination of technological-economic and geological factors. ISL is implemented through the circulation of leaching solutions within a permeable ore-bearing horizon and the recovery of pregnant leach solution (PLS) to the surface through production wells. For industrial feasibility, the presence of impermeable confining layers, controlled hydrodynamics, and regulated solution geochemistry are critical. As emphasized by the IAEA in its specialized publication on ISR operations, these requirements determine both the configuration of well fields and the monitoring regimes, and they also limit the applicability of the method according to deposit type [7].

At the global level, WNA also confirms its technological dominance: as early as 2022, a significant part of global uranium production was provided by enterprises using ISR technology, with the bulk of production in the USA, Kazakhstan and Uzbekistan coming from underground leaching [6]. This indicates that the technological leadership actually coincides with the geographical dominance of the sandstone uranium provinces and, consequently, with the concentration of market supply in a limited number of jurisdictions.

The uranium market is highly sensitive to changes in production because global supply is concentrated in a small number of countries. According to the WNA, Kazakhstan, Canada, and Namibia together accounted for about three quarters of global uranium production in 2024. Under these conditions, even relatively small changes in production plans, whether caused by delays in commissioning new capacity, logistical constraints, or regulatory factors, can noticeably affect market supply.

Kazakhstan plays a particularly important role in this structure. The country has remained the world's largest uranium producer since 2009 and also holds a substantial share of identified global uranium resources, according to the WNA country profile. The updated country profiles contain production and resource base indicators reflecting the long-term sustainability of supplies [17]. For the uranium market, not only the absolute volume of production is important, but also the technological nature of this supply: the dominance of ISR makes production rates more sensitive to hydrochemical constraints and the state of the reagent

infrastructure than to the traditional mining restrictions associated with the construction of underground mines.

The distribution of uranium production volumes among the main producing countries in 2024 is shown in Figure 2, while Figure 3 shows the distribution of production volumes among the ten largest uranium mining companies in the world according to WNA data for 2024.

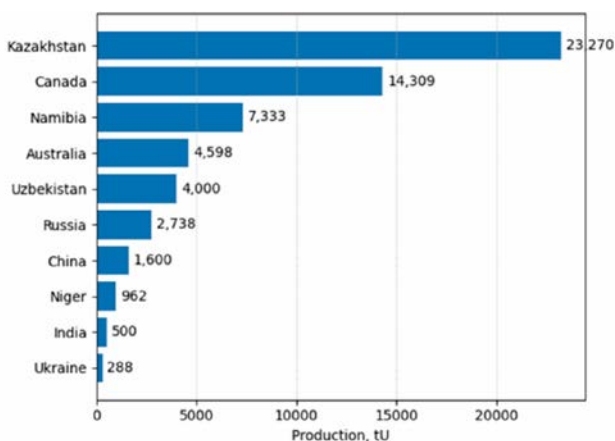


Figure 2 – Top-10 uranium-producing countries (2024), tU.

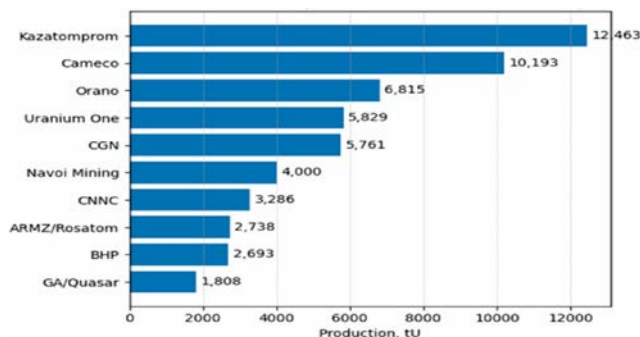


Figure 3 – Top-10 uranium-producing companies (2024), tU.

Along with the ranking of producers, the ownership structure of uranium mining companies is also of fundamental importance. According to an intergovernmental assessment presented in the Red Book (Uranium 2024 edition, data for 2022), of the total world uranium production national state-owned - companies, 15% (7,181 tons) by national private companies, 33% (16,400 tons) by foreign state-owned companies and 10% (4,970 tons) - by foreign private companies. Collectively, the Red Book indicates that in 2022, approximately 75% of global uranium production was associated with state-owned companies, while 25% was accounted for by the private sector [5, p. 95]. This configuration means

that a significant part of the uranium supply may be sensitive to national policy priorities and regulatory regimes, which is methodologically important to take into account when interpreting market signals (without assuming any political motivations beyond the information contained in the sources used).

Market data also shows that the observed spot price does not necessarily reflect the dominant segment of actual trading volumes. According to data provided by Yellow Cake, in the fourth quarter of 2024, the spot price of uranium decreased by 10.7%, decreasing from \$81.75/lb (September 30, 2024) to \$73.00/lb (December 31, 2024). After the end of the quarter, the decline continued, and as of January 27, 2025, the price of it amounted to \$67.30/lb, while the indicative long-term price for the same period decreased to \$79.00/lb. In terms of market liquidity, the quarterly trading volume was 11.1 million lb, while the cumulative annual volume in 2024 reached 45.6 million lb, compared with 56.7 million lb in 2023. At the same time, the average annual trading volume for the period 2020-2023 was 78.7 million lb, and the maximum value was recorded in 2021 (102.4 million lb) [18]. These indicators quantitatively confirm the thesis about the relatively small scale of the spot market segment and the potential volatility of price indicators in conditions of limited volume of “mobile stocks”; available for spot operations.

In terms of final demand, the contract structure of the uranium market is well illustrated by statistics for the United States. According to the U.S. Energy Information Administration (EIA), in 2024, U.S. nuclear power plant owners and operators purchased 55.9 million lb of U_3O_8 -equivalent, of which 49.8 million lb were delivered under short-, medium-, and long-term contracts, while 6.1 million lb were purchased under spot contracts. The weighted average purchase price in 2024 was \$52.71/lb, including \$71.92/lb for spot contracts and \$50.36/lb for contracts with a delivery period of more than one year. Furthermore, EIA data demonstrate the dominance of external supplies in the uranium procurement structure: of the 55.9 million lb, supplies from foreign producers accounted for 54.6 million lb, while U.S.-origin uranium accounted for only 4.3 million lb [19]. In the context of this review, these statistics serve as empirical confirmation that, even in the face of significant price fluctuations, major consumers primarily rely on multi-year contractual agreements, while the spot market serves primarily as an indicative measure.

These factors often cause discrepancies between planned production volumes and actual production levels. Energy policy creates an additional level of uncertainty. For example, in 2025, Reuters, examining the impact of government initiatives aimed at expanding nuclear energy in the United States, cited estimates indicating a possible acceleration in uranium demand growth due to reactor fleet expansion plans and the development of small modular reactors (SMR). Such trends may increase the likelihood of increased contracting activity and increase upward price pressure in the face of limited supply growth [20].

Taken together, the presented data allow us to conclude that the current structure of the uranium market-characterized by the technological dominance of

ISR, high production concentration, the return of long-term contracting, and limited spot market liquidity-increases the likelihood of periods of supply tightness as reactor fleet demand grows, even in cases where nominal production expansion plans appear sufficient on paper. The dynamics of World uranium production in 2010–2024 and the forecast of its change up to 2030 are presented in Figure 4 (according to data from [21]).

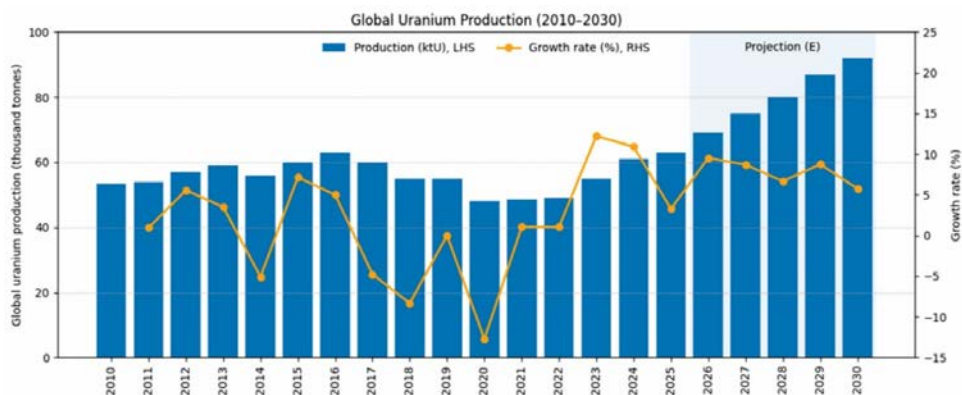


Figure 4 – World uranium production (2010–2030): production volumes (thousand tU) and growth rates (%)

As a result, the uranium market is entering a phase characterized by three interrelated characteristics: the technological dominance of ISR and its continued expansion to over half of global production; the high concentration of production in a limited number of countries and companies; and the restoration of long-term contracting as the primary mechanism for balancing supply and demand.

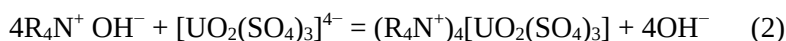
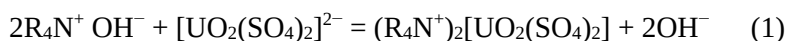
Taken together, these factors explain why even moderate changes in demand can quickly lead to a transition of the uranium market to a state of supply tension and increased price sensitivity. Under these conditions, the sustainability of uranium supplies is increasingly assessed not only in terms of resource availability but also in terms of the feasibility of production plans and the reliability of key mining centers.

3. Ion-Exchange Recovery of Uranium from Pregnant Leach Solutions of In-Situ Leaching

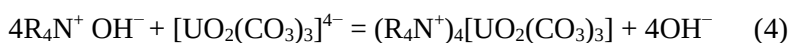
In industrial practice of uranium in-situ leaching, uranium recovery from pregnant leach solutions (PLS) is carried out by the ion-exchange method, which is based on the selective sorption of uranium(VI) anionic complexes on the functional groups of synthetic ion-exchange resins [22]. Depending on the chemical conditions of leaching, uranium in solution is present either in the form of uranyl sulfate complexes (in sulfuric-acid systems) or uranyl carbonate

complexes (in alkaline bicarbonate systems), which determines the requirements for the type of sorbent used [7].

Under conditions of acid in-situ leaching, which is widely applied at sandstone deposits in Kazakhstan where leaching is carried out with sulfuric acid, uranium (VI) is predominantly present in the form of anionic complexes $\text{UO}_2(\text{SO}_4)_2^{2-}$ and $\text{UO}_2(\text{SO}_4)_3^{4-}$ [23]. These complexes are recovered using strong-base anion exchange resins (SBA). Sorption of these complexes on the quaternary ammonium functional groups of SBA resins proceeds according to an ion-exchange mechanism that may be represented by the following reactions:



In contrast to acidic systems, at several ISR operations in the United States alkaline bicarbonate leaching is applied, in which uranium(VI) occurs predominantly in the form of uranyl-carbonate complexes $\text{UO}_2(\text{CO}_3)_2^{2-}$ and $\text{UO}_2(\text{CO}_3)_3^{4-}$ [24]. Their recovery on SBA anion exchange resins also occurs through exchange of the resin counter-ions for uranyl anionic complexes:



Under these conditions, such commercial strong-base anion exchange resins as Dowex 1X8, Purolite A-520E, Purolite A500, and Lewatit S6328A are widely used. These sorbents are applied both in resin-in-solution (RIS) column circuits and in resin-in-pulp (RIP) processes when solid particles are present in the productive solution.

For sulfuric-acid productive solutions it has been shown that the resin Dowex 1X8 provides a high sorption capacity and efficient desorption, enabling the production of eluates with uranium concentrations more than twenty times higher than those of the initial pregnant solution [25].

In carbonate ISR systems used at certain deposits in the United States, strong-base anion exchange resins resistant to high mineralization of groundwater are typically applied. In particular, column experiments have demonstrated that Dowex 21K resin can provide a loading capacity of up to 49.8 mg U g⁻¹ before breakthrough during treatment of carbonate groundwater solutions [26]. Similarly, Purolite A-520E is used in RIS processes for the recovery of uranyl-carbonate complexes from alkaline productive solutions [27].

A comparison of sorbents used in acidic and carbonate ISR circuits is presented in Table 2.

Table 2 – Sorbents Used in Acidic and Carbonate ISR Circuits

Resin brand	Sorbent type	Leaching medium	RIS	RIP
Dowex 1X8	SBA	H ₂ SO ₄	+	+
Purolite A-520E		H ₂ SO ₄ / NaHCO ₃	+	+
Purolite A500		H ₂ SO ₄	+	+
Lewatit S6328A			+	+
Dowex 21K		NaHCO ₃	+	-
Dowex 21K XLT			+	-

Thus, in modern technological schemes for uranium recovery from pregnant solutions of in-situ leaching, strong-base anion exchange resins are most widely used, providing effective sorption of uranium (VI) anionic complexes in both acidic and carbonate ISR systems. The choice of a specific resin grade is determined by the chemical composition of the pregnant solution, the type of leaching medium, and the engineering configuration of the sorption equipment.

4. The Problem of Silica Fouling of Ion-Exchange Resins in Uranium ISR Circuits

Under conditions of sulfuric-acid in-situ leaching of uranium (ISR/ISL), which is predominantly applied at sandstone deposits, pregnant leach solutions (PLS) inevitably contain, along with uranyl-sulfate complexes, significant concentrations of dissolved silicon originating from the acid decomposition of the silicate and aluminosilicate matrix of host rocks. Within the technological circuit of uranium recovery, silicon is present in a set of forms including orthosilicic acid, oligomeric polysilicic acids, and colloidal silica, and the transformation between these forms is primarily determined by pH, temperature, and the ionic composition of the solution.

Although at pH values typical of ISR solutions (pH $\approx$ 1.5–2.5) the rate of polycondensation of silicic acids may be relatively low, even minor local deviations in acidity that occur during mixing of process streams, washing zones, or interaction with hydrolyzing ions such as Fe³⁺ and Al³⁺ may initiate aggregation of low-molecular silicon species followed by the formation of hard-to-remove intrapore deposits on the surface and within the volume of ion-exchange sorbents [15, p.443].

As demonstrated by Chuuman et al. [28], the initial stage of interaction between silicon compounds and strong-base anion exchange resins proceeds through an ion-exchange mechanism between the functional quaternary ammonium groups of the polymer matrix of type R₄N⁺OH⁻ and the monosilicate anion Si(OH)₃O⁻, which may be described by the following reaction:



It should be noted that at the pH of 1.5–2.5 typical of ISR pregnant solutions and with a first dissociation constant of silicic acid of about $pK_{a1} \approx 9.8$, silicon is present mainly as the neutral species $\text{Si}(\text{OH})_4$. In the acidic sorption circuit, silica accumulation is therefore governed chiefly by polymerization and deposition of neutral silica within the pores, whereas the ion exchange described by reaction (5) is relevant primarily for the OH-form of the resin and for the alkaline regeneration stage. The sorbed monomeric forms of silicic acid subsequently undergo intrapore polycondensation with the formation of siloxane bonds (Si-O-Si), resulting in the formation of oligomeric and polymeric structures with different degrees of connectivity. According to NMR spectroscopy, these structures are identified as Q^1 – Q^3 silicate units. It has been shown that even when less than 10% of the ion-exchange capacity of the resin is occupied, monomeric forms (Q^0) transform into dimeric and linear polysilicates (Q^2 – Q^3), which is accompanied by a decrease in the mobility of the adsorbed silicon compounds and their subsequent fixation within the pore structure of the sorbent.

Practical observations in industrial ISR circuits demonstrate that the silicon content in strong-base anion exchange resins may reach 12–17 wt.%, which is accompanied by a decrease in uranium sorption capacity and deterioration of the mechanical strength of resin beads [15, p.435]. In this context, silica fouling of resins ceases to be considered a secondary analytical phenomenon and becomes a factor directly limiting the operational lifetime of sorption materials.

The mechanism of this phenomenon combines deposition of neutral silica inside the pores and competition of silicate anions with uranyl-sulfate complexes for the active sites of strong-base anion exchange resins. In the initial state, the resin exists in the hydroxide form $\text{R}_4\text{N}^+\text{OH}^-$. Upon contact with the pregnant solution of in-situ leaching, ion-exchange sorption of the anionic uranium complex $[\text{UO}_2(\text{SO}_4)_2]^{2-}$ occurs, resulting in the formation of a uranium-loaded resin form. At the same time, part of the dissolved silicon occurs as the anion $\text{Si}(\text{OH})_3\text{O}^-$, whose share rises in local zones of elevated pH and in the OH-form of the resin after regeneration and which then competes for the same quaternary ammonium sites; in the bulk acidic circuit the neutral form $\text{Si}(\text{OH})_4$ prevails and is retained mainly through intrapore polymerization.

During the desorption stage of uranium, uranyl-sulfate complexes are removed from the resin structure; however, silicon compounds may partially remain within the pores and on the functional groups of the resin. This leads to gradual accumulation of silicon in the anion-exchange matrix and to the formation of the so-called silica fouling effect, which is accompanied by a decrease in the availability of active sites and deterioration of the sorption properties of the material.

Schematically, the sequence of these stages – namely the initial state of the resin, sorption of uranyl-sulfate complexes with the competitive participation of silicates, and the subsequent partial retention of silicon after uranium desorption – may be represented as shown in Figure 5.

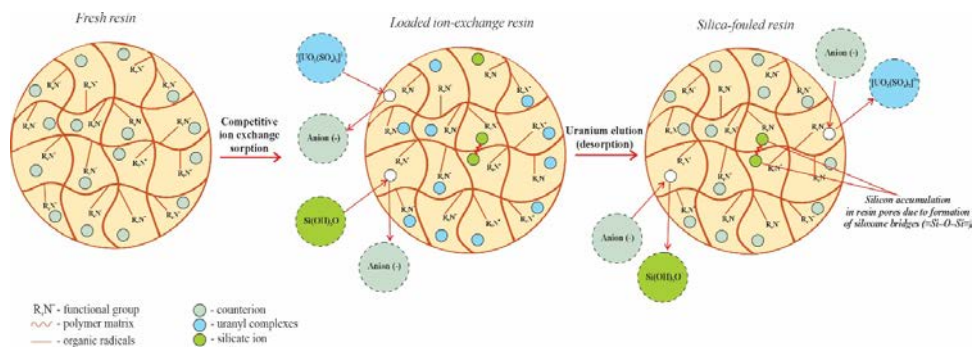


Figure 5 – Schematic representation of the competitive sorption of uranium and silicon on an anion-exchange resin.

The quantitative influence of accumulated silica on the sorption properties of resins was investigated in detail by Yahorava et al. [29]. The authors demonstrated that already at a silica content of about 6% SiO_2 in a gel-type RIP resin, the loss of maximum uranium loading after 24 hours exceeds 50%, whereas for macroporous resins a comparable decrease occurs only when silicon accumulation reaches 25–28%. At the same time, the authors reported differences in the morphology of deposits: in gel-type resins a diffusion film forms on the bead surface, whereas in macroporous resins silica penetrates deeper into the internal structure of the beads. This is confirmed by the increase in silicon concentration toward the center of the bead at high levels of contamination.

These results are consistent with the previously proposed mechanism of intrapore fouling, formulated by Zhang [30], according to which low-molecular polysilicic acids are capable of diffusing into the pore space of an anion-exchange resin, followed by aggregation and formation of intragranular deposits. In contrast, high-molecular polysilicate species are limited by pore dimensions and therefore predominantly precipitate on the resin surface. Taken together, these findings indicate that the critical factor in the degradation of sorption properties is not so much the total silicon concentration in solution but rather the presence of a reactive oligomeric silica fraction.

The obtained results also agree with experimental observations reported by Chuuman et al. [28, p.873], according to which the desorption of silicon from strong-base anion exchange resins strongly depends on the degree of polymerization of the silicate structures. Thus, structures of types Q^0 – Q^2 are relatively easily removed during treatment with 1–2% NaOH solutions, whereas more condensed Q^3 structures are practically not desorbed even when the alkali concentration is increased. This indicates the necessity of breaking siloxane bridges during sorbent regeneration.

Additional confirmation of the influence of silica fouling on the kinetics of uranium sorption is presented in the work of Litvinenko et al. [31]. The authors showed that increasing the SiO_2 content in the Purolite A500U anion exchange

resin from 0 to approximately 19.6% leads to a substantial decrease in the degree of uranium saturation at a fixed contact time. For resin containing about 28% silica, achieving equilibrium loading requires an increase in contact time up to 24 hours, whereas a fresh sorbent reaches comparable values within 6 hours. Thus, the accumulation of silicon can shift the sorption process from a kinetically controlled regime to a diffusion-limited regime, which has direct technological implications for column ISR circuits.

It should be noted that the negative impact of silicon on the operational characteristics of sorption materials in ISR circuits is not limited to mechanical blockage of the porous structure of ion-exchange resins. According to the results reported by Sharafutdinov et al. [32], silica may participate in the formation of stable organo-silicon complexes with humic and fulvic acids present in pregnant leach solutions. These compounds subsequently sorb on the surface and within the volume of both anion-exchange and cation-exchange materials.

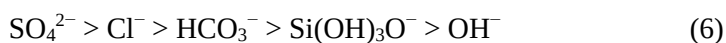
In this case, it is assumed that fixation of silicon within the ion-exchange matrix occurs not only in the form of polycondensed silicate particles but also as part of sulfoghumic compounds, which are capable of partial desorption during the regeneration stage. This results in secondary contamination of the commercial desorbate and deterioration of its technological characteristics during subsequent processing. Moreover, the sorbed organo-silicon complexes may serve as centers for further fixation of trivalent cations, particularly Fe^{3+} , predominantly in an irreversible form. This additionally reduces the efficiency of resin regeneration and promotes accumulation of ballast components within the ion-exchange phase.

Thus, the presence of silicon in ISR pregnant solutions may be considered a factor of complex chemical–physical contamination of strong-base anion exchange resins, leading to a progressive decrease in their working capacity and deterioration of cyclic stability during sorption–desorption operations.

Despite the established negative effects of silicon accumulation in ion-exchange resins, the scientific literature contains a comparatively limited number of studies devoted to the development of effective methods for its removal from the structure of sorbents. The most common approach remains alkaline desilication, based on the conversion of silica into soluble silicate forms [12, 33].

It should be taken into account that the efficiency of this process is determined not only by the concentration of alkali but also by the degree of polymerization of the adsorbed silicon compounds, since silicon removal in this case occurs mainly through alkaline hydrolysis of siloxane bonds (Si-O-Si) formed during intrapore polycondensation of silicic acid [28, p.871].

At the same time, the results of column experiments by Chuuman et al. [28, p.871] demonstrate that for the OH^- form of SBA anion exchange resin, the expected “reverse” desorption of silicon via displacement by more selective anions X^{n-} (such as Cl^- , HCO_3^- , SO_4^{2-}) is practically not realized, although the selectivity order for this system is given as:



The authors showed that regeneration of the column using H_2SO_4 , HCl , NaHCO_3 , and NaCl solutions results in incomplete elution of silicon, whereas noticeable elution occurs specifically when NaOH solution is used. This indicates that the dominant mechanism is hydrolytic destruction of polysilicates rather than simple ion exchange.

Consequently, alkaline regeneration should be considered a process limited by the rate of hydrolysis of siloxane bonds ($\equiv\text{Si}-\text{O}-\text{Si}\equiv$) within the formed intrapore polysilicates rather than solely by the concentration of exchangeable silicon anions.

Earlier studies [15, p.436] established that treatment of anion exchange resin with NaOH solutions of $30\text{--}50\text{ g dm}^{-3}$ at $25\text{--}27\text{ }^\circ\text{C}$ allows the silicon content in the resin to be reduced to 2.91% and 1.15%, respectively, while maintaining mechanical strength of approximately 94%. However, increasing the alkali concentration above 100 g dm^{-3} leads to destruction of the polymer matrix of the sorbent. Similar concerns regarding chemical degradation of functional groups during intensive alkaline treatment were reported by Brown et al. [34], who emphasized the instability of certain strong-base anion exchange resins at high pH values.

Column experiments performed by Chuuman et al. demonstrated that increasing the concentration of NaOH increases silica elution within the range of 1–2%, whereas a further increase up to 5% practically does not produce additional improvement. Thus, a concentration of 2% NaOH may be considered sufficient for elution of adsorbed silicates.

The temperature factor exhibits a non-linear influence: increasing the temperature from $25\text{ }^\circ\text{C}$ to $45\text{ }^\circ\text{C}$ enhances the degree of elution, whereas at $55\text{ }^\circ\text{C}$ a decrease is observed. The authors attribute this to possible repolymerization or precipitation of silicon within the pores as a result of increasing local concentration of monosilicate during accelerated hydrolysis [28].

This effect is important for practical technological regulations, since it demonstrates that intensification of regeneration by heating has an optimum and exceeding this optimum may lead to the opposite effect.

In this context, the attention of researchers has been directed toward fluoride-containing reagent systems, which promote the formation of soluble fluorosilicate complexes. In the work of Spirin et al. [35], it was shown that the use of a regenerant composed of 10% HNO_3 + 5% HF allows the SiO_2 content in the resin to be reduced from an initial 36.8% to 2.8% at a solid-to-liquid ratio of 1:4, and to 0.4% at 1:5, while maintaining mechanical strength at the level of 75–76%.

In a direct comparative experiment using the same batch of resin, a three-stage alkaline treatment reduced the silicon content only to 11.5%, with residual mechanical strength of approximately 40%, whereas fluoride regeneration made it possible to achieve 6.2% SiO_2 with a strength of about 77%. This residual value is higher than the 0.4–2.8% reported by Spirin et al.; the difference should be attributed to the conditions of this comparative test (initial SiO_2 loading, reagent

concentration and number of contact stages) rather than to a discrepancy between the data.

Comparable results were reported by Litvinenko et al. [36], who showed that treatment of Purolite A500Y anion exchange resin with HF or HF + HNO₃ solutions at a sorbent-to-solution ratio of 1:5 for 3 hours results in a more pronounced decrease in residual SiO₂ content while causing less deterioration of mechanical strength compared with alkaline reagents.

Table 3 presents a comparative summary of the reported chemical methods for desilication of silica-fouled ion-exchange resins.

Table 3 – Chemical methods for desilication of silica-fouled ion-exchange resins

Method type	Reagent(s)	Optimal processing conditions	Desilication effect	Limitations	Source
Alkaline desilication	NaOH	30–50 g dm ⁻³ NaOH; 25–27 °C; L:S ≈3:1; ~2 h	SiO ₂ in resin reduced to 1.15–2.91 wt.%	NaOH > 100 g dm ⁻³ damages resin matrix Partial loss of mechanical strength High alkali consumption Possible silica gel formation in column	Kylyshkanov et al. [15]
		1–2% NaOH; ~45 °C; 5–10 min	Removal of monomeric and dimeric silica (Q ⁰ –Q ²); polymerized Q ³ silica remains		Chuuman et al. [28]
		150–200 g dm ⁻³ NaOH; ≤40 °C; 6–8 h	22–35% of silica removed from fouled resin		Molchanova et al. [16]
		3–6% NaOH; 8–16 h	SiO ₂ decreases from ~3–4% to 0.1–0.3% in resin		Ritcey [33]
Fluoride desilication	HF	~5–7% HF; S:L = 1:5; 3 h; RT	~13 g dm ⁻³ Si transferred to eluate	Fluoride corrosion and waste treatment Fluoride handling	Litvinenko et al. [31, 36]
	NH ₄ F	5–9% NH ₄ F; S:L = 1:5; 3 h; RT	Strong silica desorption; Si concentration in eluate ~13–14 g dm ⁻³		
Fluoride–acid treatment	NH ₄ F + H ₂ SO ₄	~10% NH ₄ F + dilute H ₂ SO ₄ ; ~3 h; RT	Moderate silica removal (~40–60%), mechanical strength ~90% retained	Changes sulfate balance	
Alkaline–salt desilication	NaOH + (NH ₄) ₂ SO ₄	9% NaOH + 15% (NH ₄) ₂ SO ₄ ; ~3 h; RT	28–35 g dm ⁻³ Si removed into eluate	Resin strength reduced to 63–68%	
Acid–fluoride treatment	HF + HNO ₃	10% HNO ₃ + 5% HF; S:L ≈1:4–1:5; 1–2 h	Residual SiO ₂ 0.4–2.8% in resin	Highly corrosive medium	Spirin et al. [35]

The data reported by Chuuman et al. [28, p.873] indicate that the limited efficiency of alkaline desilication is determined not only by diffusion factors but also by the degree of polycondensation of the adsorbed silicon compounds, since highly cross-linked Q^3 structures remain resistant to desorption even at elevated alkali concentrations.

Despite the relatively high efficiency of fluoride-based regeneration methods, their industrial application is associated with increased requirements for corrosion resistance of equipment and for handling fluoride-containing effluents. This significantly limits their use as a routine regeneration procedure.

In this regard, a number of authors are considering preventative approaches aimed at reducing the entry of reactive forms of silicon into the sorption circuit. For example, IAEA report TRS-359 notes that high-molecular-weight polymers can be used to remove colloidal silica from productive solutions before the sorption stage [12, p. 87]. Furthermore, Mikhaylenko and van Deventer [37] emphasizes the need to maintain a balance between the rate of silicon accumulation and its removal through partial regeneration of the resin flow in kidney-loop mode.

Another approach involves the use of macroreticular anion-exchange resins, which demonstrate higher stability when operating in environments with elevated silicon content. This is reflected in the patent [38], which demonstrates the applicability of such resins in long-term contact with solutions containing 500 – 700 mg/L SiO_2 . Overall, an analysis of the presented studies shows that existing desilication methods provide varying degrees of silicon removal and simultaneously have uneven effects on the mechanical integrity of resins. In this context, the depth of purification and the preservation of the resin granule structure act as competing criteria.

In many published studies, desilication efficiency is assessed primarily based on the residual SiO_2 content and the mechanical strength of the sorbent. Data on the recovery of uranium sorption capacity after regeneration are reported significantly less frequently, making direct comparisons of different regeneration methods difficult.

Additional complications arise from differences in the criteria for assessing silicon contamination and the analytical methods used. Therefore, the results of individual studies are not always comparable, and the transfer of laboratory data to industrial ISL conditions remains limited.

The available data are insufficient to fully evaluate the efficiency of desilication under ISL conditions. Further research should focus on regeneration modes that ensure silicon removal without significantly reducing the mechanical strength and uranium sorption capacity of ion-exchange resins during repeated use.

5. Conclusion

An analysis of current trends in global uranium mining reveals the consistent dominance of the in-situ leaching method, which accounts for a significant

portion of global production. When using this technology, the efficiency of processing pregnant solutions depends largely on the stable operation of the ion-exchange sorbents used for uranium extraction.

One of the reasons for the reduced efficiency of ISL sorption systems is the accumulation of silicon compounds in ion-exchange resins. Silicon enters the pregnant solutions through the interaction of the leach solution with silicate minerals in the host rocks. Its accumulation in the anion exchange resin structure can lead to a decrease in uranium sorption capacity and deterioration of mass transfer, which gradually reduces the efficiency of the sorption process.

Despite the practical significance of this problem, the mechanisms of contamination and regeneration of ion-exchange resins from silicon-containing compounds under uranium ISL conditions have not been sufficiently studied. The proposed purification methods provide varying degrees of silicon removal, but their impact on restoring the resins' sorption properties has been significantly less studied. Therefore, further research should focus on selecting regeneration modes that remove silicon with minimal damage to the sorbent, as well as developing measures to reduce silicon accumulation in ion-exchange materials during long-term operation.

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ЖЕР АСТЫ ШАЙМАЛАУ ПРОЦЕСІНДЕГІ АНИОНАЛМАСТЫРҒЫШ ШАЙЫРЛАРДЫҢ КРЕМНИЙМЕН ЛАСТАНУЫ: ҚАЗІРГІ ТҮСІНІКТЕР ЖӘНЕ РЕГЕНЕРАЦИЯ ӘДІСТЕРІ

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Түйіндемe. Уранды әлемдік өндіруде жер асты ұңғымалық шаймалау (ЖАШ) үлесінің артуы өнімді ерітінділерді ионалмасу әдістерімен тиімді өңдеуге қойылатын талаптарды күшейтеді. Уранды бөліп алу үшін әдетте уранил-сульфатты немесе уранил-карбонатты кешендерді сорбциялайтын күшті негізді аниониттер қолданылады. Ұзақ уақыт пайдаланғанда олардың қасиеттері силикатты жыныстарды шаймалау кезінде ерітіндіге өтетін кремний қосылыстарының жиналуына байланысты нашарлайды. Шолуда ЖАШ жағдайында қолданылатын анионалмастырғыш шайырлардың кремниймен ластану механизмдері, сондай-ақ десиликация мен регенерацияның қолданыстағы тәсілдері қарастырылды. Ғылыми жарияланымдар мен техникалық материалдарды талдау кремниймен ластану негізінен кремний қышқылының шайыр кеуектеріне енуі және одан әрі полимерленуімен байланысты екенін көрсетеді. рН жергілікті жоғарылаған жағдайда силикат аниондары ионалмасу орталықтарымен де әрекеттесуі мүмкін. Олигомерлі және полимерлі силоксан құрылымдарының түзілуі масса алмасуды қиындатады, белсенді орталықтарды бөгейді және уран бойынша сорбциялық сыйымдылықты төмендетеді. Регенерация үшін NaOH ерітіндісімен сілтілік өңдеу және құрамында фторид бар реагенттер қолданылады. Сілтілік ерітінділер технологиялық жағынан қарапайым, бірақ жоғары дәрежеде полимерленген кремнийлі фазаны жоюда тиімділігі төмен және қатаң режимдерде шайырды зақымдауы мүмкін.

Фторидті жүйелер кремнийді тереңірек жояды, алайда жабдықтың коррозияға төзімділігі мен ағынды суларды тазартуға жоғары талап қояды. Сондықтан регенерация режимі шайырдың механикалық беріктігі мен уранға қатысты сорбциялық қасиеттерін елеулі төмендетпей, кремнийді тиімді жоюды қамтамасыз етуі тиіс.

Түйінді сөздер: уран, жер асты шаймалау, сорбция, кремний, кремнийден тазарту

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ЗАГРЯЗНЕНИЕ АНИОНООБМЕННЫХ СМОЛ КРЕМНИЕМ В ПРОЦЕССЕ ПОДЗЕМНОГО ВЫЩЕЛАЧИВАНИЯ УРАНА: СОВРЕМЕННОЕ ПОНИМАНИЕ И ПОДХОДЫ К РЕГЕНЕРАЦИИ

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Резюме. Рост доли подземного скважинного выщелачивания (ПВ) в мировой добыче урана повышает требования к эффективности переработки продуктивных растворов ионообменными методами. Для извлечения урана обычно применяют сильноосновные аниониты, сорбирующие уранил-сульфатные или уранил-карбонатные комплексы. При длительной эксплуатации их свойства ухудшаются из-за накопления соединений кремния, поступающих в раствор при выщелачивании силикатных пород. В обзоре рассмотрены механизмы кремниевого загрязнения анионообменных смол, используемых в ПВ, а также существующие способы десиликации и регенерации. Анализ научных публикаций и технических материалов показывает, что загрязнение связано главным образом с проникновением кремниевой кислоты в поры смолы и ее последующей полимеризацией. При локальном повышении pH силикатные анионы также могут взаимодействовать с обменными центрами. Образование олигомерных и полимерных силоксановых структур затрудняет массоперенос, блокирует активные участки и снижает сорбционную емкость по урану. Для регенерации применяют щелочную обработку NaOH и фторидсодержащие реагенты. Щелочные растворы технологически проще, но менее эффективны при сильно полимеризованной кремнеземистой фазе и при жестких режимах могут повреждать смолу. Фторидные системы обеспечивают более глубокое удаление кремния, однако предъявляют повышенные требования к коррозионной стойкости оборудования и очистке стоков. Поэтому режим регенерации должен обеспечивать удаление кремния без существенного снижения механической прочности и сорбционных свойств смолы.

Ключевые слова: уран, подземное выщелачивание, сорбция, кремний, обескремнивание

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SYNTHESIS, STRUCTURE AND MORPHOLOGY OF SmMnO_3 - LaMnO_3 PEROVSKITE COMPOSITE

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Abstract: This article discusses the synthesis, phase composition, and structural morphology of the LaMnO_3 - SmMnO_3 double- phase manganite perovskite composite. The aim of synthesizing a two-phase manganite containing the rare earth elements samarium and lanthanum is to study the structural features and properties of the resulting products compared to classical perovskite manganites and single-phase samarium and lanthanum manganites. The Pechini method, based on sol-gel synthesis, was used to synthesize the product. The purpose of selecting this method was to obtain a product with high fineness and crystallographic purity. The phase composition and crystallographic parameters were analyzed using X-ray diffraction (XRD), Fourier-transform infrared (FTIR), and morphological methods to determine the formation of bonds between Me-O; scanning electron microscopy (SEM-EDS), scanning surface area, and elemental distribution. The synthesis was carried out based on sol-gel formation in the presence of metal nitrate hydrates. Phase analysis of the product showed that SmMnO_3 has the orthorhombic Pbnm (62) structure in accordance with PDF 00-025-0747, while LaMnO_3 corresponds to the rhombohedral space group R-3C (167) in accordance with PDF card No. 01-090-6505. It was established that the intense absorption bands in the FTIR spectrum lie within the range of $750\text{--}600\text{ cm}^{-1}$, indicating the formation of Mn–O bonds. SEM-EDS results show that the average particle size of the powdered product is $0.489\text{ }\mu\text{m}$, and the product was successfully characterized using the elemental distribution map.

Keywords: perovskite, manganite, Pechini method, XRD, SEM-EDS analysis

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1. Introduction

Perovskite manganites are a class of transition metal oxides with the general chemical formula ABO_3 ($RMnO_3$ for rare-earth variants), where the A-site is occupied by trivalent rare-earth cations (La^{3+} , Nd^{3+} , Sm^{3+}) or divalent cations of alkaline earth elements (Ca^{2+} , Sr^{2+} , Ba^{2+}), while manganese (Mn) ions occupy the B sites [1–3]. Their structure consists of a three-dimensional framework of MnO_6 octahedra, the vertices of which are shared, while the cation at the A-site occupies interstitial spaces [4–6]. These materials are model systems for studying strong electronic correlations, exhibiting a wide range of electronic and magnetic phases arising from complex interactions between spin, charge, lattice, and orbital structure [5,7]. Depending on their composition and temperature, they may exhibit ferromagnetism (FM), antiferromagnetism (AFM), or paramagnetism (PM) [5,8–10]. It is known for its phenomenon of giant magnetoresistance, in which electrical resistance decreases sharply under the influence of an applied magnetic field [2,9]. In contrast, it exhibits metal-insulator transitions and semimetallic properties, making it important for spintronics [7,9,11]. Physical properties of manganites are primarily determined by two competing exchange interactions involving manganese ions: double-exchange (DE) interaction and super-exchange (SE) interaction. DE interactions occur between Mn^{3+}/Mn^{4+} ions via oxygen 2p orbitals. Electron transitions between these mixed valence states contribute to both FM and metallic conductivity [2,9,11,12]. SE CAO interactions typically give rise to antiferromagnetic insulating states, examples of which are the stoichiometric compounds $CaMnO_3$ or $LaMnO_3$ [2,3,10].

Lanthanum manganite ($LaMnO_3$) is a typical perovskite oxide (ABO_3) characterized by a flexible structure, tunable electronic states, and magnetic properties. Stoichiometric $LaMnO_3$ is an antiferromagnetic insulator, but FE can be achieved by incorporating other metals into its composition or by introducing an excess or a small amount of oxygen [8,11]. These modifications are suitable for use in supercapacitors, electrocatalysis, MRI contrast agents, and environmental remediation [1,13,14]. Researchers have employed various strategies to overcome challenges such as particle agglomeration and low conductivity. One of these is the diversity of synthesis types and the choice of synthesis method. Hydrothermal synthesis is used to create $LaMnO_3$ nanoparticles, which are combined with MXene nanoparticles to improve charge transport and increase the surface area [1]. Mesoporous silica (SBA-15) is used to produce a nanoscale product, enhancing oxygen adsorption on the surface and creating more active sites for catalytic reactions. Sol-gel synthesis is a cost-effective and rapid method that often uses oxalic or citric acid as a precursor to produce fine magnetic nanoparticles [13,15,16]. Although doped $LaMnO_3$ perovskites are of great importance for the development of clean energy and electronics, issues related to the formation of secondary phases, electrolyte reactivity, and high-temperature stability have not yet been fully resolved.

$SmMnO_3$ is characterized by properties such as being one of the best-known perovskite manganites, exhibiting colossal magnetoresistance (CMR), and

possessing complex spin textures, making it a promising material for the development of next-generation sensor, memory, and spintronic devices [17,18]. SmMnO_3 crystallizes primarily in the orthorhombic perovskite structure (space group Pbnm). Substitution of samarium with other ions, such as strontium (Sr) [17], europium (Eu), or yttrium (Y), leads to significant changes in the lattice structure. Eu or Y dopants lead to lattice contraction and a decrease in lattice constants. Calculations of the Goldschmidt tolerance coefficient (0.9) and the cohesive energy confirm that the structure remains stable even at high doping levels (up to 25% for Eu and Y). Mechanical analysis shows that SmMnO_3 is flexible, as evidenced by a G/B ratio below 0.57. Y doping increases the material's hardness (Young's modulus), while Eu doping typically reduces it [19]. From highly efficient supercapacitors to multiferroic devices operating at room temperature, SmMnO_3 is a key product of innovation in materials science and functional electronics [18,20,21].

This study aims to synthesize the biphasic perovskite manganite LaMnO_3 - SmMnO_3 and to investigate the effect of the phase mixture on structural and morphological properties compared to the individual components LaMnO_3 and SmMnO_3 . Particular attention is paid to lattice distortion, phase formation, particle morphology, and the potential improvement in functional properties associated with the coexistence of orthorhombic and rhombohedral phases, using FTIR, XRD, and SEM-EDS methods.

2. Experimental part

Dual-phase perovskite manganites (LaMnO_3 - SmMnO_3) were first synthesized separately using the Pechini method [22] and weighed in a 1:1 ratio to obtain a homogeneous composite; they were then mixed in a ball mill in the presence of ethanol for 15 minutes. For the synthesis of LaMnO_3 , 10 mmol of lanthanum(III) nitrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4.33 g) and 10 mmol of manganese(II) nitrate $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.51 g) were used. To prepare SmMnO_3 , 10 mmol of samarium(III) nitrate $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (4.45 g) and 10 mmol of manganese(II) nitrate $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (2.51 g) were used. The starting salts were dissolved in 10 mL of distilled water with constant stirring on a magnetic stirrer. Citric acid (1.92 g, 10 mmol) and ethylene glycol (0.93 mL, 15 mmol) were then added to the solutions in a molar ratio of metal: citric acid: ethylene glycol = 1:1:1.5. The resulting mixture was held at a temperature of 70-90 °C for 15 minutes until a gel-like mass formed. The resulting gel was dried at 200 °C for 5 hours, after which it was heat-treated in the temperature range of 600-1100 °C to form a perovskite structure. LaMnO_3 and SmMnO_3 powders were first prepared separately and then mixed in a 1:1 mass ratio to form a two-phase composite. To do this, 1 g of each powder was taken and mechanically ground in a ball mill in the presence of three drops of ethanol for 15 minutes to achieve a homogeneous phase distribution. The resulting wet powder was further calcined at 800 °C for 2 hours to remove residual organic components and increase the crystallinity of the composite. We

analyzed the two-phase perovskite using FTIR, XRD, and SEM-EDS to confirm that manganites had been obtained.

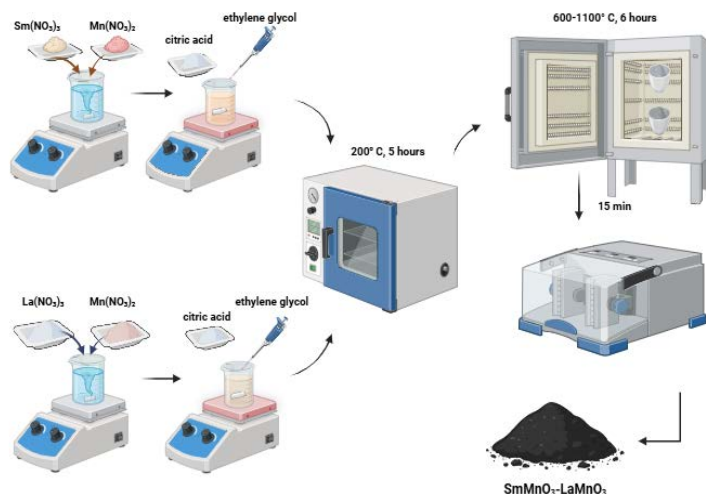


Figure 1 – Synthesis of a two-phase perovskite manganite.

Reagents used to prepare the two-phase product: manganese(II) nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$, Buchs, Switzerland); lanthanum(III) nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, TU 6-09-4676-83); citric acid ($\text{C}_6\text{H}_8\text{O}_7$, GOST 908-79); ethyl alcohol, 96% (medical grade) and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) (GOST 10164-75); samarium nitrate ($\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Ch.P, GOST 10928-90).

We used the following measuring instruments and methods: a laboratory agate (diameter-13 cm (130 mm)) (QIANGFU, ASIN, B0DNB1MQ28, China), an AM vibrating ball mill (China), and a “SNOL” laboratory furnace. The phase composition was determined using X-ray diffraction (Rigaku Miniflex 600 benchtop X-ray diffractometer (Rigaku, Tokyo, Japan)) and a field-emission scanning electron microscope (Thermo Scientific ChemSEM Axia, USA). IR spectroscopy was performed using a Bruker ALPHA FTIR spectrometer in the range of $400\text{--}4000\text{ cm}^{-1}$.

3. Results and discussion

3.1. XRD analysis

The formation of biphasic perovskite manganites was confirmed by determining the crystallographic parameters and phase composition of the resulting product using X-ray phase analysis (XRD). Measurements were performed using a Rigaku Miniflex 600 X-ray diffractometer, and the parameters of the crystalline phase were analyzed using the PDF-5 software.

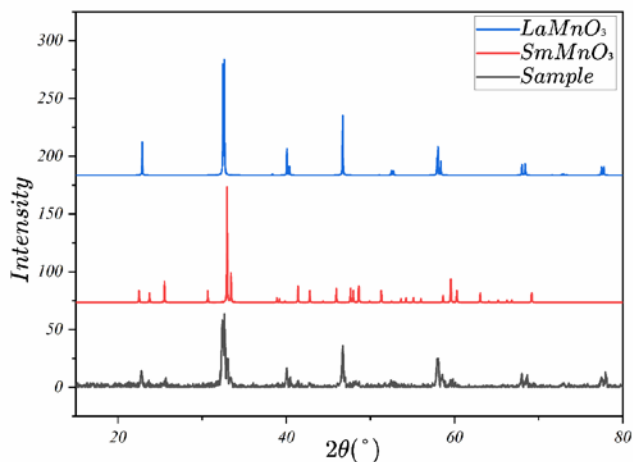


Figure 2 – LaMnO_3 - SmMnO_3 diffractogram.

Figure 2 shows synthesized two-phase perovskite manganites and the diffraction patterns of samarium manganite and lanthanum manganite. The sharpness of the diffraction peaks and the retention of peaks characteristic of the dual phase in the composite indicate the formation of the product. Samarium manganite crystallizes in orthorhombic space group $Pbnm$ [62] according to PDF 00-025-0747, while lanthanum manganite forms rhombohedral $R\text{-}3C$ (167) structure according to PDF 01-090-6505 (table 1).

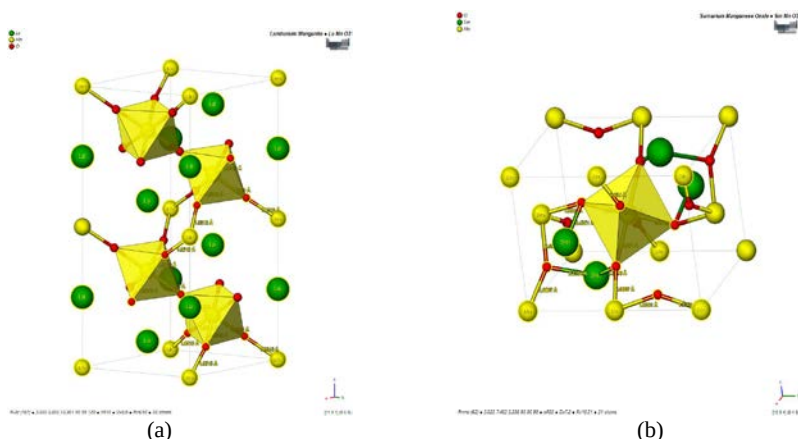


Figure 3 – Phase structures of LaMnO_3 (a) and SmMnO_3 (b).

Figure shows the crystal structure of the perovskite-like compounds LaMnO_3 and SmMnO_3 . In both phases, manganese atoms coordinate with oxygen atoms to form MnO_6 clusters and a 3D perovskite lattice. The lattice exhibits significant octahedral distortion due to the fact that the radius of the Sm^{3+} ion is smaller than

that of the La^{3+} ion, and also because LaMnO_3 structure is relatively symmetric, resulting in the formation of a rhombohedral structure.

Table 1 – Results of crystallographic quantitative analysis

№	Name of compound	Crystal System	a, Å	b, Å	c, Å	V, (Å ³)	Z	PDF Number	Space Group	Density $\rho_{\text{x-rays}}$ g/cm ³
1	SmMnO_3	Orthorhombic	5.825	7.483	5.358	233.55	4	00-025-0747	Pbnm (62)	7.20
2	LaMnO_3	Rhombohedral	5.511	5.511	13.396	352.27	6	01-090-6505	R-3c (167)	6.84

Table 1 lists the crystallographic parameters of two-phase product. Lattice parameters of SmMnO_3 are $a = 5.825$ Å, $b = 7.483$ Å, and $c = 5.358$ Å, with a unit cell volume of 233.55 cm³. Density of the X-ray structure is 7.20 g/cm³. Lattice parameters of the LaMnO_3 compound are $a = 5.511$ Å, $b = 5.511$ Å, and $c = 13.396$ Å, with a unit cell volume of 352.27 Å³. Density of the X-ray structure of this compound is 6.84 g/cm³.

3.2. FTIR analysis

FTIR spectroscopic analysis was performed using a Bruker ALPHA spectrometer (Ettlingen, Germany) at room temperature with a spectral resolution of 1 cm⁻¹. Measurements were taken in the frequency range of 4000 – 400 cm⁻¹ using KBr pellets.

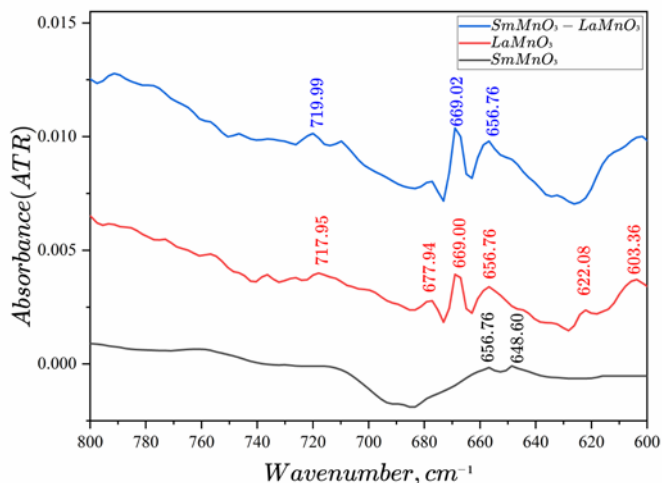


Figure 4 – IR spectrum of LaMnO_3 , SmMnO_3 , and $\text{LaMnO}_3\text{-SmMnO}_3$.

Figure 4 shows the FTIR spectrum of LaMnO_3 , SmMnO_3 , and $\text{LaMnO}_3\text{-SmMnO}_3$ samples. The correspondence between Mn-O bonds and vibrations in 800 – 600 cm⁻¹ absorption region explains the formation of the perovskite

structure. LaMnO_3 compound is identified by absorption bands at 717.95, 677.94, 669.00, 656.76, 622.08, and 603.36 cm^{-1} . SmMnO_3 compound was observed near 656.76 and 648.60 cm^{-1} . In $\text{LaMnO}_3\text{-SmMnO}_3$ composite, an increase in the intensity of the bands in the regions of 719.99, 669.02, and 656.76 cm^{-1} can be observed.

3.2. SEM-EDS analysis

SEM-EDS analysis was performed using a Thermo Scientific ChemSEM Axia (USA) in a 99.999% pure nitrogen (N_2) atmosphere. The quantitative and qualitative elemental composition was determined by SEM and EDS analysis.

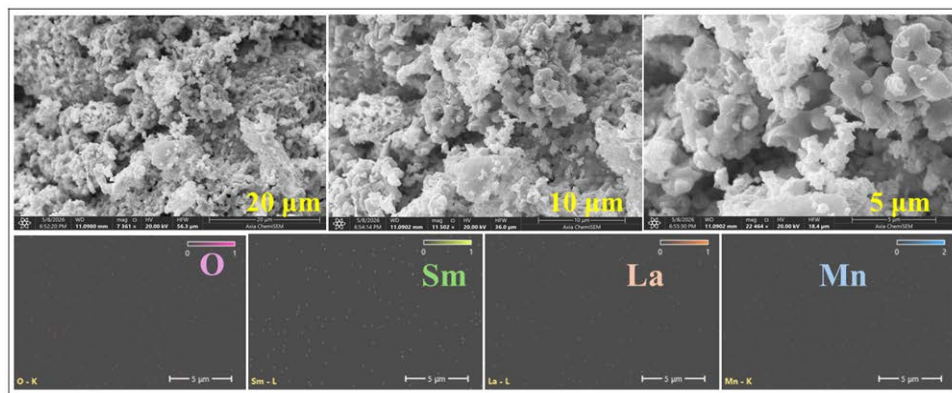


Figure 5 – SEM images of the surface of $\text{LaMnO}_3\text{-SmMnO}_3$ at 20, 10, and 5 μm , and elemental distribution.

Figure shows SEM images and EDS elemental distribution maps of the $\text{LaMnO}_3\text{-SmMnO}_3$ perovskite composite at sizes of 20, 10, and 5 μm . The SEM images show that the product is agglomerated and has a fine-grained morphology. The EDS map indicates that the constituent elements are evenly distributed and confirms that the composite has a homogeneous structure.

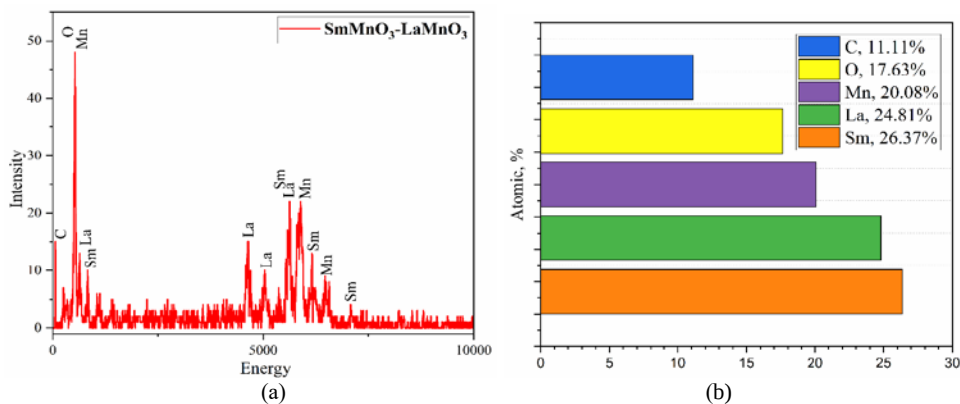


Figure 6 – SEM-EDS diagram (a) and atomic percentage, % (b) of $\text{LaMnO}_3\text{-SmMnO}_3$ composite.

EDS diagram shows the composition of the composite, confirming the presence of La, Mn, O, and Sm; the atomic composition of these elements serves as evidence of the composite's formation. The presence of carbon in the diagram is also explained by the fact that it was detected by placing the sample on a carbon label in scanning electron microscope.

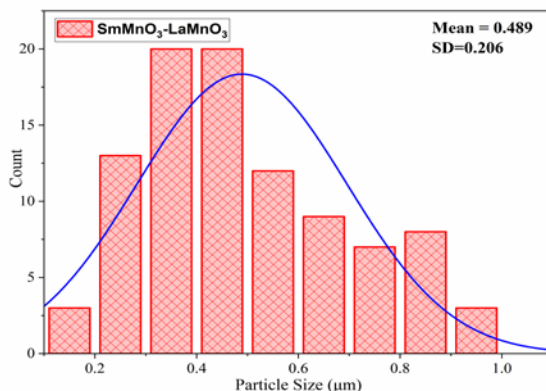


Figure 7 – Average particle size of LaMnO₃-SmMnO₃ at 5 μm.

Figure 7 shows that the average particle size of the two-phase manganite in the SEM range of 5 μm was 0.489 μm, with a standard deviation of 0.206 μm. The primary particle sizes ranged from 0.1 to 1.1 μm. The measurements were taken using ImageJ software.

4. Conclusion

LaMnO₃-SmMnO₃ composite was synthesized using the Pecchini method. Crystallographic and phase characteristics of the product were determined by X-ray analysis. Based on the results, the a, b, and c parameters, the space group, and the crystal system types were determined. The orthorhombic *pbnm* samarium manganite (62) crystallizes in the space group, while the lanthanum manganite exhibits a rhombohedral *R-3C* (167) structure. The FTIR results corresponded to Mn-O bond vibrations in the absorption range of 800–600 cm⁻¹. Surface area and elemental distribution were analyzed using SEM-EDS data. The average microparticle size in the 5 μm range was 0.489 μm. The results presented confirm the formation of a two-phase perovskite manganite composite.

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SmMnO₃-LaMnO₃ ПЕРОВСКИТТИ МАНГАНИТТИҢ СИНТЕЗІ, ҚҰРЫЛЫСЫ ЖӘНЕ МОРФОЛОГИЯСЫ**Нурбекова М.А., Матаев М.М., Сарсенбаева* З.Б., Абдраймова М.Р., Көшкімбаева А.Қ.***«Қазақ ұлттық қыздар педагогикалық университеті» КеАҚ, Алматы, Қазақстан*

Түйіндемесі: Бұл мақалада LaMnO₃-SmMnO₃ қос манганитті перовскитті композиттің синтезі және фазалық құрамы мен құрылыс-морфологиясы қарастырылады. Құрамында самарий және лантан сирек элементтері бар қос фазалы манганитті синтездеудегі мақсат алынған өнімдерді классикалық перовскитті манганиттерден және бір фазалы самарийдің және лантанның манганиттерімен құрылыс мен қасиеттерін ерекшеліктерді зерттеу. Өнімді синтездеу үшін золь-гельді синтезге негізделген Печини әдісі қолданылды. Бұл әдісті таңдаудағы мақсат ұсақтығы жоғары және кристаллографиялық таза өнім алуға бағытталды. Фазалық құрамы мен кристаллографиялық параметрлерін рентген фазалық талдау (XRD), Me–O арасындағы байланыстың түзілгенін анықтау үшін Фурье-ИК (FTIR) және морфологиясын; беттік өлшемі мен элементтік таралуын сканерлеуші электронды микроскоп (SEM-EDS) әдістері арқылы талданды. Синтез үшін металл нитраттарының гидраттары қатысында золь-гель түзуге негізделі жүргізілді. Өнімнің түзілгенін фазалық талдау жүргізіп құрамындағы SmMnO₃ PDF 00-025-0747 сәйкес орторомбалы Pbnm (62) пішінді, ал LaMnO₃ PDF №01-090-6505 картасына сәйкес ромбоэдрлік R-3c (167) кеңістіктік топқа сәйкес екендігі анықталды. FTIR мәндері бойынша интенсивті жұтылу жолақтары 750-600 см⁻¹ аралығында жатқаны анықталып, Mn – O байланыстың түзілгенін көрсетеді. SEM-EDS нәтижелері бойынша ұнтақ өнімнің орташа беттік өлшемі 0,489 μm екені және элементтердің таралу картасы арқылы өнімнің сәтті түзілгенін көрсетеді.

Түйінді сөздер: перовскит, манганит, Печини әдісі, XRD, SEM-EDS талдау

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СИНТЕЗ, СТРУКТУРА И МОРФОЛОГИЯ ПЕРОВСКИТНОГО КОМПОЗИТА SmMnO₃-LaMnO₃**Нурбекова М.А., Матаев М.М., Сарсенбаева* З.Б., Абдраймова М.Р., Көшкімбаева А.Қ.***НАО «Казахский национальный женский педагогический университет», Алматы, Казахстан*

Резюме: в этой статье рассматривается синтез и фазовый состав, и строительно-морфология двойного манганитового перовскитного композита LaMnO₃-SmMnO₃. Целью синтеза двухфазного манганита, содержащего редкоземельные элементы самарий и лантан, является изучение особенностей строения и свойств полученных продуктов из классических перовскитных манганитов и манганитов однофазного Самария и лантана. Для синтеза продукта использовался метод Печини, основанный на синтезе Золя-геля. Цель выбора этого метода была направлена на получение продукта с высокой тонкостью и кристаллографической чистотой. Фазовый состав и кристаллографические параметры были проанализированы с помощью методов рентгенофазного анализа (XRD), Фурье-ИК (FTIR) и морфологии для определения образования связи между Me – O; электронного микроскопа (SEM-EDS), сканирующего размер поверхности и распределение элементов. Для проведения синтеза проводились на основе образования золь-геля в присутствии

гидратов нитратов металлов. Фазовый анализ образования продукта показал, что SmMnO_3 имеет орторомбальную форму Pbnm (62) в соответствии с PDF 00-025-0747, а LaMnO_3 соответствует ромбоэдрической пространственной группе $R\text{-}3\text{C}$ (167) в соответствии с картой PDF №01-090-6505. Установлено, что интенсивные полосы поглощения по значениям FTIR лежат в пределах $750\text{--}600\text{ см}^{-1}$, что указывает на образование связи $\text{Mn} - \text{O}$. Результаты SEM-EDS показывают, что средний размер поверхности порошкообразного продукта составляет $0,489\text{ мкм}$, и продукт был успешно сформирован с помощью карты распределения элементов.

Ключевые слова: перовскит, манганит, метод Печини, XRD, SEM-EDS анализ

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DEVELOPMENT OF AN INNOVATIVE AND IMPROVED TECHNOLOGY FOR PROCESSING OIL WASTE FROM JSC “OZENMUNAYGAZ” INTO USEFUL PRODUCTS

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Abstract. *Introduction.* Oil and gas activities generate oil-contaminated waste, which poses an environmental hazard. The development of effective technologies for its treatment and reuse is an important task. *Objective.* To develop and evaluate the efficiency of a technology for processing oil-contaminated waste from JSC «Ozenmunaigas» to produce treated soil suitable for road construction and technical land reclamation. *Methods.* Pilot-scale industrial tests were conducted using a surfactant, a polymer composite, and technical water. The components were mixed for 10–15 minutes, followed by settling for 20–30 minutes. The concentration of petroleum hydrocarbons was determined using the fluorometric method. *Results.* The concentration of petroleum hydrocarbons decreased from 102,600 to 900 mg/kg, corresponding to a removal efficiency of 99.12%. The resulting treated soil was proposed for use in road construction and technical land reclamation. The developed technology provides effective processing of oil-contaminated waste and reduces the technogenic impact on the environment.

Keywords: oil-contaminated waste, waste processing, petroleum hydrocarbons, surfactants, environmental safety, technical land reclamation

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1. Introduction

The production activities of hydrocarbon extraction and processing facilities have a certain impact on environmental components. According to the Environmental Code of the Republic of Kazakhstan, natural resource users are required to process oil waste [1].

One of the most important tasks for subsoil users and scientists during the operation of oil and gas fields is environmental protection. In this regard, it is necessary to carry out environmental protection work in the zone of potential impact of subsoil use facilities.

From an environmental perspective, the greatest danger is posed by the contamination of land surfaces and water bodies with petroleum products, as well as the penetration of petroleum products into aquifers [1, 2, 3-5]. The problem of disposing of waste accumulated as a result of the activities of enterprises in the oil and gas sector remains relevant and is linked to a significant increase in the volume of oil and gas production.

In accordance with the principles of sustainable development and the transition of the Republic of Kazakhstan to a “green economy,” the development of effective technologies for the processing oil-containing waste is an important and relevant task. Technologies that reduce the anthropogenic impact on the environment and produce products suitable for further economic use are of particular importance [3–5].

In this regard, the development and improvement of methods for processing oil-containing waste are of scientific and practical interest.

The aim of the study is to develop and evaluate the efficiency of a technology for processing oil-containing waste from JSC “Ozenmunaigas” to obtain purified soil suitable for use in road construction and technical reclamation of disturbed lands.

The scientific novelty of the study lies in the development of an effective method for processing oil waste using an energy-accumulating additive, surfactants, and composite materials, which ensures a reduction in the content of petroleum products and produces a product for further use.

The practical significance of the work lies in the possibility of applying the developed technology for processing oil-containing waste at oil and gas industry facilities, reducing the anthropogenic impact on environmental components, and rationally utilizing the products obtained from the processing.

2. Materials and methods of research

Within the framework of this study, oil-containing waste stored at the landfill of JSC “Ozenmunaigas” was used as the initial material. The sample was taken from the accumulated oil-containing waste intended for processing.

The research involves developing technological solutions for the processing of oil-contaminated waste using an energy-accumulating additive based on composite materials with surfactants, which contain a mixture of oxides of

alkaline-earth metals, including CaO and MgO, to produce materials used in road construction.

The essence of the technology for processing oil-containing waste is that the oil waste is treated, while being mixed, with an energy-accumulating additive based on composite materials with surfactants, which includes a mixture of alkaline earth metal oxides containing Ca and Mg oxides. At the same time, the oxide of the alkaline-earth metal forms a hydroxide with water, as a result of which petroleum products are evenly absorbed by it, producing a dry, storage-stable powdery substance consisting of granules (the size ranges from 2 mm to 15 mm), which, in terms of their chemical composition, are particles of neutralized petroleum waste evenly distributed throughout the product mass. Adding an energy-accumulating additive and petroleum-containing waste from composite materials at the time of mixing makes it possible to obtain materials used in road construction. Composite materials that make it possible to obtain hydroxyl powder are supplied in measured quantities at the moment of mixing the energy-accumulating additive and oil-containing waste. The method is based on the properties of mineral oxide sorbents to increase the specific surface area by 15–30 times and thereby transform into a bulk binding substance with high absorption capacity for high-molecular substances, and in particular for petroleum hydrocarbons, which results in a sharp increase in the specific surface area. During the processing of oil-containing waste, volatile unsaturated hydrocarbons are released into the atmospheric air; their concentration depends on the content of petroleum products in the waste.

The energy-accumulating additive with composite materials based on surfactants is a multi-purpose product that has neutralizing and sorbing properties in relation to crude oil [6–7]. The energy-accumulating additive promotes the decomposition of crude oil and intensifies the natural processes of soil self-purification. Its application contributes to the enrichment of the soil with nitrogen and biologically active compounds, which stimulates the growth of microorganisms and accelerates the decomposition of oil contained in the waste.

The processed product can be used as an additive or as an integral component in the production of the following materials and structures: asphalt concrete mixtures for highways and on-field roads, structural elements of roads, thermal insulation, hydro-barrier, and additional layers of the roadbed, as well as for creating parking areas for equipment and constructing on-site roads, for profiling the surface of solid waste landfills, and others.

The process proceeds with the release of heat, which results in a sharp increase in the specific surface area. The resulting salts provide hydrophobicity and strength to the granules of the reaction product of the EAD with hydrocarbons. Composite materials make it possible to obtain a moisture-absorbing material used for the preparation of concrete mixtures for road pavement.

The processing of oil-containing waste includes four main stages:

- 1) Receipt and placement of reagents for processing oil-containing waste delivered by road transport;
- 2) Physico-chemical analysis and preparation of oil-containing waste from JSC “Ozenmunaigas” for processing on a special concrete site;
- 3) Mixing and blending of the components;
- 4) Unloading of the neutralized soil and physicochemical analysis of the samples.

To obtain a product from recycled waste that can subsequently be used for road construction, special substances – composite materials based on inorganic salts are added at the site during the mixing of the energy-accumulating additive and oil-containing waste.

The addition of composite materials during the mixing of the energy-accumulating additive and oil-containing waste ensures the production of materials used in the construction of field roads. Bone meal or fish meal, containing up to 90% CaCO_3 , can be used as composite materials. The composite materials are delivered in bags of a specified weight, which makes it possible to supply them to the oil-containing waste processing site from a warehouse located under a canopy after weighing them in containers on scales in a specified dosage ratio of 1:3 to the other mixing components. After mixing the oil-containing waste with the EAD and composite materials, water is supplied from water storage tanks using submersible pumps through flexible pipelines or by water tankers. During active mixing, the processes of processing and granulation of the neutralized oil-containing waste take place in accordance with the technology described above.

The final product of processing the neutralized oil-containing waste, with the addition of composite materials, is recycled soil, which is an environmentally safe material used in the construction of on-site roads and in the technical reclamation of soils. Unloading and storage of the recycled soil are carried out using a front-end loader.

The finished processed soil, after the addition of composite materials in the “Horizontal Mixer (SM)”, UNZG, and PTK-INSTEB-ECO-5 units, is transformed into a mixture used in road construction. The resulting mixture is discharged through the mixer’s discharge port into the loader’s bucket, after which it is temporarily stored in a specially designated area or transferred to dump trucks and transported for reclamation work.

To improve the mixing process and accelerate the reactions involved in the processing of oil-containing waste, JSC “Ozenmunaigas” is to prepare oil-containing waste using special equipment, and a site for mixing and blending reagents is to be set up. The preparatory stage involves setting up the work site:

- the site for installing the equipment must have a solid surface with a waterproof coating – 1 area for primary processing measuring 10 x 20 meters and 1 area for placing the equipment measuring 10 x 10 meters;
- the storage area for the energy-accumulating additive with a waterproofing coating – 1 (one) covered site measuring 10 × 30 meters;

- the entrance to the site is equipped with portable truck scales with the capability to print the total weight of the vehicle, ensuring accurate accounting of the oil-containing waste delivered for processing;
- the presence of a water storage tank on the site;
- the removal of oil-contaminated waste is carried out from an unequipped sludge storage facility;
- upon entry to the work site, the oil-contaminated waste is weighed;
- before the tests begin, the oil-contaminated waste is sorted and mechanically cleaned, with foreign objects that cannot be processed being removed;
- uniform mechanical crushing of large soil inclusions is carried out on a specially prepared site.

The main stage:

- cleaning of oil-containing waste by mixing with the addition of an energy-accumulating additive containing surfactants, composite materials, and process water using specialized mixing equipment;
- during the addition, the dosage of the energy-accumulating additive and composite materials with surfactants must be strictly observed.

Pilot-scale tests of a new technology for processing paste-like oil waste with the addition of surfactants and a polymer composite, using a screw mixer, were carried out at the test site of JSC “Ozenmunaigas”.

During the tests, the following materials were used:

1. 0.5 m³ of process water;
2. 1 litre of surfactant, 0.02% polymer composite.

The system for supplying surfactants and polymer composite has been redesigned and connected to the system; at the oil waste processing facility, there is a concrete platform measuring 20 x 30 meters for storing oil waste; changes have been made to the mixer design.

The required amounts of surfactants, polymer composite, and process water have been determined. The possibility of recycling process water with surfactants and collecting it in a tank has been tested.

The content of petroleum products in the oil waste and purified soil was determined by the fluorimetric method using the “Fluorat 02-3M” instrument in accordance with the PNDF 16.1:2.21-98 methodology. The petroleum product content in the initial oil waste was 102,600 mg/kg.

3. Results and Discussion

Figure 1 shows the results of an IR spectroscopic analysis of the used oil-containing waste, which consists of asphalt-resin-paraffin deposits (ARPD). The sample contains signs of moisture, clay, and organic components. Figure 1 shows that the IR spectra have characteristic absorption frequencies for hydrocarbons. The absorption band frequencies in the IR spectra with wavenumbers 722–1462 and 2851–2921 cm⁻¹ are attributed to paraffin components. For aromatic structures with C=C bonds, absorption bands at 1604,

871, and 811 cm^{-1} are characteristic. Absorption bands at 1700–1750 cm^{-1} , typical of CO groups in carbonyl compounds, are absent. O–H-containing components may be present in small amounts. Assigning specific absorption bands to particular functional groups is difficult due to the multicomponent nature of the oil-containing samples under study.

The paraffinic petroleum deposit has a complex hydrocarbon composition with the presence of aromatic, resinous, and, probably, mineral components, which provides an overall characterization of the ARPD. The combination of absorption bands at 2851–2921 and 722–1462 cm^{-1} indicates a significant content of long-chain aliphatic hydrocarbons characteristic of the paraffinic component of ARPD. The band at 1604.9 cm^{-1} indicates the presence of aromatic structures. Overall, the spectrum corresponds to a paraffinic petroleum deposit of complex composition.

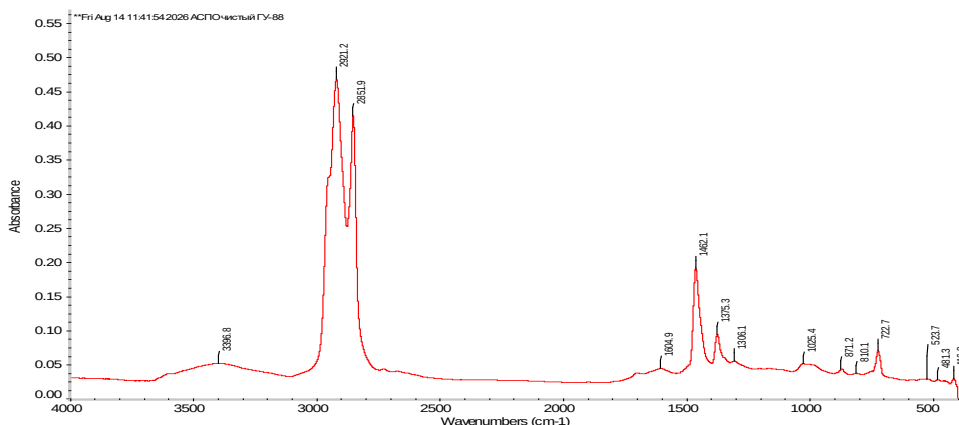


Figure 1 – Results of the IR spectroscopic analysis of ARPD from the NGDU-1 landfill of JSC “Ozenmunaigas”.

The results of the analysis of asphalt-resin-paraffin deposits, presented in Table 1, indicate a significant content of paraffins and saturated hydrocarbons, which contribute to the formation of dense deposits on the process equipment. The detected presence of resins and asphaltenes indicates a complex multicomponent composition of the studied deposits, which should be taken into account when selecting effective methods for their cleaning and preventing their formation.

Table 1 – Results of physic-chemical studies of the asphalt-resin-paraffin deposit from JSC “Ozenmunaigas”

№	Indicators	Content
1	Density, g/cm^3	0,878
2	Pour point, $^{\circ}\text{C}$	35

3	Viscosity at 50 °C	13,8
4	pH	8
5	Total mineralization, g/L	55,9
6	Water content, %	8
	Petroleum products, content, %:	
8	sulfur	0,19
9	resins	16,5
10	asphaltenes	1,37
11	paraffins	24,6
12	saturated hydrocarbons C ₁₂ –C ₁₉	28,6

As a result of the pilot-industrial tests, the efficiency of the technology for processing oil-containing waste from JSC “Ozenmunaigas” was evaluated. The main indicator of the process efficiency was the change in the petroleum product content in the initial oil-containing waste and in the purified soil obtained after treatment. The results of the physicochemical analysis are presented in Table 2.

Table 2 — Content of petroleum products in the initial and purified material

№	Sample name	Petroleum products, mg/kg
1	Initial oil waste	102 600
2	Purified soil	900

As a result of the tests conducted, it was established that the application of the new technology makes it possible to significantly reduce the petroleum product content in oil-containing waste. The petroleum product content in the initial oil-containing waste was 102,600 mg/kg. After treatment using the developed technology, the petroleum product content in the purified soil decreased to 900 mg/kg. The degree of reduction in petroleum product content was 99.12%.

After a series of tests, the optimal technological conditions for the process were established. The mixing time in the reactor-mixer was 10–15 minutes. Upon completion of mixing, settling was carried out for 20–30 minutes, resulting in the separation of the purified soil and the water-oil emulsion. The water-oil emulsion was removed through the drain valve, while the purified soil was discharged through the mixer hatch.

The obtained results demonstrate the high efficiency of the new technology for processing oil waste at the landfills of JSC “Ozenmunaigas.” The necessary additional equipment was connected, and the test results demonstrated positive outcomes.

The obtained purified soil is proposed for use as an additive or component in the production of the following materials and structures: asphalt concrete mixtures for highways and field roads, structural elements of roads, thermal

insulation, waterproofing and additional layers of roadbeds, as well as for the construction of equipment parking areas and on-site roads, profiling the surface of solid municipal waste landfills, and others.

Thus, the results of the pilot and industrial tests indicate the possibility of effectively reducing the content of petroleum products in oil-containing waste, resulting in a product suitable for further use in construction and reclamation work.

4. Conclusion

The results of industrial tests have demonstrated the high efficiency of the new technology for processing oil waste at the landfills of JSC "Ozenmunaigas".

As a result of the tests conducted, the petroleum product content in the oil-containing waste decreased from 102,600 mg/kg to 900 mg/kg, corresponding to a 99.12% reduction in petroleum product content.

The optimal conditions for the technological process were established as a mixing time of 10–15 minutes in the reactor-mixer, followed by settling for 20–30 minutes.

The obtained purified soil is proposed for use in road construction and for the technical reclamation of disturbed lands.

The developed technology for processing oil-containing waste is of practical significance for reducing the anthropogenic impact on the environment, rational use of natural resources, and reuse of the products obtained from the processing.

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"ӨЗЕНМҰНАЙГАЗ" АҚ МҰНАЙ ҚАЛДЫҚТАРЫН ПАЙДАЛЫ ӨНІМДЕРГЕ ӨНДЕУДІҢ ИННОВАЦИЯЛЫҚ ЖӘНЕ ЖЕТІЛДІРІЛГЕН ТЕХНОЛОГИЯСЫН ӘЗІРЛЕУ

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Түйіндемe. Кіріспе. Мұнай-газ өндірісінде қоршаған ортаға кері әсер ететін мұнайлы қалдықтар түзіледі. Осы қалдықтарды тиімді қайта өңдеу және қайта пайдалану экологиялық мәселелерді шешудің маңызды бағыттарының бірі болып табылады. Мақсаты. «Өзенмұнайгаз» АҚ-ның мұнайлы қалдықтарын қайта өңдеу технологиясын әзірлеу және оның тиімділігін бағалау, сондай-ақ жол құрылысы мен техникалық рекультивацияда пайдалануға болатын тазартылған топырақ алу. Әдісі. БАЗ, полимерлік композит және техникалық суды қолдану арқылы тәжірибелік-өнеркәсіптік сынақтар жүргізілді. Қоспалар 10–15 минут аралығында араластырылып, кейін 20–30 минут тұндырылды. Мұнай өнімдерінің мөлшері флуориметриялық әдіспен анықталды. Нәтижелері. Мұнай өнімдерінің мөлшері 102 600 мг/кг-нан 900 мг/кг-ға дейін төмендеді, тазарту дәрежесі 99,12%-ды құрады. Алынған тазартылған топырақты жол құрылысында және техникалық рекультивация кезінде пайдалануға ұсынуға болады. Әзірленген технология мұнайлы қалдықтарды

тиімді қайта өңдеуге және қоршаған ортаға түсетін техногендік жүктемені азайтуға мүмкіндік береді.

Түйінді сөздер: мұнайлы қалдықтар, қалдықтарды қайта өңдеу, мұнай өнімдері, БАЗ, экологиялық қауіпсіздік, техникалық рекультивация

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РАЗРАБОТКА ИННОВАЦИОННОЙ И УЛУЧШЕННОЙ ТЕХНОЛОГИИ ПЕРЕРАБОТКИ НЕФТЕОТХОДОВ АО «ОЗЕНМУНАЙГАЗ» В ПОЛЕЗНЫЕ ПРОДУКТЫ

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Резюме. *Введение.* Нефтегазовая деятельность сопровождается образованием нефтесодержащих отходов, представляющих экологическую опасность. Разработка эффективных технологий их переработки и повторного использования является актуальной задачей. *Цель.* Разработка и оценка эффективности технологии переработки нефтесодержащих отходов АО «Озенмунайгаз» с получением очищенного грунта для дорожного строительства и технической рекультивации. *Метод.* Проведены опытно-промышленные испытания с применением ПАВ, полимерного композита и технической воды. Перемешивание осуществляли в течение 10–15 минут с последующим отстаиванием 20–30 минут. Содержание нефтепродуктов определяли флуориметрическим методом. *Результаты.* Содержание нефтепродуктов снизилось с 102 600 до 900 мг/кг, степень очистки составила 99,12%. Полученный очищенный грунт рекомендован для использования в дорожном строительстве и технической рекультивации. Разработанная технология обеспечивает эффективную переработку нефтесодержащих отходов и снижение техногенной нагрузки на окружающую среду.

Ключевые слова: нефтесодержащие отходы, переработка отходов, нефтепродукты, ПАВ, экологическая безопасность, техническая рекультивация

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PHYSICOCHEMICAL ASPECTS OF POLYELECTROLYTE INTERACTIONS IN AQUEOUS FILM-FORMER DISPERSIONS

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Abstract. *Introduction.* Waterborne coating materials offer environmental and technological advantages; however, the coatings they form may exhibit structural heterogeneity and increased porosity. One approach to controlling the properties of such systems is the introduction of functional modifiers. *Objective.* The aim of this study was to determine the effect of polyethylene polyamine on the surface and bulk properties of aqueous polyurethane and acrylic-polyurethane dispersions, as well as on the porosity of the coatings formed from them. *Methodology.* At 293 K, surface tension, specific and molar electrical conductivity, pH, and coating porosity were determined in systems containing 0-0.0024 mol/dm³ PEPA. *Results and Discussion.* In the binary «water-PEPA» system, changes in the character of the concentration dependences of surface tension, molar conductivity, and pH were observed in the region CPEPA = 0.0012 mol/dm³, corresponding to the critical association concentration. In ternary systems, the nature of changes in the investigated parameters depended on the film-former chemistry; the most pronounced decrease in surface tension was observed for the acrylic-polyurethane dispersion, from 39.60 to 35.15 mN/m. With increasing PEPA concentration, the porosity of the polyurethane coating decreased from 73.70 to 40.56%, while that of the acrylic-polyurethane coating decreased from 37.69 to 4.62%. *Conclusion.* The results demonstrate that PEPA affects the surface and bulk properties of the investigated aqueous dispersions and the structure of the coatings formed. The observed changes are consistent with the possibility of associative interactions between PEPA and the components of the studied systems, with the most pronounced modification effect established for the acrylic-polyurethane composition.

Keywords: acrylic-polyurethane; polyurethane; surface and bulk properties; polyethylene polyamine; aqueous film-former dispersions

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1. Introduction

Waterborne coating materials are widely used because of their environmental and technological advantages over solvent-borne systems. At the same time, the coatings formed from these materials may exhibit structural heterogeneity, increased porosity, and insufficient corrosion resistance [1-3].

One approach to controlling the properties of such materials is modification of heterochain film-forming polymers containing polar ester ($-\text{COO}-$), amide ($-\text{CONH}-$), and urethane ($-\text{NH}-\text{CO}-\text{O}-$) groups capable of participating in intermolecular interactions [3-5]. Another approach is the introduction of multifunctional surfactants that can alter the surface and bulk properties of aqueous dispersions [6, 7].

Amine-containing modifiers are of particular interest because they are capable of forming ion pairs and hydrogen bonds with polar groups of the polymer phase [6-8]. Polyethylene polyamine (PEPA) belongs to this class of compounds and contains primary and secondary amino groups. Therefore, the aim of this work was to establish the effect of PEPA on the surface and bulk properties of aqueous polyurethane and acrylic-polyurethane dispersions and on the porosity of the coatings formed from them.

2. Experimental part

The following materials were used: a waterborne polyurethane dispersion, TU 2313-001-254543-2015; a waterborne acrylic-polyurethane dispersion, TU 20.30.12-041-29525189-2019; and polyethylene polyamine, TU 2413-357-00203447-99. The composition and structural features of the samples were characterized by FTIR spectroscopy using a Shimadzu instrument (resolution 4 cm^{-1} , 45 scans, Happ-Genzel apodization). The spectra obtained are shown in Figure 1.

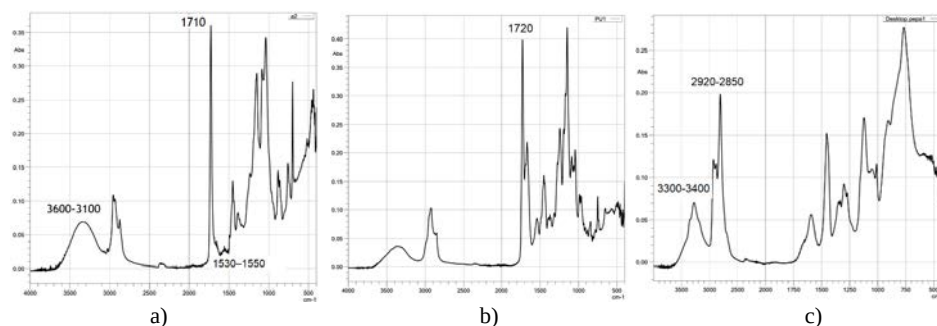


Figure 1 – FTIR spectra of the investigated samples: a – polyurethane; b – acrylic-polyurethane; c – polyethylene polyamine.

FTIR spectra (Figure 1) confirmed the characteristic functional groups of the investigated components. Polyurethane exhibited N-H stretching bands at $3600\text{--}3100\text{ cm}^{-1}$, a urethane $\text{C}=\text{O}$ band near 1710 cm^{-1} , and C-N vibrations at 1530--

1550 cm⁻¹ (Figure 1a) [9, 10]. The acrylic-polyurethane spectrum additionally showed an intense C=O band of the acrylate component near 1720 cm⁻¹ (Figure 1b) [9, 10]. PEPA was characterized by N-H stretching at 3300–3400 cm⁻¹ and CH₂ bands at 2920–2850 cm⁻¹ (Figure 1c) [11].

The studies were carried out in binary «water-PEPA» systems and ternary «polyurethane/acrylic-polyurethane-water-PEPA» compositions. The concentration of the amine-containing modifier was varied from 0 to 0.0024 mol/dm³ in increments of 0.0004 mol/dm³. Freshly prepared solutions and compositions were used for all measurements, which were performed at 293 K.

PEPA solutions of the required concentrations for the binary systems were prepared in a specified volume of distilled water under stirring until complete homogenization. Ternary compositions were prepared by adding PEPA to a calculated volume of the polyurethane or acrylic-polyurethane dispersion, followed by stirring until a visually homogeneous system without visible aggregates was obtained. Surface tension, specific electrical conductivity, and pH were monitored over time until stable readings were established, which for the investigated systems occurred predominantly after 30–40 min. Statistical treatment was performed using the results of three independent replicate determinations ($n=3$) recorded after stabilization of the corresponding parameter. For each experimental point, the arithmetic mean ($\bar{x}$), standard deviation (SD), and relative standard deviation (RSD) were calculated:

$$\bar{x} = \frac{\sum_{i=1}^n x_i}{n}; SD = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n-1}}; RSD = \frac{SD}{\bar{x}} \times 100\%, \quad (1)$$

where x_i – the result of an individual determination;

n – the number of replicate measurements.

Experimental data in the figures are presented as $\bar{x} \pm SD$.

Surface tension σ was determined using an automated ACAM instrument by the pendant-drop method. The drop profile was recorded by a video-imaging system, and σ was calculated by the instrument software using the Young-Laplace equation [12].

Specific electrical conductivity χ was measured using a Multitest conductivity meter calibrated with a standard solution. Molar conductivity λ_m was calculated from the experimentally measured specific conductivity according to [13]:

$$\lambda_m = \frac{\chi}{C}, \quad (2)$$

where λ_m – molar conductivity, S·cm²/mol;

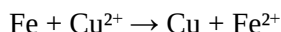
χ – specific electrical conductivity, mS/cm;

C – the molar concentration of PEPA, mol/dm³.

The pH values were measured using a laboratory pH-150MI pH meter equipped with an ESK-10603/7 combination electrode and automatic temperature compensation. Before measurements, the instrument was calibrated using standard buffer solutions.

Coating porosity was determined by indicator deposition of metallic copper with quantitative evaluation of the relative area of the formed copper-deposition sites [14]. Steel plates measuring 3×9 cm were sequentially ground with P800 and P1000 abrasive paper, degreased with ethanol, and dried at room temperature. The test compositions were applied by wiping with a lint-free cotton cloth and dried for 5 days. The actual mass of the formed coatings was 0.0038-0.0065 g for the polyurethane system and 0.0069-0.0123 g for the acrylic-polyurethane system.

A 1.0 mL aliquot of solution containing 10% CuSO_4 and 0.5% H_2SO_4 was uniformly distributed over a 2×2 cm² area of the coating bounded by an adhesive contour and maintained at 295 K for 30 min. Penetration of the electrolyte through coating defects was accompanied by reduction of copper ions on the steel surface:



After removal of the solution, the surface was photographed under constant imaging conditions. The images were processed using Particle Analyzer v2.0 with color-segmentation and contour-analysis algorithms implemented in Python using the OpenCV library. Coating porosity CP (%) was calculated as the ratio of the total area of copper-deposition sites S_p to the total analyzed area S_0 :

$$\overline{CP} = \frac{S_p}{S_0} \times 100\%, \quad (3)$$

For each experimental point, three independent porosity determinations were performed; the results were expressed as $\overline{CP} \pm SD$.

3. Results and Discussion

The experimental data showed high reproducibility: RSD values did not exceed 0.26% for pH, 3.44% for specific electrical conductivity, and 2.41% for surface tension.

3.1 «Water-PEPA» system

The effect of additive concentration on the surface tension of water is shown in Figure 2.

The surface-tension isotherm (σ_{T-g}) of aqueous polyethylene polyamine solutions at 293 K is characterized by two concentration regions. As C_{PEPA} increased from 0 to 0.0012 mol/dm³, the surface tension decreased by 1.49 mN/m to 71.28 mN/m, after which it remained practically unchanged, forming a plateau region.

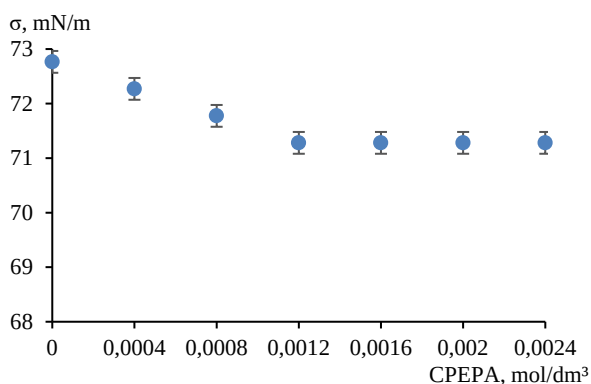


Figure 2 – Surface-tension isotherm of the «water-PEPA» system ($T = 293$ K).

The change in the character of the concentration dependence at $C_{PEPA} = 0.0012$ mol/dm³ allows this concentration to be considered the critical association concentration (CAC), which is consistent with literature data [6] and is confirmed by changes in the bulk characteristics of the corresponding systems (Figures 3 and 4).

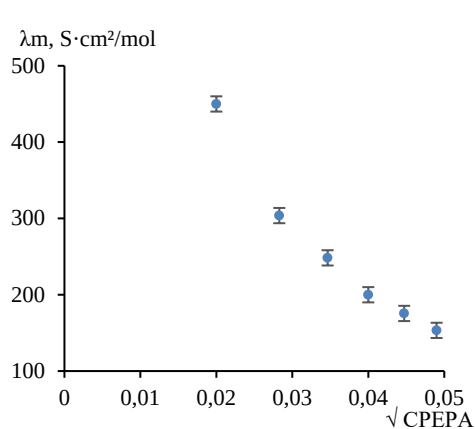


Figure 3 – Dependence of molar conductivity in the binary «water-PEPA» system on the square root of PEPA concentration.

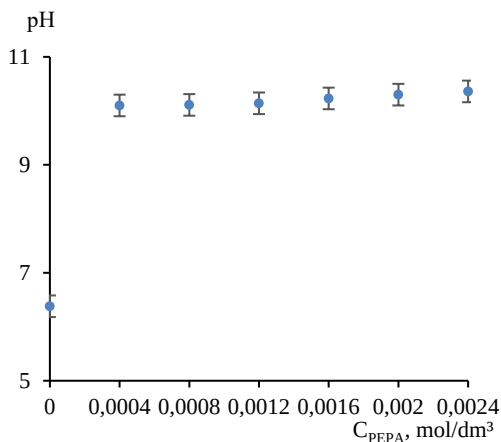


Figure 4 – Effect of polyethylene polyamine concentration on pH in the binary «water-PEPA» system.

In the concentration range $C_{PEPA}=0.0004$ – 0.0012 mol/dm³, the observed decrease in molar conductivity from 442.5 to 248.1 S·cm²/mol is consistent with gradual protonation of PEPA amino groups in aqueous medium [15] (Figure 3). Binding of protons from water by the amino groups is accompanied by formation of hydroxide ions, which is manifested by a shift of the medium from near-neutral ($C_{PEPA}=0$ mol/dm³) to alkaline ($C_{PEPA} = 0.0012$ mol/dm³) and is confirmed by the increase in pH from 6.38 to 10.14 (Figure 4).

The change in the character of the molar-conductivity (Figure 3) and pH (Figure 4) dependences near $C_{\text{PEPA}}=0.0012 \text{ mol/dm}^3$, together with formation of a plateau in the surface-tension isotherm (Figure 2), suggests a transition of the system toward an associated state [16]. Formation of PEPA associates may be governed by a combination of hydrophobic interactions between methylene segments, hydrogen bonding, and electrostatic interactions involving protonated amino groups [16, 17]. Upon association, the mobility of the resulting structures decreases relative to individual polyions, which may contribute to the decrease in molar conductivity.

With a further increase in PEPA concentration from 0.0012 to 0.0024 mol/dm^3 , molar conductivity decreased from 248.1 to 153.2 $\text{S}\cdot\text{cm}^2/\text{mol}$ (Figure 3), whereas the change in pH became less pronounced, from 10.14 to 10.36 (Figure 4). Over the same concentration interval, surface tension remained practically unchanged at approximately 71.28 mN/m (Figure 2), which is consistent with formation of a plateau after the CAC had been reached.

3.2 «Water-film former-PEPA» systems

The effects of film-former chemistry and additive concentration on the surface tension of the investigated systems are shown in Figure 5.

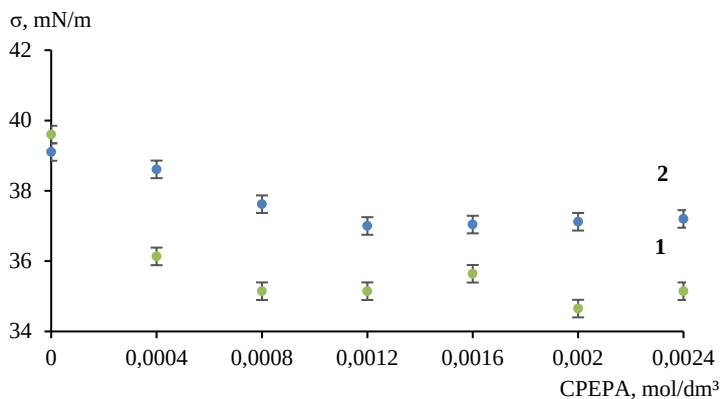


Figure 5 – Surface-tension isotherm ($T = 293 \text{ K}$): 1 – acrylic-polyurethane; 2 – polyurethane.

In the absence of PEPA, the aqueous dispersions of both film formers exhibited similar surface-tension values, $\sigma_{\text{l-g}}=39.11\text{--}39.60 \text{ mN/m}$. The similarity of these values may be related to the presence of polar urethane ($-\text{NH}-\text{CO}-\text{O}-$) and ether ($-\text{O}-$) groups in both systems (Figure 1). The small difference between the polyurethane and acrylic-polyurethane dispersions ($\Delta\sigma_{\text{l-g}}=0.49 \text{ mN/m}$) may be associated with the functional composition of the acrylic-polyurethane film former, which also contains acrylate fragments.

The surface tension of the initial film-former dispersions ($\sigma_{\text{l-g}}=39.11\text{--}39.60 \text{ mN/m}$) was substantially lower than that of water (72.77 mN/m), indicating pronounced surface activity of the dispersion components and formation of an

adsorption layer at the liquid-air interface [12]. After PEPA addition, differences between the investigated film formers became apparent in the way surface tension changed with increasing additive concentration (Figure 5).

For the acrylic-polyurethane system, surface tension decreased from 39.60 to 35.15 mN/m. This effect may be associated with additional intermolecular interactions between PEPA amino groups and polar groups of the acrylic-polyurethane film former, including hydrogen bonding and acid-base interactions [15, 16]. The results suggest that such interactions contribute to changes in the composition and organization of the surface layer.

For the polyurethane dispersion, the change in surface tension upon addition of PEPA was less pronounced: after the initial decrease, σ_{l-g} changed only slightly over the subsequent concentration range (Figure 5). The different concentration dependences of the two film formers indicate that the chemical nature of the polymer phase affects its interaction with PEPA.

Comparison of the acid-base characteristics of the aqueous dispersions in the absence of PEPA showed pH values of 8.19 for the acrylic-polyurethane dispersion and 6.87 for the polyurethane dispersion, whereas the pH of water was 6.38 (Table 1). These differences in initial pH characterize the acid-base state of the dispersions and may affect subsequent interactions between functional groups of the film formers and PEPA.

Table 1 – Effect of additive concentration on the pH of water, acrylic-polyurethane, and polyurethane compositions

$C_{PEPA}, \text{mol/dm}^3$	0	0.0004	0.0008	0.0012	0.0016	0.0020	0.0024
pH (polyurethane)	6.87	8.69	9.46	9.85	9.94	10.23	10.41
pH (acrylic-polyurethane)	8.19	8.85	9.37	9.81	10.10	10.98	11.08
pH (water)	6.38	10.10	10.11	10.14	10.23	10.30	10.36

The shift in pH toward the alkaline region after PEPA addition to the film former-water systems is consistent with the protonation of amino groups by water molecules discussed for the binary system, accompanied by release of hydroxide ions (OH^-). The pH increased continuously with increasing PEPA concentration and reached maximum values at $C_{PEPA}=0.0024 \text{ mol/dm}^3$: 10.41 for polyurethane and 11.08 for acrylic-polyurethane. These values are close to the pH of 10.36 measured for the binary «water-PEPA» system at the same additive concentration (Table 1).

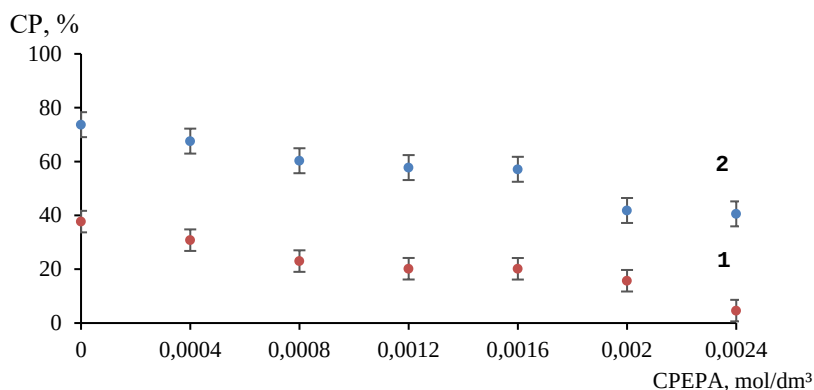
Concentration-dependent changes in the specific electrical conductivity of the investigated systems are presented in Table 2.

Table 2 – Effect of additive concentration on the specific electrical conductivity of water, acrylic-polyurethane, and polyurethane compositions

C_{PEPA} , mol/dm ³	0	0.0004	0.0008	0.0012	0.0016	0.0020	0.0024
χ (polyurethane), mS/cm	1.39	1.39	1.34	1.29	1.24	1.29	1.26
χ (acrylic-polyurethane), mS/cm	3.80	3.71	3.42	3.50	3.19	3.06	2.57
χ (water), mS/cm	0.0052	0.1770	0.2427	0.2977	0.3197	0.3507	0.3677

The overall tendency toward lower specific electrical conductivity after PEPA addition may be related to changes in the state of polar film-former groups and in the mobility of charged species as a result of intermolecular interactions with protonated PEPA amino groups. The results are consistent with the possibility of heteroassociative interactions between PEPA and the hydrophilic fragments of both film formers [18].

The change in porosity of the formed coatings reflects the effect of PEPA on the structural organization of the film-forming matrix. In the absence of PEPA, the porosity of the polyurethane coating was 73.70%, whereas that of the acrylic-polyurethane coating was 37.69% (Figure 6). The lower initial porosity of the acrylic-polyurethane coating may be related to the chemical composition of the hybrid polymer system and to conditions favoring formation of a more homogeneous film structure [19].

**Figure 6** – Porosity of coatings based on acrylic-polyurethane (1) and polyurethane (2) film formers as a function of PEPA concentration.

Replicate determinations confirmed the reproducibility of the observed concentration dependence of porosity. For polyurethane coatings, RSD values ranged from 3.27 to 5.89%. For acrylic-polyurethane coatings, the relative scatter increased as the absolute porosity decreased, reaching its maximum value at the minimum porosity of 4.62%.

As the additive concentration increased from 0 to 0.0024 mol/dm³, the porosity of the polyurethane coating decreased from 73.70 to 40.56%. This

decrease corresponded to the maximum pH value of 10.41 and the minimum specific electrical conductivity of 1.26 mS/cm. For the acrylic-polyurethane coating, the decrease was more pronounced: porosity decreased from 37.69 to 4.62%, while the corresponding pH and specific electrical conductivity values were 11.08 and 2.57 mS/cm, respectively.

Thus, addition of PEPA was accompanied by a decrease in the porosity of both coatings, with the strongest effect observed for the acrylic-polyurethane system. The change in porosity, together with changes in pH, electrical conductivity, and surface tension, is consistent with possible involvement of intermolecular interactions between PEPA and polar groups of the film former in the formation of a less porous coating with a porosity of 4.62%.

4. Conclusion

The «water-PEPA» system exhibited concentration-dependent changes, with the region near $C_{PEPA}=0.0012$ mol/dm³ interpreted as the critical association concentration based on concurrent changes in surface tension, molar conductivity, and pH. Increasing PEPA from 0.0004 to 0.0024 mol/dm³ reduced molar conductivity from 442.5 to 153.2 S·cm²/mol. The modifier affected the two film formers differently: the acrylic-polyurethane system showed the stronger response, including a decrease in surface tension from 39.60 to 35.15 mN/m. PEPA also reduced coating porosity from 73.70 to 40.56% for polyurethane and from 37.69 to 4.62% for acrylic-polyurethane. These results are consistent with possible intermolecular interactions between PEPA and polar groups of the film formers and support its use for controlling the surface and structural properties of waterborne coating systems.

Conflict of Interest: The authors declare no conflict of interest.

ҚАБЫҚ ТҮЗГІШТЕРДІҢ СУЛЫ ДИСПЕРСИЯЛАРЫНДАҒЫ ПОЛИЭЛЕКТРОЛИТ ӨЗАРА ӘРЕКЕТТЕСУІНІҢ ФИЗИКА-ХИМИЯЛЫҚ АСПЕКТІЛЕРІ

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Түйіндемe. *Kіріспе.* Сулы-дисперсиялық лак-бояу материалдары экологиялық және технологиялық артықшылықтарға ие, алайда олар түзетін жабындар құрылымдық біртексіздікпен және жоғары кеуектілікпен сипатталуы мүмкін. Мұндай жүйелердің қасиеттерін реттеу тәсілдерінің бірі функционалдық модификаторларды енгізу болып табылады. *Жұмыстың мақсаты.* Полиэтиленполиаминнің сулы полиуретандық және акрил-полиуретандық дисперсиялардың беттік және көлемдік қасиеттеріне, сондай-ақ олар түзетін жабындардың кеуектілігіне әсерін анықтау. *Әдістеме.* Құрамында 0-0,0024 моль/дм³ ПЭПА бар жүйелерде 293 К температурада беттік керілу, меншікті және молярлық электрөткізгіштік, рН және жабындардың кеуектілігі анықталды. *Нәтижелер және талқылау.* «Су-ПЭПА» бинарлық жүйесінде беттік керілу, молярлық электрөткізгіштік және рН концентрациялық тәуелділіктерінің сипатының өзгеруі $C_{ПЭПА}=0,0012$ моль/дм³ аймағында байқалды, бұл ассоциацияның критикалық концентрациясына сәйкес келеді. Үш компонентті жүйелерде зерттелген көрсеткіштердің өзгеру сипаты қабық түзгіштердің табиғатына тәуелді болды; беттік керілудің ең айқын төмендеуі акрил-полиуретандық дисперсия үшін байқалды – 39,60-тан 35,15 мН/м-ге дейін. ПЭПА концентрациясының

жоғарылауымен полиуретандық жабынның кеуектілігі 73,70-тен 40,56%-ға дейін, ал акрил-полиуретандық жабынның кеуектілігі 37,69-дан 4,62%-ға дейін төмендеді. Қорытынды. Алынған нәтижелер ПЭПА-ның зерттелген сулы дисперсиялардың беттік және көлемдік қасиеттеріне және түзілетін жабындардың құрылымына әсер ететінін көрсетеді. Байқалған өзгерістер ПЭПА-ның зерттелген жүйелер компоненттерімен ассоциативтік өзара әрекеттесу мүмкіндігімен үйлеседі; модификациялаудың ең айқын әсері акрил-полиуретандық композиция үшін анықталды.

Түйінді сөздер: акрил-полиуретан, полиуретан, беттік және көлемдік қасиеттер, полиэтиленполиамин, қабық түзгіштердің сулы дисперсиялары

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ФИЗИКО-ХИМИЧЕСКИЕ АСПЕКТЫ ВЗАИМОДЕЙСТВИЯ ПОЛИЭЛЕКТРОЛИТА В ВОДНЫХ ДИСПЕРСИЯХ ПЛЕНКООБРАЗУЮЩИХ

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Резюме. Введение. Водно-дисперсионные лакокрасочные материалы обладают экологическими и технологическими преимуществами, однако формируемые ими покрытия могут характеризоваться структурной неоднородностью и повышенной пористостью. Одним из подходов к регулированию свойств таких систем является введение функциональных модификаторов. *Цель* настоящей работы – определить влияние полиэтиленполиамин на поверхностные и объемные свойства водных полиуретановых и акрил-полиуретановых дисперсий, а также пористость формируемых ими покрытий. *Методология.* При 293 К в системах, содержащих 0-0,0024 моль/дм³ ПЭПА, определяли поверхностное натяжение, удельную и молярную электропроводность, pH, пористость покрытий. *Результаты и обсуждение.* В бинарной системе «вода-ПЭПА» изменение характера концентрационных зависимостей поверхностного натяжения, молярной электропроводности и pH наблюдалось в области $C_{\text{ПЭПА}}=0,0012$ моль/дм³, соответствующей критической концентрации ассоциации. В тройных системах характер изменения исследуемых показателей зависел от природы пленкообразующих; наиболее выраженное снижение поверхностного натяжения наблюдалось для акрил-полиуретановой дисперсии – с 39,60 до 35,15 мН/м. При увеличении концентрации ПЭПА пористость полиуретанового покрытия снизилась с 73,70 до 40,56%, а акрил-полиуретанового – с 37,69 до 4,62%. *Заключение.* Полученные результаты свидетельствуют о влиянии ПЭПА на поверхностные и объемные свойства исследуемых водных дисперсий и структуру формируемых покрытий. Наблюдаемые изменения согласуются с возможностью ассоциативных взаимодействий ПЭПА с компонентами исследуемых систем, наиболее выраженный эффект модифицирования установлен для акрил-полиуретановой композиции.

Ключевые слова: акрил-полиуретан; полиуретан; поверхностные и объемные свойства; полиэтиленполиамин; водные дисперсии пленкообразующих

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A REVIEW OF MODERN FLOTATION COLLECTORS FOR TUNGSTEN MINERALS: FROM BIFUNCTIONAL MOLECULES TO DFT-GUIDED DESIGN (REVIEW)

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Abstract. The flotation efficiency of tungsten minerals depends largely on the structure of the collector and the nature of its adsorption on the mineral surface. Traditional fatty acids, hydroxamates, and organophosphorus reagents are well studied; however, their limited selectivity stimulates the development of more complex molecular systems. *The purpose* of this review is to examine current developments in the collector design for scheelite and wolframite, focusing on the bifunctional, multifunctional, and DFT-guided approaches. A conditional division of the collectors into generations is proposed: from traditional and chelating reagents to bifunctional and multifunctional systems and further to rationally designed collectors, using DFT and molecular modeling. This review examines the collectors containing various combinations of active groups, including amine–hydroxyl, thioether–hydroxamate, bis-hydroxamate, amino–hydroxamate, amidoxime–phosphonate, and hydroxamate–phosphonate systems. Their interactions with the surface Ca, Fe, Mn, and W sites are discussed, as well as the roles of electrostatic attraction, coordination bonding, hydrogen bonding, and hydrophobicity. Particular attention is paid to the increasing application of the density functional theory (DFT), molecular dynamics, electronic structure analysis, and hydrophobicity calculations in the collector design. The current research shows that the computational methods are increasingly being used not only to elucidate the adsorption mechanisms, but also to optimize spacer length, electron donation capacity, hydrophobicity, and ligand combinations prior to or in parallel with the experimental validation. This review focuses on the studies published between 2020 and 2026, with the earlier studies included where necessary to understand the background to the development of the modern approaches to the collector design.

Keywords: tungsten flotation; scheelite, wolframite, flotation collectors, bifunctional collectors, DFT, rational molecular design

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1. Introduction

For Kazakhstan, the development of the tungsten industry has acquired particular significance in recent years. The country possesses one of the world's largest raw material bases for this metal and, according to the official data from the Republic of Kazakhstan, ranks first in the world in explored tungsten reserves [1,2]. The most significant deposits include the Verkhneye Kayraktinskoye and Severny Katpar deposits in the Karaganda region, as well as the Boguty deposit in the Almaty region. The commencement of the industrial development of the Boguty deposit and the development of the capacity for the further processing of tungsten concentrate indicate a renewed interest in the creation of a full-fledged processing chain for the tungsten-containing raw materials in Kazakhstan [3,4]. Under these conditions, improving tungsten-ore beneficiation technologies, including the development of more efficient and selective organic flotation collectors, is of significant scientific and practical interest.

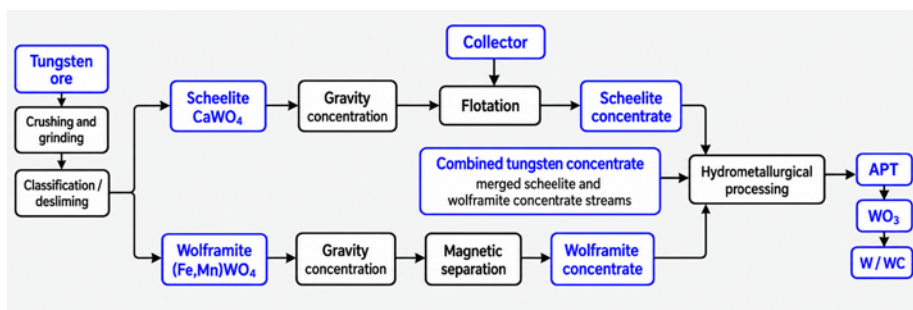


Figure 1 – General beneficiation routes for tungsten minerals.

To understand the place of flotation enrichment in the overall process chain of processing the tungsten-containing raw materials, it is important to consider the mineralogical form of tungsten and the corresponding methods of its extraction. The main industrially significant minerals are scheelite CaWO₄ (~ 70% of the world's tungsten resources) and wolframite (Fe/Mn)WO₄ (~ 30%), for which different, but often combined, enrichment schemes are used [5-7]. In general, the main stages of processing tungsten ores - from crushing and classification to obtaining a concentrate and subsequent hydrometallurgical processing - are presented in Figure 1. A special place in this scheme is occupied by the flotation of the scheelite-containing ores, the efficiency of which is largely determined by the choice of a collector.

The choice of a collector for the flotation of tungsten minerals is determined by its ability to simultaneously ensure a strong interaction with the target mineral surface and sufficient hydrophobization of the particles. Historically, relatively simple organic reagents have been used for these purposes - primarily fatty acids and their salts, classical hydroxamic acids, and individual organophosphorus compounds [8-10]. Oleic acid and oleates, benzohydroxamic and

octylhydroxamic acids, which remain convenient model and industrially significant collectors to this day [11], have been used.

To systematize modern approaches to the development of flotation reagents, this review proposes to consider organic collectors for tungsten minerals as several sequential stages of their molecular evolution. This division is conditional and primarily reflects the evolution of approaches to molecular design: from traditional reagents to chelating agents, then to bi- and polyfunctional systems, and to rational design using DFT and molecular modeling. Moreover, these areas may develop in parallel and partially overlap.

The 1st generation –traditional collectors. Fatty acids and their salts, primarily oleic acid and oleates. They are characterized by a high collecting capacity but limited selectivity.

The 2nd generation – chelating collectors. Hydroxamates, oximes, amidoximes, and simple organophosphorus reagents. Their advantage lies in their more specific coordination interactions with the surface Ca, Fe, and Mn centers.

The 3rd generation – bi- and polyfunctional collectors. The molecules containing two or more active moieties, such as hydroxamate–phosphonate and amidoxime–phosphonate. Such reagents provide multi-site binding to the mineral surface and potentially higher selectivity.

The 4th generation – rationally designed and environmentally oriented systems. The collectors whose structure is optimized using DFT, adsorption modeling, and molecular dynamics, simultaneously taking into account selectivity, reagent consumption, and environmental safety. Traditional fatty acid and classical chelating collectors, primarily hydroxamates and organophosphorus reagents, have already been reviewed in considerable detail in the literature [12–15]. Therefore, the main focus of this review is on more modern approaches –bi- and polyfunctional collectors and their rational molecular design.

Currently, DFT calculations, molecular modeling, and electronic structure analysis are increasingly being used directly in the development and interpretation of the mechanism of action of new collectors [16–22]. Therefore, the boundary between the generations III and IV is becoming largely arbitrary: many bi- and polyfunctional reagents are simultaneously objects of computationally-directed design. Therefore, in this review, generations III and IV are considered together – as a single direction for the multifunctional and rationally designed collectors.

The novelty of this review lies in its examination of collectors for the flotation of tungsten minerals from the perspective of the evolution of molecular design principles – from bi- and polyfunctional reagents to systems, including those rationally designed using DFT. Particular attention is paid to the relationship between molecular architecture, electronic and spatial characteristics, interaction with the mineral surface, and flotation selectivity.

2. Materials and Methods

To prepare this review, a search of scientific literature on modern flotation collectors for tungsten minerals has been conducted, using Scopus, Web of

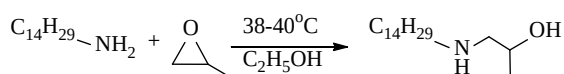
Science, ScienceDirect, and Google Scholar databases. The focus has been on publications made between 2020 and 2026; the earlier studies have been included in the analysis if they represented the initial research on traditional collectors, adsorption mechanisms, or the development of modern approaches to molecular design. The information on the status and development of the tungsten industry in Kazakhstan, deposits, and projects for processing tungsten-containing raw materials has been obtained from the official information resources of the Government of the Republic of Kazakhstan and the Gov.kz portal.

3. Results and Discussion

One of the key research directions is the creation of collectors with multiple functional sites, providing a more selective interaction with the surface of tungsten minerals. Bifunctionality can combine two coordination-active moieties or a chelating site with an auxiliary group that enhances adsorption and hydrophobization. DFT and molecular modeling allow the identification of the reactive sites and the evaluation of their interactions with the Ca, Fe, and Mn sites [23,24].

In this review, a distinction should be made between bi- and polyfunctional collectors, which are individual molecules with several functional centers, and multiligand or multicomponent systems in which the functional interaction is realized between several chemical components. The latter are not bifunctional collectors in the strict molecular sense, but are considered here as a further development of the principle of cooperative interaction of several functional centers with a mineral surface.

One early example of a functionally bifunctional approach is N-tetradecylisopropanolamine (NTIA), which combines an amine and a hydroxyl site. NTIA has been prepared by the addition of tetradecylamine (TDA) to propylene oxide in anhydrous ethanol at 38–40°C (Scheme 1) [25].



Scheme 1 – The synthetic route of NTIA.

The protonated amine center provides predominantly an electrostatic interaction with the negatively charged surface of scheelite, while the OH group is involved in hydrogen bonding [25,26]. Using ethetraditional collectors DDA (dodecylamine) and NaOL (sodium oleate), the WO₃ content in the concentrate has been 40.44 and 39.60%, respectively, while the use of NTIA at pH 7.0 and a concentration of 50 mg/L increased this figure up to 62.56% with a recovery of 96.44%, confirming its higher efficiency and selectivity in scheelite flotation (Figure 2).

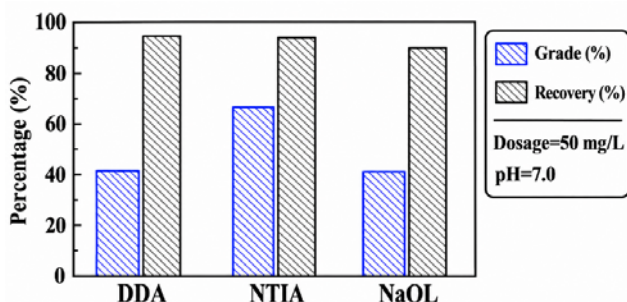


Figure 2 – The flotation performance of DDA, NTIA, and NaOL.

A more pronounced cooperative effect is realized in 2-(benzylthio)aceto-hydroxamic acid (BTHA) [27], applied for the separation of wolframite and fluorite [28]. BTHA combines the thioether and hydroxamate moieties, which are jointly anchored on Fe-centers of the wolframite surface to form the Fe–S bonds and a five-membered hydroxamate-(O,O)-Fe complex (Figure 3). The DFT analysis has identified S- and O-atoms as the main reaction centers, and the MD modeling has shown a significantly stronger interaction of BTHA with wolframite (–128.90 kJ/mol) than with fluorite (–10.84 kJ/mol). The obtained calculated data have been confirmed by the flotation tests and XPS, demonstrating the efficiency of combining bifunctional design and computational prediction of the collector selectivity.

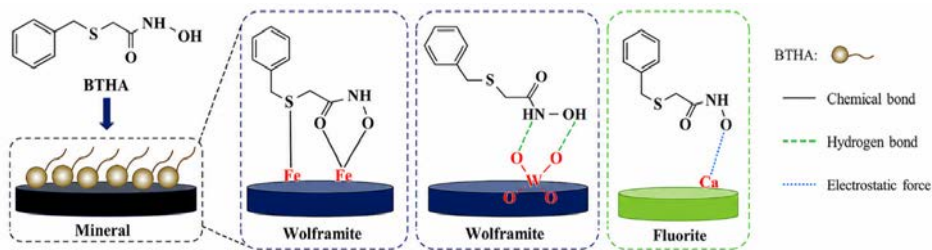
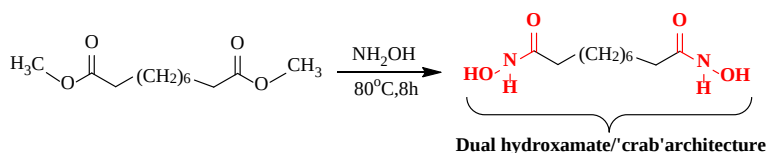


Figure 3 – The proposed interaction mechanism of BTHA with wolframite and fluorite.

Another type of bifunctional design is represented by sebacoylhydroxamic acid (SHA), which contains two hydroxamate groups (Scheme 2). In the work of Zhang et al. [29], it has been shown that SHA, due to its “crab” structure, provides a high extraction of wolframite without Pb^{2+} activation [29], and outperforms the traditional BHA/ $Pb(NO_3)_2$ system [30], which is especially important considering the toxicity and bioaccumulation of lead [31–33]. In later studies [34,35], the mechanism of action of SHA has been further investigated by XPS and DFT methods. The two $-C(O)NHOH$ groups interact preferentially with the Fe centers of the wolframite surface to form five-membered chelate rings, and

a smaller HOMO–LUMO gap compared to BHA (0.1557 vs. 0.2132 a.u.) indicates a higher reactivity of SHA [35].



Scheme 2 – The synthetic route of SHA.

A similar bis-hydroxamate design has been implemented for DHA (dodecanediohydroxamic acid), for which DFT confirmed the high reactivity of both hydroxamate groups [36].

For scheelite, a promising example is N-(3-(octylamino))hydroxamic acid (NOHA), developed as an efficient amphoteric collector for scheelite enrichment without a prior activation by $\text{Pb}(\text{NO}_3)_2$ [37]. At pH 8.0 and a concentration of 2.0×10^{-4} mol L^{-1} , NOHA has provided >95% scheelite recovery without prior Pb^{2+} activation. The molecular design of NOHA is based on the combination of a selective hydroxamate group with an amine center: the hydroxamate moiety provides an interaction with the Ca sites on the scheelite surface, which has been confirmed in a number of studies by DFT and XPS [34,38], while the protonated amino group additionally increases the affinity of the collector for the negatively charged mineral surface and enhances its adsorption [37,39].

A more complex heterobifunctional architecture is realized in the DHAHEP (dihexyl (2-amino-2-(hydroxyimino)ethyl) phosphonate) collector, whose molecule combines amidoxime and phosphonate moieties [40]. According to FTIR, XPS, and DFT data, DHAHEP adheres to wolframite in a mixed manner: the cationic form of the collector predominantly interacts electrostatically with the WO_4^{2-} surface sites, while the amidoxime and phosphoryl centers participate in chemical binding with the surface Fe sites (Figure 4). Thus, DHAHEP combines several adsorption mechanisms in a single molecule, ensuring a high affinity for wolframite and its efficient separation from quartz.

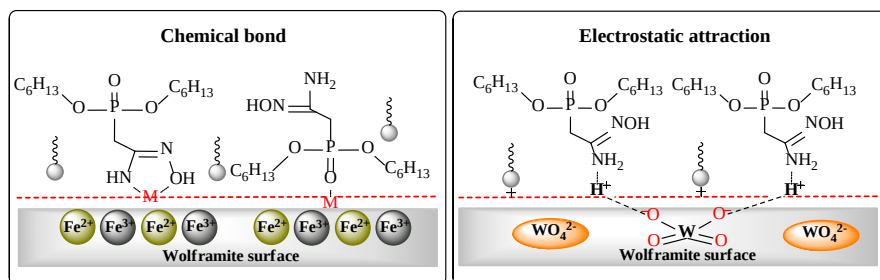


Figure 4 – The proposed adsorption mechanisms of DHAHEP on the wolframite surface: chemical bonding and electrostatic attraction.

Microflotation has demonstrated the high collection capacity of DHAHEP for wolframite: at pH 2–4.5, its recovery has exceeded 90%, while for quartz it has remained below 60%. In a wolframite–quartz mixture at pH ~4 and 8×10^{-5} mol L⁻¹ DHAHEP, the wolframite recovery has been 64.5% at the content of 48.9%.

Another variant of functional interaction is observed for DHHAOEP (dihexyl (2-(hydroxyamino)-2-oxoethyl) phosphonate), a hydroxamate-phosphonate collector of scheelite [41]. Unlike DHAHEP, the P=O group here is practically not directly involved in chemical adsorption: according to XPS and DFT data, binding to the surface occurs predominantly through the hydroxamate fragment. However, DFT has shown that the presence of a phosphoryl group alters the geometry of the active site: the distance between the two O-atoms of the DHHAOEP hydroxamate fragment is 2.889 Å and is almost identical to the distance between the adjacent O-atoms in the surface WO₄²⁻ fragment of scheelite (2.899 Å). This geometric correspondence facilitates the formation of a five-membered surface complex and increases selectivity for scheelite (Figure 5).

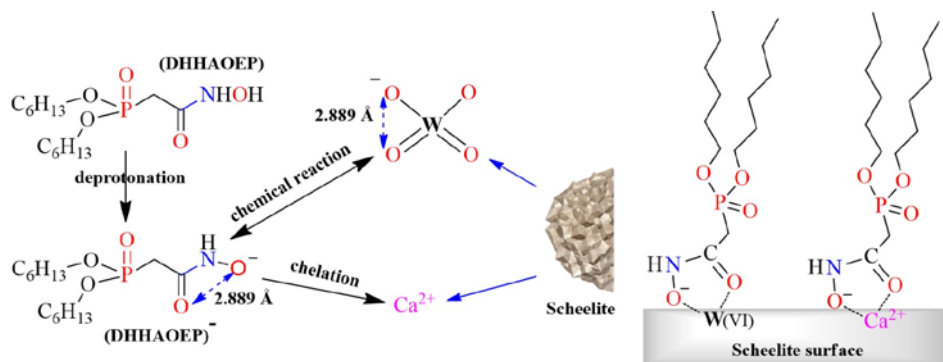


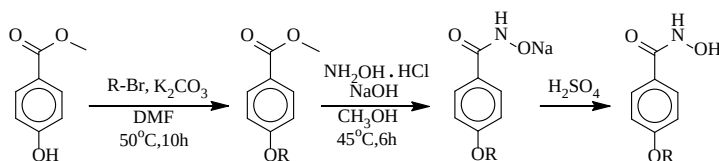
Figure 5 – The proposed adsorption mechanism of DHHAOEP⁻ on the scheelite surface.

Thus, the role of the second functional center in multifunctional collectors can vary significantly: from the direct cooperative coordination binding, as in BTHA [27] and DHAHEP [40], to the structural and electronic optimization of the main chelating center, as in DHHAOEP [41]. These examples clearly demonstrate the importance of DFT and molecular modeling not only for interpreting the adsorption mechanism, but also for rational design of new collectors.

A more direct example of the rational computational design is presented by a series of bifunctional dicarboxyl collectors CS_n for scheelite [42]. In this work, the length of the carbon spacer has been considered as a key parameter determining the relative position of the two carboxyl groups of the collector. TheDFT calculations have shown that the most favorable adsorption on the scheelite surface is characteristic of CS₇, which is associated with a good spatial

correspondence between the carboxyl centers and the Ca sites of CaWO_4 . An analysis of the electron density and charges has confirmed the predominantly ionic nature of the O–Ca interaction. At the theoretical stage, the bifunctional molecule has demonstrated an adsorption energy advantage over single molecules. Further flotation results have confirmed the operating principle of the bifunctional collector structure. This work clearly illustrates the use of DFT at the stage of the targeted collector structure optimization.

Rationally designed systems include the p-alkoxy derivatives of benzohydroxamic acid (AOBHAs), for which the DFT and hydrophobicity calculations have been used for the targeted structure optimization. [43]. For the experimental verification, the four derivatives (MOBHA, EOBHA, POBHA, BOBHA) have been synthesized by sequential alkylation of methyl p-hydroxybenzoate with the corresponding alkyl bromide, subsequent oximation with hydroxylamine, and acidification to yield free hydroxamic acids (Scheme 3). After recrystallization, the purity of the products has exceeded 98%.



Scheme 3 – The synthetic route of AOBHAs.

The alkoxy substituent does not act as an independent coordination center, but due to p- π conjugation it increases the electron-donating ability of the hydroxamate group, while an increase in the length of the alkyl chain enhances the surface hydrophobization (Figure 6). The calculated prediction has been confirmed by the flotation tests, which have shown a consistent increase in the collecting capacity in the series $\text{BHA} < \text{MOBHA} < \text{EOBHA} < \text{POBHA} < \text{BOBHA}$ [43].

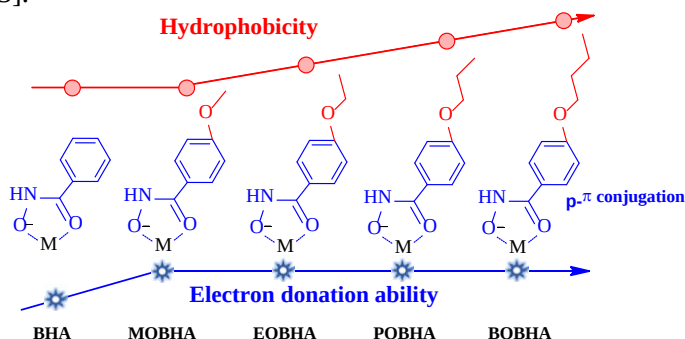


Figure 6 – The structure–property relationship of the p-alkoxy benzohydroxamic acid collectors: hydrophobicity and electron-donating ability.

The subsequent work [44] on the C₃-derived POB, IPOB, and AOB has demonstrated that a higher HOMO energy does not always correspond to better flotation activity: despite the highest electron-donating capacity of IPOB, the more hydrophobic POB has exhibited the highest collecting capacity (Figure 7). These results highlight the need to simultaneously consider both the electronic and hydrophobic characteristics in rational collector design.

It should be noted that individual DFT descriptors, including HOMO/LUMO energies, atomic charges, and interaction energies, are not direct indicators of flotation performance. Their predictive value increases only when solvation, protonation, mineral surface state, and collector hydrophobicity are taken into account jointly. A illustrative example is the POB/IPOB/AOB series, where the highest electron-donating capacity did not correspond to the maximum flotation activity.

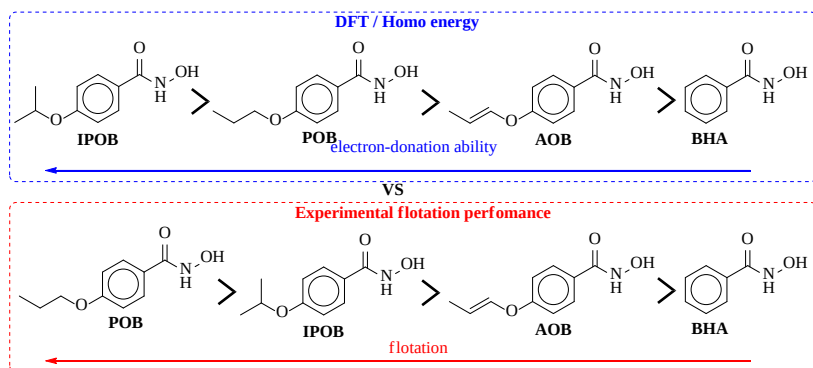


Figure 7 – The DFT-predicted electron-donating ability versus the experimental flotation performance of the C₃ alkoxybenzohydroxamate collectors.

In the work of Deng et al. [45], *m*-methylbenzohydroxamate (3MBHA) has been developed based on BHA. The introduction of a methyl substituent at the meta position has increased the hydrophobicity of the molecule and enhanced its complexation with Pb(II). Compared to BHA, 3MBHA has been characterized by a higher logP and a more pronounced decrease in the surface tension, while a UV–Vis analysis has revealed a stronger interaction with Pb(II) and the formation of a larger number of Pb–hydroxamate complexes. This has been accompanied by an increased adsorption on the scheelite surface and an increase in its flotation recovery. The obtained results demonstrate that the efficiency of hydroxamate collectors can be enhanced by simultaneously optimizing the electronic and hydrophobic properties of the molecule [45].

Another rational design approach considers not only the collector structure but also the chemistry of the specific mineral surface. For the specially selected hydroxamate collector DPHA (N-dodecanoyl-N-phenylhydroxylamine), selectivity in the scheelite–calcite system is attributed to a combination of the Ca-

coordinating hydroxamate center, a hydrophobic organic moiety, and differences in the behavior of surface Ca with changing pH [46]. A similar principle has been implemented using the trisiloxane collector AATS (N-(2-aminoethyl)-3-aminopropyltrisiloxane) for the separation of scheelite and calcite, where the correspondence of the cationic amine center to the differences in the charge state of the mineral surfaces plays a significant role [47]. Thus, the object of rational design is no longer only the collector molecule itself, but also its correspondence to the chemical and electrostatic state of the target mineral surface.

A similar surface-targeted approach was implemented for the modified oleate collector Ca-DBOA (α -bromooleic acid), developed for the selective separation of scheelite and calcite. According to AFM, ζ -potential, FTIR, and XPS data, Ca-DBOA chemically adsorbs on scheelite even in the presence of liquid glass, whereas its adsorption on calcite is significantly suppressed [48].

This approach is widely used: it expands the concept of molecular design, where the object of optimization is no longer only the reagent molecule but also the correspondence of its properties to the specific state of the mineral surface [49].

An interesting direction of rational design, standing somewhat apart, is represented by a series of studies by Wei et al. [50–55] on the creation of organometallic and multiligand collectors based on the Pb–BHA system. In the early studies, the structure of Pb–BHA complexes and the features of their adsorption on the scheelite surface have been investigated using XPS and TOF-SIMS [50] (Figure 8, a). Subsequently, the structure of these complexes has been studied in detail in the crystalline state, solution, and at the solid/liquid interface, which has provided a better understanding of the role of Pb(II) and BHA coordination in the formation of an adsorption-active system [51,52] (Figure 8, b). The next step was an introduction of additional organic ligands. Thus, the multiligand systems Pb–BHA–SDS (sodium dodecyl sulfate) and Pb–BHA–CPF (cupferron) have been developed, for which the enhanced adsorption and increased flotation activity have been shown compared to the original Pb–BHA system (Figure 8, c) [53,54].

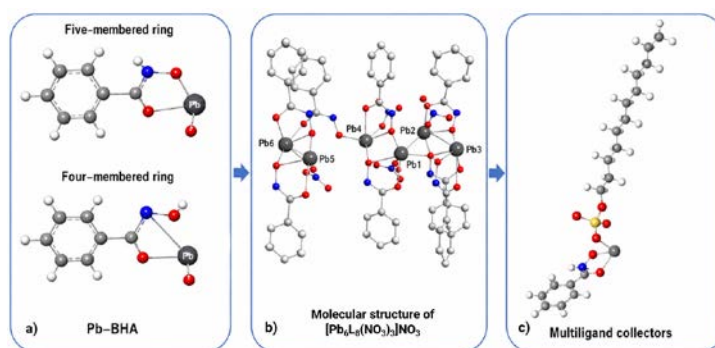


Figure 8 – Evolution of Pb–BHA-based multi-ligand collectors in the studies of Wei et al [50–55].

Further development of this approach has led to the concept of multiple-ligand metal–organic framework collectors (ML-MOF), in which the selection of an additional ligand has been carried out using a quantum chemical analysis, hydrophobicity assessment, and calculations of the interactions with the mineral surfaces. Among the combinations studied, Pb–BHA–SDS and Pb–BHA–OHA have been identified as the most promising, the efficiency of which has been subsequently confirmed by the microflotation tests [55]. Although such systems are not bifunctional collectors in the strict molecular sense, they are conceptually close to them: several functional centers participate in the formation of an adsorption-active system, but belong to different ligands united by a common metal center. In this regard, the multiligand approach can be viewed as a development of the principle of functional cooperation characteristic of bi- and polyfunctional collectors. In this series of studies (Wei et al.), the computational methods have been used at virtually every stage of the concept's development - from the analysis of the electronic structure and adsorption mechanisms to the evaluation of the multiligand complexes and, ultimately, the targeted molecular design of ML-MOFs. As the approach has evolved, the role of DFT has gradually shifted from the interpretation of the experimental data to a tool for the preliminary selection and optimization of the new collector systems.

Another example of a multicomponent design is the Pb–BHA–NaOL system, which, at a component ratio of 6:6:1, provided selective separation of scheelite and calcite at pH 9. The increased selectivity is attributed to the preferential adsorption of positively charged Pb–BHA–NaOL particles on the scheelite surface and their stronger interaction with its surface Ca- and O-sites [56].

To summarize the approaches discussed, the described collectors for scheelite and wolframite, their structural features, adsorption mechanisms, and rational design are compared in Table 1.

Table 1 – Tungsten flotation collectors discussed in this review

Collector [Ref.]	Target mineral	Functional architecture	Main surface site	Main interaction	Computa- tional approach	Pb invol- vement	Design principle
NTIA [25]	Sch	amine–OH	negatively charged sch. surface	electrostatic adsorption + H-bonding	–	No	auxiliary functionality
BTHA [27,28]	Wol	thioether– hydroxamate	Fe	Fe–S bonding + O, O-chelation	DFT, MD	No	cooperative binding
SHA [29,34,35]	Wol	dual hydroxamate	Fe	hydroxamate chelation	DFT	No	dual- hydroxamate design
DHA	Wol	dual	wol. surface	hydroxamate - driven	DFT	No	dual- hydroxamate

[36]		hydroxamate		adsorption			design
NOHA [37]	Sch	amino- hydroxamate	Ca	Ca- hydroxamate chemisorp- tion + amino- assisted adsorption	–	No	amphoteric/c ooperative design
DHAHEP [40]	Wol	amidoxime- phosphonate	Fe/WO ₄ sites	chemical + electrostatic	DFT	No	Heterobifunc- tional design
DHHAOEP [41]	Sch	hydroxamate – phosphonate	Ca / W- containing surface sites	hydroxamate - dominated chemisorp- tion	DFT	No	geometric matching
CS ₇ [42]	Sch	dicarboxylate	Ca	ionic O–Ca interaction	DFT	No	spacer/site matching
AOBHAs [43]	Wol	alkoxy- modified BHA	Pb-activated sites	Pb-mediated hydroxamate adsorption	DFT + logP	Yes	electronics + hydrophobi- city
3MBHA [45]	Sch	methyl- modified BHA	Pb-associated surface sites	Pb- hydroxamate complex formation + adsorption	logP	Yes	electronics + hydrophobi- city
DPHA [46]	Sch	N-substituted hydroxamate	Ca	selective Ca coordination	DFT	No	pH- and surface- specific design
AATS [47]	Sch	diamino- trisiloxane	negatively charged sch. surface	electrostatic adsorption via protonated amino group	DFT	No	surface- charge matching
Ca-DBOA [48]	Sch	modified oleate	sch. surface / Ca-related sites	selective chemisorp- tion; suppression on calcite by water glass	–	No	surface- targeted modification
ML-MOF [50-55]	Sch, Wol	Pb–BHA + multiple ligands	mineral surface sites	metal- mediated multiligand adsorption	quantum- chemical screening	Pb- containin g system	multiligand design

Pb-BHA- NaOL [56]	Sch	self- assembled Pb-BHA- oleate system	O / Ca sites	chemical + electrostatic adsorption	–	Pb- containin g system	self- assembled multicompo- nent design
Note - Sch – scheelite, Wol – wolframite							

4. Conclusion

The analysis shows that the modern development of flotation collectors for scheelite and wolframite is primarily associated with a shift from the selection of individual functional groups to the targeted design of the entire molecular architecture of the reagent. High efficiency is determined not by the number of functional centers per se, but by their chemical nature, spatial arrangement, and ability to interact with the active sites on the mineral surface.

For bi- and polyfunctional collectors, several main modes of action can be distinguished: the coordinate binding of several centers, the combination of the main chelating moiety with an auxiliary group that enhances adsorption, and the structural and electronic influence of the second moiety on the geometry and reactivity of the main center. Therefore, functional cooperation is becoming a more important parameter than the formal number of donor groups in the molecule.

A separate selectivity factor is the spatial correspondence of the collector's active centers to the surface Ca, Fe, Mn, and W sites.

Equally important is the combined consideration of electronic and hydrophobic properties. Therefore, rational design should consider a complex set of the interrelated molecule characteristics, rather than a single descriptor.

DFT, molecular modeling, and electronic structure and hydrophobicity analysis are now used not only to elucidate the adsorption mechanism after the experiment, but also to pre-select the structure, spacer length, substituents, and composition of the multiligand systems. Thus, computational methods are gradually becoming a tool for targeted design, but their results should be considered in conjunction with the flotation and surface chemistry experiments.

Overall, the most promising direction appears to be the creation of collectors, which simultaneously optimize selective binding to the mineral surface, the spatial organization of the active sites, electronic properties, and hydrophobicity, while also reducing the need for toxic activators. Of particular practical interest are collectors capable of providing high efficiency without preliminary Pb²⁺ activation; however, their direct quantitative comparison requires standardized flotation test conditions. This approach allows for a transition from empirical reagent searches to a more substantiated molecular design, tailored to a specific mineral and its surface properties.

ВОЛЬФРАМ МИНЕРАЛДАРЫНА АРНАЛҒАН ЗАМАНАУИ ФЛОТАЦИЯЛЫҚ ЖИНАҒЫШТАРҒА ШОЛУ: БИФУНКЦИОНАЛДЫ МОЛЕКУЛАЛАРДАН DFT НЕГІЗІНДЕГІ ЖОБАЛАУҒА ДЕЙІН (ШОЛУ)

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Түйіндеме. Вольфрам минералдарын флотациялау тиімділігі көп жағдайда жинағыштың құрылымына және оның минерал бетінде адсорбциялану сипатына байланысты. Дәстүрлі май қышқылдары, гидроксаматтар және фосфорорганикалық реагенттер жақсы зерттелген, алайда олардың шектеулі селективтілігі күрделірек молекулалық жүйелерді әзірлеуге ынталандырады. Осы шолудың мақсаты – бифункционалды, көпфункционалды және DFT-бағытталған тәсілдерге ерекше назар аударып, шеелит пен вольфрамитке арналған жинағыштарды жобалаудағы заманауи әзірлемелерді қарастыру. Біз жинағыштарды шартты түрде буындарға бөлуді ұсынамыз: дәстүрлі және хелаттаушы реагенттерінен бастап би- және полифункционалды жүйелерге дейін және одан әрі DFT және молекулалық модельдеуді пайдалана отырып рационалды жобаланған жинағыштарға дейін. Шолуда белсенді топтардың әртүрлі үйлесімдерін қамтитын, оның ішінде амин–гидроксидті, тиоэфир–гидроксаматты, бис-гидроксаматты, амина–гидроксаматты, амидоксим–фосфонатты және гидроксамат–фосфонатты жүйелер бар жинағыштар қарастырылады. Олардың беткі Са-, Fe-, Mn- және W-сайттарымен әрекеттесуі, сондай-ақ электростатикалық тартылыс, координациялық байланыс, сутектік байланыстар мен гидрофобтылықтың рөлі талқыланады. Жинағыштарды әзірлеуде тығыздық функционалы теориясын (DFT), молекулалық динамиканы, электрондық құрылымды талдаудың және гидрофобтық есептеулердің қолданылуының артуына ерекше назар аударылған. Заманауи зерттеулер көрсеткендей: есептеу әдістері тек адсорбция механизмінен түсіндіру үшін ғана емес, сонымен қатар тәжірибелік тексеруге дейін немесе онымен параллельді түрде спейсер ұзындығын, электрондонорлық қабілеттің, гидрофобтығын және лигандтар комбинацияларын оңтайландыру үшін де барған сайын кеңінен қолданылуда. Шолуда негізгі назар 2020–2026 жылдары жарияланған зерттеулерге шоғырландырылады, сондай-ақ заманауи жинағыштарды жобалау тәсілдерінің дамытудың алғышарттарын түсіну қажет болған жағдайларда ертерек жарияланған жұмыстар енгізілген.

Түйінді сөздер: вольфрам флотациясы, шеелит, вольфрамит, флотациялық жинағыштар, бифункционалды жинағыштар, DFT, рационалды молекулалық жобалау

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ОБЗОР СОВРЕМЕННЫХ ФЛОТАЦИОННЫХ КОЛЛЕКТОРОВ ДЛЯ ВОЛЬФРАМОВЫХ МИНЕРАЛОВ: ОТ БИФУНКЦИОНАЛЬНЫХ МОЛЕКУЛ ДО ПРОЕКТИРОВАНИЯ НА ОСНОВЕ DFT (ОБЗОР)

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Резюме. Эффективность флотации вольфрамовых минералов во многом зависит от структуры коллектора и характера его адсорбции на минеральной поверхности. Традиционные жирные кислоты, гидроксаматы и фосфорорганические реагенты хорошо изучены, однако их ограниченная

селективность стимулирует разработку более сложных молекулярных систем. Цель настоящего обзора – рассмотреть современные разработки в области дизайна коллекторов для шеелита и вольфрамита, уделяя особое внимание бифункциональным, многофункциональным и DFT-направленным подходам. Нами предлагается условное разделение коллекторов на поколения: от традиционных и хелатирующих реагентов к би- и полифункциональным системам и далее к рационально спроектированным коллекторам с использованием DFT и молекулярного моделирования. В обзоре рассматриваются коллекторы, содержащие различные сочетания активных групп, включая амин–гидроксильные, тиозфир–гидроксаматные, бис-гидроксаматные, амино–гидроксаматные, амидоксим–фосфонатные и гидроксамат–фосфонатные системы. Обсуждаются их взаимодействия с поверхностными Ca-, Fe-, Mn- и W-сайтами, а также роль электростатического притяжения, координационного связывания, водородных связей и гидрофобности. Особое внимание уделено всё более широкому применению теории функционала плотности (DFT), молекулярной динамики, анализа электронной структуры и расчётов гидрофобности при разработке коллекторов. Как показывают современные исследования: вычислительные методы всё чаще используются не только для объяснения механизмов адсорбции, но и для оптимизации длины спейсера, электронодонорной способности, гидрофобности и комбинаций лигандов до или параллельно с экспериментальной проверкой. Основное внимание в обзоре концентрируется на исследованиях, опубликованных в 2020–2026 гг., при этом более ранние работы включены там, где это необходимо для понимания предпосылок развития современных подходов к дизайну коллекторов.

Ключевые слова: флотация вольфрама, шеелит, вольфрамит, флотационные коллекторы, бифункциональные коллекторы, DFT, рациональное молекулярное проектирование

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DOCKING AND ADMET EVALUATION OF ASTRAGALUS-DERIVED PHYTOCHEMICALS AGAINST GLYCOGEN SYNTHASE KINASE-3 β **E.M. Yergaliyeva¹, V.V. Vazhev², A.B. Uzakova^{3*}, D.B. Zhusupova¹, M.A. Gubenko¹, S.B. Abeuova⁴**¹ Akhmet Baitursynuly Kostanay Regional University, Kostanay, Kazakhstan² Kostanay Social-Technical University named after academician Zulkarnay Aldamzhar, Kostanay, Kazakhstan³ Abai Kazakh National Pedagogical University, Almaty, Kazakhstan⁴ Astana International University, Astana, Kazakhstan*Corresponding author e-mail: a.uzakova@abaiuniversity.edu.kz

Abstract. Glycogen synthase kinase-3 β (GSK-3 β) regulates cellular processes associated with inflammation, apoptosis, and neurodegeneration and is a validated therapeutic target. Interest in natural compounds capable of interacting with the GSK-3 β active site is driven by the toxicity and adverse effects associated with many existing kinase inhibitors. This study aimed to evaluate *Astragalus* phytocomponents as potential GSK-3 β ligands *in silico* using molecular docking and ADMET prediction. The docking methodology was validated by redocking the native ligand FKB501 from the cocrystallized X-ray structure, yielding an RMSD of 1.83 Å. To assess affinity for the GSK-3 β active site, a library of 96 *Astragalus* compounds was screened. Based on binding affinity and ADMET characteristics, six compounds were selected for detailed analysis: soyasapogenol B, soyasapogenol E, chlorogenic acid, neochlorogenic acid, isoliquiritigenin, and echinatin. Their binding energies were comparable to or exceeded, in absolute value, that of FKB501 (-7.546 kcal/mol), with the lowest values observed for soyasapogenol B (-8.523 kcal/mol) and soyasapogenol E (-8.176 kcal/mol). Interaction analysis revealed key active-site residues, including Ile62, Phe67, Val70, Ala83, Lys85, Val135, Gln185, Leu188, Cys199, and Asp200. ADMET prediction indicated that isoliquiritigenin and echinatin had the most balanced pharmacological and toxicological profiles, whereas sapogenins, despite their higher docking affinity, were limited by low solubility and high lipophilicity. The selected *Astragalus* phytocomponents are therefore promising candidates for further experimental evaluation as potential GSK-3 β inhibitors.

Keywords: GSK-3 β , *Astragalus*, molecular docking, ADMET, phytocomponents, soyasapogenol, chlorogenic acid, isoliquiritigenin, echinatin

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1. Introduction

The involvement of glycogen synthase kinase-3 β (GSK-3 β) in processes related to the regulation of glycogen synthase activity, insulin signaling, inflammation, apoptosis, and neurodegenerative processes makes GSK-3 β an important therapeutic target [1]. However, many known ATP-competitive inhibitors have limited use due to risks associated with low selectivity and safety concerns [2, 3]. Therefore, natural compounds remain a promising source in the search for new GSK-3 β ligands with favorable pharmacological and toxicological profiles.

The rich phytochemical composition and extensive study of *Astragalus membranaceus* and the genus *Astragalus* in general make them interesting targets for the above-mentioned research. The main groups of compounds found in *Astragalus* plants include triterpene saponins, flavonoids, isoflavonoids, and phenolic metabolites [4]. Also, according to sources, representatives of the genus exhibit inhibitory effects on α -glucosidase, α -amylase, cholinesterases, tyrosinase, β -glucuronidase, hCA II, COX-2, and bacterial targets. However, the type and intensity of activity depend on the plant species, organ, extract composition, and chemical class of compounds [4–7]. Therefore, we believe it would be appropriate to screen *Astragalus* phytocomponents for potential GSK-3 β inhibitors.

To prioritize such compounds, molecular docking and ADMET prediction are commonly used as complementary tools at the early stages of computer-aided drug discovery [8]. Docking makes it possible to evaluate the spatial orientation of a ligand within the protein active site and to compare its predicted affinity for the molecular target [9]. However, docking score alone is insufficient for selecting promising candidates, since compounds with favorable binding energy may still exhibit poor solubility, low permeability, undesirable interactions with CYP enzymes or hERG channels, or potential toxicity [10, 11]. Therefore, ADMET filtering provides an additional level of selection by assessing the predicted biopharmaceutical limitations and safety-related risks of candidate molecules. In the present study, this combined docking–ADMET strategy was applied to select *Astragalus*-derived phytocomponents capable of binding to the active site of GSK-3 β while retaining acceptable predicted properties for subsequent experimental investigation.

2. Experimental part

The crystal structure of GSK-3 β was downloaded from the Protein Data Bank, PDB ID: 6H0U, at 2.3 Å resolution [12]. During protein preparation in AutoDockTools 1.5.7, water molecules and ions, as well as the original ligand, were removed from the structure. The structure was saved in PDBQT after adding polar hydrogen atoms and Kollman charges.

Based on *Astragalus* phytocomponents described in the literature, a ligand library was created, comprising 96 compounds in SMILES format. The original structures of the compounds were converted to SDF format, and geometry was

optimized using Open Babel 3.1.1. Meeko 0.7.1 was used to add hydrogen atoms, calculate Gasteiger charges, and save the structure in PDBQT.

The active site of GSK-3 β was determined based on the position of the native ligand FKB501. The center of the calculation box was defined by the coordinates: X = -5.560 Å, Y = -28.948 Å, Z = -16.272 Å. The box size was 15 × 15 × 15 Å.

The docking protocol was validated by redocking the native ligand FKB501. The RMSD value between the experimental and predicted poses was 1.83 Å, which meets the generally accepted criterion for successful docking protocol validation: RMSD < 2.0 Å [13].

Molecular docking was performed in AutoDock Vina 1.2.3 [14] with an exhaustiveness setting of 32. For each ligand, the best binding energy was recorded, and the most favorable conformation was analyzed. Visualization of complexes and 2D interaction diagrams was performed in PyMOL and Discovery Studio Visualizer.

ADMETlab 3.0 [15] was used to evaluate molecular weight, the number of hydrogen bond donors and acceptors, TPSA, lipophilicity, drug-likeness, predicted absorption, distribution, metabolism, toxicity, and integrated indicators of compound suitability for further analysis. All 96 compounds were screened, and then, for a more in-depth analysis of binding parameters, bioavailability, and pharmacological and toxicological profiles, selection was performed based on a combination of high affinity, absence of Lipinski's rule violations, and absence of critical toxicological risks in ADMETlab 3.0.

3. Results and Discussion

The initial set of 96 *Astragalus*-associated compounds was ranked by docking affinity to the GSK-3 β active site and subsequently filtered according to predicted drug-likeness and toxicological parameters. Six compounds with the most favorable combination of docking score, phytochemical relevance, and ADMET profile were selected for detailed interaction analysis (Table 1).

Table 1 – Molecular docking scores and key interactions of selected *Astragalus*-derived compounds with GSK-3 β

Compound	Binding affinity, kcal/mol	Key interactions with GSK-3 β
FKB501	-7.546	Conventional H-bond: Gln185 (2.56 Å); π -donor H-bond: Phe67 (4.00 Å); π -sulfur interaction: Cys199 (4.03 Å); π - π stacked interactions: Phe67 (5.30–5.62 Å); alkyl interactions: Ala83 (3.77 Å), Leu188 (4.43 Å), Cys199 (5.11 Å); π -alkyl interactions: Phe67 (5.29 Å), Val70 (4.64 Å)
Soyasapogenol B	-8.523	Conventional H-bond: Val135 (2.61 Å); alkyl interactions: Ile62 (3.72–5.47 Å), Val70 (5.02 Å); π -alkyl interactions: Phe67 (5.05 Å), Tyr134 (4.62 Å)
Soyasapogenol E	-8.176	Conventional H-bonds: Lys183 (2.20 Å), Asn64 (2.40 Å); alkyl interactions: Ile62 (4.77 Å), Val70 (5.09 Å), Leu188 (5.22 Å), Cys199 (5.45 Å); π -alkyl interaction: Tyr134 (4.61 Å)

Chlorogenic acid	-7.739	Conventional H-bonds: Asp200 (2.13 Å), Asn64 (2.03 Å), Gln185 (2.88 Å); π -alkyl interactions: Ala83 (3.50 Å), Leu188 (4.99 Å)
Neochlorogenic acid	-7.675	Conventional H-bonds: Val135 (2.15 Å), Asp200 (2.64 Å), Lys85 (2.92 Å); π -alkyl interactions: Ala83 (3.57 Å), Leu188 (4.85 Å)
Isoliquiritigenin	-7.436	Conventional H-bonds: Val135 (1.87 and 2.15 Å), Asn186 (2.04 Å), Asp200 (2.63 Å); π -alkyl interactions: Ala83 (3.72 Å), Leu188 (4.99 Å), Val70 (5.43 Å)
Echinatin	-7.263	Conventional H-bond: Asp200 (2.37 Å); π -sulfur interaction: Cys199 (4.11 Å); π - π stacked interaction: Phe67 (4.52 Å); π -alkyl interactions: Ala83 (5.05 Å), Val70 (5.27 Å), Leu188 (5.36 Å)

Soyasapogenol B and Soyasapogenol E showed the most favorable docking scores among the selected phytocomponents. Soyasapogenol B formed one conventional hydrogen bond with Val135 (2.61 Å), a residue previously reported as important for the stabilization of ATP-competitive GSK-3 β inhibitors [2]. In addition to this polar contact, the complex was stabilized by several hydrophobic interactions involving Ile62, Val70, Phe67, and Tyr134. The predominance of alkyl and π -alkyl contacts is consistent with the triterpene structure of Soyasapogenol B, whose extended hydrophobic skeleton may favor anchoring in the nonpolar region of the GSK-3 β active site (Fig. 1). Soyasapogenol E formed two conventional hydrogen bonds with Lys183 and Asn64 and additional hydrophobic contacts with Ile62, Val70, Leu188, Cys199, and Tyr134. Compared to soyasapogenol B, the binding energy was less favorable, despite the higher number of hydrogen bonds. This may be due to the orientation of the ligand and the efficiency of the hydrophobic packing within the binding pocket.

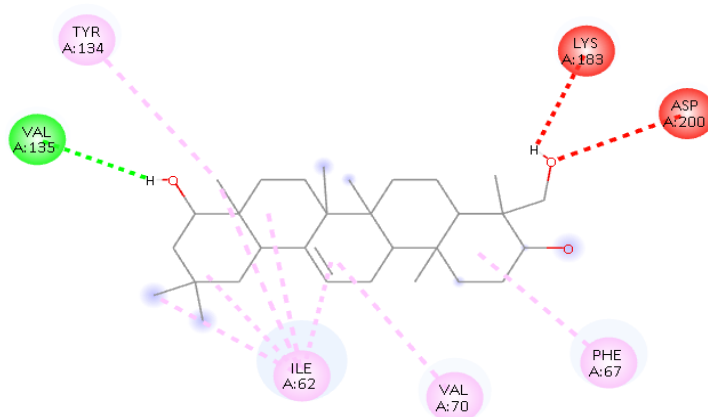


Figure 1 – 2D diagram of the interactions of Soyasapogenol B with the active site of GSK-3 β . Conventional hydrogen bonds are shown in green, π -alkyl hydrophobic interactions in pink, and unfavorable acceptor-acceptor contacts in red.

Chlorogenic acid formed three conventional hydrogen bonds with residues Asp200, Asn64, and Gln185. The shortest bonds were observed with Asn64 (2.03 Å) and Asp200 (2.13 Å), which may be the main contributor to complex stabilization. Additionally, the aromatic moiety of the ligand participated in hydrophobic π -alkyl interactions with Ala83 and Leu188. The contact with Gln185 is important, as this residue has already been noted to be important for binding of the native ligand FKB501 in the active site of GSK-3 β . Like chlorogenic acid, neochlorogenic acid formed hydrophobic π -alkyl interactions with Ala83 and Leu188, but instead of hydrogen contacts with Asn64 and Gln185, it was characterized by interactions with Lys85 and Val135.

Isoliquiritigenin formed an extensive network of conventional hydrogen bonds with residues Val135, Asn186, and Asp200. The shortest bond was observed between Val135 and the ligand oxygen atom (1.87 Å), indicating a significant contribution of this contact to complex stabilization. Additionally, the aromatic system of isoliquiritigenin participated in π -alkyl interactions with Ala83, Leu188, and Val70. Despite its less favorable docking affinity compared to sapogenins, the presence of several directional hydrogen bonds and hydrophobic contacts confirms stable fixation of the molecule in the GSK-3 β active site.

Echinatin formed one conventional hydrogen bond with Asp200 (2.37 Å), as well as several aromatic and hydrophobic contacts important for stabilizing the chalcone backbone in the GSK-3 β active site. Of particular significance are the π -sulfur interaction with Cys199 and π - π stacking with Phe67, as these residues are also noted to be important for ligand binding in the ATP-binding pocket of GSK-3 β . The molecule additionally formed π -alkyl contacts with Ala83, Val70, and Leu188. Despite its weaker docking affinity compared to sapogenins, the interaction profile of echinatin is qualitatively interesting due to the involvement of Cys199 and Phe67.

The native ligand FKB501 formed one conventional hydrogen bond with Gln185 (2.56 Å) and a π -donor hydrogen bond with Phe67 (4.00 Å). Aromatic and hydrophobic contacts significantly contributed to the stabilization of the complex: π -sulfur interaction with Cys199 (4.03 Å), π - π stacking with Phe67 (5.30–5.62 Å), and alkyl/ π -alkyl interactions with Val70, Ala83, Leu188, Cys199, and Phe67. Comparison with the native ligand FKB501 revealed that the selected phytocomponents are stabilized in the GSK-3 β active site through different mechanisms. Chlorogenic acid most clearly mimics the polar contact with Gln185 characteristic of FKB501. Echinatin, on the other hand, is closer to the native ligand in its aromatic-hydrophobic profile, interacting with Phe67 and Cys199. Soyasapogenol B and Soyasapogenol E exhibit the highest calculated affinities, but their binding is largely determined by the hydrophobic packing of the triterpene skeleton.

To assess the pharmacokinetic suitability of the selected compounds, a comparative analysis was conducted using ADMETlab 3.0. Table 2 lists the most informative parameters characterizing drug-likeness, solubility, lipophilicity,

polarity, predicted absorption, distribution, and toxicological risks; parameters that do not affect candidate ranking were omitted.

Table 2 – Comparative ADMET profile of selected *Astragalus*-derived compounds predicted by ADMETlab 3.0

Indicator	Soyasapogenol B	Soyasapogenol E	Chlorogenic acid	Neochlorogenic acid	Isoliquiritigenin	Echinatin
MW	458.38	456.36	354.10	354.10	256.07	270.09
QED	0.415	0.454	0.234	0.234	0.583	0.662
TPSA, Å ²	60.69	57.53	164.75	164.75	77.76	66.76
logP	4.27	3.73	1.04	0.84	2.52	2.83
logS	-5.25	-4.66	-2.96	-2.76	-3.46	-3.90
Caco-2	-5.39	-5.18	-6.43	-6.33	-4.84	-4.83
HIA	0.99	0.96	0.99	1.00	0.49	0.26
BBB	0.97	0.95	0.56	0.42	0.07	0.19
PPB, %	87.92	91.97	64.83	56.53	96.10	94.46
hERG	0.03	0.03	0.03	0.01	0.19	0.23
DILI	0.14	0.28	0.29	0.23	0.24	0.35
Ames	0.32	0.55	0.39	0.39	0.29	0.37
LD50 oral	0.657	0.739	0.597	0.584	0.923	0.883

Note - MW, molecular weight; QED, quantitative estimate of drug-likeness; TPSA, topological polar surface area; HIA, human intestinal absorption; BBB, blood-brain barrier penetration; PPB, plasma protein binding; DILI, drug-induced liver injury.

For the overall assessment, the quantitative estimate of drug-likeness (QED) metric provided by ADMETlab 3.0 was used, which integrally reflects a molecule's compliance with the typical properties of drug-like compounds. The highest QED values were calculated for the chalcones echinatin (0.662) and isoliquiritigenin (0.583). Isoliquiritigenin and echinatin, with moderate polarity (TPSA = 77.76 and 66.76 Å²) and acceptable lipophilicity (logP = 2.52 and 2.83), demonstrate the most balanced physicochemical profile.

Sapogenins demonstrated the most favorable docking scores; however, the low solubility and increased lipophilicity of Soyasapogenol B (logS = -5.25; logP = 4.27) and Soyasapogenol E (logS = -4.66; logP = 3.73) indicate limited bioavailability. In contrast, the hydrophilicity (logS = -2.96 and -2.76) and high polarity (TPSA = 164.75 Å²) of chlorogenic acid and neochlorogenic acid may limit their membrane permeability.

However, the toxicological predictors for all selected compounds remained within the acceptable range, consistent with the logic of preliminary ADMET filtration.

Thus, soyasapogenol B and soyasapogenol E demonstrated the highest affinity for the GSK-3β active site, while isoliquiritigenin and echinatin, whose binding energies are comparable to those of the native ligand, are preferred based on their pharmacological properties. Chlorogenic acid and its isomer, neochlorogenic acid, demonstrated acceptable affinity, but their high polarity may limit biopermeability.

4. Conclusion

Ninety-six phytocomponents of the genus *Astragalus* were evaluated *in silico* as potential GSK-3 β ligands, from which six compounds were selected for their combination of good affinity and favorable pharmacological and toxicological profiles. Molecular docking showed that soyasapogenol B and soyasapogenol E exhibited more favorable binding energies than the native ligand FKB501. Analysis of ligand-receptor interactions revealed the involvement of Phe67, Val70, Val135, Leu188, Cys199, and Asp200.

ADMET prediction allowed for refinement of the pharmacokinetic potential of the selected compounds. Sapogenins demonstrated the highest calculated affinity for GSK-3 β , but had limitations related to lipophilicity and solubility. Meanwhile, isoliquiritigenin and echinatin exhibited more balanced drug-like properties, making them interesting candidates for further research.

Thus, the obtained results confirm the feasibility of further studying *Astragalus* phytocomponents as potential GSK-3 β -targeting compounds. The results of this study can be used to select candidates for experimental testing, expand libraries of natural GSK-3 β inhibitors, and develop further research in the field of computer-aided discovery of biologically active compounds.

Conflict of Interest: The authors declare no conflict of interest.

АСТРАГАЛДАН АЛЫНҒАН ФИТОХИМИЯЛЫҚ ҚОСЫЛЫСТАРДЫ ГЛИКОГЕНСИНТАЗАКИНАЗА-3 β -ҒА ҚАТЫСТЫ ДОКИНГТІК ЖӘНЕ ADMET-БАҒАЛАУ

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Түйіндемесі. Гликогенсинтазакиназа-3 β (GSK-3 β) қабыну, апоптоз және нейродегенерациямен байланысты жасушалық үдерістерді реттейді және расталған терапиялық нысана болып табылады. GSK-3 β белсенді орталығымен әрекеттесуге қабілетті табиғи қосылыстарға қызығушылық осы киназаның көптеген қолданыстағы ингибиторларына тән уыттылық пен жанама әсерлерге байланысты. Зерттеудің мақсаты молекулалық докинг және ADMET қасиеттерін болжау әдістерін пайдалана отырып, астрагал фитокомпоненттерін GSK-3 β -ның әлеуетті лигандтары ретінде *in silico* бағалау болды. Докинг әдістемесі кокрystalданған рентгендік құрылымдағы FKB501 нативті лигандының қайта докингін жүргізу арқылы тексерілді; RMSD мәні 1,83 Å құрады. GSK-3 β белсенді орталығына аффинділікті бағалау үшін астрагалдың 96 қосылысынан тұратын кітапхана скринингтен өткізілді. Аффинділік және ADMET сипаттамалары негізінде егжей-тегжейлі талдау үшін алты қосылыс таңдалды: соясапогенол В, соясапогенол Е, хлороген қышқылы, неофлороген қышқылы, изоликирритигенин және эхинатин. Олардың байланысу энергиялары FKB501 байланысу энергиясымен (-7,546 ккал/моль) салыстырмалы болды немесе абсолюттік мәні бойынша одан жоғары болды, ал ең төмен мәндер соясапогенол В (-8,523 ккал/моль) және соясапогенол Е (-8,176 ккал/моль) үшін анықталды. Өзара әрекеттесулерді талдау белсенді орталықтың Ile62, Phe67, Val70, Ala83, Lys85, Val135, Gln185, Leu188, Cys199 және Asp200 негізгі қалдықтарын анықтады. ADMET болжамы бойынша изоликирритигенин мен эхинатиннің фармакологиялық және токсикологиялық профильдері ең теңгерімді болды, ал сапогениндер

докинг кезінде жоғары аффинділік көрсеткеніне қарамастан, төмен ерігіштігімен және жоғары липофильділігімен сипатталды. Осылайша, таңдалған астрагал фитокомпоненттері GSK-3 β әлеуетті ингибиторлары ретінде әрі қарай эксперименттік бағалау үшін перспективалы кандидаттар болып табылады.

Түйінді сөздер: GSK-3 β , астрагал, молекулалық докинг, ADMET, фитокомпоненттер, соясапогенол, хлороген қышқылы, изоликвиритигенин, эхинатин.

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ДОКИНГ И ADMET-ОЦЕНКА ФИТОХИМИЧЕСКИХ СОЕДИНЕНИЙ АСТРАГАЛА В ОТНОШЕНИИ ГЛИКОГЕНСИНТАЗАКИНАЗЫ-3 β

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Резюме. Гликогенсинтазакиназа-3 β (GSK-3 β) регулирует клеточные процессы, связанные с воспалением, апоптозом и нейродегенерацией, и является подтвержденной терапевтической мишенью. Интерес к природным соединениям, способным взаимодействовать с активным центром GSK-3 β , обусловлен токсичностью и побочными эффектами, характерными для многих существующих ингибиторов этой киназы. Целью исследования была *in silico* оценка фитокомпонентов астрагала как потенциальных лигандов GSK-3 β с использованием молекулярного докинга и прогнозирования ADMET. Методика докинга была валидирована путем редоклинга нативного лиганда FKB501 из кокристаллизованной рентгеновской структуры; значение RMSD составило 1,83 Å. Для оценки сродства к активному центру GSK-3 β была проведена проверка библиотеки из 96 соединений астрагала. На основании аффинности и ADMET-характеристик для детального анализа были выбраны шесть соединений: соясапогенол В, соясапогенол Е, хлорогеновая кислота, неохлаорогеновая кислота, изоликвиритигенин и эхинатин. Их энергии связывания были сопоставимы или превосходили по абсолютному значению энергию связывания FKB501 (-7,546 ккал/моль), при этом наиболее низкие значения отмечены для соясапогенола В (-8,523 ккал/моль) и соясапогенола Е (-8,176 ккал/моль). Анализ взаимодействий выявил ключевые остатки активного центра, включая Ile62, Phe67, Val70, Ala83, Lys85, Val135, Gln185, Leu188, Cys199 и Asp200. По результатам ADMET-прогнозирования наиболее сбалансированными фармакологическими и токсикологическими профилями обладали изоликвиритигенин и эхинатин, тогда как сапогенины, несмотря на более высокую аффинность при докинге, характеризовались низкой растворимостью и высокой липофильностью. Таким образом, выбранные фитокомпоненты астрагала являются перспективными кандидатами для дальнейшей экспериментальной оценки в качестве потенциальных ингибиторов GSK-3 β .

Ключевые слова: GSK-3 β , астрагал, молекулярный докинг, ADMET, фитокомпоненты, соясапогенол, хлорогеновая кислота, изоликвиритигенин, эхинатин

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EFFECT OF β -CYCLODEXTRIN AND LACTIC ACID-BASED SUPRADES ON ASPHALTENE AGGREGATION PROCESSES

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Abstract. *Introduction.* Asphaltene precipitation and aggregation complicate petroleum production, transport, and refining. *Aim.* To evaluate β -cyclodextrin–L-lactic-acid SUPRADES as a modifier of asphaltene aggregation in model oil prepared from Karazhanbas crude oil. *Methods.* Asphaltenes were isolated according to GOST 11858-66. SUPRADES was prepared at a 1:60 molar ratio and characterized by FT-IR, UV–Vis, thermogravimetry, and ¹H and ¹³C NMR, including COSY, HMQC, and HMBC. *Results and discussion.* FT-IR indicated a hydrogen-bonded network, TGA revealed multistage decomposition, and NMR confirmed the lactic-acid fragment and its principal correlations. Near 292 nm, absorbance decreased from approximately 0.88 to 0.59 after SUPRADES addition, an apparent decrease of about 33%. Because replicate-level variability was unavailable, the comparison is semiquantitative. *Conclusion.* The system may modify asphaltene aggregation, but quantitative inhibition must be confirmed at defined concentrations with independent replicates.

Keywords: β -cyclodextrin, lactic acid, asphaltenes, aggregation, FT-IR spectroscopy, UV–Vis spectroscopy, SUPRADES

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1. Introduction

Prevention of asphaltene deposition is one of the key tasks of the petrochemical industry, since aggregation and subsequent flocculation lead to deposits that impair the transport and operational characteristics of oil. Asphaltene inhibitors can shift the onset of deposition and reduce both the amount of sediment formed and particle size. Nonionic surfactants capable of stabilizing asphaltene particles in a dispersed medium have proved effective in this regard. Historically, aromatic organic solvents such as toluene and xylene have been used because they dissolve asphaltene aggregates. However, their toxicity, volatility, and environmental impact significantly limit their use in modern processes. Alternative inhibitors therefore include nonionic surfactants and polymer additives that stabilize asphaltenes through peptization and prevent aggregation [1].

In recent decades, considerable attention has been paid to ionic liquids with physicochemical properties such as low volatility, high thermal stability, and structural tunability, making them promising candidates as asphaltene inhibitors [2]. Further development of this field led to deep eutectic solvents (DES), which combine efficiency with ease of preparation and relatively low cost; their combination with macrocyclic host molecules has opened additional opportunities for molecular recognition [3]. Supramolecular chemistry focuses on non-covalent interactions and molecular recognition mechanisms that form stable host–guest complexes [4]. In this context, supramolecular deep eutectic solvents (SUPRADES) were proposed in 2020 as an extension of the DES class. These systems are formed using cyclodextrins (CDs) or their derivatives together with hydrogen-bond donors, particularly carboxylic acids [5, 6]. This approach combines the advantages of DES with the selectivity and encapsulation ability of macrocyclic compounds. Cyclodextrin-based systems are especially widespread because of their natural origin, availability, low cost, and molecular-recognition properties [7]. β -Cyclodextrin is frequently used because its cavity size enables interaction with a broad range of organic molecules and it is economically accessible [8]. Depending on composition and synthesis strategy, CD-based SUPRADES can be classified as binary or ternary systems [9]. SUPRADES can retain high stability in aqueous media [10], although molecular-dynamics studies show that water can markedly affect their structure and dynamics [11]. Complementary host–guest interactions and hydrogen bonding govern the organization and functional properties of these systems and enable selective capture of molecules of suitable shape, size, and polarity [12]. Their versatility has also been demonstrated in analytical separations, including chiral capillary electrophoresis [13].

2. Experimental part

Asphaltene isolation. Asphaltenes were isolated from Karazhanbas crude oil (Western Kazakhstan) according to GOST 11858-66. The crude oil was treated

with n-hexane as the precipitant, allowed to stand for 24 h, and filtered without disturbing the settled phase. The filtration stage is shown in Figure 1.



Figure 1 – Asphaltene filtration from Karazhanbas oil.

Purification and recovery. The precipitate retained on the filter paper was subjected to Soxhlet extraction with toluene to separate the asphaltene fraction from co-extracted resins and oils. Toluene was refluxed at approximately 116 °C using an oil bath maintained at 120 °C. The extraction cycle was repeated 4–5 times. The recovered asphaltenes were dried at 100 °C for 24 h and then cooled to room temperature in a desiccator.

Model oil and SUPRADES treatment. The isolated asphaltenes were dissolved in toluene (purity $\geq 99.8\%$) at 0.5 wt%. The solution was stirred for 2 h and equilibrated for 24 h. SUPRADES was evaluated over the verified working concentration range of 100–1000 ppm, and the samples were magnetically stirred for 10–30 min. n-Hexane was then added at an n-hexane:model-oil ratio of 40:1, and the mixtures were left for 24 h at room temperature. The available experimental record did not retain the exact SUPRADES dose and mixing time linked to the representative spectrum in Figure 3; therefore, the UV–Vis result is reported as a semiquantitative comparison rather than as a concentration–response experiment.

Preparation of SUPRADES. SUPRADES was prepared by mixing β -cyclodextrin (98%, Macklin Biochemical Co., Ltd., China) and L-(+)-lactic acid ($\geq 85\%$, Macklin Biochemical Co., Ltd., China) at a 1:60 molar ratio [14]. The components were heated at 80 °C with continuous magnetic stirring at 350 rpm until a clear homogeneous liquid formed [15].

3. Results and discussion

3.1. Physico-chemical properties

In this work, the properties of pure lactic acid (LA), β -cyclodextrin (β -CD), and their mixture at a 1:60 molar ratio were considered. At 30 °C, pure LA has a density of approximately 1200 kg m⁻³ and a viscosity below 50 mPa·s. Pure β -CD is a crystalline solid with low water solubility, whereas contact with LA produces a liquid supramolecular deep eutectic solvent through extensive hydrogen bonding. The viscosity of β -LA is 111.74 mPa·s at 30 °C and decreases to approximately 40 mPa·s at 60 °C [14]. The density of β -LA was 1245 kg m⁻³ at 20 °C. Because the density values for pure LA and β -LA refer to different

temperatures, they are reported separately and are not used for direct quantitative comparison. At 25.5 °C, β -LA had a pH of 1.08 and an electrical conductivity of 26.5 mS cm⁻¹. The pH meter was calibrated with pH 4.00, 7.00, and 10.00 buffers. pH and conductivity measurements were performed in triplicate, and mean values were reported. Measurements were conducted at the stated temperatures and atmospheric pressure.

3.2. FT-IR spectroscopy

FT-IR spectroscopy was used to characterize β -cyclodextrin–lactic-acid SUPRADES (1:60) and to examine its interaction with components of the model oil. The corresponding spectra are shown in Figure 2.

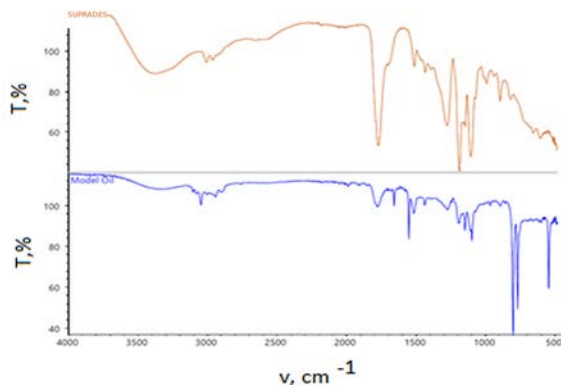


Figure 2 – FT-IR spectra of SUPRADES and model oil.

The broad band at 3300–3400 cm⁻¹ was assigned to O–H stretching and is consistent with extensive intermolecular hydrogen bonding between β -cyclodextrin hydroxyl groups and lactic-acid carboxyl groups. Bands at 2920–2950 cm⁻¹ were assigned to aliphatic C–H stretching. The band at approximately 1715–1720 cm⁻¹ corresponds to C=O stretching of the lactic-acid carboxyl group. C–H and O–H bending modes occur at 1450–1380 cm⁻¹. Intense bands at 1200–1000 cm⁻¹, particularly 1120–1030 cm⁻¹, were assigned to C–O–C and C–O stretching in the glucopyranose units of β -cyclodextrin, indicating retention of the cyclic carbohydrate framework. The model-oil spectrum contains bands at approximately 3030 cm⁻¹ (aromatic C–H), 2920 and 2850 cm⁻¹ (aliphatic C–H), approximately 1600 cm⁻¹ (aromatic C=C), and 1000–700 cm⁻¹ (out-of-plane aromatic C–H bending). Taken together, these data are consistent with formation of a hydrogen-bonded SUPRADES system containing functional groups capable of interacting with polar and aromatic asphaltene fragments; FT-IR alone, however, does not prove a specific host–guest complex.

3.3. UV–Vis spectroscopy

Representative UV–Vis spectra of the model oil without and with SUPRADES were compared over the 200–800 nm range shown in Figure 3. The available record did not include the spectrophotometer model, optical path length,

or replicate-level acquisition metadata; therefore, no unverified instrumental details were added.

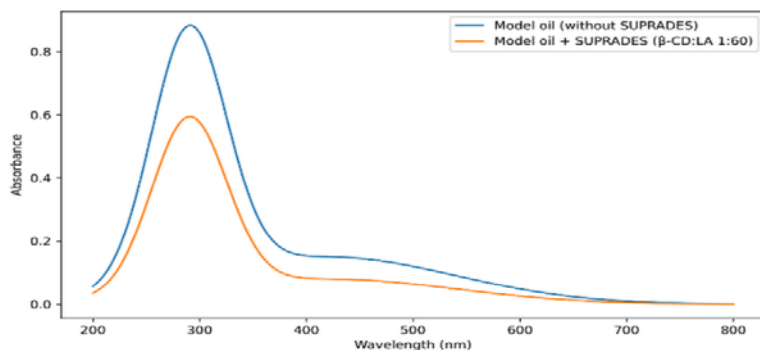


Figure 3 – Representative UV–Vis spectra of model oil without and with SUPRADES.

Both representative spectra show a maximum near 292 nm, associated with the optical response of aromatic asphaltene structures. From the plotted curves, the absorbance decreased from approximately 0.88 for the model oil without SUPRADES to approximately 0.59 after SUPRADES addition. The apparent relative absorbance decrease, calculated as $(0.88 - 0.59)/0.88 \times 100\%$, was approximately 33%. This value describes the optical change in the plotted spectra and should not be interpreted as a statistically validated aggregation-inhibition efficiency. Replicate-level raw spectra and variability estimates were unavailable; consequently, standard deviations, error bars, and inferential significance are not reported. Under otherwise comparable sample preparation, the lower absorbance is consistent with reduced aggregation or dispersion of asphaltene-containing structures. Hydrogen bonding between polar asphaltene fragments and the hydroxyl/carboxyl groups of SUPRADES, together with possible host–guest interactions involving the β -cyclodextrin cavity, may contribute to this behavior, but these mechanisms require independent confirmation.

3.4. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed to assess the thermal stability of the synthesized supramolecular deep eutectic solvent based on β -cyclodextrin and lactic acid (β -CD:LA, 1:60). This method makes it possible to determine the temperature ranges of thermal decomposition, as well as to establish the resistance of the resulting system to thermal effects. The study of the thermal behavior of SUPRADES is an important step to assess the possibility of its practical application in petrochemical processes, since asphaltene deposition inhibitors must maintain stability at elevated temperatures of oil transportation and refining. The resulting TG curve is shown in Figure 4.

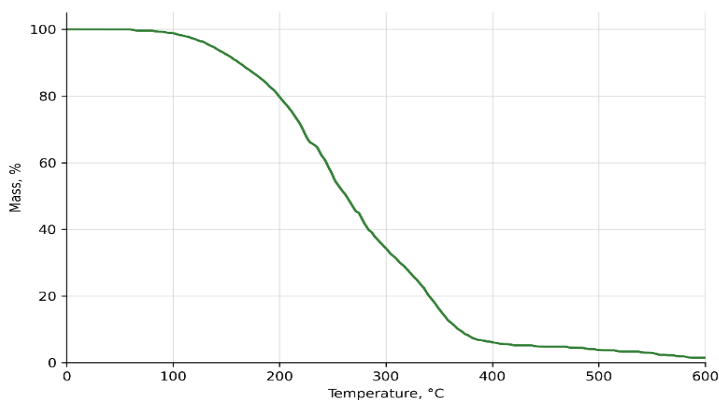


Figure 4 – TG curve of SUPRADES.

The TG curve shows multistage mass loss. The initial loss at approximately 40–120 °C is attributed to physically adsorbed moisture, water in the β -cyclodextrin cavity, and possible evaporation of weakly bound lactic acid. At approximately 120–220 °C, mass decreases as weak intermolecular interactions and the hydrogen-bonded network are disrupted. The main decomposition step at approximately 230–350 °C is assigned to β -cyclodextrin degradation and cleavage of glycosidic bonds. Above approximately 400 °C, the remaining organic fragments decompose and a carbonaceous residue forms. The curve indicates that major decomposition accelerates above approximately 200 °C; therefore, the material may warrant further evaluation under lower-temperature petrochemical conditions, but application stability should be confirmed under process-specific conditions.

3.5. NMR analysis of SUPRADES

The ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-ECA 400 spectrometer at 399.78 and 100.53 MHz, respectively, using D_2O as the solvent. Chemical shifts were referenced to the residual solvent signal. In the ^1H NMR spectrum of SUPRADES, the methyl protons H-3 of lactic acid appeared as a three-proton multiplet at 0.95–0.96 ppm, while the methine proton H-2 appeared as a one-proton multiplet at 3.89–3.95 ppm. The hydroxyl proton H-1 and carboxyl proton H-6 were not observed because of rapid proton/deuterium (H/D) exchange with D_2O . The low concentration of β -cyclodextrin did not allow its signals to be identified in solution. The ^1H – ^1H COSY spectrum showed a correlation between the methyl (H-3) and methine (H-2) protons. In the ^{13}C NMR spectrum, lactic-acid carbon signals were observed at 19.11 ppm (C-3), 66.14 ppm (C-2), and 177.86 ppm (C-4). The ^1H – ^{13}C HMQC correlations confirmed direct one-bond connections H-3/C-3 (0.95, 19.09 ppm) and H-2/C-2 (3.91, 66.06 ppm). The ^1H – ^{13}C HMBC spectrum showed long-range correlations H-3/C-2 (0.95, 66.61 ppm), H-3/C-4 (0.95, 178.16 ppm), H-2/C-3 (3.90, 19.18 ppm), and

H-2/C-4 (3.90, 178.16 ppm). The ^1H spectrum is presented in Figure 5, and the ^{13}C spectrum in Figure 6.

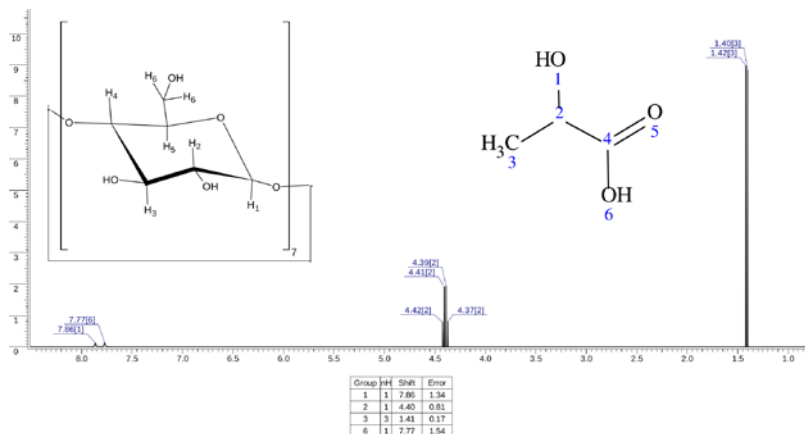


Figure 5 – ^1H NMR spectrum of SUPRADES in D_2O .

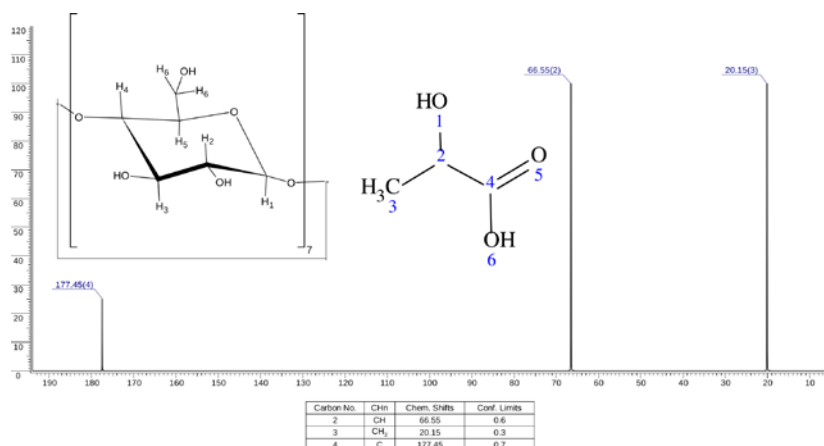


Figure 6 – ^{13}C NMR spectrum of SUPRADES in D_2O .

The structure of the compound was further examined by two-dimensional ^1H - ^1H COSY spectroscopy in D_2O . Characteristic homonuclear spin-spin correlations between neighboring lactic-acid protons were observed. Cross-peaks between the methyl (H-3) and methine (H-2) protons at 0.94/3.92 ppm and 3.92/0.94 ppm confirm their scalar coupling through three chemical bonds. One-bond ^1H - ^{13}C correlations were established by HMQC spectroscopy in D_2O . The COSY spectrum is shown in Figure 7.

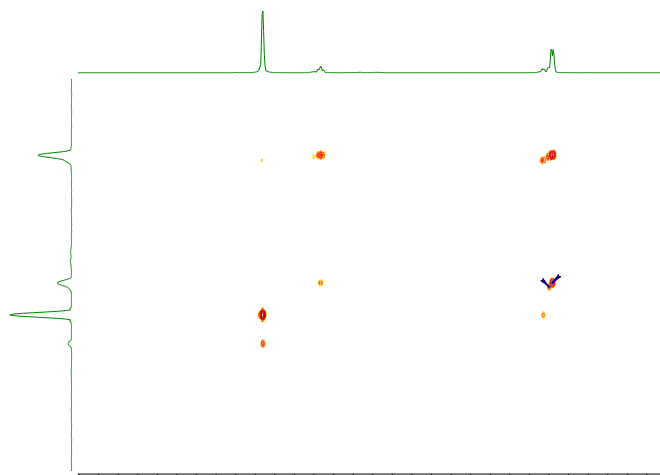


Figure 7 – COSY spectrum of SUPRADES in D₂O.

The following direct correlations were detected in the HMQC spectrum of SUPRADES: H-3/C-3 (0.95, 19.09 ppm) and H-2/C-2 (3.91, 66.06 ppm), confirming the lactic-acid fragment in the studied compound. Correlation signals of β -cyclodextrin were not detected because of its low concentration in the sample. Long-range heteronuclear correlations through two or more bonds were established by HMBC spectroscopy in D₂O. The H-3/C-2 (0.95, 66.61 ppm), H-3/C-4 (0.95, 178.16 ppm), H-2/C-3 (3.90, 19.18 ppm), and H-2/C-4 (3.90, 178.16 ppm) correlations support the constitutional connectivity of the lactic-acid fragment. The HMQC and HMBC spectra are presented in Figure 8.

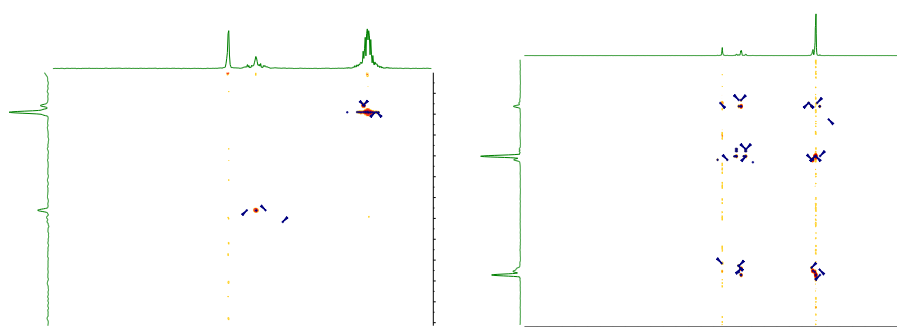


Figure 8 – (a) HMQC and (b) HMBC spectra of SUPRADES in D₂O.

4. Conclusion

This study evaluated β -cyclodextrin–lactic-acid SUPRADES as a potential modifier of asphaltene aggregation in a model oil prepared from Karazhanbas crude oil. FT-IR data were consistent with formation of a hydrogen-bonded

supramolecular network, TGA characterized the multistage thermal decomposition of the system, and ^1H , ^{13}C , COSY, HMQC, and HMBC NMR data confirmed the lactic-acid fragment and its principal correlations. In the representative UV–Vis spectra, absorbance near 292 nm decreased from approximately 0.88 to 0.59 after SUPRADES addition, corresponding to an apparent relative decrease of about 33%. Because the exact SUPRADES dose and mixing time linked to Figure 3 and replicate-level variability were not retained in the available record, this result is semiquantitative and should not be interpreted as a validated inhibition efficiency. Further work should use predefined SUPRADES concentrations, independent replicates, and complementary particle-size or precipitation measurements to establish dose–response behavior and quantitative inhibition performance.

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β-ЦИКЛОДЕКСТРИН МЕН СҮТ ҚЫШҚЫЛЫ НЕГІЗІНДЕГІ SUPRADES-тің АСФАЛЬТЕНДЕРДІҢ АГРЕГАЦИЯЛАНУ ПРОЦЕСТЕРІНЕ ӘСЕРІ

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Түйіндемe. *Kіріспе.* Асфальтендердің тұнуы мен агрегациялануы мұнайды өндіруді, тасымалдауды және өндеуді қиындатады. *Мақсаты.* β-Циклодекстрин мен L-сүт қышқылы негізіндегі SUPRADES жүйесінің Қаражанбас мұнайынан дайындалған модельдік мұнайдағы асфальтен агрегациясына әсерін бағалау. *Әдістері.* Асфальтендер ГОСТ 11858-66 бойынша бөлінді. SUPRADES 1:60 мольдік қатынаста алынып, FT-IR, УК–көрінетін спектроскопия, термогравиметрия және ^1H , ^{13}C , COSY, HMQC, HMBC ЯМР әдістерімен зерттелді. *Нәтижелері және талқылау.* FT-IR сутектік байланыстар желісін, TGA көпсатылы ыдырауды, ал ЯМР сүт қышқылы фрагменті мен негізгі корреляцияларды көрсетті. 292 нм маңында оптикалық тығыздық шамамен 0,88-ден 0,59-ға дейін төмендеді, яғни көрінетін төмендеу шамамен 33% болды. Қайталама өлшеулердің шашырауы болмағандықтан, нәтиже жартылай сандық деп түсіндірілді. *Қорытынды.* Жүйе асфальтен агрегациясын өзгертуі мүмкін, бірақ сандық тиімділік нақты концентрациялар мен тәуелсіз қайталамаларда расталуы тиіс.

Түйінді сөздер: β-циклодекстрин, сүт қышқылы, асфальтендер, агрегация, FT-IR-спектроскопия, УК–көрінетін спектроскопия, SUPRADES

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ВЛИЯНИЕ SUPRADES НА ОСНОВЕ β -ЦИКЛОДЕКСТРИНА И МОЛОЧНОЙ КИСЛОТЫ НА ПРОЦЕССЫ АГРЕГАЦИИ АСФАЛЬТЕНОВ

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Резюме. Введение. Осаждение и агрегация асфальтенов осложняют добычу, транспортировку и переработку нефти. Цель. Оценить влияние SUPRADES на основе β -циклодекстрина и L-молочной кислоты на агрегацию асфальтенов в модельной нефти, приготовленной из нефти Каражанбас. Методы. Асфальтены выделяли по ГОСТ 11858-66. SUPRADES получали при мольном соотношении 1:60 и исследовали методами FT-IR- и УФ-видимой спектроскопии, термогравиметрии и ¹H-, ¹³C-, COSY-, HMQC- и HMBC-ЯМР. Результаты и обсуждение. FT-IR указала на сеть водородных связей, TGA выявила многостадийное разложение, а ЯМР подтвердил фрагмент молочной кислоты и основные корреляции. При 292 нм оптическая плотность снизилась примерно с 0,88 до 0,59, то есть приблизительно на 33%. Из-за отсутствия данных о вариабельности повторных измерений результат интерпретирован как полуколичественный. Заключение. Система может изменять агрегацию асфальтенов, однако количественную эффективность необходимо подтвердить при заданных концентрациях и в независимых повторях.

Ключевые слова: β -циклодекстрин, молочная кислота, асфальтены, агрегация, FT-IR-спектроскопия, УФ-видимая спектроскопия, SUPRADES

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RESEARCH ON THE TECHNOLOGY FOR PRODUCING ZINC SULFATE MONOHYDRATE FROM ZINC-CONTAINING WASTE

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Abstract. Zinc sulfate is an important chemical compound widely used in various industries. It is applied in agriculture to increase crop yields, as well as in the production of paints, pharmaceuticals, beer, and other products. The main element, zinc, promotes the active growth and development of plants. A technology for producing zinc sulfate monohydrate was studied and developed. Powders containing 75-99% zinc and 25% sulfuric acid were used as research materials. In order to increase the interaction rate between the components, the powders were preliminarily mixed with water. The amount of concentrated sulfuric acid added was regulated so that, after addition, a sulfuric acid solution with a concentration of 25% was obtained. Hydrogen peroxide was used to remove impurities such as iron, copper, cadmium, and nickel. According to XRD analysis, the obtained product consisted of single-phase zinc sulfate monohydrate. A laboratory-scale procedure for the production of zinc sulfate monohydrate was developed.

Keywords: zinc sulfate monohydrate, waste, zinc oxide, zinc-containing raw materials, chemical composition, sulfuric acid, hydrogen peroxide, laboratory procedure, filtration, evaporation, drying.

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1. Introduction

Zinc sulfate is widely used in agriculture, pharmaceuticals, chemical production, electroplating, and feed additives [1-4]. Zinc sulfate monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) is particularly important due to its high zinc content, stability, and favorable storage properties. Growing demand for zinc products has increased interest in recovering zinc from industrial waste for value-added applications [5-7].

Zinc sulfate is mainly produced by hydrometallurgical processing of zinc-containing raw materials and wastes [8-10]. Sulfuric acid leaching enables efficient zinc recovery with relatively low energy consumption and is suitable for low-grade materials [11,12]. Thus, zinc recovery from industrial waste provides both environmental and technological benefits.

Zinc oxide production wastes are promising zinc sources but contain impurities that complicate the production of high-purity zinc sulfate [13,14]. Purification involves methods such as cementation, oxidation, precipitation, filtration, and solvent extraction [15-17]. Hydrogen peroxide enables Fe^{2+} oxidation to Fe^{3+} without introducing additional metal ions, facilitating zinc sulfate purification.

Zinc recovery from zinc-containing waste depends on acid concentration, temperature, particle size, solid-to-liquid ratio, and mixing conditions. Optimizing sulfuric acid concentration and temperature is essential to ensure efficient zinc dissolution and controlled crystallization of zinc sulfate monohydrate.

Limited information is available on the controlled production of phase-pure $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ from zinc oxide production waste. The effects of sulfuric acid concentration, temperature, and purification conditions on zinc sulfate formation and monohydrate crystallization require further investigation.

The novelty of this study is the development of a laboratory-scale method for producing phase-pure $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ from zinc-containing waste by optimizing sulfuric acid concentration and thermal conditions. The products were purified and characterized by X-ray diffraction to confirm their phase composition.

The aim of this study was to develop a laboratory-scale method for producing $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ from zinc-containing waste and optimize the acid concentration and processing conditions.

2. Experimental part

Several zinc-containing waste samples were used in this study. Samples ZO1 and ZO2 were cream-colored powders, whereas samples Z3 and Z4 were silver-colored bars. The zinc content of the investigated materials ranged from 75.35 to 99.13 wt.%, indicating that all samples were characterized by a high zinc content and were therefore considered suitable feedstocks for zinc sulfate production.

Prior to the determination of the major and minor elemental composition, the mercury content of the samples was analyzed separately and was found to be in the range of 0.005-0.016 mg/kg. The concentrations of the remaining elements

were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). The results are presented in Table 1.

Table 1 – Chemical composition of zinc-containing waste samples determined by ICP-OES

Sample	Fe	Si	Al	Ti	Sr	Ba	Mn,	Cu	Cr
	%			mg/kg					
ZO1	0,29	0,26	0,31	42	4	<1	31	292	3
ZO2	0,88	0,72	0,51	162	3	208	101	118	4
Z4	0,05	0,05	0,27	n/o	3	9	12	42	5
Z3	0,18	0,02	0,47	n/o	<1	118	11	32	9
Sample	Zn	K	Pb	Ca	Mg	Na	Ni	Co	Mo
	%						mg/kg		
ZO1	76,00	0,15	0,19	0,11	0,04	0,14	85	2	1
ZO2	75,35	0,13	0,40	0,08	0,01	0,10	26	2	1
Z4	99,13	<0,01	0,03	0,02	0,05	0,12	<1	1	<1
Z3	98,81	<0,01	0,01	0,02	0,04	<0,1	<1	20	7

As shown in Table 1, zinc was the predominant element in all samples. Z3 and Z4 contained 98.81 and 99.13 wt.% Zn, respectively, indicating predominantly metallic zinc, whereas the lower Zn contents in ZO1 and ZO2 (76.00 and 75.35 wt.%) were attributed to its oxidized form. Recalculation of the ZO1 and ZO2 compositions as oxides gave 94.6 and 93.8 wt.% ZnO, respectively, confirming ZnO as the main zinc-containing phase. The major impurities were Al_2O_3 and SiO_2 , with smaller amounts of Fe_2O_3 .

The selection of these materials for subsequent acid treatment was based on their high zinc content and the different chemical forms of zinc represented in the waste: predominantly oxidized zinc in ZO1 and ZO2 and predominantly metallic zinc in Z3 and Z4. This composition enabled the evaluation of sulfuric-acid treatment for zinc-containing wastes with different initial chemical states. In particular, sulfuric acid was selected because it can react with both metallic zinc and zinc oxide to form zinc sulfate, which is the target product of the proposed process.

To increase the contact area between the zinc-containing waste and the sulfuric acid solution and to promote more uniform interaction between the components, the zinc-containing powders were pre-mixed with water before acid treatment. The powder-to-water mass ratio was maintained at 1:1. The resulting slurry was thoroughly homogenized prior to the addition of sulfuric acid. Maintaining a constant powder-to-water ratio ensured reproducible moisture conditions and uniform distribution of the liquid phase throughout the powder, thereby facilitating subsequent acid-solid interaction.

The sulfuric acid solution used for the treatment was prepared by diluting concentrated H_2SO_4 with water to obtain a final concentration of 25 wt.%. When 98 wt.% concentrated H_2SO_4 was used, the required amount of concentrated acid

was calculated according to the mass balance to obtain the target 25 wt.% concentration. The corresponding mass ratio of concentrated H_2SO_4 to water was approximately 1.00:2.92. The concentrated acid was added gradually to water with continuous stirring, and the resulting solution was homogenized before use.

Based on the stoichiometric recalculation, 48.0 g of zinc-containing raw material, expressed as ZnO , was required for the synthesis of zinc sulfate monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$). The required amount of 25 wt.% H_2SO_4 was calculated based on the stoichiometric amount necessary for the conversion of ZnO to ZnSO_4 . The calculated quantities of the starting materials are summarized in Table 2.

Table 2 – Stoichiometric calculation of the starting materials for $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ synthesis

Parameter	Value
Zinc-containing raw material (as ZnO), g	48.0
ZnO molar mass, g/mol	81.38
Amount of ZnO , mol	0.590
H_2SO_4 molar ratio	1:1
Required H_2SO_4 , mol	0.590
Pure H_2SO_4 required, g	57.78
Concentration of H_2SO_4 solution, wt. %	25
25 wt. % H_2SO_4 solution required, g	231.1
Water in 25 wt. % H_2SO_4 solution, g	173.3
Zinc-containing raw material (as ZnO), g	48.0

The calculated amount of 25 wt.% H_2SO_4 solution was then used for the acid treatment of the zinc-containing raw material. The reaction temperature was maintained above 70 °C to promote the dissolution of the zinc-containing phase and formation of zinc sulfate.

The resulting mixture was stirred for 0.5 h (30 min) to ensure sufficient contact between the zinc-containing solid phase and the sulfuric acid solution and to promote dissolution of the zinc-containing components. Therefore, 30 min was used as the standard mixing time for the subsequent experiments.

Hydrogen peroxide was used as an oxidizing agent during the subsequent purification step to facilitate the removal of impurity elements, particularly iron, copper, cadmium, and nickel. H_2O_2 was selected because of its strong oxidizing properties and its ability to promote the oxidation and subsequent separation of transition-metal impurities under the applied aqueous conditions. In addition, hydrogen peroxide decomposes to water and oxygen, which minimizes the introduction of additional persistent chemical contaminants into the process.

At this concentration, ZnO can be readily converted to soluble ZnSO_4 , while metallic Zn undergoes dissolution according to the following reaction:



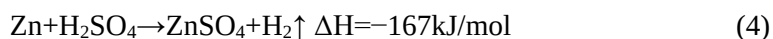
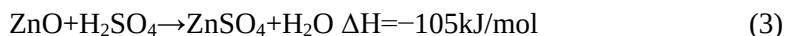
For zinc oxide, the corresponding reaction is:



Thus, the selected acid concentration was intended to provide effective conversion of both oxidized and metallic zinc into zinc sulfate while avoiding unnecessarily high acid concentrations. The use of a common 25 wt.% H_2SO_4 concentration for all samples also ensured comparable experimental conditions and allowed the effect of the initial chemical form of zinc on zinc sulfate formation to be evaluated.

3. Results and discussion

The conducted experiments on the production of zinc sulfate in the form of zinc vitriol ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$) and the possibility of converting it into the monohydrate form ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) made it possible to determine the stages of this process. The reactions between zinc-containing waste and sulfuric acid proceed according to the following equations:



The reactions are exothermic and proceed easily without additional heating (due to the released heat, the acid is heated to boiling) at temperatures above 70 °C [18].

Zinc sulfate hydrate crystallization depends on temperature: $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ forms at –7–39 °C, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ at 39–70 °C, and $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ above 70 °C, with dehydration to anhydrous ZnSO_4 at 238 °C. Therefore, ZO1 and ZO2 wastes were dried at 105 °C, dispersed in water for 10 min, and treated with concentrated H_2SO_4 to obtain a 25 wt.% solution; direct acid treatment was avoided due to poor wetting and vigorous reaction.

In industrial practice, zinc-containing raw materials are added in excess to diluted acid until the acid concentration decreases to 1–2 g/L. Due to the highly exothermic ZnO – H_2SO_4 reaction, no preliminary heating is required above 70 °C. Reagent-grade zinc dust dissolved within 5 min at 7–45 wt.% H_2SO_4 , whereas ZO1 and ZO2 required 30 min due to complex zinc compounds. Tin, if present, may hinder filtration; in its absence, the acid can be diluted to 180 g/L and heated to boiling.

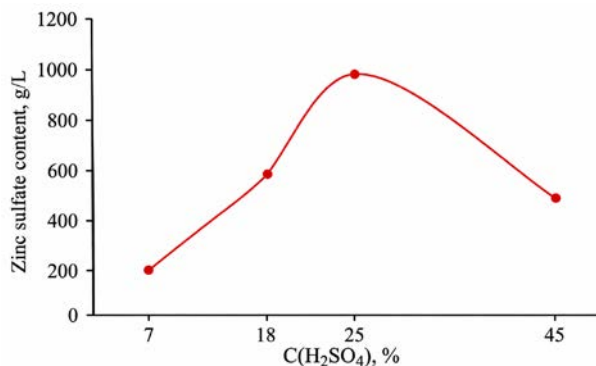
The raw material was pre-ground to increase the reaction rate, while foaming indicated the presence of metallic zinc and hydrogen evolution. The resulting ZnSO_4 solution was purified from Cu, Cd, Ni, and Fe by acid treatment, zinc-dust cementation, Fe^{2+} oxidation, precipitation, and filtration; tin-containing solutions were settled for 10–15 h before purification.

Hydrogen peroxide can also be used as an oxidizing agent.

As a result of the experiments, the zinc sulfate content was determined as a function of sulfuric acid concentration (Table 3, Fig. 1).

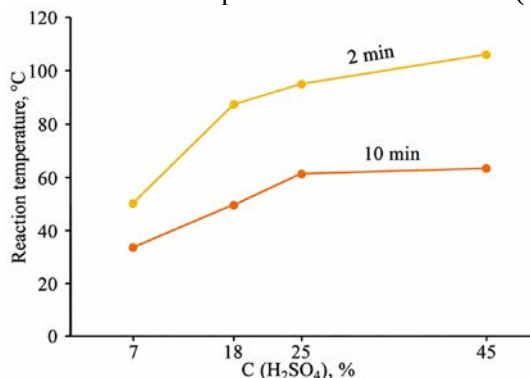
Table 3 – Zinc sulfate content as a function of initial sulfuric acid concentration

H ₂ SO ₄ (% mass.)	T ₀ (°C)	T _i (°C) after 2 min	T _f (°C) (after 10 min)	C _{ZnSO₄} (g/l)	C _{H₂SO₄ free.} (g/l)
45	22,9	107,9	63,1	503	29,4
25	26,5	95,8	61,9	985	24,7
18	23,5	88,3	50,6	589	23,76
7	24,1	50,7	34,6	204	3,43

**Figure 1** – Dependence of zinc sulfate content on the concentration of initial sulfuric acid.

As shown in Figure 1, the maximum zinc sulfate concentration (985 g/l) was achieved at an initial sulfuric acid concentration of 25 wt.%. Both lower and higher acid concentrations resulted in decreased zinc sulfate content. This behavior indicates that the interaction between sulfuric acid and zinc-containing waste is strongly dependent on acid concentration, and that 25 wt.% provides the most favorable conditions for zinc sulfate formation.

A change in the temperature of the products as a function of the initial sulfuric acid concentration in the suspension is also observed (Fig. 2).

**Figure 2** – Dependence of Product Temperature on the Concentration of Initial Sulfuric Acid in the Suspension.

At a high initial sulfuric acid concentration (45 wt.%), the reaction temperature increased rapidly from 22.9 °C to 107.9 °C within the first 2 minutes, indicating an intensive exothermic interaction between sulfuric acid and zinc-containing waste. With decreasing acid concentration, the maximum reaction temperature also decreased, which may be associated with a lower reaction rate and reduced heat release during zinc sulfate formation. The observed temperature changes are influenced not only by sulfuric acid concentration, but also by heat transfer processes, evaporation, and the thermal capacity of the reaction medium.

Temperature gradients for the reaction between sulfuric acid and zinc oxide production waste were also calculated (Fig. 3).

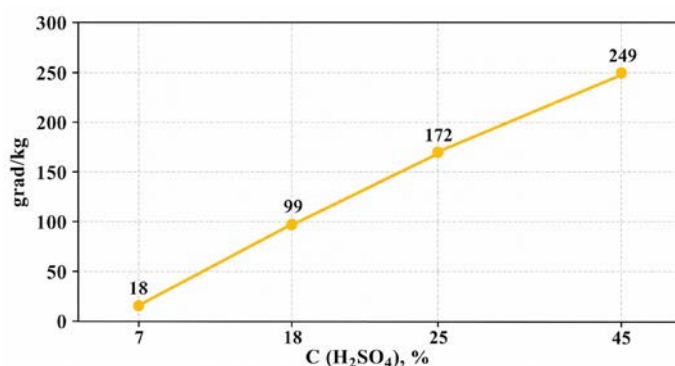


Figure 3 – Temperature gradient of the reaction between H₂SO₄ and zinc oxide production waste.

This curve makes it possible to derive a heat balance equation required for process scaling. Analysis of the curve confirms that the choice of a 25 wt.% acid concentration is appropriate.

Based on the obtained data, the conditions for further application to zinc-containing waste were selected.

It is known that the production of 1 ton of zinc vitriol consumes 0.47 tons of zinc (as metal) and 0.72 tons of sulfuric acid (100%). After recalculation, it was determined that for the synthesis of zinc sulfate monohydrate, 48.0 g of zinc-containing raw material (in terms of oxide) should be used, along with 25% sulfuric acid to maintain the required temperature regime (above 70°C). First, the acid is diluted to 25% by adding 210 g of distilled water to the reaction vessel, followed by 40.74 mL of 95% sulfuric acid.

In all cases, the obtained product consisted of single-phase ZnSO₄·H₂O. Figures 4-5 and Table 4 present the diffraction patterns of the samples, confirming the formation of pure zinc sulfate monohydrate.

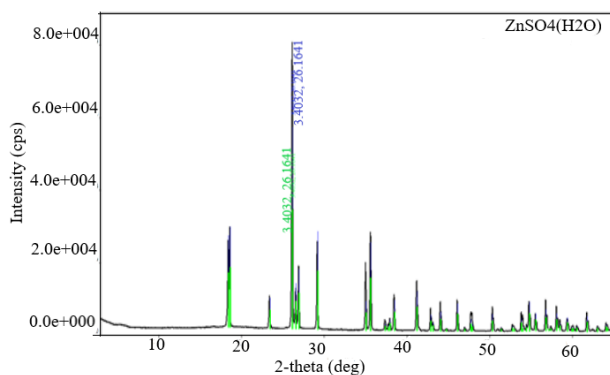


Figure 4 – X-ray diffraction pattern of zinc sulfate monohydrate obtained from sample ZO1.

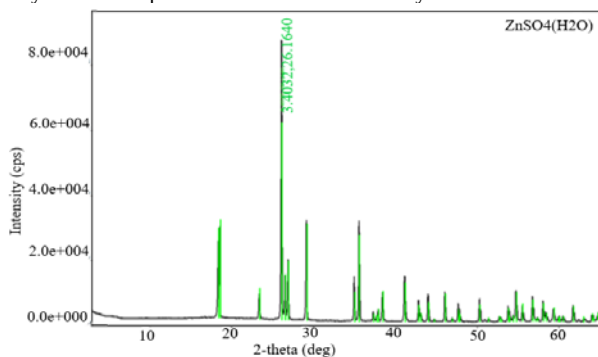


Figure 5 – X-ray diffraction pattern of zinc sulfate monohydrate obtained from sample ZO2.

Table 4 – Phase composition of the samples

Samples	Phase composition	Content, wt. %
ZO1	ZnSO ₄ ·H ₂ O; C2/c (15), ICDD PDF-2; 01-074-1331, RIR = 2.24	100
ZO2	ZnSO ₄ ·H ₂ O C2/c (15), ICDD PDF-2; 01-074-1331, RIR = 2.24	

The mercury content in the obtained samples did not exceed 4 ppm. Lead and cadmium compounds were not detected. The remaining mother liquor is retained and added to subsequent batches of solution for evaporation. If evaporation is carried out at temperatures below 70°C, zinc vitriol crystals are formed.

4. Conclusion

A laboratory-scale technology for the production of zinc sulfate monohydrate from zinc-containing waste was developed. The influence of sulfuric acid concentration on the synthesis process was investigated, and the optimal concentration was determined to be 25 wt.%, which provided the highest zinc sulfate concentration in solution.

The study showed that preliminary mixing of zinc-containing powders with water ensures stable interaction with sulfuric acid and improves the dissolution

process. Hydrogen peroxide was successfully applied for purification of the zinc sulfate solution from iron and other impurity compounds.

XRD analysis confirmed the formation of phase-pure zinc sulfate monohydrate ($\text{ZnSO}_4 \cdot \text{H}_2\text{O}$) in samples obtained from both “ZO1” and “ZO2” wastes. The developed approach demonstrates the possibility of efficient recycling of zinc oxide production waste into a valuable commercial product.

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МЫРЫШ ҚҰРАМДЫ ҚАЛДЫҚТАРДАН МЫРЫШ СУЛЬФАТЫНЫҢ МОНОГИДРАТЫН АЛУ ТЕХНОЛОГИЯСЫН ЗЕРТТЕУ

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Түйіндеме. Цинк сульфаты - әртүрлі өнеркәсіп салаларында кеңінен қолданылатын маңызды химиялық қосылыс. Ол ауыл шаруашылығында өнімділікті арттыру үшін, сондай-ақ бояулар, фармацевтикалық препараттар, сыра және басқа да өнімдерді өндіруде қолданылады. Негізгі элемент - мырыш - өсімдіктердің белсенді өсуі мен дамуына ықпал етеді. Цинк сульфаты моногидратын алу технологиясы зерттеліп, әзірленді. Зерттеу материалы ретінде 75-99% мырыштан тұратын ұнтақтар және 25% күкірт қышқылы қолданылды. Компоненттердің өзара әрекеттесу жылдамдығын арттыру үшін ұнтақтар алдын ала сумен араластырылды. Қосылатын концентрлі күкірт қышқылының мөлшері, қосқаннан кейін 25% концентрациялы күкірт қышқылы ерітіндісі алынатындай етіп реттелді. Темір, мыс, кадмий және никель сияқты қоспаларды жою үшін сутек асқын тотығы қолданылды. Осы технология бойынша 100% цинк сульфаты моногидраты алынды. Мырыш сульфатының моногидратын алудың зертханалық регламенті жасалды.

Түйінді сөздер: Цинк сульфаты моногидраты, қалдық, мырыш оксиді, мырышқұрамды шикізат, химиялық құрамы, күкірт қышқылы, сутек асқын тотығы, зертханалық регламент, сүзу, буландыру, кептіру

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ИССЛЕДОВАНИЕ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ МОНОГИДРАТА СУЛЬФАТА ЦИНКА ИЗ ЦИНКСОДЕРЖАЩИХ ОТХОДОВ

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Резюме. Сульфат цинка является важным химическим соединением, широко применяемым в различных отраслях промышленности. Он используется в сельском хозяйстве для повышения урожайности, а также в производстве красок, фармацевтических препаратов, пива и других продуктов. Основным элементом – цинк – способствует активному росту и развитию растений. Была изучена и разработана технология получения моногидрата сульфата цинка. В качестве исследуемых материалов использовали порошки, содержащие 75-99% цинка, и 25% серную кислоту. Для увеличения скорости взаимодействия между компонентами порошки предварительно смешивали с водой. Количество вводимой концентрированной серной кислоты регулировали таким образом, чтобы после добавления получался раствор серной кислоты с концентрацией 25%. Для удаления примесей, таких как железо, медь, кадмий и никель, использовали перекись водорода. По данной технологии был получен 100% моногидрат сульфата цинка. Разработан лабораторный регламент получения моногидрата сульфата цинка.

Ключевые слова: Цинк сульфат моногидрат, отходы, оксид цинка, цинксоодержащее сырьё, химический состав, серная кислота, перекись водорода, лабораторный регламент, фильтрация, выпаривание, сушка

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SYNTHESIS AND EVALUATION OF OCTADECYL METHACRYLATE-VINYLMIDAZOLE COPOLYMERS AS COLD-FLOW IMPROVERS FOR DIESEL FUEL

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Abstract. *Introduction.* The formation and aggregation of wax crystals at low temperatures impair the flow and filtration properties of diesel fuel. Comb-like copolymers containing long alkyl side chains can modify wax crystallization and improve the low-temperature performance of diesel fuel. *This study aimed* to synthesize octadecyl methacrylate-vinylimidazole (ODMA-VI) copolymers with different monomer feed ratios and evaluate their effects on the cold filter plugging point (CFPP), cloud point (CP) and pour point (PP) of diesel fuel. *Results and Discussion.* ODMA-VI copolymers with ODMA:VI monomer feed ratios of 9:1, 6:1 and 4:1 were synthesized by free-radical solution copolymerization and characterized by ¹H NMR, FTIR spectroscopy and gel permeation chromatography. Their effects on the low-temperature properties of diesel fuel were evaluated at dosages ranging from 1000 to 3000 ppm. The observed changes depended on the monomer feed ratio and additive dosage. Among the investigated samples, the copolymer prepared at an ODMA:VI monomer feed ratio of 4:1 resulted in the largest reductions at 3000 ppm, decreasing the CFPP from -7 to -10 °C, the CP from -3 to -8 °C and the PP from -10 to -18 °C. Optical microscopy showed that the copolymer reduced the size and aggregation of wax crystals and promoted their more uniform dispersion in diesel fuel. *Conclusion.* The results indicate that the ODMA:VI monomer feed ratio influences the depressant performance of the synthesized copolymers. Among the investigated samples, the copolymer prepared at an ODMA:VI monomer feed ratio of 4:1 showed the most pronounced effects on wax-crystal morphology and the measured low-temperature properties of diesel fuel.

Keywords: octadecyl methacrylate, vinylimidazole, diesel fuel, cold-flow improver, low-temperature properties

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1. Introduction

Diesel fuel contains a complex mixture of hydrocarbons, including normal paraffins that provide a high cetane number but adversely affect fuel performance at low temperatures. During cooling, long-chain paraffins lose solubility and begin to crystallize [1]. Further crystal growth and aggregation can produce an interconnected wax network that restricts fuel flow and blocks fuel lines and filters. The low-temperature operability of diesel fuel is commonly assessed using the cloud point (CP), pour point (PP) and cold filter plugging point (CFPP). These parameters characterize different stages of wax formation, from the initial appearance of crystals to the loss of fluidity and filterability. Therefore, improving these properties is important for the storage, transportation, and use of diesel fuel under cold climatic conditions [2].

Several approaches have been proposed to improve the low-temperature properties of petroleum fuels, including dewaxing, dilution with low-wax fractions, and the addition of cold-flow improvers [3]. Among these methods, polymeric additives are particularly attractive because they can be applied at relatively low dosages without substantially changing other fuel properties. They modify wax nucleation, crystal growth, morphology, and aggregation [4]. Their nonpolar segments can interact or co-crystallize with paraffin molecules, while other structural units remain at the crystal surface and hinder the formation of large, interconnected aggregates.

Comb-like polymers containing long alkyl side chains are widely investigated as cold-flow improvers because their molecular architecture resembles that of the paraffins present in diesel fuel. Polyacrylates, polymethacrylates, ethylene-vinyl acetate copolymers, and maleic anhydride-based copolymers have been reported as effective wax-crystal modifiers [5]. Recent studies have demonstrated that copolymers containing octadecyl acrylate or methacrylate units can reduce wax crystal size, weaken the three-dimensional crystal network and improve the low-temperature flow properties of wax-containing hydrocarbon systems [6]. However, additive performance depends strongly on molecular structure, including alkyl-chain length, co-monomer type and content, molecular weight and polymer conformation [7].

The balance between nonpolar and polar structural units is particularly important in designing an effective copolymer. Long alkyl chains promote interaction with crystallizing paraffins, whereas polar groups can influence polymer solubility, adsorption at the wax-crystal surface and the subsequent aggregation of crystals [8]. Variations in monomer ratio can therefore alter both the hydrodynamic behavior of the copolymer in solution and its ability to modify wax crystallization. Recent studies have emphasized the relationship between polymer composition, molecular characteristics, wax-crystal morphology and depressant efficiency [9,10]. Nevertheless, octadecyl methacrylate-vinylimidazole copolymers have received limited attention as cold-flow improvers for diesel fuel produced by the Shymkent Oil Refinery. Incorporation of vinylimidazole

provides nitrogen-containing polar units, allowing the polarity and hydrodynamic characteristics of the copolymer to be adjusted by changing the ODMA-VI ratio.

In this study, ODMA-VI copolymers with ODMA:VI monomer feed ratios of 9:1, 6:1 and 4:1 were synthesized by free-radical solution copolymerization. The obtained samples were characterized by ^1H NMR, FTIR spectroscopy and gel permeation chromatography (GPC). Their performance as cold-flow improvers for Shymkent Oil Refinery diesel fuel was evaluated at different dosages by measuring CFPP, CP and PP.

2. Experimental part

2.1 Materials

Octadecylmethacrylate ($\geq 98\%$, Sigma Aldrich), 1-vinylimidazole ($\geq 99\%$, Sigma Aldrich), benzoyl peroxide ($\geq 99.0\%$, Sigma-Aldrich), toluene (99.8% , Sigma-Aldrich) and ethanol ($\geq 99.5\%$, Sigma-Aldrich) were used without further purification.

A diesel fuel sample obtained from the Shymkent Oil Refinery was used to evaluate the low-temperature performance of the synthesized additives.

2.2 Synthesis of ODMA-VI copolymers

ODMA-VI copolymers with an ODMA:VI monomer feed ratio of 9:1 were synthesized via free-radical solution copolymerization of 3.00 g of octadecyl methacrylate (ODMA) and 0.093 g of vinylimidazole (VI) in 6 mL of toluene under a nitrogen atmosphere. The synthetic route is shown in Figure 1. Benzoyl peroxide was used as the initiator at 1 wt % of the reactants. The reaction mixture was heated to $80\text{ }^\circ\text{C}$ and the initiator was added portionwise at 30 min intervals over 2 h. The copolymerization was subsequently conducted at $110\text{ }^\circ\text{C}$ for 6 h. The resulting copolymer was precipitated in 50 mL of ethanol and dried under vacuum at room temperature to a constant mass. Unreacted VI may have remained soluble in ethanol and been removed during precipitation. ODMA-VI copolymers with ODMA:VI monomer feed ratios of 6:1 and 4:1 were similarly prepared using 0.139 and 0.208 g of VI, respectively. The samples were designated OV-91, OV-61 and OV-41 according to their ODMA:VI monomer feed ratios.

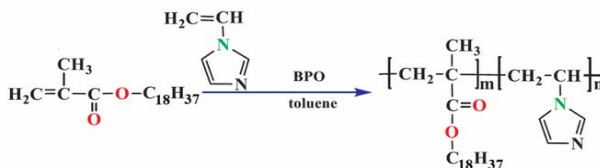


Figure 1 – Synthesis scheme of the ODMA-VI copolymer.

2.3 Characterization methods

The n-alkane distribution of diesel fuel obtained from the Shymkent Oil Refinery was analyzed using an AutoSystem XL gas chromatograph

(PerkinElmer, USA) equipped with an ELITE PS 2887 capillary column and a flame ionization detector (FID).

The copolymer was added to diesel fuel as a 30 wt.% solution in toluene. The dosages from 1000 to 3000 ppm refer to the amount of the prepared copolymer solution. The treated fuel samples were mixed at room temperature for 20 min and then tested. Standard test methods for diesel fuel characterization and its composition are presented in Figure 2 and Table 1, respectively.

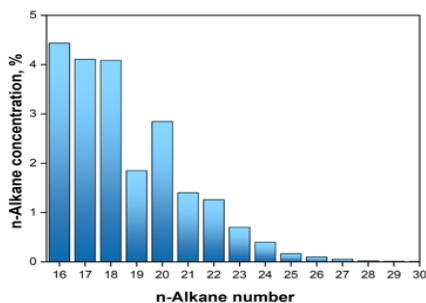


Figure 2 – Carbon number distribution of the diesel fuel.

Table 1 – Standard test methods for fuel characterization

Test	Method
Cold filter plugging point (CFPP), °C	ASTM D 6371
Cloud point (CP), °C	ASTM D 2500
Pour point (PP), °C	ASTM D 97

All CFPP, CP and PP measurements were performed in triplicate and the results are reported as mean values. The molecular weights of the synthesized polymers were measured by gel permeation chromatography (GPC) using a PSS SECcurity² system equipped with a refractive index detector. The ¹H NMR spectra were recorded on a JEOL JNM-ECA 400 spectrometer operating at 399.78 MHz using CDCl₃ as the solvent. The chemical structures of the synthesized samples were characterized by FTIR spectroscopy using a Nicolet 5700 spectrometer over the range of 4000-400 cm⁻¹. The morphology of wax crystals in diesel fuel samples was examined using a Nikon ECLIPSE LV150N polarized optical microscope (Nikon, Japan) equipped with a temperature-controlled heating and cooling stage. Certain amounts of the samples were placed between glass slides, thermostated and purged with a stream of dry nitrogen to prevent condensation. Wax crystal images were recorded at intervals of 1° and observed in real time.

3. Results and Discussion

The molecular weights, dispersities and yields of the synthesized ODMA-VI copolymers are summarized in Table 2.

Table 2 – Characteristics of the synthesized ODMA-VI copolymers

Sample	M_w , g mol ⁻¹	M_n , g mol ⁻¹	$\bar{D}$	Yield, %
OV-91	60 013	21 436	2.79	84.12
OV-61	57 952	22 883	2.53	82.43
OV-41	41 236	22 354	1.84	87.41

Table 2 shows that the synthesized ODMA-VI copolymers have M_w and M_n values ranging from 41 236 to 60 013 g mol⁻¹ and from 21 436 to 22 883 g mol⁻¹, respectively. As the VI proportion increased, M_w and dispersity decreased, whereas M_n remained nearly unchanged. The $\bar{D}$ values ranged from 1.84 to 2.79, indicating moderately broad molecular weight distributions. The decrease in M_w and dispersity with increasing VI content, while M_n remained nearly unchanged, indicates a reduced contribution of the high-molecular-weight fraction and a narrower molecular-weight distribution. All copolymers were obtained in high yields of 82.43–87.41%.

Figure 3 shows the ¹H NMR spectra of OV-91, OV-61 and OV-41.

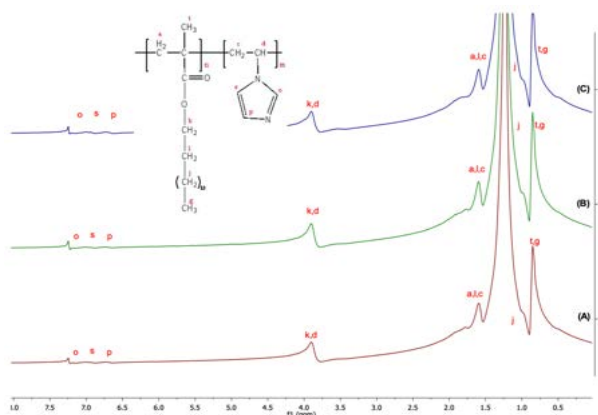


Figure 3 – ¹H NMR spectra of OV-91 (A), OV-61 (B) and OV-41 (C).

The signals at 6.7-7.3 ppm were assigned to the three protons of the imidazole ring (Figure 3). The signal near 3.9 ppm was attributed to the OCH₂ protons of the ODMA units. The intense signals at 1.1-1.5 and 0.9 ppm correspond to the methylene and terminal methyl groups of the long ODMA alkyl chains, respectively. The absence of vinyl proton signals at 5.0-6.5 ppm confirms monomer consumption during copolymerization. The imidazole signals increased in intensity from OV-91 to OV-41, indicating greater incorporation of VI units. Signal integration gave ODMA-VI molar ratios of 26.53:1 for OV-91, 24.51:1 for OV-61 and 16.63:1 for OV-41.

The chemical structures of the synthesized ODMA-VI copolymers were characterized by FTIR spectroscopy (Figure 4).

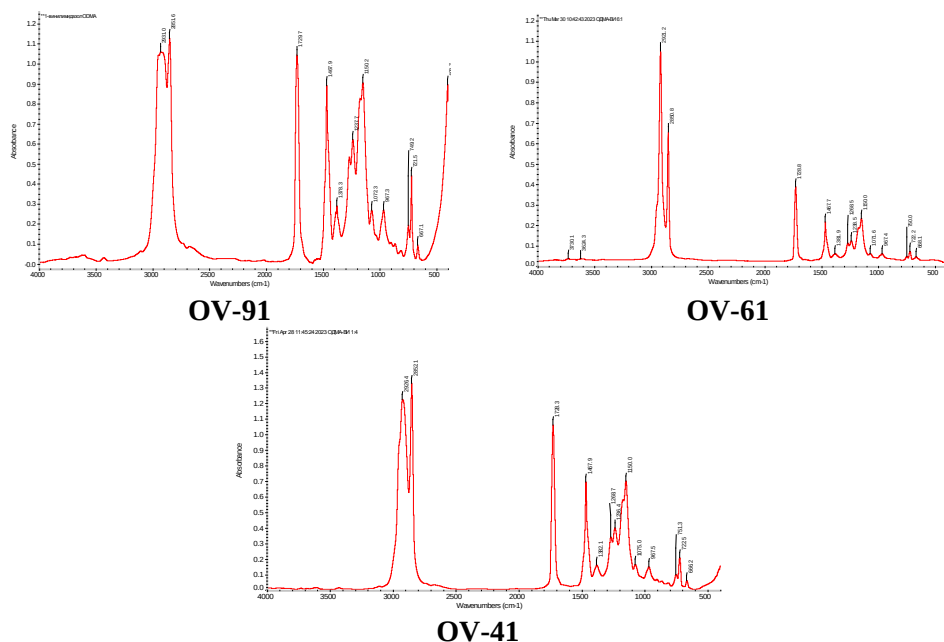


Figure 4 – FTIR spectra of ODMA-VI copolymers synthesized at different ODMA:VI monomer feed ratios.

The FTIR spectra of OV-91, OV-61 and OV-41 showed similar absorption patterns, indicating the presence of the same principal structural features in all three samples (Figure 4). The absorption bands at 2921–2931 and 2851–2852 cm^{-1} were assigned to the asymmetric and symmetric stretching vibrations of CH_2 groups in the long alkyl chains, respectively. The strong bands at 1728–1730 cm^{-1} corresponded to the $\text{C}=\text{O}$ stretching vibrations of the ester groups. The bands at 1467–1468 and 1378–1383 cm^{-1} were attributed to the bending vibrations of CH_2 and CH_3 groups, respectively. The bands in the regions of 1236–1269, 1150 and 1072–1075 cm^{-1} were assigned mainly to the $\text{C}-\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching vibrations of the ester groups. Within this region, the band at approximately 1268 cm^{-1} , observed for OV-61 and OV-41, may include a contribution from $\text{C}-\text{N}$ stretching vibrations. In the OV-91 spectrum, this band was not distinguishable because of the low concentration of 1-vinylimidazole units in the copolymer. The weak bands at approximately 967, 749–751 and 666–668 cm^{-1} may include contributions from deformation vibrations of the imidazole ring.

The synthesized copolymers were introduced into untreated diesel fuel at dosages ranging from 1000 to 3000 ppm. Solvent-only control experiments confirmed that toluene had no effect on the CFPP, CP and PP of the diesel fuel. Figure 5 shows the effects of copolymer composition and dosage on the CFPP of

diesel fuel. The OV-91 showed negligible activity over the investigated dosage range, whereas the OV-61 reduced the CFPP from -7 to -8 °C at 2000 and 3000 ppm. The most pronounced dose-dependent change among the investigated samples was observed for the OV-41, which decreased the CFPP to -9 and -10 °C at 2000 and 3000 ppm, respectively.

The effect of the copolymer solutions on the CP of diesel fuel is shown in Figure 6. All copolymers reduced the CP of diesel fuel from its initial value of -3 °C. For the OV-91, the CP decreased to -6 °C at 1000 and 2000 ppm and to -7 °C at 3000 ppm. The OV-61 copolymer lowered the CP to -6 °C at 1000 ppm and to -7 °C at 2000 and 3000 ppm. The lowest CP was observed for the OV-41, which lowered the CP to -7 °C at 1000 and 2000 ppm and to -8 °C at 3000 ppm.

Figure 7 shows the PP lowering performance of the copolymers. The untreated diesel fuel exhibited a PP of -10 °C. Addition of the OV-91 lowered the PP by 5 °C to -15 °C at all tested dosages, indicating that increasing the dosage above 1000 ppm provided no further improvement. The OV-61 showed a smaller effect, reducing the PP to -13 °C at 1000 and 2000 ppm and to -14 °C at 3000 ppm. In contrast, the effect of the OV-41 became more pronounced with increasing dosage. The PP decreased to -14 °C at 1000 ppm, -15 °C at 2000 ppm and -18 °C at 3000 ppm. Thus, the OV-41 at 3000 ppm provided the lowest PP, corresponding to an 8 °C reduction relative to untreated diesel fuel.

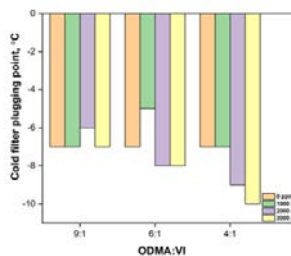


Figure 5 – CFPP of diesel fuel treated with ODMA-VI copolymers prepared at different ODMA:VI monomer feed ratios.

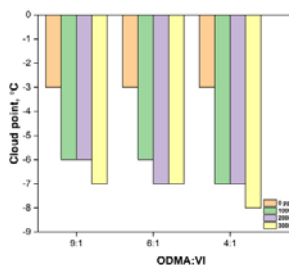


Figure 6 – Effect of the ODMA:VI monomer feed ratio and additive dosage on the CP of diesel fuel.

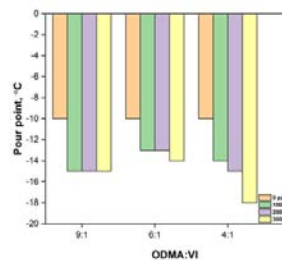


Figure 7 – Effect of the ODMA:VI monomer feed ratio and additive dosage on the PP of diesel fuel.

For comparison, the effects of OV-41 on the CFPP, CP and PP of diesel fuel are summarized in Table 3 alongside the corresponding values for untreated diesel fuel.

Table 3 – Low-temperature properties of untreated diesel fuel and diesel fuel treated with OV-41

Sample	Concentration, ppm	Temperature, °C		
		CFPP	CP	PP
Diesel fuel	-	-7	-3	-10
OV-41	1000	-7	-7	-14
	2000	-9	-7	-15
	3000	-10	-8	-18

According to the data in Table 3, the addition of 1000 ppm OV-41 reduced the CP from -3 to -7 °C and the PP from -10 to -14 °C, while the CFPP remained unchanged at -7 °C. At 2000 ppm, the CFPP and PP decreased to -9 and -15 °C, respectively, whereas the CP remained at -7 °C. Increasing the dosage to 3000 ppm resulted in the greatest improvement, reducing the CFPP to -10 °C, the CP to -8 °C, and the PP to -18 °C.

Among the investigated samples, the copolymer prepared at an ODMA:VI monomer feed ratio of 4:1 showed the most pronounced reductions in CFPP, CP and PP. This behavior may be attributed to a favorable balance between the long C₁₈ alkyl side chains of ODMA and the polar VI units. The alkyl chains can co-crystallize with diesel paraffins, while the VI-containing polymer backbone limits wax crystal growth and aggregation [11, 12]. The higher VI proportion may also improve polymer dispersion and reduce self-association of the ODMA-rich segments, which could result in smaller, less interconnected wax crystals and suppression of the continuous wax network [13]. OV-41 also combined the highest VI content with the lowest M_w and dispersity among the investigated samples. Its enhanced performance may reflect the combined effects of copolymer composition and molecular-weight distribution on wax-crystal modification.

Figure 8 presents micrographs of paraffin crystals in untreated diesel fuel and in diesel fuel treated with the copolymer at a concentration of 3000 ppm at different temperatures.

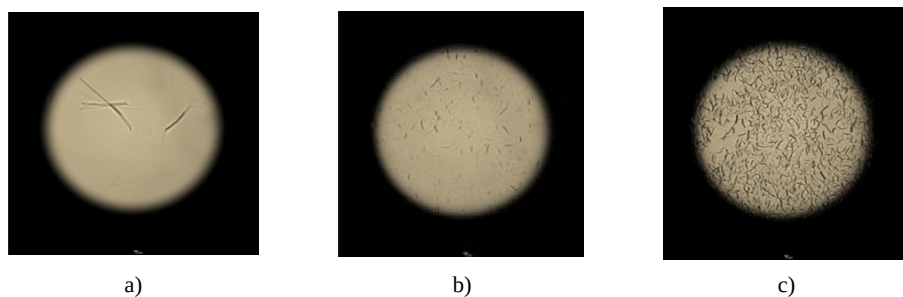


Figure 8 – Micrographs of untreated diesel fuel (a) and diesel fuel treated with 3000 ppm of OV-41 at -5 °C (b) and -10 °C (c).

As shown in Figure 8a, in the absence of the additive, separate large needle-like and plate-like paraffin crystals are observed. The addition of 3000 ppm of the copolymer results in the formation of smaller and more uniformly distributed crystalline particles at -5 °C (Figure 8b). Upon further cooling to -10 °C, the number of crystals increases significantly, but they remain relatively small and dispersed throughout the fuel (Figure 8c). These results indicate that the copolymer modifies the morphology of paraffin crystals by limiting their growth and the formation of a dense three-dimensional network, thereby improving the low-temperature flowability and filterability of diesel fuel.

4. Conclusion

ODMA-VI copolymers with ODMA:VI monomer feed ratios of 9:1, 6:1 and 4:1 were synthesized by free-radical solution copolymerization and characterized by ^1H NMR, FTIR spectroscopy and gel permeation chromatography. Their effects on the low-temperature properties of diesel fuel were evaluated using CFPP, CP, PP and optical microscopy measurements. The results depended on the monomer feed ratio and additive dosage. Among the investigated samples, OV-41 produced the highest changes in the measured parameters. At 3000 ppm, it reduced the CFPP from -7 to -10 °C, the CP from -3 to -8 °C and the PP from -10 to -18 °C. Optical microscopy showed smaller and more uniformly distributed wax crystals in the treated diesel fuel. These findings indicate that OV-41 affects wax crystallization and the low-temperature behavior of diesel fuel. However, further optimization of its composition and dosage, comparison with commercial additives and techno-economic assessment are required to determine its practical applicability.

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Conflict of Interest: The authors declare no conflict of interest.

ОКТАДЕЦИЛМЕТАКРИЛАТ ПЕН ВИНИЛИМИДАЗОЛДЫҢ СОПОЛИМЕРЛЕРІН ДИЗЕЛЬ ОТЫНЫНЫҢ ТӨМЕН ТЕМПЕРАТУРАЛЫҚ КӨРСЕТКІШТЕРІН ЖАҚСАРТАТЫН ҚОСПАЛАР РЕТІНДЕ СИНТЕЗДЕУ ЖӘНЕ ОЛАРДЫ БАҒАЛАУ

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Түйіндеме. Кіріспе. Төмен температурада парафин кристалдарының түзілуі мен агрегациясы дизель отынының ағу және сүзгілену қасиеттерін нашарлатады. Құрамында ұзын алкилді бүйір тізбектері бар тарақ тәрізді сополимерлер парафиндердің кристалдану процесін өзгертіп, дизель отынының төмен температуралық қасиеттерін жақсартып алады. Зерттеудің мақсаты бастапқы қоспадағы мономерлердің әртүрлі молярлық қатынастарында октадецилметакрилат-винилимидазол (ОДМА-ВИ) сополимерлерін синтездеу және олардың дизель отынының шекті сүзгілену температурасына (CFPP), бұлдырлану температурасына (CP) және қату температурасына (PP) әсерін бағалау болды. Нәтижелер және талқылау. ОДМА:ВИ мономерлерінің бастапқы молярлық қатынастары 9:1, 6:1 және 4:1 болатын сополимерлер ерітіндіде еркін радикалды сополимерлеу әдісімен синтезделіп, ^1H ЯМР спектроскопиясы, Фурье түрлендірулі инфрақызыл спектроскопия және гель-өткізгіш хроматография әдістерімен зерттелді. Олардың дизель отынының төмен температуралық қасиеттеріне әсері 1000–3000 ppm аралығындағы дозаларда бағаланды. Байқалған өзгерістер мономерлердің бастапқы молярлық қатынасы мен қоспа дозасына байланысты болды. Зерттелген үлгілердің ішінде ОДМА:ВИ мономерлерінің бастапқы молярлық қатынасы 4:1 болған кезде алынған сополимер 3000 ppm дозада көрсеткіштердің ең айқын төмендеуін қамтамасыз етті: CFPP көрсеткіші -7-ден -10 °C-қа дейін, CP -3-тен -8 °C-қа дейін, ал PP -10-нан -18 °C-қа дейін төмендеді. Оптикалық микроскопия сополимердің парафин кристалдарының мөлшері мен агрегациясын азайтып, олардың дизель отынында біркелкі таралуына ықпал ететінін көрсетті. Қорытынды. Алынған нәтижелер ОДМА:ВИ мономерлерінің бастапқы молярлық қатынасы синтезделген сополимерлердің депрессорлық әсеріне ықпал ететінін көрсетті. Зерттелген үлгілердің ішінде ОДМА:ВИ мономерлерінің бастапқы молярлық қатынасы

4:1 болған кезде алынған сополимер парафин кристалдарының морфологиясына және дизель отынының төмен температуралық қасиеттеріне ең айқын әсер етті.

Түйінді сөздер: октадецилметакрилат, винилимидазол, дизель отыны, төмен температуралық қасиеттерді жақсартқыш, төмен температуралық қасиеттер.

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СИНТЕЗ И ОЦЕНКА СОПОЛИМЕРОВ ОКТАДЕЦИЛМЕТАКРИЛАТА И ВИНИЛИМИДАЗОЛА В КАЧЕСТВЕ ПРИСАДОК ДЛЯ УЛУЧШЕНИЯ НИЗКОТЕМПЕРАТУРНЫХ СВОЙСТВ ДИЗЕЛЬНОГО ТОПЛИВА

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Резюме. Введение. Образование и агрегация кристаллов парафина при низких температурах ухудшают текучесть и фильтруемость дизельного топлива. Гребнеобразные сополимеры, содержащие длинные алкильные боковые цепи, способны изменять процесс кристаллизации парафинов и улучшать низкотемпературные свойства дизельного топлива. Целью работы являлись синтез сополимеров октадецилметакрилата и винилимидазола (ОДМА-ВИ) при различных молярных соотношениях мономеров в исходной смеси и оценка их влияния на предельную температуру фильтруемости (CFPP), температуру помутнения (CP) и температуру застывания (PP) дизельного топлива. Результаты и обсуждение. Сополимеры ОДМА-ВИ с молярными соотношениями мономеров 9:1, 6:1 и 4:1 были синтезированы методом свободнорадикальной сополимеризации в растворе и охарактеризованы с помощью спектроскопии ¹H ЯМР, ИК-Фурье-спектроскопии и гель-проникающей хроматографии. Их влияние на низкотемпературные свойства дизельного топлива оценивали при дозировках от 1000 до 3000 ppm. Наблюдаемые изменения зависели от молярного соотношения мономеров и дозировки присадки. Среди исследованных образцов сополимер, полученный при молярном соотношении мономеров ОДМА:ВИ 4:1, обеспечил наиболее выраженное снижение показателей при дозировке 3000 ppm: CFPP снизилась с -7 до -10 °C, CP с -3 до -8 °C, а PP с -10 до -18 °C. Оптическая микроскопия показала, что сополимер уменьшает размер и агрегацию кристаллов парафина и способствует их более равномерному распределению в дизельном топливе. Заключение. Полученные результаты показывают, что молярное соотношение мономеров ОДМА:ВИ влияет на депрессорное действие синтезированных сополимеров. Среди исследованных образцов сополимер, полученный при молярном соотношении мономеров ОДМА:ВИ 4:1, оказал наиболее выраженное влияние на морфологию кристаллов парафина и низкотемпературные свойства дизельного топлива.

Ключевые слова: октадецилметакрилат, винилимидазол, дизельное топливо, низкотемпературная присадка, низкотемпературные свойства

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STRUCTURAL OPTIMIZATION OF BIOCOMPOSITES USING MULTIVALENT IONS AND MODIFIED MONTMORILLONITE

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Abstract. *Introduction.* In modern biomedicine and pharmacology, one of the central challenges is the development of highly efficient therapeutic systems with controlled drug release. *Objective.* This study investigates the influence of cation valence and concentration on the degree of crosslinking in polymer networks of alginate hydrogels prepared via ionotropic gelation. *Results and Discussion.* The structural characteristics of the synthesized materials were examined using physicochemical analysis. A detailed evaluation was conducted on the swelling kinetics and the release profiles of immobilized drugs in physiological saline. Stimuli-responsive (pH-dependent) ionotropic biocomposites capable of adapting to changes in environmental acidity were successfully synthesized. Particular attention was given to the differences in insulin release kinetics from alginate-gelatin biocomposites upon the incorporation of montmorillonite and its magnetized form. It was demonstrated that the inclusion of magnetized montmorillonite nanoparticles not only prolongs the release of the protein drug but also enables prospects for targeted transport under the influence of an external magnetic field. *Conclusion.* The findings highlight effective strategies for controlling the structure and physicochemical properties of biocomposite hydrogels. These advances represent an important step toward the development of therapeutic systems for controlled and targeted drug delivery.

Keywords: hydrogel, ionotropic biocomposites, montmorillonite, magnetosensitivity, particles, modification, swelling degree

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1. Introduction

The high density of reactive functional groups offers polysaccharides a wide range of applications. Their use in drug encapsulation preserves the biological activity and integrity of loaded drugs, regulate their distribution within the body, reduce side effects, and protects them from adverse environmental influences [1-5].

In this context, bionanocomposites are commonly formed through ionotropic crosslinking of polysaccharides with multivalent ions: cations and anions. This mechanism enhances the polymers' resistance to water and improves their mechanical properties. Comparative studies have analyzed the strength and swelling behavior of hydrogels crosslinked with different multivalent cations (Ca^{2+} , Ba^{2+} , Sr^{2+}), demonstrating that ion type significantly influences mechanical stability and structural optimization. Both equilibrium swelling and mechanical properties of hydrogels prepared with various cations have been investigated, with emphasis placed on optimizing ion concentration to achieve the desired characteristics [6-8]. A protocol for immobilizing INS1E cells in alginate hydrogels has also been reported [9], highlighting high biocompatibility and preservation of cell functionality during encapsulation. The regulation of hydrogel degradation through oxidation has been explored in another study [10]. Sodium periodate was used to oxidize alginate, varying its concentration in the range of 0%, 2.5%, 5%, and 7%. At 2.5% oxidation, the material exhibited sufficient stability to retain insulin while simultaneously degrading and integrating into tissue, underscoring the potential of alginate for injectable biodegradable drug delivery systems. Polymer hydrogels represent a promising class of biomaterials for targeted drug delivery due to their high biocompatibility and favorable physicochemical properties [11]. Their swellable and porous matrix enables absorption of large amounts of water and biological fluids, making them particularly suitable for controlled and sustained drug release [12].

The aim of this research is to optimize the matrix architecture of alginate-gelatin hydrogels via ionotropic gelation with multivalent cations, and to establish the quantitative relationship between montmorillonite (MMT) and its magnetized form, the swelling ratio in media of varying pH, and the kinetics of prolonged insulin release.

The primary novelty of this work lies in the development of a ternary biocomposite system - based on the compatibility of biopolymers and magnetized montmorillonite - designed to facilitate the delivery of protein-based drugs (specifically insulin) through a dual-factor mechanism involving pH and magnetic fields. The study elucidates how the dense layered structure of the magnetized montmorillonite acts as a physical barrier, suppressing the initial "burst" release of insulin in model medium. Moreover, the incorporation of magnetized montmorillonite imparts magnetic responsiveness to the pH-sensitive polymer matrix, thereby establishing a theoretical foundation for targeted therapeutic delivery controlled by external stimuli.

The structure of such biocomposites can be further tailored by introducing natural water-soluble polymers during ionotropic hydrogel formation. The addition of gelatin, a polyampholyte, confers pH sensitivity [13–15], while the incorporation of colloidal montmorillonite particles containing magnetic components imparts magnetosensitive properties [16, 17].

2. Experimental part

2.1 Materials

Sodium alginate (19–40 kDa, Sisco Research Laboratories, Turkey), gelatin (The Kraft Heinz Company, CHIA), calcium chloride (Sinopharm Chemical Reagent Co., Ltd, China), insulin-isophane (human genetically engineered, Novo Nordisk A/S, Denmark), iron chloride (Sigma-Aldrich Chemie GmbH Eschenstrasse 5 D-82024 Taufkirchen, Germany), buffer solutions with pH values of pH=1.0; pH=4.0; pH=7.0; pH=9.18 (Reagecon, Ireland), montmorillonite – bentonite clay powder, Eastern section 12 horizon, light gray.

2.2 Preparation of sodium alginate particles by ionotropic gelation

Alginate hydrogel particles were prepared by dropwise addition of a 1% sodium alginate solution into CaCl_2 and FeCl_3 crosslinker solutions using a syringe pump. To optimize particle formation, crosslinker solutions of varying concentrations (0.5%, 1.0%, 1.5%, and 2.0%) were tested. The particles were incubated in the crosslinker solution for 30 minutes, collected by filtration, and subsequently washed with deionized water.

2.3 Determination of particles swelling in simulated gastrointestinal media

The swelling degree of particles was determined by measuring the increase in particle mass over time. Particles were placed in model solutions simulating different sections of the gastrointestinal tract, and their mass was recorded at 30-minute intervals over a total period of 180 minutes.

Table 1 - Model solutions and their pH values used in the experiment

№	Model solution	pH value
1.	0.1 N HCl solution	1.00
2.	Potassium hydrogen phthalate, saturated at 25°C	4.00
3.	Phosphate buffer	7.00
4.	0.01 mol/kg sodium tetraborate solution	9.18

The degree of swelling was calculated using the following equation:

$$K = \frac{m_t}{m_0} \quad (1)$$

Where m_t - particle mass over time, mg; m_0 - mass of particles at the initial time, mg.

In this context, the parameter K represents the swelling rate constant. Physically, K governs the diffusion velocity of water molecules into the biocomposite network and reflects the structural resistance of the crosslinked polymer matrix during expansion.

2.4 Production of biocomposites for protein drug immobilization by ionotropic gelation

The biocomposite was prepared by mixing a 1% sodium alginate solution with an 8% gelatin solution in a 1:1 ratio ($V_1:V_2$). The resulting mixture was introduced into a crosslinking agent solution using a syringe pump. The formed alginate - gelatin biocomposites were incubated in the crosslinking solution for 30 minutes, collected by filtration, and washed with deionized water.

2.5 Preparation of Magnetically Responsive Biocomposites

Magnetic montmorillonite (MMT), synthesized using the established Elmore method, was incorporated into the sodium alginate - gelatin biocomposite at concentrations of 0.1 g, 0.25 g, and 0.5 g for different sample batches. The mixture was homogenized until a uniform dispersion was achieved and subsequently injected into a 1.5% CaCl_2 solution using a syringe pump. The biocomposites were incubated in the crosslinking solution for 30 minutes, collected by filtration, and washed with deionized water.

2.6 Study of insulin release from biocomposites

Insulin release was quantified using a UV-7504 spectrophotometer (Shanghai Hansom Technology & Sales Limited, China; wavelength range: 200–1000 nm) at the characteristic absorbance maximum of 280 nm, corresponding to aromatic amino acid residues (tyrosine) in the insulin structure. Optical density (absorbance) was measured in the UV-visible range using a spectrophotometer and a quartz cuvette with an optical path length of 1 cm. Drug-loaded biocomposites were immersed in 20 mL of buffer solution with a pH of 7.4 and incubated at 37°C with stirring (100 rpm). At predetermined intervals, aliquots of the buffer were withdrawn and analyzed for insulin concentration. Each aliquot was replaced with an equal volume of fresh buffer to maintain constant volume.

The cumulative drug release was calculated using the following equation:

$$\text{Drug released (\%)} = \frac{C_t}{C_\infty} \cdot 100 \% \quad (2)$$

where (C_t) represents the concentration of the drug released at time (t), determined via the UV-Vis calibration curve equation ($\text{Abs} = m \cdot C + b$) and (C_∞) is the theoretical concentration of insulin upon complete release from the biocomposite.

2.7 Infrared spectroscopy

IR spectra of samples (sodium alginate, gelatin, CaCl_2 , montmorillonite) were recorded using a Cary 660 Agilent FTIR spectrometer (Agilent Technologies, USA), range 7900 - 375 cm^{-1} , signal-to-noise ratio 10000:1.

3. Results and Discussion

3.1 The effect of cation valence and concentration on the network density of ionotropically formed alginate hydrogels

Alginate hydrogels were obtained via ionotropic gelation using multivalent cations (Ca^{2+} and Fe^{3+}) at varying concentrations (0.5–2.0%). Hydrogels cross-linked with calcium ions exhibited greater stability than those formed with Fe^{3+} , with stability increasing proportionally to cation concentration. The study demonstrated that the cation valence influences the structure of the hydrogels and their behavior in an aqueous environment. The swelling kinetics (K) of alginate gels, shown in Figures 1 and 2, demonstrated that Ca^{2+} -crosslinked samples continued to swell for 180 minutes across all CaCl_2 concentrations. The highest swelling rate was observed at 1.5% CaCl_2 , where K values exceeded those of 0.5%, 1.0%, and 2.0% solutions by 1.08, 0.65, and 0.79 arbitrary units, respectively. During hydrogel synthesis, the 1.5% CaCl_2 concentration was identified as optimal, producing more pronounced swelling compared to other concentrations (Figure 1).

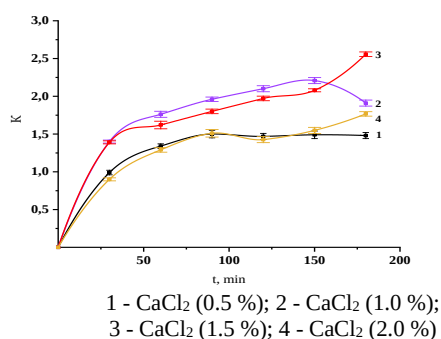


Figure 1 – Swelling kinetics of alginate hydrogels crosslinked with Ca^{2+} ions in aqueous media.

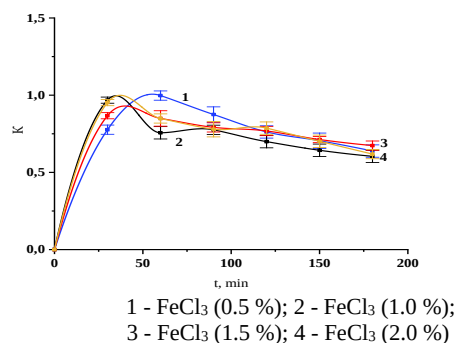


Figure 2 - Swelling kinetics of alginate hydrogels cross-linked with Fe^{3+} ions in aqueous media.

In contrast, hydrogels crosslinked with Fe^{3+} ions exhibited markedly lower swelling capacity. The maximum swelling kinetics for Ca^{2+} -based gels reached 2.55 arbitrary units, whereas Fe^{3+} -based gels did not exceed 1.0 arbitrary units (Figure 2).

3.2 Synthesis of stimuli-responsive (pH-Sensitive) and magneto-sensitive ionotropic biocomposites

To obtain pH-sensitive ionotropic biocomposite hydrogels, gelatin was introduced into sodium alginate. Specifically, gelatin was added to the sodium alginate solution at concentrations of 2%, 5%, and 8% at a 1:1 ($V_1:V_2$) ratio. The swelling kinetics of these gels in aqueous medium were subsequently investigated (Figure 3). The study demonstrated that the swelling rate of alginate - gelatin hydrogels at gelatin concentrations of 2%, 5%, and 8% exceeded that of pure alginate gels by 1.06, 1.6, 1.35, and 2.66 u.c., respectively. The highest swelling

kinetics were observed with the incorporation of 8% gelatin, identifying this concentration optimal for the synthesis of pH-sensitive biocomposite hydrogels. To impart magnetic responsiveness, magnetic montmorillonite particles were incorporated into the hydrogel matrix. In the initial step, magnetite particles were introduced into the alginate–gelatin solution prior to gelation, resulting in the formation of biocomposites containing magnetic montmorillonite.

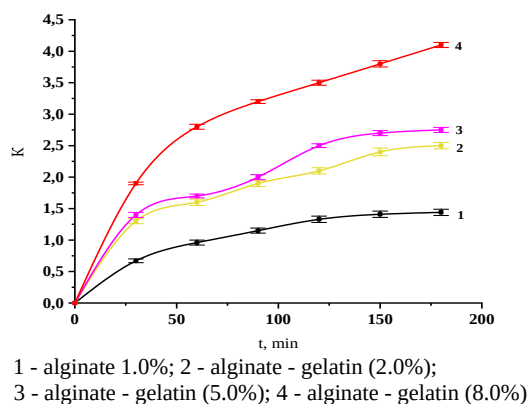


Figure 3 - Changes in the swelling kinetics of biocomposite hydrogels in aqueous medium.

Magnetic properties were confirmed using an external magnet. The resulting samples were dried at room temperature (Figure 4), after which their swelling kinetics were evaluated (Figure 5).

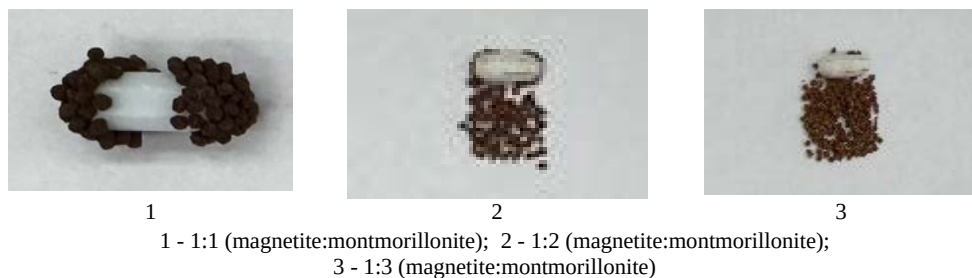


Figure 4 - Synthesized samples of biocomposite hydrogels with magnetically sensitive properties

The resonant frequency values of hydrogel-gelatin composites are given below in Table 2.

Table 2 - Resonant frequency values of biocomposites

Mass of introduced magnetite	0.1 g	0.25 g	0.5 g
Magnetite:MMT ratio			
1:1	4.314 MHz	4.312 MHz	4.310 MHz
1:2	4.348 MHz	4.346 MHz	4.345 MHz

1:3	4.335 MHz	4.345 MHz	4.354 MHz
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The magnetic properties of the synthesized biocomposites were indirectly evaluated by measuring the shift in the resonant frequency of the inductive circuit. As shown in Table 2, the resonant frequency values (expressed in MHz) vary depending on the mass of the introduced magnetite and the Magnetite:MMT ratio. The introduction of magnetic nanoparticles into the polymer matrix alters the magnetic core inductance within the measuring coil, which consequently shifts the resonant frequency. This frequency response serves as an indicator of the magnetic loading and distribution within the alginate-gelatin biocomposite network. Specifically, for the control biocomposite sample without magnetic additives, the resonant frequency was found to be 4.318 MHz. Upon the incorporation of magnetic components into the matrix, a systematic decrease in the resonant frequency was observed, signifying a pronounced increase in the magnetic sensitivity of the material. This effect is primarily attributed to the presence of structured magnetite particles capable of interacting with an external magnetic field [18-24]. Beyond the magnetic characteristics, the structural integration of the mineral phase, particularly montmorillonite (MMT), significantly influences the matrix behavior. As a result, the introduction of MMT markedly affects the swelling capacity of the biocomposites, with the overall effect being strictly dependent on the pH of the medium and the total filler content (Figure 5).

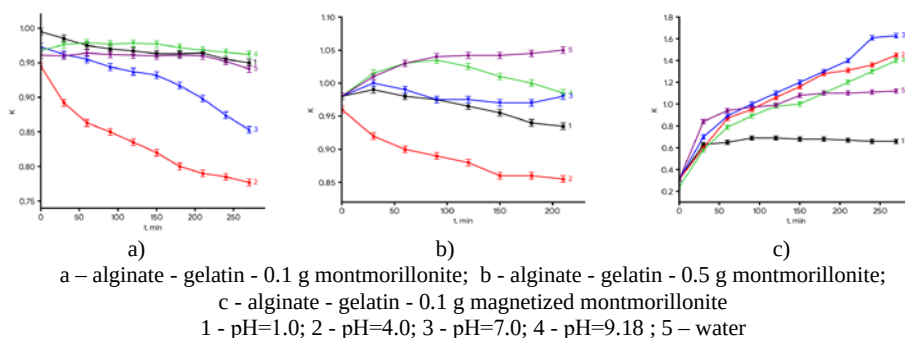
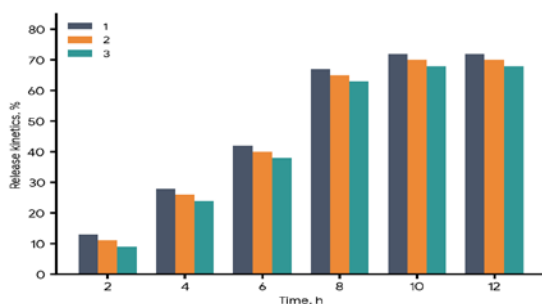


Figure 5 - Dependence of the swelling kinetics of biocomposites in the presence of montmorillonite

At low pH (1.0 - 4.0), swelling of the biocomposites is restricted due to protonation of the carboxyl groups of sodium alginate, which reduced hydrophilicity. Under neutral and slightly alkaline conditions (pH 7.0 - 9.18), dissociation of these groups enhances hydration through electrostatic repulsion between polymer chains. The addition of 0.1 g of montmorillonite increases swelling as a result of additional water sorption, however, increasing the montmorillonite mass to 0.5 g leads to structural compaction and reduced polymer chain mobility. Magnetized montmorillonite (0.1 g) exerts a more pronounced effect owing to its enhanced sorption capacity and uniform particle

distribution, while also enabling controlled manipulation under an external magnetic field. Thus, modification of biocomposites with montmorillonite provides a means of regulating swelling behavior, and the incorporation of magnetic fillers establishes a foundation for the development of biomaterials with tunable properties. Differences in the kinetics of insulin release from biocomposites were examined following the addition of montmorillonite and its magnetized form at pH 7.4 (Figure 6). The original sample exhibited a relatively high insulin diffusion rate -approximately 72% - due to the pronounced hydrophilicity and porous structure of the polysaccharide matrix. Upon incorporation of montmorillonite, the release rate decreased as a result of additional intermolecular interactions between the functional groups of the polysaccharides and the mineral layers. This modification increased gel density and restricted diffusion pathways for the insulin macromolecule.



1 – alginate - gelatin; 2 – alginate - gelatin - montmorillonite;
3 – alginate - gelatin - magnetized montmorillonite

Figure 6 - Kinetics of insulin release from biocomposites with the addition of montmorillonite in a physiological solution at pH = 7.4

Of particular interest was the system containing magnetized montmorillonite, in which insulin release was further delayed. This effect can be attributed to additional coordination and electrostatic interactions between the iron-containing centers and the polar groups of the protein, thereby enhancing the matrix's retention capacity. Consequently, the incorporation of montmorillonite-especially in its magnetized form-ensures prolonged release of the biologically active compound [21-23]. The influence of montmorillonite on the structure of alginate-gelatin polymer hydrogels was also studied using IR spectroscopy (Table 3).

Table 3 - Characteristic absorption bands in the IR spectra of the starting components and composite hydrogels

Sample/ Component	Wave number (cm ⁻¹)	Intensity	Assignment/ Functional Group
Sodium alginate	2636 1605 1100–1020	Weak/ Moderate Strong, sharp Very strong	Asymmetric C-H stretching Carboxylate (COO ⁻) stretching C-O-C carbohydrate skeleton

Gelatin	3300 1230–1245	Broad, strong Medium	Amide A stretching Amide I (C=O) & Amide III stretching
Alginate-gelatin- MMT	Shifted 1045–1030 470–520	Strong / Variable Very strong Moderate	Asymmetric COO ⁻ vibrations Si-O-Si silicate framework Si-O and M-O-Si stretching
Alginate-gelatin- mag-MMT	516 Shifted	Moderate / Sharp Strong, modified	Fe-O band appearance COO ⁻ & Amide II stretching (shifted)

The introduction of montmorillonite into the alginate-gelatin system resulted in a shift in the absorption band of carboxylate groups (COO⁻) and a change in the peaks of the carbohydrate skeletal peaks within the 1100–1020 cm⁻¹ region. These spectral changes indicate the formation of electrostatic interactions and hydrogen bonding between the polymer matrix and the silicate layers of montmorillonite. Following modification of montmorillonite with magnetite, the spectrum exhibited a distinct and intense peak at a frequency of 516 cm⁻¹, corresponding to the stretching vibrations of the Fe-O bond. This serves as direct physicochemical confirmation of the successful magnetization process [26–30].

Furthermore, coordination of iron ions with the carboxyl groups of alginate and the amide structures of gelatin resulted in a pronounced band shift and a change in peak intensity in the IR spectrum. The resulting spectral effects indicate the formation of a highly stable magnetic composite.

4. Conclusion

The principal outcome of this study is the development of an optimal technology for synthesizing a new generation of biocomposites with tunable polymer network density, achieved by varying the content of chemical, ionotropic, and physical crosslinking units. These biocomposites exhibit dual stimuli-responsiveness (pH and magnetic sensitivity) and demonstrate a more sustained release of immobilized drugs compared to conventional ionotropic polysaccharide hydrogels. The enhanced ability to prolong the physiological action of drugs underscores the practical significance of this approach and highlights its potential for advanced therapeutic applications.

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Conflict of Interest: The authors declare no conflicts of interest requiring disclosure in this article.

КӨПВАЛЕНТТІ ИОНДАР ЖӘНЕ МОДИФИКАЦИЯЛАНҒАН МОНТМОРИЛЛОНИТ НЕГІЗІНДЕ БИОКОМПОЗИТТЕРДІ ҚҰРЫЛЫМДЫҚ ОҢТАЙЛАНДЫРУ

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Түйіндемe. *Кіріспе.* Қазіргі заманғы биомедицина мен фармакологиядағы негізгі міндеттердің бірі – дәрілік заттардың бөлінуі реттелетін жоғары тиімді терапиялық жүйелерді әзірлеу. *Мақсаты.* Бұл зерттеу ионотропты геледену әдісімен алынған альгинатты гидрогельдердегі полимерлік торлардың айқаспалы байланысу дәрежесіне катиондардың валенттілігі мен концентрациясының әсерін қарастырады. *Нәтижелер және талқылау.* Синтезделген материалдардың құрылымдық ерекшеліктері физика-химиялық талдау әдістері арқылы сипатталды. Физиологиялық тұзды ерітіндіге иммобилизделген дәрілік заттардың бөліну жылдамдығы мен ісіну кинетикасына егжей-тегжейлі талдау жасалды. Қоршаған ортаның қышқылдығының өзгеруіне жауап бере алатын, тітіркендіргіштерге сезімтал (рН-қа тәуелді) ионотропты биокөмпозиттер синтезделді. Монтмориллонит пен оның магниттелген түрін енгізу кезінде альгинат-желатин биокөмпозиттерінен инсулиннің бөліну кинетикасындағы айырмашылықтарды зерттеуге ерекше назар аударылды. Магниттелген монтмориллонит нанобөлшектерін енгізу ақуыздық препараттың бөлінуін ұзартып қана қоймай, сонымен қатар сыртқы магнит өрісінің әсерімен мақсатты тасымалдауға мүмкіндік беретіні анықталды. *Қорытынды.* Алынған нәтижелер биокөмпозиттік гидрогельдердің құрылымы мен физика-химиялық қасиеттерін мақсатты түрде реттеудің тиімді тәсілдерін көрсетеді; бұл дәрілік заттарды бақыланатын және мақсатты жеткізуге арналған терапиялық жүйелерді құру жолындағы маңызды қадам болып табылады.

Түйінді сөздер: гидрогель, ионотропты биокөмпозиттер, монтмориллонит, магнитті сезімталдық, бөлшектер, модификация, ісіну дәрежесі

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СТРУКТУРНАЯ ОПТИМИЗАЦИЯ БИОКОМПОЗИТОВ С ИСПОЛЬЗОВАНИЕМ МНОГОВАЛЕНТНЫХ ИОНОВ И МОДИФИЦИРОВАННЫХ МОНТМОРИЛЛОНИТА

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Резюме. *Введение.* В современной биомедицине и фармакологии одной из ключевых задач является создание высокоэффективных терапевтических систем с контролируемым высвобождением лекарственных веществ. *Цель.* В работе исследовано влияние валентности катионов и их концентрации на степень сшивки полимерных сеток в альгинатных гидрогелях, полученных методом ионотропного гелеобразования. *Результаты и обсуждение.* Методами физико-химического анализа изучены структурные особенности синтезированных материалов. Проведен детальный анализ кинетики набухания и скорости высвобождения иммобилизованных лекарственных препаратов в физиологический раствор. Синтезированы стимулчувствительные (рН-зависимые) ионотропные биокөмпозиты, способные реагировать на изменение кислотности среды. Особое внимание уделено изучению различий в кинетике высвобождения инсулина из альгинат-желатиновых биокөмпозитов при введении монтмориллонита и его магнетизированной формы. *Заключение.* Установлено, что включение магнетизированных наночастиц монтмориллонита позволяет не только пролонгировать выход белкового препарата, но и открывает перспективы для направленного транспорта под воздействием внешнего магнитного поля. Полученные результаты демонстрируют эффективные подходы к направленному управлению

структурой и физико-механическими свойствами биокompозитных гидрогелей, что является важным шагом для создания терапевтических систем контролируемого и адресного высвобождения лекарственных веществ.

Ключевые слова: гидрогель, ионотропные биокompозиты, монтмориллонит, магниточувствительность, частиц, модификация, степень набухания

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RESEARCH OF THE TECHNOLOGY FOR PRODUCING A GRANULATED COMPOSITION BASED ON MONOMETHYLOUREA, COPPER AND ZINC PHYTOCOMPOUNDS, CALCIUM PHOSPHATES OF MONOETHANOLAMINE

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Abstract: *Introduction.* Conventional active substances used for cotton and grain seed treatment belong to toxicity classes II–III, negatively affecting soil fertility and agricultural product quality. This study focuses on low-toxic (class IV) preparations. *Objective.* To study the pilot-scale production technology of a granulated multifunctional composition based on monomethylolurea, copper and zinc phytocompounds, mono- and dicalcium phosphate, and phosphate monoethanolamine. *Methods.* Experiments were conducted at the pilot plant of LLP “Scientific and Production Association Ana-Zher” using a screw granulator (L = 4.7 m, D = 0.8 m). *Results.* The optimal solid-to-liquid composition ratio was 0.80:0.20. At a 30-min residence time, the yield of 1–4 mm granules was 83% for MMM and FSCu • MCP (150 kg/h; moisture 0.95%), 85% for MMM and FSZn • DCP (160 kg/h; 0.93%), and 82% for MMM • FMEA (145 kg/h; 0.94%). *Conclusion.* The selected parameters ensure production of a high-quality granulated preparation with favorable physicochemical and commercial properties.

Keywords: monomethylol urea, phytochemistry of copper, phytochemistry of zinc, monocalcium phosphate, dicalcium phosphate, phosphate monoethanolamine, technology, physical and chemical characteristics

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1. Введение

Действующие вещества применяемые в растениеводстве композиции для протравливания семян хлопчатника и зерновых относятся к токсичным соединениям (II, III класс), что негативно влияет на почвенное плодородие и качество получаемой сельхозпродукции [1-8]. Так действующие вещества фунгицидной части инсекто-фунгицидной композиции, по данным [1, 2, 4, 6], а также по патентам RU 2773310C1 и RU 1614163C состоят из прохлораза, пираклостробина, тебуконазола, по патенту US 2010/0248960A1 – эпоксиконазола/метконазола, по патенту RU 2722755C1 – тиаметоксама + дифеноконазола + флудиоксонила, которые пагубно влияют на полезную микрофлору почвы, обеспечивающие питание растений. Препаративная форма композиции – суспензия, что усложняет его перевозку, хранение.

В данной статье рассматривается технология получения препаративной формы гранулированной композиции полифункционального действия с протравливающим эффектом семян хлопчатника и зерновых на основе: монометиолмочевины (МММ) и фитосоединения меди (ФССu)• монокальцийфосфата (МКФ); монометиолмочевины (МММ) и фитосоединения цинка (ФСZn)•дикальцийфосфата (ДКФ) [9]; монометиолмочевины (МММ)• фосфатмоноэтаноламина (ФМЭА) [10] в опытно-промышленных условиях ТОО «Научно-производственное объединение Ана-Жер» (лицензионный номер на эксплуатацию 22017311 от 20.09.2022 г.).

2. Экспериментальная часть

2.1 Объекты исследования и технические характеристики оборудования

Объектами исследования является препараты полифункционального действия с протравливающим эффектом семян хлопчатника и зерновых на основе МММ и ФССu•МКФ, МММ и ФСZn•ДКФ, МММ•ФМЭА. Технологические исследования проведены на опытно-промышленной установке ТОО НПО «Ана Жер», основные технические характеристики, которых представлены в таблице 1.

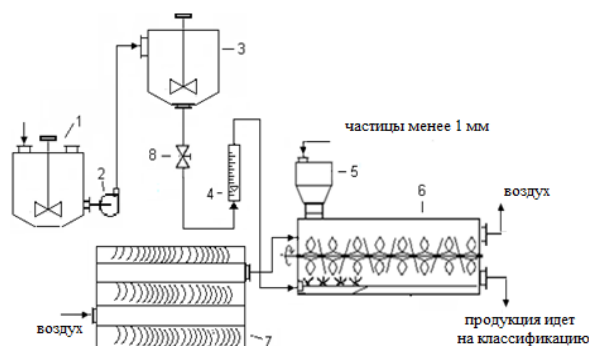
Таблица 1 – Технические характеристики оборудования для получения гранулированной композиции

Наименование	Кол-во	Материалы изготовления	Техническая характеристика
Шнековый гранулятор	1	нерж. сталь (н/ж) 316L	L = 4,7 м, D = 0,8 м
Реактор	1	сталь 3 с титановой футеровкой	V = 1200 л
Напорная емкость	1	н/ж 316L	V = 1200 л
Насос центробежный	1	н/ж 316L	BAW-1, 0,37 кВт, d = 25 – 89мм, 2740 об/мин

Расходомер	1	н/ж 316L	Расход до – 50л/мин
Калорифер биметаллический, спирально-накатный	1	КСк 3-6	L – 650 мм; Н – 602 мм; В – 575 мм; масса – 34 кг

2.2 Описание технологии получения препаративной формы композиции

Упрощенная технологическая схема получения препаративной формы гранулированной композиции полифункционального действия на основе смеси МММ и ФССу•МКФ, МММ и ФСЗп•ДКФ, МММ•ФМЭА исследована на опытно-промышленной установке ТОО НПО «Ана Жер» (рисунок 1).



1 – сборник суспензированной смеси МММ и ФССу•МКФ, МММ и ФСЗп•ДКФ, МММ•ФМЭА; 2 – насос; 3 – напорная емкость; 4 – расходомер; 5 – бункер; 6 – шнековый гранулятор; 7 – калорифер; 8 – вентиль.

Рисунок 1 – Упрощенная технологическая схема получения препаративной формы композиции полифункционального действия на основе МММ и ФССу•МКФ, МММ и ФСЗп•ДКФ, МММ•ФМЭА в опытно-промышленных условиях.

Суспензированная композиция готовится реакторе 1 при мольном отношении 1:1 исходных реагентов, температуре 25-35 °С и времени перемешивания 30-40 минут, далее посредством насоса 2 поступает в напорную емкость 3, откуда через расходомер 4 подается в шнековый гранулятор 6 и распыляется на завесу твердой композиции размером частиц менее 1 мм, поступающей из бункера 5. Для сушки продукции горячий воздух с температурой 80-85 °С подается из калорифера 7. Готовый продукт выгружается на классификацию и затаривание.

3. Результаты и их обсуждение

Входными параметрами при определении оптимальных технологических параметров гранулированной композиции полифункционального действия с протравливающим эффектом семян хлопчатника и зерновых явились: массовое отношение твердой композиции

к суспензированной (ТК:СК), равное 0,90:0,10; 0,80:0,20; 0,70:0,30, время пребывания реагентов в реакционной зоне 30 мин (таблица 2).

Выходными параметрами явились: выход гранул размером менее 1 мм, 1–4 мм, более 4 мм, производительность, влажность продукции (φ) (таблица 2), диаметр сводообразующего отверстия, просеиваемость по Мерингу, угол естественного откоса (таблица 3).

Обоснование входного параметра при определении оптимальных технологических параметров гранулированной композиции. Выбор массового отношения (ТК:СК), равный 0,90:0,10; 0,80:0,20; 0,70:0,30, определен оптимальными соотношениями ТК:СК при гранулообразовании за счет слипания отдельных частиц. Равновесная влажность ТК при относительной влажности атмосферы (ϕ_k) 80 % на основе МММ и ФССу•МКФ – 3,5 мас.%, МММ и ФСЗп•ДКФ – 3,3 мас.%, МММ•ФМЭА – 3,8 мас.% определяет получение продукции с хорошими физико-химическими товарными свойствами. Время пребывания реагентов в зоне грануляции 30 мин определено временем пребывания реагентов в опытно-промышленном шнековом грануляторе.

Результаты технологических исследований получения гранулированной композиции протравливающим эффектом семян хлопчатника и зерновых на основе МММ и ФССу•МКФ, МММ и ФСЗп•ДКФ, МММ•ФМЭА, а также их физико-химические и товарные характеристики представлены в таблицах 2 и 3.

Таблица 2 – Результаты технологических исследований получения гранулированной композиции протравливающим семян эффектом на основе МММ и ФССу•МКФ, МММ и ФСЗп•ДКФ, МММ•ФМЭА

Входные параметры		Выходные параметры				
массовое отношение ТК : СК	время пребывания реагента в реакционной зоне, мин	выход гранул, %			производи- тельность, кг/час	влажность продукции (φ), масс. %
		менее 1 мм	1 – 4 мм	более 4 мм		
МММ и ФССu•МКФ						
0,90 : 0,10	30	43	50	7	160	0,83
0,80 : 0,20		7	83	10	150	0,95
0,70 : 0,30		10	65	25	145	0,98
МММ и ФСЗп•ДКФ						
0,90 : 0,10	30	40	52	8	165	0,85
0,80 : 0,20		5	85	10	160	0,93
0,70 : 0,30		8	72	20	150	0,97
МММ•ФМЭА						
0,90 : 0,10	30	38	47	15	150	0,90
0,80 : 0,20		4	82	14	145	0,94
0,70 : 0,30		6	69	25	138	0,98

Из полученных данных технологических исследований (таблица 2) в случае композиции на основе МММ и ФССu•МКФ при массовом отношении на твердой композиции к суспензированной (ТК:СК) равной 0,90:0,10 выход гранул размером менее 1 мм составляет 43%, более 4 мм – 7% и товарной продукции размером 1–4 мм всего 50%. Также неудовлетворительные данные получены при массовом отношении ТК:СК = 0,70:0,30. Выход товарной продукции составила 65%, при гранул размером менее 1 мм – 10%, более 4 мм – 25%. Оптимальным является отношения ТК:СК = 0,80:0,20, где выход товарной продукции имеет значение 83%, при влажности продукции (ϕ) – 0,95%.

В случае МММ и ФСZn•ДКФ при массовом отношении на твердой композиции к суспензированной (ТК:СК) равной 0,90:0,10 выход гранул размером менее 1 мм составляет 40%, более 4 мм – 8% и товарной продукции размером 1–4 мм всего 52%. Также неудовлетворительные данные получены при массовом отношении ТК:СК = 0,70:0,30. Выход товарной продукции составила 72%, при гранул размером менее 1 мм – 8%, более 4 мм – 20%. Оптимальным является отношения ТК:СК = 0,80:0,20, где выход товарной продукции имеет значение 85%, при влажности продукции (ϕ) – 0,93%.

Аналогическая закономерность наблюдается в случае композиции на основе МММ•ФМЭА. При массовом отношении твердой композиции к суспензированной (ТК:СК) равной 0,90:0,10 выход гранул размером менее 1 мм составляет 38%, более 4 мм – 15% и товарной продукции размером 1 – 4 мм всего 47%. Данные полученные при массовом отношении ТК:СК=0,70:0,30 составляет: выход товарной продукции – 69%, при гранул размером менее 1 мм – 6%, более 4 мм – 25%. Оптимальным является отношения ТК:СК=0,80:0,20, где выход товарной продукции имеет значение 82%, при влажности продукции (ϕ) – 0,94%.

Полученные товарные продукты МММ и ФССu•МКФ, МММ и ФСZn•ДКФ, МММ•ФМЭА с выходом 83%, 85% и 82% соответственно (таблица 3), обладают хорошими физико-химическими и товарными свойствами, характеризующийся равновесной влажностью при относительной влажности 80%, влажностью гранулированной продукции, диаметром сводообразующего отверстия, просеиваемостью по Мерингу, углом естественного откоса.

Таблица 3 – Физико-химические и товарные характеристики гранулированной композиции протравливающим семян эффектом на основе МММ и ФССu•МКФ, МММ и ФСZn•ДКФ, МММ•ФМЭА

Композиции	Равновесная влажность композиции при относитель. влаж. 80%, $\phi_{\text{к}}$	Влажность готовый продукции ϕ , масс. %,	Диаметр сводообразующего отверстия гранул размером 1-4мм, мм	Просеиваемость по Мерингу гранул размером 1-4 мм, балл	Угол естественного откоса гранул размером 1-4 мм, град.
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МММ и ФССu•МКФ	3,5	0,95	10	более 8	31
МММ и ФCZn•ДКФ	3,3	0,93	10	более 8	29
МММ•ФМЭА	3,8	0,94	10	более 8	30

4. Заключение

На опытно-промышленной установке, состоящей из шнекового гранулятора, реактора, сборника, центробежного насоса, расходомера, калорифера биметаллической спирально-накатанной исследована малоотходная технология, получения гранулированной композиции полифункционального действия с протравливающим эффектом семян хлопчатника и зерновых на основе МММ и ФССu•МКФ, МММ и ФCZn•ДКФ, МММ•ФМЭА.

Определены следующие оптимальные технологические параметры получения гранулированного препарата на основе:

– МММ и ФССu•МКФ – массовое отношение ТК:СК = 0,80:0,20, время пребывания реагентов в реакционной зоне 30 мин, при которых выход гранул размером 1–4 мм – 83 %, производительность установки – 150 кг/ч, влажность продукции (φ) – 0,95 %, диаметр сводообразующего отверстия 10 мм, просеиваемость по Мерингу более 8 баллов, угол естественного откоса 31°;

– МММ и ФCZn•ДКФ – массовое отношение ТК:СК = 0,80:0,20, время пребывания реагентов в реакционной зоне 30 мин, при которых выход гранул размером 1–4 мм 85 %, производительность установки – 160 кг/ч, влажность продукции (φ) – 0,93 %, диаметр сводообразующего отверстия 10 мм, просеиваемость по Мерингу более 8 баллов, угол естественного откоса 29°;

– МММ•ФМЭА – массовое отношение ТК:СК = 0,80:0,20, время пребывания реагентов в реакционной зоне 30 мин, при которых выход гранул размером 1–4 мм 82%, производительность установки – 145 кг/ч, влажность продукции (φ) – 0,94 %, диаметр сводообразующего отверстия 10 мм, просеиваемость по Мерингу более 8 баллов, угол естественного откоса 30°.

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МОНОМЕТИЛОЛМОЧЕВИНА, МЫС ПЕН МЫРЫШТЫҢ ФИТОҚОСЫЛЫСТАРЫ ЖӘНЕ МОНОЭТАНОЛАМИН КАЛЬЦИЙ ФОСФАТТАРЫ НЕГІЗІНДЕ ТҮЙІРШІКТЕЛГЕН КОМПОЗИЦИЯ АЛУ ТЕХНОЛОГИЯСЫН ЗЕРТТЕУ

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Түйіндемесі: *Кіріспе.* Мақта және дәнді дақылдар тұқымдарын өңдеуде қолданылатын дәстүрлі әсер етуші заттар уыттылықтың II–III кластарына жатады, бұл топырақ құнарлылығына және ауыл шаруашылығы өнімдерінің сапасына кері әсер етеді. Зерттеуде уыттылығы төмен, IV класқа жататын заттар негізіндегі препараттар қарастырылды. *Мақсаты.* Монометилломочевина, мыс және мырыш фитокосылыстары, моно- және дикальцийфосфат, сондай-ақ моноэтанолламин фосфаты негізіндегі көпфункционалды композицияның түйіршіктелген дәрілік түрін пилоттық жағдайда өндіру технологиясын зерттеу. *Әдістері.* Зерттеулер «Ана-Жер» ғылыми-өндірістік бірлестігі» ЖШС пилоттық қондырғысында L = 4,7 м, D = 0,8 м шнекті грануляторды пайдалану арқылы жүргізілді. *Нәтижелері.* Қатты және сұйық композициялардың оңтайлы массалық қатынасы 0,80:0,20 болды. 30 минут реакциялық аймақта болған кезде 1–4 мм түйіршіктердің шығымы MMM және FSCu • MCP үшін 83% (150 кг/сағ; ылғалдылығы 0,95%), MMM және FSZn • DCP үшін 85% (160 кг/сағ; 0,93%), ал MMM • FMEA үшін 82% (145 кг/сағ; 0,94%) құрады. *Қорытынды.* Таңдалған технологиялық параметрлер физика-химиялық және тауарлық қасиеттері жақсы, сапалы түйіршікті препарат алуды қамтамасыз етеді.

Түйінді сөздер: монометилломочевина, мыс фитокосылысы, мырыш фитокосылысы, монокальций фосфаты, дикальций фосфаты, фосфатмоноэтанолламин, технология, физика-химиялық сипаттамалары.

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ИССЛЕДОВАНИЕ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ ГРАНУЛИРОВАННОЙ КОМПОЗИЦИИ НА ОСНОВЕ МОНОМЕТИЛОЛМОЧЕВИНЫ, ФИТОСОЕДИНЕНИИ МЕДИ И ЦИНКА, КАЛЬЦИЙФОСФАТОВ МОНОЭТАНОЛАМИНА

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Резюме. *Введение.* Традиционные действующие вещества, применяемые для обработки семян хлопчатника и зерновых культур, относятся ко II–III классам токсичности, отрицательно влияя на плодородие почвы и качество сельскохозяйственной продукции. В работе рассматриваются препараты на основе малотоксичных веществ IV класса. *Цель.* Изучить технологию получения в

условиях пилотной установки гранулированной полифункциональной композиции на основе монометилломочевина, фитосоединений меди и цинка, моно- и дикальцийфосфата и фосфата моноэтаноламина. *Методы.* Исследования проведены на пилотной установке ТОО «Научно-производственное объединение Ана-Жер» с использованием шнекового гранулятора ($L = 4,7$ м, $D = 0,8$ м). *Результаты.* Оптимальное соотношение твердой и жидкой композиций составило 0,80:0,20. При времени пребывания 30 мин выход гранул размером 1–4 мм составил 83% для МММ и FSCu • MCP (150 кг/ч; влажность 0,95%), 85% для МММ и FSZn • DCP (160 кг/ч; 0,93%) и 82% для МММ • FMEA (145 кг/ч; 0,94%). *Заключение.* Выбранные параметры обеспечивают получение качественного гранулированного препарата с благоприятными физико-химическими и товарными свойствами.

Ключевые слова: монометилломочевина, фитосоединение меди, фитосоединение цинка, монокальцийфосфат, дикальцийфосфат, фосфатмоноэтаноламин, технология, физико-химические характеристики.

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FORMATION OF A POROUS SILICA-RICH MATRIX FROM CHRYSOTILE-ASBESTOS WASTE FOR POTENTIAL APPLICATION IN SILICON REMOVAL FROM PROCESS SOLUTIONS

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Abstract: Silicon-containing species in uranium-bearing process solutions can accumulate on ion-exchange materials, impairing mass transfer and sorption efficiency. Inexpensive porous inorganic materials for preliminary silicon removal are therefore of practical interest. This study aimed to evaluate how thermal, chemical and mechanical post-treatment affects the porous structure of a silica-rich product obtained by hydrochloric acid leaching of chrysotile-asbestos waste, in order to select a promising matrix for sorption studies. Raw material underwent magnetic separation followed by HCl leaching. Five products were examined: material calcined at 650 °C; material calcined at 850 °C (1 h) and modified with 5% NiSO₄ and 10% MoO₄; material calcined at 650 °C for 52 h; leached product before attrition; and the same product after attrition. Textural properties were assessed via low-temperature N₂ adsorption using BET, Langmuir, t-plot and BJH methods. The BET specific surface area of the samples varied from 56.55 to 169.02 m²/g. The most favorable textural characteristics were observed for the leaching product without additional grinding: the specific surface area was 169.02 m²/g, the micropore area was 44.72 m²/g, the t-plot micropore volume was 0.0180 cm³/g, and the average pore diameter was 3.89 nm. After attrition, surface area remained high (165.99 m²/g) while total pore volume increased to 0.1951 cm³/g. Calcination at 650 °C and prolonged 52-h calcination reduced surface area to 106.61 and 91.41 m²/g, respectively; combined 850 °C treatment with Ni–Mo modification gave the lowest value (56.55 m²/g). HCl leaching was the key step forming the porous silica matrix. The unattrited leached product was selected as the most promising matrix for silicon removal from uranium solutions.

Keywords: chrysotile-asbestos waste, hydrochloric acid leaching, amorphous silica, inorganic adsorbent, BET, BJH, porosity, silicon removal, uranium process solutions

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1. Introduction

Chrysotile asbestos production waste is a large-scale man-made magnesium silicate raw material, the recycling of which is of interest from both an environmental and resource-saving perspective [1-3]. The main mineral in this waste is chrysotile, with the composition $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$, whose structure can be significantly transformed by acid exposure. During acid leaching, magnesium predominantly passes into solution, while the solid residue is enriched with silica and, due to the destruction of the original magnesium silicate structure, acquires a developed porous surface [4-5]. This creates the preconditions for the production of silica-containing materials from chrysotile-asbestos waste, potentially suitable as matrices for sorption and other functional materials.

The functional properties of silica-containing materials are largely determined by their textural characteristics, including specific surface area, total pore volume, micro- to mesopore ratio, and pore size distribution. A well-developed porous structure ensures surface accessibility for interaction with solution components, while the presence of surface silanol groups enables further chemical modification of the silica matrix [6]. In this regard, acid processing of magnesium silicate man-made raw materials is of interest not only as a method for extracting soluble components, but also as an approach to the formation of a porous silica-containing product with potential sorption properties.

One potential application for such materials is the preliminary removal of silicon-containing components from hydrometallurgical process solutions. In particular, in uranium productive solutions, dissolved and colloidal forms of silicon can accumulate in the pore space and on the surface of ion-exchange materials, impairing mass transfer and reducing the efficiency of uranium sorption extraction [7,8]. Therefore, the development of inexpensive porous materials for preliminary silicon reduction before the main ion-exchange stage is of practical interest [9,10]. At this stage, however, the primary task is to obtain and texturally evaluate a suitable porous matrix, while its effectiveness directly in the silicon removal process requires separate experimental study.

For Kazakhstan, this area is of additional importance due to the presence of man-made waste from chrysotile asbestos production. Work on processing waste from the Zhitikarinskoye deposit demonstrated the possibility of combining magnetic separation and acid leaching to produce silica-containing products with a developed surface area [11]. However, the production of a silica-containing product alone does not determine its suitability as a matrix for a functional material, as subsequent thermal, chemical, and mechanical processing steps can significantly alter the resulting pore structure. The impact of such processing on the specific surface area, pore volume, and pore size distribution of products from the acid processing of chrysotile asbestos waste requires separate assessment.

The aim of the work is to establish the patterns of change in the specific surface area and porous structure of the silica-containing product of hydrochloric acid leaching of chrysotile asbestos waste with various methods of subsequent processing and to justify the choice of the most promising matrix base for the

creation of an inorganic chemisorbent intended for the preliminary removal of silicon compounds from process solutions before the sorption extraction of uranium.

2. Experimental part

The textural characteristics of the samples were determined by low-temperature nitrogen adsorption on an EASY-V3210 analyzer using an N_2 –He gas system. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method and the Langmuir model. Micropore and external surface area were estimated using the t-Plot method; mesopore size distribution, cumulative pore area, and pore volume were estimated using the Barrett–Joyner–Halenda (BJH) method using the adsorption and desorption isotherms.

The feedstock used was man-made waste from chrysotile asbestos production, with a particle size of -1.0 to $+0.25$ mm. The feedstock was subjected to dry magnetic separation to produce magnetic (17.5–18.0%) and non-magnetic (82.0–82.5%) fractions. The composition of the non-magnetic fraction sent for subsequent leaching was, wt. %: MgO – 39,0–41,3; SiO_2 – 33,4–36,5; CaO – 0,5–1,4; Fe_2O_3 – 2,7; Fe_3O_4 – 4,9. The non-magnetic fraction was leached with an HCl solution with a concentration of 0.45 mol/l at a solid-to-liquid ratio (S:L) = 1:5, a temperature of 75 °C and a duration of 3 hours from the moment the operating temperature was reached. The resulting solid residue was washed with water at an S:L ratio of 1:2, then filtered and dried. The content of the silica component in the resulting product reached 78–80 wt. %. The scheme of preliminary magnetic separation of the source material is shown in Figure 1.

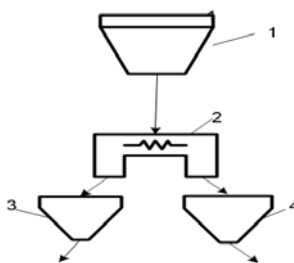


Figure 1 – Hardware diagram of magnetic separation of chrysotile-asbestos waste: 1 – feedstock bin; 2 – magnetic separator; 3 – non-magnetic fraction; 4 – magnetic fraction.

Magnetic separation separated the original chrysotile asbestos waste into magnetic and non-magnetic fractions. The magnetic fraction was separated from the main process stream, while the non-magnetic fraction, enriched in magnesium silicate, was sent for hydrochloric acid leaching, followed by the production of a silica-containing product. To evaluate the influence of subsequent thermal, chemical and mechanical treatment on its porous structure, five samples were prepared, the conditions for obtaining which are given in Table 1.

Table 1 – Conditions for obtaining the test samples

№	Sample	Treatment conditions of the product after leaching
1	Sand 1	Calcination at 650 °C
2	Sand 2	Calcination at 850 °C for 1 h and modification with 5% NiSO ₄ and 10% MoO ₄
3	Sand 3	Calcination at 650 °C for 52 h
4	Sand 4	Product before the abrasion operation
5	Sand 5	Product after the abrasion operation

3. Results and Discussion

Hydrochloric acid leaching was accompanied not only by changes in the chemical composition but also by a significant restructuring of the original magnesium silicate structure. X-ray diffraction (XRD) analysis was performed using a Rigaku MiniFlex 600 diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$), operated at 40 kV and 15 mA. The diffraction patterns were recorded over a 2θ range of $5\text{--}80^\circ$ with a step size of 0.02° and a scanning rate of $[\text{specify}]^\circ/\text{min}$.

The X-ray diffraction pattern of the product after leaching showed a decrease in the intensity of the characteristic diffraction peaks and diffuse scattering in the 2θ range of approximately $15\text{--}35^\circ$, indicating the formation of a disordered, predominantly amorphous silica-containing component.

Thermogravimetric analysis performed using a Q-1500D derivatograph (Paulik–Paulik–Erdey system, Hungary) revealed successive stages of water removal at 110, 140, and 170 °C. The total loss of hydration water over the temperature range of $40\text{--}310^\circ\text{C}$ was 8.45%. The presence of various forms of bound water and OH groups was consistent with the structural heterogeneity of the surface after acid treatment.

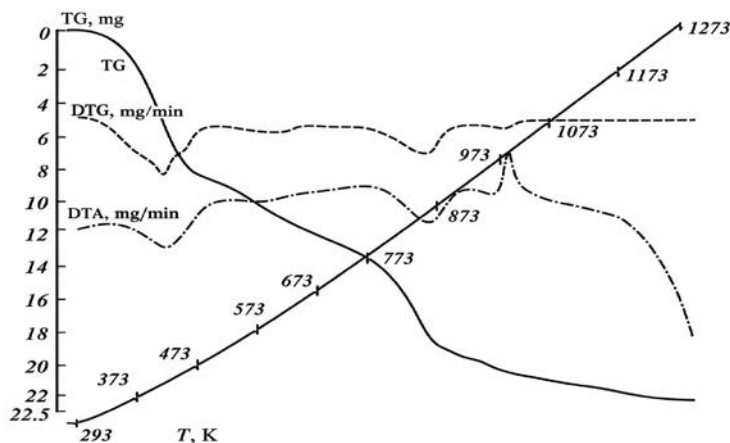


Figure 2 – Thermogravimetric curves of the residue after leaching.

To confirm the extent of structural disordering, X-ray phase analysis was performed on the leached product, comparing peak positions and intensities with the initial crystalline phase (Figure 3).

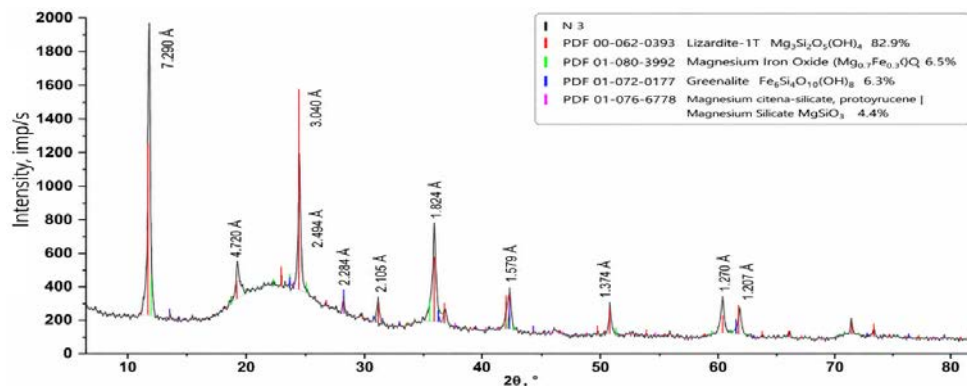


Figure 3 – X-ray diffraction pattern of the residue after leaching.

FTIR spectroscopy was additionally used to characterize surface functional groups and confirm the presence of OH groups and silica-containing fragments consistent with the acid-leached structure (Figure 4).

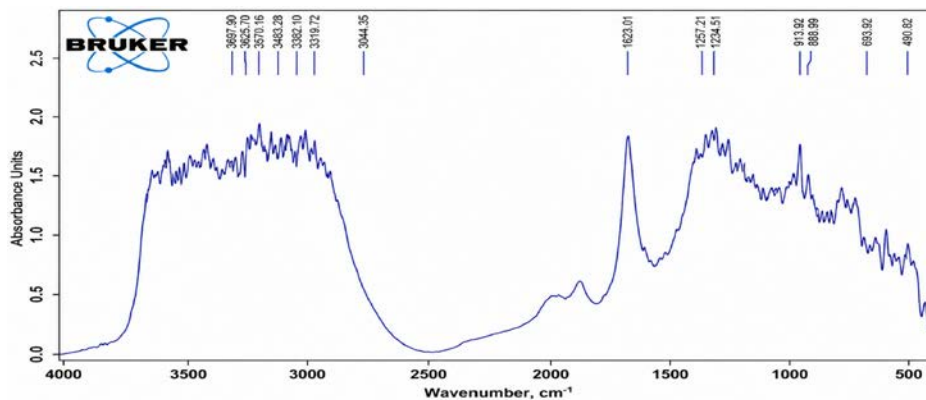


Figure 4 – IR spectrum of the product after leaching.

The results showed a significant dependence of textural characteristics on the type of post-treatment applied (Table 2). The specific surface area of BET varied from 56.55 to 169.02 m²/g across the five samples studied.

Table 2 – Main textural characteristics of the studied samples

Sample	Specific surface area BET, m ² /g	Specific surface area of Langmuir, m ² /g	Micropore area, m ² /g	Outer surface, m ² /g	Total pore volume, sm ³ /g	Micropore volume t-Plot, sm ³ /g	Average pore size, nm
1 650 °C	106,61	168,39	4,74	101,87	0,1179	0,00151	4,42
2 850 °C + Ni–Mo	56,55	73,72	5,30	51,25	0,1211	0,00185	8,57
3* 650 °C, 52 h	91,41	135,29	—	—	0,1556	0	6,81
4* before abrasion	169,02	214,27	44,72	124,31	0,1644	0,01802	3,89
5 after abrasion	165,99	192,77	42,31	123,68	0,1951	0,01779	4,70
<i>Note – BET is the Brunauer–Emmett–Teller specific surface area; t-Plot is the method for assessing the microporous and external surface area Sample 4 (highlighted) was selected as the most promising matrix; t-Plot micro/outer surface values for Sample 3 were not determined.</i>							

The maximum surface area was determined for Sample 4 (product after leaching, before the attrition operation): S_{BET} = 169.02 m²/g, micropore area = 44.72 m²/g, external surface area = 124.31 m²/g, total pore volume = 0.1644 cm³/g, and average pore size = 3.89 nm – identifying it as the most promising matrix among all samples tested (Table 3).

Table 3 – Comparative interpretation of textural characteristics

Sample	S _{BET} , m ² /g	Key features	Interpretation
4 – before abrasion	169,02	Maximum BET-surface area and micropore area	The most promising matrix
5 – after abrasion	165,99	Maximum total pore volume 0,1951 sm ³ /g	Abrasion increases pore volume
1 – 650 °C	106,61	Surface reduction after firing	Heat treatment reduces the available surface
3 – 650 °C, 52 h	91,41	Average pore size 6,81 nm	Long firing further reduces S _{BET}
2 – 850 °C + Ni–Mo	56,55	Smallest S _{BET} ; pore size 8,57 nm	Cumulative treatment produces the coarsest pore structure

Firing at 650 °C (sample 1) was accompanied by a decrease in S_{BET} to 106.61 m²/g and micropore area to 4.74 m²/g. With prolonged exposure at 650°C for 52 hours (sample 3), the specific surface area further decreased to 91.41 m²/g, and the average pore size increased to 6.81 nm. This indicated a decrease in

accessible surface area with increasing thermal exposure. The lowest value of $S_{\text{BET}} = 56.55 \text{ m}^2/\text{g}$ was obtained for sample 2, which was fired at 850°C for 1 h and subsequently modified with NiSO_4 and MoO_4 compounds. The average pore size of this material was 8.57 nm . Since the processing temperature and surface chemical composition were changed simultaneously for this sample, the available data characterize the combined effect of these factors and do not allow a separate assessment of the contribution of each of them. Mechanical abrasion altered the pore space differently. After abrasion, S_{BET} decreased only from 169.02 to $165.99 \text{ m}^2/\text{g}$, while the total pore volume increased from 0.1644 to $0.1951 \text{ cm}^3/\text{g}$, and the average pore size increased from 3.89 to 4.70 nm . Consequently, mechanical action primarily affected the volumetric and size characteristics of the pores without further development of the specific surface area.

To preserve the original experimental data and visually compare the adsorption pattern, Figure 8 shows the initial N_2 adsorption-desorption isotherms from the EASY-V3210 analyzer reports for all five samples. The highest adsorption capacity was observed for samples 4 and 5, consistent with their maximum specific surface area values.

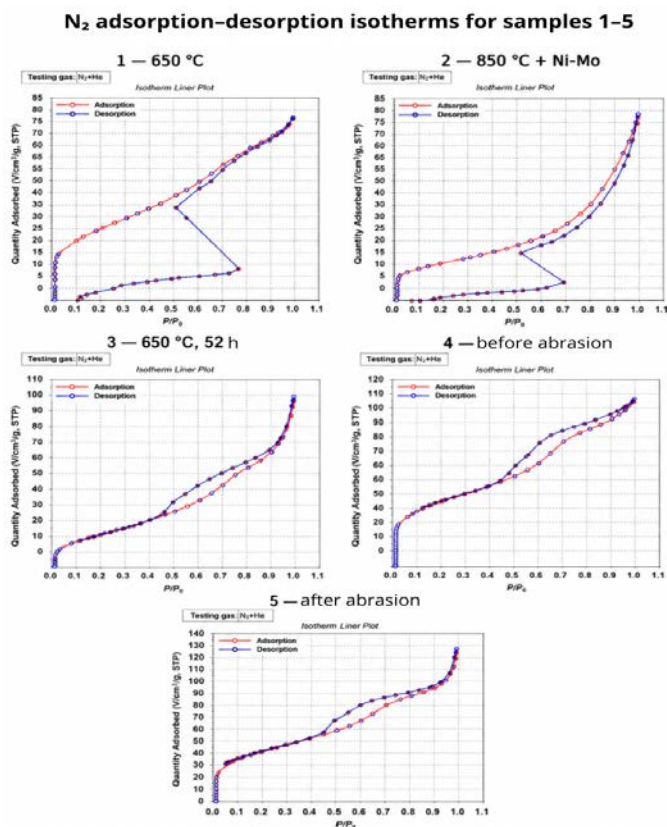


Figure 8 – N_2 adsorption-desorption isotherms for samples 1-5.

The pore size distribution calculated using the BJH method confirmed a significant change in the mesoporous component during thermal and mechanical treatment. For the thermally treated materials, the characteristic pore sizes shifted toward larger values, while sample 4 combined the maximum specific surface area with a smaller average pore size. The pore size distribution calculated by the BJH method for samples 1-5 is shown in Figure 9.

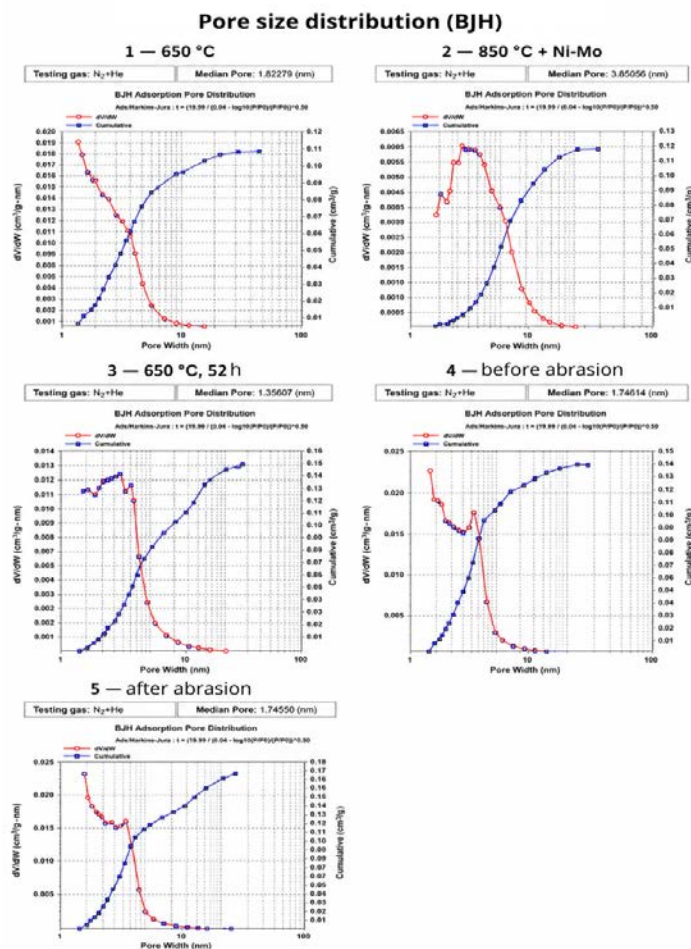


Figure 9 – Pore size distribution by the BJH method for samples 1–5.

According to the specific surface area of BET, the samples were arranged in the following sequence: 4 (169.02) > 5 (165.99) > 1 (106.61) > 3 (91.41) > 2 (56.55 m^2/g). Thus, the most developed surface was formed immediately after hydrochloric acid leaching and was preserved until additional thermal treatment. The obtained result is consistent with the literature data on the formation of

porous amorphized silica during acid destruction of chrysotile and serpentinite matrices [9–11].

Based on a combination of textural parameters, sample 4 was selected as the most promising matrix for further development of an inorganic chemisorbent. However, BET/BJH characteristics alone do not directly demonstrate high silicon sorption capacity; a final assessment must be made based on the results of individual sorption experiments to determine the degree of silicon removal and sorption capacity.

4. Conclusion

Hydrochloric acid leaching of chrysotile asbestos waste produced a silica-rich porous matrix containing 78–80 wt.% SiO₂. The leached product obtained before attrition exhibited the most favorable textural properties, with a BET specific surface area of 169.02 m²/g, a micropore area of 44.72 m²/g, a total pore volume of 0.1644 cm³/g, and an average pore diameter of 3.89 nm. These results demonstrate that acid leaching is the key stage responsible for magnesium removal and the development of the porous structure.

Subsequent processing affected the pore structure differently. Heat treatment at 650 °C, particularly prolonged annealing, reduced the accessible surface area, indicating partial densification or restructuring of the porous matrix. The combination of calcination at 850 °C and Ni–Mo modification produced the lowest BET specific surface area of 56.55 m²/g. In contrast, mechanical attrition had little effect on the BET surface area but increased the total pore volume to 0.1951 cm³/g, suggesting enlargement or improved accessibility of the pore system.

Overall, the leached product obtained before attrition provided the best balance of silica content, specific surface area, and pore characteristics. It was therefore selected as the most promising matrix for further investigation of the preliminary removal of silicon-containing species from process solutions prior to the sorption recovery of uranium. Future studies should evaluate its removal efficiency, selectivity, regeneration behavior, and performance under conditions representative of industrial process solutions.

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ТЕХНОЛОГИЯЛЫҚ ЕРІТІНДІЛЕРДЕН КРЕМНИЙДІ ЖОЮДА ӘЛЕУЕТТІ ҚОЛДАНУ
ҮШІН ХРИЗОТИЛ-АСБЕСТ ҚАЛДЫҚТАРЫНАН КЕУЕКТІ КРЕМНЕЗЕМҚҰРАМДЫ
МАТРИЦА ҚАЛЫПТАСТЫРУ

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Түйіндеме. Уран құрамдас ерітінділердегі кремний құрамдас түрлері ион алмасу материалдарында жиналып, масса алмасу мен сорбция тиімділігін төмендетуі мүмкін. Сондықтан кремнийді алдын ала кетіруге арналған арзан кеуекті бейорганикалық материалдар практикалық қызығушылық тудырады. Бұл зерттеу сорбциялық зерттеулер үшін перспективалы матрицаны таңдау мақсатында хризотил-асбест қалдықтарын тұз қышқылымен сілтілеу арқылы алынған кремнийге бай өнімнің кеуекті құрылымына термиялық, химиялық және механикалық өңдеуден кейінгі әсер етуді бағалауға бағытталған. Шикізат магниттік бөлуден, содан кейін HCl сілтілеуден өтті. Бес үлгі зерттелді: 650 °C-та күйдірілген өнім; 850 °C-та 1 сағ күйдіріліп, 5 % NiSO₄ және 10 % MoO₄ қосылыстарымен модификацияланған өнім; 650 °C-та 52 сағ күйдірілген өнім; үйкеліс операциясына дейінгі және одан кейінгі шаймалау өнімдері. Кеуектілік сипаттамалары азоттың төмен температуралық адсорбциясы, BET, Langmuir, t-Plot және BJH әдістерімен анықталды. Үлгілердің БЭТ әдісі бойынша меншікті бет ауданы 56,55-тен 169,02 м²/г-ға дейін өзгерді. Ең жақсы текстуралық сипаттамалар қосымша ұнтақтауға ұшыратылмаған сілтісіздендіру өнімінде байқалды: меншікті бет ауданы 169,02 м²/г, микрокеуектер ауданы 44,72 м²/г, t-график әдісі бойынша микрокеуектер көлемі 0,0180 см³/г, ал кеуектердің орташа диаметрі 3,89 нм болды. Үйкелістен кейін S_BET 165,99 м²/г деңгейінде сақталып, жалпы кеуек көлемі 0,1951 см³/г дейін артты. 650 °C температурада күйдіру және ұзаққа созылған 52 сағаттық күйдіру бетінің ауданын сәйкесінше 106,61 және 91,41 м²/г-ға дейін азайтты; Ni-Mo модификациясымен 850 °C температурада біріктірілген өңдеу ең төменгі мәнді берді (56,55 м²/г). Дамыған кремнеземді кеуекті матрицаны қалыптастыратын негізгі кезең тұз қышқылымен шаймалау болып табылды. Уран ерітінділерінен кремнийді кетіру үшін ең перспективалы матрица ретінде сілтісіздендіру өнімі таңдалды.

Түйінді сөздер: хризотил-асбест қалдықтары, тұз қышқылымен шаймалау, аморфты кремнезем, бейорганикалық адсорбент, BET, BJH, кеуектілік, кремнийді жою, уран ерітінділері

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ФОРМИРОВАНИЕ ПОРИСТОЙ КРЕМНЕЗЕМСОДЕРЖАЩЕЙ МАТРИЦЫ ИЗ ОТХОДОВ ХРИЗОТИЛ-АСБЕСТА ДЛЯ ПОТЕНЦИАЛЬНОГО ПРИМЕНЕНИЯ ПРИ УДАЛЕНИИ КРЕМНИЯ ИЗ ТЕХНОЛОГИЧЕСКИХ РАСТВОРОВ

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Резюме. Соединения кремния, присутствующие в технологических растворах, содержащих уран, могут накапливаться на ионообменных материалах, ухудшая массообмен и снижая эффективность сорбции. В связи с этим практический интерес представляют недорогие пористые неорганические материалы для предварительного удаления кремния. Целью данной работы было изучение влияния термической, химической и механической постобработки на пористую структуру продукта с высоким содержанием диоксида кремния, полученного путем солянокислотного выщелачивания отходов хризотил-асбеста, с целью выбора перспективной матрицы для сорбционных исследований. Исходное сырье подвергалось магнитной сепарации с последующим

выщелачиванием соляной кислотой. Были исследованы пять образцов: материал, прокаленный при 650 °C; материал, прокаленный при 850 °C (в течение 1 ч) и модифицированный 5% NiSO₄ и 10% MoO₄; материал, прокаленный при 650 °C в течение 52 ч; продукт выщелачивания до измельчения (аттриции); и тот же продукт после измельчения. Текстуальные характеристики оценивали методом низкотемпературной адсорбции азота с использованием моделей БЭТ (БЕТ), Ленгмюра, t-графика и метода Барретта-Джойнера-Халенды (ВЖН). Удельная площадь поверхности образцов по методу БЭТ варьировалась от 56,55 до 169,02 м²/г. Наилучшие текстурные характеристики были установлены для продукта выщелачивания без дополнительного измельчения: удельная площадь поверхности составила 169,02 м²/г, площадь микропор - 44,72 м²/г, объём микропор по методу t-графика - 0,0180 см³/г, а средний диаметр пор - 3,89 нм. После измельчения удельная площадь поверхности осталась высокой (165,99 м²/г), а общий объём пор увеличился до 0,1951 см³/г. Прокаливание при 650 °C и длительное прокаливание (52 ч) привели к снижению удельной площади поверхности до 106,61 и 91,41 м²/г соответственно; комбинированная обработка при 850 °C с модифицированием Ni–Mo дала наименьшее значение (56,55 м²/г). Выщелачивание соляной кислотой стало ключевой стадией формирования пористой кремнеземной матрицы. Продукт выщелачивания, не подвергавшийся измельчению, был выбран в качестве наиболее перспективной матрицы для удаления кремния из урансодержащих растворов.

Ключевые слова: отходы хризотил-асбеста, сернокислотное выщелачивание, аморфный кремнезем, неорганический адсорбент, БЕТ, ВЖН, пористость, удаление кремния, урановые растворы

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SYNTHESIS OF AMINOPHTHALIDES BASED ON MORPHOLINE AND CYTISINE ALKALOID

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Abstract. This work describes the investigation of the reactions between *o*-formylbenzoic acid and morpholine, as well as the alkaloid cytosine. This study is aimed at the synthesis of new aminophthalide derivatives as compounds of potential interest for biological evaluation. The interactions between the starting reagents were studied, and optimal synthesis conditions were determined to ensure high the amounts of desired compounds obtained. The structures, electronic properties of the initial substances, intermediates, and synthesized compounds were analyzed using quantum-chemical computations are based on density functional theory using a quantum-chemical research method. The molecular constitution of the obtained products were established based on their Infrared spectral data, one-dimensional ¹H, ¹³C and two-dimensional Nuclear Magnetic Resonance spectroscopy (COSY, HMQC, HMBC), and mass spectrometry. A possible reaction pathway accounting for the formation of aminophthalides is presented, involving the nucleophilic addition of secondary amines to the carbonyl group of *o*-formylbenzoic acid, followed by intramolecular cyclization. The spectral analysis is fully consistent with the proposed structure of the obtained compounds. The findings reveal the effectiveness of the established procedure for synthesizing aminophthalides based on morpholine and cytosine and provide the basis for further studies of their reactivity, physicochemical characteristics, and potential biological activity.

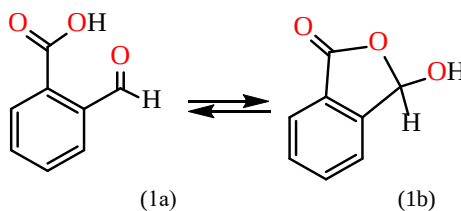
Keywords: *o*-formylbenzoic acid, morpholine, cytosine, aminophthalides, quantum chemical calculations, NMR spectroscopy, mass spectrometry

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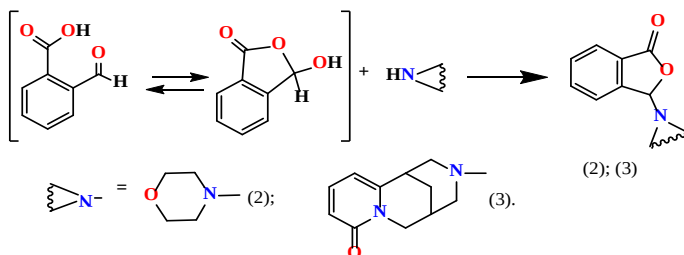
1. Introduction

The phthalide moiety serves as a key structural scaffold for compounds of practical importance, such as dyes, fungicides, natural oils (butylphthalide), and pharmaceuticals (isoxepac, vatalanib, hydralazine) [1-3]. Due to its broad spectrum of biological activity, the phthalide moiety is considered a promising pharmacophore platform. Of particular interest is the design of hybrid molecules ("dual drugs") containing two pharmacophore fragments, a strategy that can yield novel biological activity [4]. Aromatic compounds bearing active *ortho*-substituents are widely used in the synthesis of fused heterocyclic systems [5-7]. The presence of aldehyde and carboxyl groups in the *ortho*-position of such systems facilitates intramolecular cyclization [8]. A prime example is 2-formylbenzoic acid, which exists predominantly in the closed form in the solid state, whereas in solution, it exists in equilibrium between the open form (1a) and the cyclic 3-hydroxyphthalide form (1b)-an instance of ring-chain tautomerism. With the advancement of combinatorial chemistry, the scope of application for this compound continues to expand [9-12].

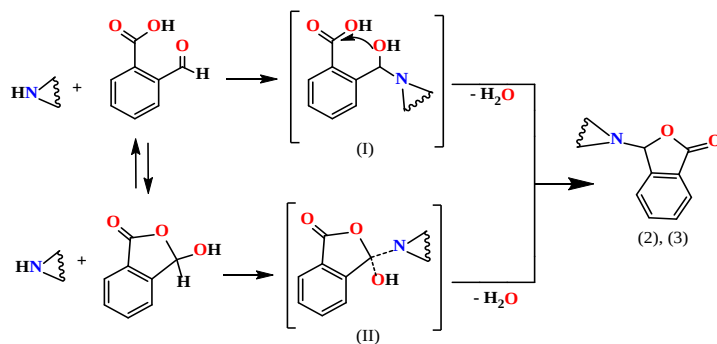


2. Results and discussion

In the search for new biologically active compounds, we investigated the reaction of *o*-formylbenzoic acid with morpholine and the alkaloid cytosine, yielding the corresponding 3-(3-oxo-1,3-dihydroisobenzofuran-1-yl)amines (2) and (3), respectively.



The formation of aminophthalides (2) and (3) can proceed via two mechanisms: through the nucleophilic addition of an amine to the aldehyde group of the open form of *o*-formylbenzoic acid, followed by intramolecular cyclization (I), or in a single step via the S_N^2 mechanism when an amine interacts with its cyclic form (II).



To study the geometric and electronic characteristics of the compounds under study, we carried out quantum chemical calculations using the density functional theory (DFT) method at the B3LYP/6-311G(d,p) level. Geometry optimization was performed without symmetry restrictions, and calculations were carried out in Gaussian 16W [13] with visualization of structures in GaussView 6.0 [14]. The resulting optimized structures are presented in Figure 1.

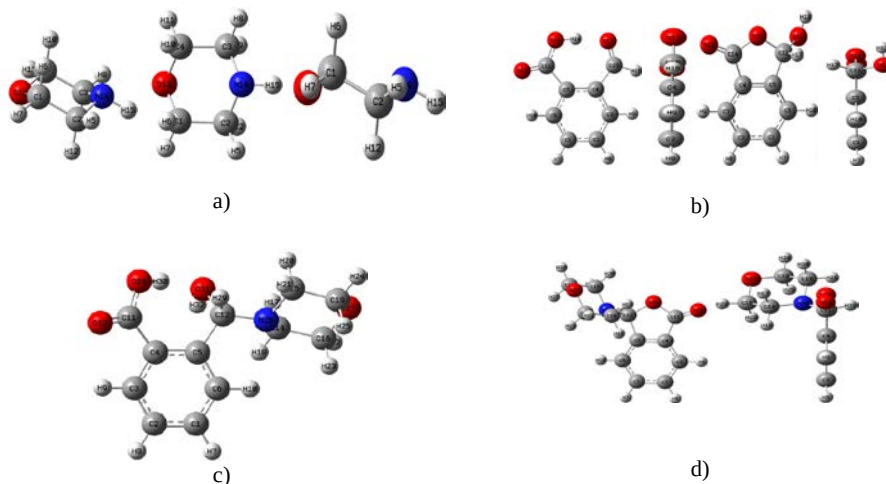


Figure 1 - Optimized 3D molecular configurations using the B3LYP/6-311G(d, p) method (top and side views; C atoms are shown in gray, Red - O, blue -N, white - H): a) morpholine; b) o-formylbenzoic acid; c) gem-amino alcohol; d) aminophthalide.

The calculated geometric parameters correspond to the energy minimum and are consistent with the standard values of chemical bonds and bond angles. For the systems under study, molecular characteristics have been determined, including the total energy (E_n), zero-point energy (E_0), ionization potential (IP), electron affinity (E_A), dipole moment (μ), entropy (S), and molar heat capacity (C_v).

Table 1 - Physicochemical characteristics of compounds (a-d) (method B3LYP/6-311G(d, p))

Characteristic	Optimized 3D molecular structures			
	a	b	c	d
E_p , a.u.	-287.8742681	-534.283849 (-534.283873)*	-822.1610836	-745.7149453
E_o , a.u.	0.134636	0.1249707 (0.126386)	0.2640155	0.2365821
μ , D	1.561	6.726 (4.286)	5.420	4.908
E_{HOMO} , eV	-6.225	-7.242 (-7.576)	-6.820	-6.682
E_{LUMO} , eV	1.084	-2.423 (-1.687)	-1.575	-1.611
ΔE , eV	-	3.22 (4.33)	-	-
S , cal/mol*K	73.077	93.274 (89.443)	120.572	111.681
C_v , cal/mol*K	20.567	33.027 (32.297)	57.451	50.243

Note – Values in parentheses refer to the closed form of *o*-formylbenzoic acid

According to calculations, the stability of molecules is determined by their structure and composition. The closed form of *o*-formylbenzoic acid is 63 J/mol more energetically stable than the open form, which indicates the possibility of their equilibrium. The dipole moment characterizes the distribution of electron density, while the ionization potential and electron affinity reflect the electronic properties of molecules and are assessed based on the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in accordance with Koopmans' theorem.

In the reaction, morpholine acts as a nucleophile, and *o*-formylbenzoic acid acts as an electrophile. The reactivity is determined by the energy gap between the highest occupied molecular orbital (HOMO) of the nucleophile and the lowest unoccupied molecular orbital (LUMO) of the electrophile: a reduction in this gap promotes the reaction. For the open form of the acid, this gap is smaller, which indicates its higher reactivity and the preferential formation of a *gem*-amino alcohol.

As a result of the interaction between *o*-formylbenzoic acid and morpholine and cytosine, new aminophthalide derivatives (2) and (3) were synthesized. The structure of the synthesized compounds (2) and (3) has been confirmed by IR, ^1H NMR, ^{13}C NMR, COSY, HMQC, HMBC spectroscopy and mass spectrometry. In the IR spectra, aminophthalides are characterized by intense bands of carbonyl absorption (1715–1750 cm^{-1}) and C–O–C bond vibrations (1050–1096 and 847–900 cm^{-1}). In the ^1H and ^{13}C NMR spectra of compound (2), signals from the morpholine and phthalide fragments were detected, while compound (3) showed

characteristic signals of the cytosine and phthalide fragments, which confirms the structure of the obtained compounds.

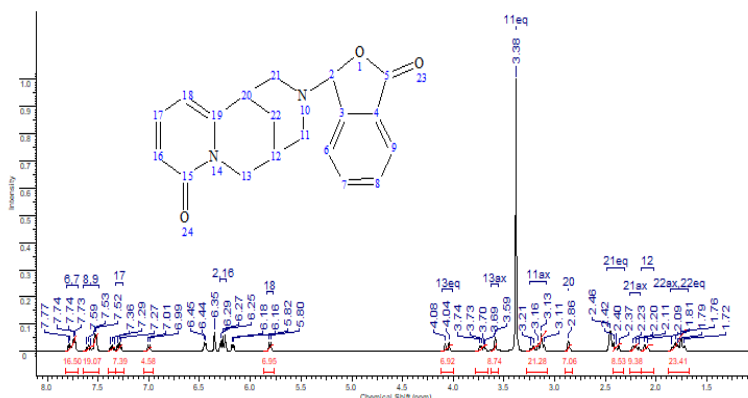


Figure 2 - ^1H NMR characteristics of compound (3)/

In the ^1H NMR spectrum of compound (3), the proton signals of the *bis*-piperidine fragment are observed in the region of 2.09–4.08 ppm, the aromatic protons of the cytosine fragment are observed at 5.80–7.31 ppm, and the phthalide fragment is observed at 7.51–7.79 ppm. In the ^{13}C NMR spectrum, the signals of the carbon atoms in the cytosine and phthalide fragments are located in characteristic ranges, which confirms the structure of the synthesized compound (3).

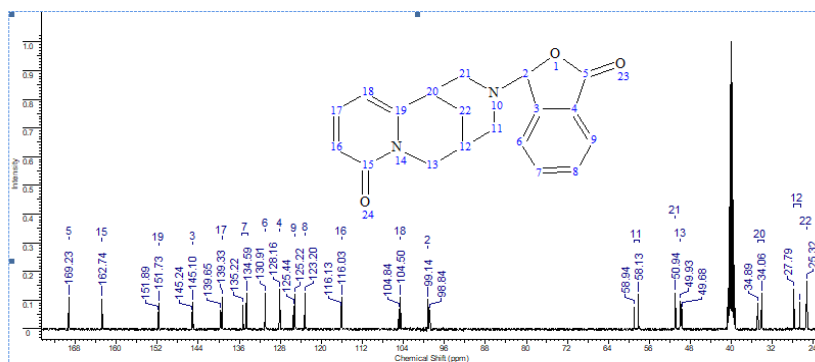


Figure 3 – NMR ^{13}C spectrum of compound (3).

The structure of compounds (2) and (3) was further confirmed using two-dimensional NMR spectroscopy methods: ^1H - ^1H COSY, ^1H - ^{13}C HMQC, and ^1H - ^{13}C HMBC. The identified short-range and long-range correlations between protons and carbon atoms correspond to the proposed structure of compound (2), confirming the relative arrangement of the morpholine, phthalide, and aromatic fragments. The ^1H - ^1H and ^1H - ^{13}C NMR connectivities determined by COSY, HMQC, and HMBC experiments for molecule (2) are depicted in Figure 4.

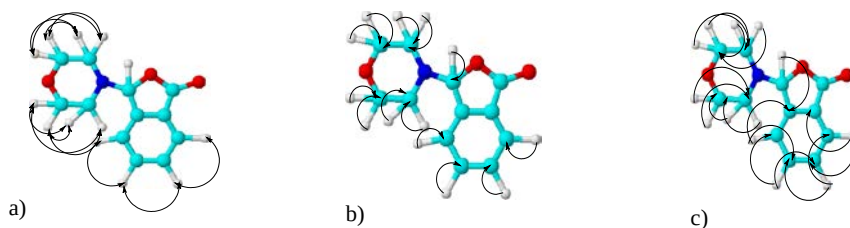


Figure 4 - Coupling diagram in the COSY (^1H - ^1H) (a), HMQC (^1H - ^{13}C) (b), and HMBC (^1H - ^{13}C) (c) spectra of compound (2).

The structure of compound (3) is additionally confirmed by data from two-dimensional NMR spectroscopy. In the ^1H - ^1H COSY and ^1H - ^{13}C HMQC spectra, characteristic correlations of protons with adjacent and directly bonded carbon atoms of the cytosine and phthalide fragments are established. The ^1H - ^{13}C HMBC method revealed distant correlations, confirming the relative arrangement of the functional groups and the correspondence of the obtained data to the proposed structure of compound (3). The observed COSY (^1H - ^1H), HMQC (^1H - ^{13}C) and HMBC (^1H - ^{13}C) NMR correlations within the molecule (3) shown in the Figure 5.

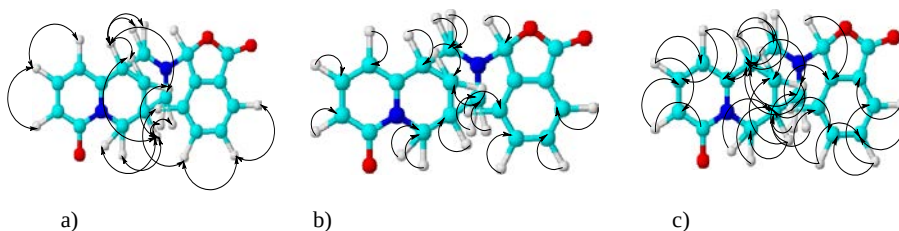


Figure 5 - COSY (a), HMQC (b), HMBC (c) correlation patterns observed for compound (3).

In the mass spectrum of compound (3), at $t = 23.95$ min, the molecular ion m/z 322.14 $[\text{M}]^+$ was detected, corresponding to the molecular mass of the compound. The most intense peak was observed at m/z 133.07. Characteristic fragment ions at m/z 146.08, 189.14, 207.05, 176.09, 160.09, 117.07, 105.07, and 77.10 were also observed, resulting from molecular fragmentation under electron impact. The obtained data confirm the structure and molecular mass of compound (3) (Fig. 6). Chromatographic-mass spectrometric analysis was carried out using a Trace GC Ultra-DSQ II gas chromatograph (Thermo Fisher Scientific, USA; 2006–2007).

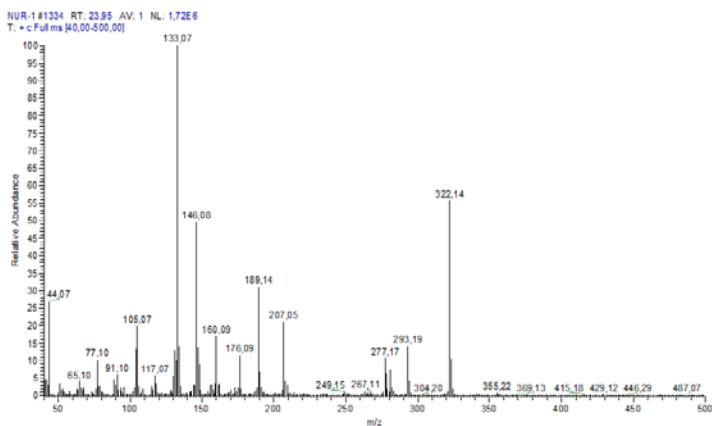


Figure 6 - Mass spectrum of compound (3), $t=23.95$

3. Experimental part

^1H and ^{13}C NMR measurements were carried out using a JNM-ECA Jeol 400 spectrometer operating at 399.78 and 100.53 MHz, respectively. DMSO- d_6 and CDCl_3 were employed as solvents. Chemical shifts were referenced to the residual proton and carbon resonances of the corresponding deuterated solvents. Melting points were measured with an «SMP10» apparatus. The synthesized products were monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates using ethyl acetate as a solvent system and visualization of spots in iodine vapor. For the original compound, $R_f \approx 0.44$, whereas for the synthesized 3-morpholinoisobenzofuran-1(3H)-one, $R_f \approx 0.34$.

Methods for the synthesis of aminophthalides morpholine (2) and cytosine (3).

3-Morpholinoisobenzofuran-1(3H)-one (2). A mixture of 2-carboxybenzaldehyde (3.4 g, 0.02 mol) and morpholine (2.0 g, 0.02 mol) in isopropyl alcohol (25 ml) was stirred at 40 °C for 3 hours, then 1–2 drops of glacial acetic acid were added. After cooling, the precipitate was filtered out. Yield: 3.9 g (83%), mp 129–130°C.

3-(Cytisin-1-yl)isobenzofuran-1(3H)-one (3). To the solution of cytosine (1.3 g, 0.0068 mol) in 25 ml of dry benzene, 2-carboxybenzaldehyde (1.02 g, 0.0068 mol) was added, and the mixture was heated for 3 hours with a Dean-Stark trap. After distilling off 2/3 of the solvent, a white precipitate formed upon cooling. The yield was 2.02 g (92.5%), with a melting point of 170–173°C.

4. Conclusion

The reaction of 2-formylbenzoic acid with amines (morpholine and cytosine) occurs under mild conditions and leads to the formation of 3-morpholinoisobenzofuran-1(3H)-one and 3-(cytisin-1-yl)isobenzofuran-1(3H)-one derivatives in high yields. The proposed reaction mechanism involves the nucleophilic addition of secondary amines to o-formylbenzoic acid followed by

intramolecular cyclization. Quantum chemical DFT calculations at the B3LYP/6-311G(d,p) level of theory determined the energy characteristics, dipole moments, ionization potentials, and electron affinities of the studied compounds.

МОРФОЛИН ЖӘНЕ АЛКАЛОИД ЦИТИЗИН НЕГІЗІНДЕГІ АМИНОФТАЛИДТЕРДІҢ СИНТЕЗІ

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Түйіндемe. Бұл мақалада *o*-формилбензой қышқылының морфолинмен және алкалоид цитизинмен реакциясын зерттеу нәтижелері ұсынылған. Бұл зерттеу болашағы зор биологиялық белсенді қосылыстар ретінде қызығушылық тудыратын жаңа аминфталид туындыларын синтездеуге бағытталған. Бастапқы, аралық және соңғы қосылыстардың геометриялық құрылымын, электрондық құрылымын және физика-химиялық сипаттамаларын зерттеу үшін B3LYP/6-311G(d,p) деңгейіндегі тығыздық функционалдық теориясын (ТФТ) қолданатын кванттық-химиялық есептеулер жүргізілді. Синтезделген қосылыстардың құрылымы ИК, бір өлшемді ¹H, ¹³C және екі өлшемді ЯМР спектроскопиясы (COSY, HMQC, HMBC) және масс-спектрометрия арқылы расталды. Бастапқы реагенттер арасындағы өзара әрекеттесулер зерттелді және мақсатты өнімдердің жоғары өнімділігін қамтамасыз ету үшін оңтайлы синтез жағдайлары анықталды. Аминфталидтердің түзілу механизмі ұсынылды, ол *o*-формилбензой қышқылының карбонил тобына екінші реттік аминдерді нуклеофильді қосуды, содан кейін молекулалық цикленуді қамтиды. Спектрлік талдау алынған қосылыстардың ұсынылған құрылымына толығымен сәйкес келеді. Алынған нәтижелер морфолин мен цитизин негізінде аминфталидтерді синтездеудің әзірленген әдісінің тиімділігін көрсетеді және олардың реактивтілігін, физика-химиялық сипаттамаларын және әлеуетті биологиялық белсенділігін одан әрі зерттеу үшін негіз болады.

Түйінді сөздер: *o*-формилбензой қышқылы, морфолин, цитизин, аминфталидтер, кванттық химиялық есептеулер, ЯМР спектроскопия, масс-спектрометрия

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СИНТЕЗ АМИНОФТАЛИДОВ НА ОСНОВЕ МОРФОЛИНА И АЛКАЛОИДА ЦИТИЗИНА

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Резюме. В работе представлены результаты исследования реакции *o*-формилбензойной кислоты с морфолином и алкалоидом цитизиним, направленной на синтез новых аминоталидных производных, представляющих интерес в качестве перспективных биологически активных соединений. Для исследования геометрического строения, электронной структуры и физико-химических характеристик исходных, промежуточных и конечных соединений проведены квантово-химические расчёты проведены с использованием теории функционала плотности (DFT) на уровне B3LYP/6-311G(d,p). Структуры синтезированных соединений подтверждены данными ИК, одномерной ¹H и ¹³C и двумерной ЯМР-спектроскопии (COSY, HMQC, HMBC), а также масс-спектрометрии. Изучены особенности взаимодействия исходных реагентов и определены оптимальные условия проведения синтеза, обеспечивающие получение целевых продуктов с высокими выходами. Предложен механизм образования аминоталидов, включающий нуклеофильное присоединение вторичных аминов к карбонильной группе *o*-формилбензойной кислоты с последующей внутримолекулярной циклизацией. Выполненный спектральный анализ полностью согласуется с предложенным строением полученных соединений. Полученные результаты свидетельствуют об эффективности разработанного метода синтеза аминоталидов на основе морфолина и цитизина и создают основу для дальнейших исследований их реакционной способности, физико-химических характеристик и потенциальной биологической активности.

Ключевые слова: *o*-формилбензойная кислота, морфолин, цитизин, аминоталиды, квантово-химические расчеты, ЯМР-спектроскопия, масс-спектрометрия.

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SYNTHESES AND STRUCTURE OF ALKYL AND DIALKYL
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Abstract. *Introduction.* Dithiocarbamates and their derivatives are promising sulfur-containing compounds used as flotation reagents in the flotation enrichment of mineral raw materials. Variations in the structure of the hydrocarbon substituent and the introduction of additional functional fragments make it possible to regulate their surface properties. The *aim* of this study was to synthesize new alkyl and dialkyl thioethers based on isopentylthiocarbamates and to establish their structures using IR and NMR spectral methods. *Results and discussion.* The reaction of isopentylamine with carbon disulfide in an alkaline medium yielded disodium isopentylbis(dithiocarbamate) and sodium isopentylthiocarbamate in 58% and 30% yields, respectively. The subsequent reaction of the salts with hexyl, heptyl, octyl, nonyl, and decyl bromides allowed the synthesis of a series of alkyl and dialkyl thioethers in 75–98% yields. The composition and structure of the synthesized compounds were confirmed by elemental analysis, IR, ¹H, and ¹³C NMR spectroscopy. Spectral characteristics indicate the presence of a dithiocarbamate fragment, an isopentyl substituent, and alkyl substituents of varying lengths. *Conclusion.* Synthetic conditions for a series of new isopentylthiocarbamate thioethers have been developed. The synthesized isopentylthiocarbamate thioethers with variable alkyl fragment lengths are of interest for further study of their flotation properties and the possibility of using them as flotation reagents.

Keywords: isopentylthiocarbamate, alkyl and dialkyl thioether, alkylation reaction, structure, IR, ¹H, and ¹³C NMR spectroscopy

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1. Introduction

Flotation remains one of the most widely used mineral beneficiation methods because it can separate minerals with very close physical characteristics. The problem of searching for new organic collectors, which ensure high recovery of valuable components with separation selectivity, becomes a priority.

Xanthates are the main flotation reagents for sulfide minerals. Although these compounds have been widely used in industry, there have been some limitations regarding selectivity, the possibility of forming toxic decomposition products, and the dependence of the action on environmental parameters. For these reasons, over the last few decades, there has been intensive research into alternative sulfur-containing compounds, among which dithiocarbamates have been considered one of the most promising classes of flotation reagents [1-3].

Dithiocarbamates exhibit high reactivity due to the presence of the $-NCS_2$ functional group, which enables complexation with surface metal ions. Interaction with the mineral surface results in the formation of stable metal-sulfur complexes, which alter the hydrophilicity and surface energy of the particles. This makes them suitable for use as both collectors and depressants in the separation of various types of mineral raw materials [4,5].

Among dithiocarbamine compounds, dithiocarbamates based on aliphatic amines are of particular interest, since they are distinguished by the availability of the starting components and the possibility of regulating the properties by changing the length and structure of the hydrocarbon substituent.

Studies have shown that simple aliphatic dithiocarbamates can effectively modify the surface properties of minerals. For example, sodium dimethyldithiocarbamate has a selective effect on the pyrite surface, reducing its hydrophobicity through the formation of hydrophilic complexes with surface iron cations [5]. In a lead-zinc mineral separation system, the combined use of $ZnSO_4$ and dimethyldithiocarbamate increased the efficiency of sphalerite suppression due to the competitive adsorption of reagents on the mineral surface [6].

Sodium diethyldithiocarbamate has also demonstrated high efficiency in the flotation of oxidized copper minerals. Its use in combination with xanthates was found to promote the formation of a more hydrophobic malachite surface due to the formation of Cu-S compounds and enhanced collector adsorption [7]. In the flotation of smithsonite, the use of a mixture of dodecylamine and diethyldithiocarbamate increased zinc recovery due to the combined physical and chemical adsorption of reagent system components [8]. In recent years, research on modified dithiocarbamate compounds containing additional functional groups has advanced significantly. These reagents possess multiple active sites for interaction with mineral surfaces and demonstrate increased efficiency in the flotation of difficult-to-process minerals. For example, dithiocarbamate-hydroxamate compounds have demonstrated excellent results in the recovery of bastnaesite, cassiterite, galena, chalcopyrite, and wolframite. Their high activity is explained by the formation of stable complexes between the reagent's functional groups and surface metal atoms [9-14].

Despite a significant amount of research devoted to dithiocarbamates, the synthesis and application of dithiocarbamates based on aliphatic amines, particularly their derivatives with a modified thioether structure, remain understudied. However, modification of dithiocarbamates can significantly affect their hydrophobicity, stability, and ability to interact with mineral surfaces.

In this regard, the preparation of new alkyl thioethers based on sodium isopentyl dithiocarbamate is of interest. The introduction of a thioether moiety into the dithiocarbamate structure can alter the electronic and surface properties of the molecule, potentially enabling the production of effective flotation reagents with improved collection properties.

The aim of this work is to synthesize alkyl thioethers based on sodium isopentyl dithiocarbamate as potential flotation reagents.

2. Experimental part

The reaction control and product purity were monitored by thin-layer chromatography (TLC) on Silufol UV-254 plates, with spot visualization performed using iodine vapor. The eluent consisted of a mixture of ethanol and acetone/hexane (1/4). Infrared (IR) spectra were recorded on a Nicolet 5700 FTIR spectrometer using KBr pellets and thin-layer films. Melting points were determined with a Hanon MP450 apparatus. The ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a JNM-ECA 400 spectrometer (JEOL), operating at 400 MHz for ^1H and 100 MHz for ^{13}C , using deuterated D_2O and CDCl_3 as solvents. Elemental analysis was performed with a THERMO FlashSmart CHNS/O elemental analyzer (USA, 2024).

Disodium isopentyl-bis(dithiocarbamate) (1). A solution of 8.0 g (0.2 mol) of NaOH in 3 mL of water was added to a solution of 8.717 g (0.1 mol) of isopentylamine in 110 mL of ethanol. Then a solution of 15.2 g (0.2 mol) of carbon disulfide was added dropwise at room temperature under stirring. After the complete addition of carbon disulfide, the reaction mixture was stirred at room temperature for four hours. The solvent was removed under reduced pressure using a water-jet vacuum pump and the solid residue was purified by recrystallization from ethanol. Yield 16.44 g (58%), $R_f = 0.84$ (ethanol/benzene, 1/2), $T_m = 296\text{--}297^\circ\text{C}$. Found, %: C, 29.27; H, 4.11; N, 4.69; Na, 16.32; S, 45.55. $\text{C}_7\text{H}_{11}\text{NNa}_2\text{S}_4$. Calculated, %: C, 29.67; H, 3.91; N, 4.94; Na, 16.22; S, 45.25. IR spectra, ν , cm^{-1} : 2931, 2852 (CH_2 , CH_3); 1470, 1421 (CH_2 , CH_3); 1221 ($=\text{C}-\text{N}$); 1109 ($\text{N}-\text{C}(\text{S})=\text{S}$); 966 ($\text{C}=\text{S}$); 883 ($\text{C}-\text{S}$). NMR ^1H spectra (D_2O), δ , ppm: 1.48 (7H, 2CH_3 , CH); 1.54 (2H, CH_2); 4.12 (t, 2H, $\text{N}-\text{CH}_2$). NMR ^{13}C spectra (D_2O), δ , ppm: 25.64 (CH_2 , 2CH_3); 23.78 (CH); 53.06 ($\text{N}-\text{CH}_2$); 205.05 ($2\text{C}=\text{S}$).

Sodium isopentyl dithiocarbamate (2). Yield 5.56 g (30%), $R_f = 0.93$ (ethanol/benzene, 1/2), $T_m = 107\text{--}108^\circ\text{C}$. Found, %: C, 39.05; H, 6.33; N, 7.29; Na, 12.71; S, 34.73. $\text{C}_6\text{H}_{12}\text{NNaS}_2$. Calculated, %: C, 38.90; H, 6.53; N, 7.56; Na, 12.41; S, 34.61. IR spectra, ν , cm^{-1} : 3369 (NH); 2936, 2852 (CH_2 , CH_3); 1470, 1421 (CH_2 , CH_3); 1221 ($=\text{C}-\text{N}$); 1131, 1111 ($\text{N}-\text{C}(\text{S})=\text{S}$); 1003, 967 ($\text{C}=\text{S}$); 883 ($\text{C}-\text{S}$). NMR ^1H spectra (D_2O), δ , ppm: 1.23 (t, 6H, 2CH_3); 1.50 (m, 2H, CH_2);

1.56 (m, 1H, CH); 4.35 (dt, 2H, N-CH₂). NMR ¹³C spectra (D₂O), δ, ppm: 13.63 (2CH₃); 23.80 (CH); 25.66 (CH₂); 53.08 (N-CH₂); 204.28 (C=S).

General procedure for the Synthesis of alkyl and dialkyl thioesters (3-12)

The corresponding alkyl bromide (hexyl, heptyl, octyl, nonyl and decyl) was added dropwise to a solution of dithiocarbamate in acetone. The reaction mixture was stirred at room temperature (22 °C) for five hours. After completion of the reaction, the mixture was filtered through a Schott funnel using a vacuum pump. The resulting solution was concentrated under reduced pressure using a water-jet vacuum pump, and the product was purified by recrystallization from hexane. The synthesis was applied to a series of alkyl bromides. As a result, the corresponding alkyl isopentyldithiocarbamate and dialkyl isopentyl bis(dithiocarbamate) derivatives were obtained.

Dihexyl isopentyl-bis(carbamodithioate) (3). Yield 9.30 g (76%), oil, R_f = 0.64 (acetone/hexane, 1/3), n_D^{20} 1.4031. Found, %: C, 55.64; H, 9.29; N, 3.67; S, 31.75. C₁₉H₃₇NS₄. Calculated, %: C, 55.97; H, 9.15; N, 3.44; S, 31.45. IR spectra, ν, cm⁻¹: 2930, 2856 (CH₂, CH₃); 1473, 1424 (CH₂, CH₃); 1241, 1226 (=C-N); 1133, 1116 (N-C(S)=S); 1006, 979 (C=S); 893, 854 (C-S). NMR ¹H spectra (CDCl₃), δ, ppm: 0.82 (s, 6H, 2CH₃ (hexyl)); 1.26 (s, 6H, 2CH₃ (isopentyl)); 1.36 (s, 1H, CH); 1.63 (s, 18H, 9CH₂); 3.22 (t, 4H, 2(S-CH₂)); 3.84-4.23 (br., d, N-CH₂). NMR ¹³C spectra (CDCl₃), δ, ppm: 14.10 (2CH₃ (hexyl)); 22.60 (2CH₃ (isopentyl)); 24.41 (2CH₂CH₃); 25.99, 25.56 (CH); 28.70, 28.78 (6CH₂); 31.46 (N-CH₂-CH₂); 37.37 (S-CH₂); 51.27, 52.75 (N-CH₂); 196.14 (2C=S).

Diheptyl isopentyl-bis(carbamodithioate) (4). Yield 9.94 g (76%), oil, R_f = 0.75 (acetone/hexane, 1/3), n_D^{20} 1.4032. Found, %: C, 57.45; H, 9.24; N, 3.54; S, 29.71. C₂₁H₄₁NS₄. Calculated, %: C, 57.88; H, 9.48; N, 3.21; S, 29.43. IR spectra, ν, cm⁻¹: 2928, 2855 (CH₂, CH₃); 1472, 1424 (CH₂, CH₃); 1228 (=C-N); 1133, 1116 (N-C(S)=S); 1006, 979 (C=S); 892, 854 (C-S). NMR ¹H spectra (CDCl₃), δ, ppm: 0.80 (s, 6H, 2CH₃ (heptyl)); 1.21 (br. s, 6H, 2CH₃ (isopentyl), CH₂); 1.34 (s, 1H, CH); 1.62 (br. s, 20H, 10CH₂); 3.21 (S-CH₂); 3.8-4.21 (N-CH₂). NMR ¹³C spectra (CDCl₃), δ, ppm: 14.14 (2CH₃ (heptyl)); 22.65 (2CH₃ (isopentyl)); 24.40 (2CH₂CH₃); 25.96, 25.57 (CH); 28.74, 28.94, 29.06 (8CH₂); 31.76 (N-CH₂-CH₂); 37.36 (2S-CH₂); 51.26, 52.72 (N-CH₂); 196.14 (2C=S).

Diocetyl isopentyl-bis(carbamodithioate) (5). Yield 13.64 g (98%), oil, R_f = 0.71 (acetone/hexane, 1/3), n_D^{20} 1.4033. Found, %: C, 59.21; H, 9.67; N, 3.31; S, 27.33. C₂₃H₄₅NS₄. Calculated, %: C, 59.56; H, 9.78; N, 3.02; S, 27.65. IR spectra, ν, cm⁻¹: 2927, 2856 (CH₂, CH₃); 1470, 1424 (CH₂, CH₃); 1238 (=C-N); 1133 (N-C(S)=S); 1007, 980 (C=S); 893, 854 (C-S). NMR ¹H spectra (CDCl₃), δ, ppm: 0.84 (t, 6H, 2CH₃ (octyl)); 1.24 (s, 18H, 2CH₃ (isopentyl), 6CH₂); 1.38 (s, 3H, CH, CH₂); 1.65 (t, 12H, 6CH₂); 3.25 (t, 4H, 2S-CH₂); 3.85, 4.25 (2s, 2H, N-CH₂). NMR ¹³C spectra (CDCl₃), δ, ppm: 14.21 (2CH₃ (octyl)); 22.74 (2CH₃ (isopentyl)); 24.44 (2CH₂CH₃); 25.82 (CH); 28.77, 29.15, 29.28 (10CH₂); 31.90 (N-CH₂-CH₂); 37.40 (2S-CH₂); 51.28, 52.79 (N-CH₂); 196.15 (2C=S).

Dinonyl isopentyl-bis(carbamodithioate) (6). Yield 12.7 g (86 %), oil, $R_f = 0.76$ (acetone:hexane = 1:3). n_D^{20} 1.4034. Found, %: C, 61.17; H, 10.3; N, 2.69; S, 25.74. $C_{25}H_{49}NS_4$. Calculated, %: C, 61.04; H, 10.04; N, 2.85; S, 26.07. IR spectra, ν , cm^{-1} : 2927, 2855 (CH_2 , CH_3); 1456, 1424 (CH_2 , CH_3); 1243, 1226 ($=C-N$); 1133, 1117 ($N-C(S)=S$); 1006, 981 ($C=S$); 893, 854 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.85 (t, 6H, 2 CH_3 (nonyl)); 1.23 (s, 18H, 2 CH_3 (isopentyl), 6 CH_2); 1.38 (s, 3H, CH, CH_2); 1.66 (t, 16H, 8 CH_2); 3.25 (t, 4H, 2S- CH_2); 3.86, 4.26 (2s, 2H, N- CH_2). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.21 (2 CH_3 (nonyl)); 22.76 (2 CH_3 (isopentyl)); 24.44 (2 $\underline{CH_2}CH_3$); 25.57, 26.05 (CH); 28.26, 28.70, 28.87, 29.15, 29.35, 29.56 (12 CH_2); 31.95 (N- $CH_2-\underline{CH_2}$); 37.41 (2S- CH_2); 51.27, 52.79 (N- CH_2); 196.18 (2C=S).

Didecyl isopentyl-bis(carbamodithioate) (7). Yield 13.9 g (89 %), oil, $R_f = 0.74$ (acetone/hexane, 1/3), n_D^{20} 1.4036. Found, %: C, 62.17; H, 10.44; N, 2.85; S, 24.36. $C_{27}H_{53}NS_4$. Calculated, %: C, 62.37; H, 10.27; N, 2.69; S, 24.66. IR spectra, ν , cm^{-1} : 2925, 2854 (CH_2 , CH_3); 1469, 1424 (CH_2 , CH_3); 1227, 1226 ($=C-N$); 1133, 1117 ($N-C(S)=S$); 1007, 981 ($C=S$); 892, 853 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.84 (t, 6H, 2 CH_3); 1.23 (s, 20H, 2 CH_3 , 7 CH_2); 1.38 (s 5H, CH, 2 CH_2); 1.65 (t, 16H, 8 CH_2); 3.25 (t, 4H, 2S- CH_2); 3.86, 4.26 (2s, 2H, N- CH_2). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.22 (2 CH_3 (decyl)); 22.77 (2 CH_3 (isopentyl)); 24.44 (2 $\underline{CH_2}CH_3$); 25.59, 26.04 (CH); 28.77, 29.15, 29.32, 29.41, 29.60, 29.65 (14 CH_2); 31.98 (N- $CH_2-\underline{CH_2}$); 37.42 (2S- CH_2); 52.81, 51.29 (N- CH_2); 196.20 (2C=S).

Hexyl isopentylcarbamodithioate (8). Yield 9.3 g (75 %), oil, $R_f = 0.72$ (acetone/hexane, 1/4, n_D^{20} 1.4037. Found, %: C, 58.06; H, 10.32; N, 5.81; S, 25.57. $C_{12}H_{25}NS_2$. Calculated, %: C, 58.24; H, 10.18; N, 5.66; S, 25.91. IR spectra, ν , cm^{-1} : 2928, 2858 (CH_2 , CH_3); 1463, 1425 (CH_2 , CH_3); 1217 ($=C-N$); 1133 ($N-C(S)=S$); 1053 ($C=S$); 855 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.86 (t, 6H, 2 CH_3 (hexyl)); 1.28 (t, 7H, 2 CH_3 (isopentyl), CH); 1.39 (t, 6H, 3 CH_2); 1.65 (t, 4H, N- $CH_2-\underline{CH_2}$, S- $CH_2-\underline{CH_2}$); 3.08 (t, 2H, S- CH_2); 4.61 (q, 2H, N- CH_2). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.11 (CH_3 (hexyl)); 22.60 (CH_3 (isopentyl)); 24.45 (CH); 28.42, 28.67, 28.74, 28.83 (4 CH_2); 31.39 (N- $CH_2-\underline{CH_2}$); 36.00 (S- CH_2); 69.82 (N- CH_2); 215.32 (C=S).

Heptyl isopentylcarbamodithioate (9). Yield 11.51 g (88 %), oil, $R_f = 0.81$ (acetone/hexane, 1/4), n_D^{20} 1.4038. Found, %: C, 59.31; H, 10.27; N, 5.55; S, 24.78. $C_{13}H_{27}NS_2$. Calculated, %: C, 59.71; H, 10.41; N, 5.36; S, 24.52. IR spectra, ν , cm^{-1} : 2927, 2856 (CH_2 , CH_3); 1466, 1425 (CH_2 , CH_3); 1219 ($=C-N$); 1145, 1133 ($N-C(S)=S$); 1054 ($C=S$); 855 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.85 (t, 3H, CH_3 (heptyl)); 1.25 (s, 6H, 2 CH_3 (isopentyl)); 1.39 (t, CH); 1.65 (t, 4H, 2 CH_2); 3.08 (t, 2H, S- CH_2); 4.61 (q, 2H, N- CH_2). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.17 (CH_3 (heptyl)); 22.68 (2 CH_3 (isopentyl)); 24.45 (CH); 28.46, 28.89, 28.95 (5 CH_2); 31.76 (N- $CH_2-\underline{CH_2}$); 36.00 (S- CH_2); 69.81 (N- CH_2); 215.32 (C=S).

Octyl isopentylcarbamodithioate (10). Yield 12.40 g (90 %), oil, $R_f = 0.9$ (acetone/hexane, 1/4), n_D^{20} 1.4040. Found, %: C, 60.76; H, 10.91; N, 5.26; S, 22.97. $C_{14}H_{29}NS_2$. Calculated, %: C, 61.03; H, 10.61; N, 5.08; S, 23.27. IR spectra, ν , cm^{-1} : 2926, 2855 (CH_2 , CH_3); 1468, 1425 (CH_2 , CH_3); 1218 ($=C-N$); 1145, 1133 ($N-C(S)=S$); 1055 ($C=S$); 853 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.85 (t, 3H, CH_3 (octyl)); 1.25 (s, 12H, $2CH_3$ (isopentyl), $3CH_2$); 1.39 (t, 5H, CH , $2CH_2$); 1.65 (m, 4H, $2CH_2$); 3.08 (t, 2H, $S-CH_2$); 4.61 (q, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.21 (CH_3 (octyl)); 22.74 ($2CH_3$ (isopentyl)); 24.45 (CH); 28.45, 28.99, 29.17, 29.23, 29.28 ($6CH_2$); 31.87 ($N-CH_2-CH_2$); 36.01 ($S-CH_2$); 69.86 ($N-CH_2$); 215.41 ($C=S$).

Nonyl isopentylcarbamodithioate (11). Yield 13.2 g (91 %), oil, $R_f = 0.85$ (acetone/hexane, 1/4), n_D^{20} 1.4042. Found, %: C, 61.91; H, 10.93; N, 4.65; S, 21.94. $C_{15}H_{31}NS_2$. Calculated, %: C, 62.22; H, 10.79; N, 4.84; S, 22.15. IR spectra, ν , cm^{-1} : 2926, 2854 (CH_2 , CH_3); 1464, 1425 (CH_2 , CH_3); 1217 ($=C-N$); 1133 ($N-C(S)=S$); 1055 ($C=S$); 855 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.85 (t, 3H, CH_3 (nonyl)); 1.24 (s, 14H, $2CH_3$ (isopentyl), $4CH_2$); 1.39 (t, 5H, CH , $2CH_2$); 1.66 (m, 4H, $2CH_2$); 3.08 (t, 2H, $S-CH_2$); 4.62 (q, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.21 (CH_3 (nonyl)); 22.76 ($2CH_3$ (isopentyl)); 24.45 (CH); 28.46, 28.99, 29.16, 29.23, 29.33, 29.57 ($7CH_2$); 31.95 ($N-CH_2-CH_2$); 36.01 ($S-CH_2$); 69.81 ($N-CH_2$); 215.34 ($C=S$).

Decyl isopentylcarbamodithioate (12). Yield 12.8 g (84 %), oil, $R_f = 0.9$ (acetone/hexane, 1/4), n_D^{20} 1.4045. Found, %: C, 63.06; H, 10.82; N, 4.91; S, 21.25. $C_{16}H_{33}NS_2$. Calculated, %: C, 63.31; H, 10.96; N, 4.61; S, 21.12. IR spectra, ν , cm^{-1} : 2926, 2854 (CH_2 , CH_3); 1464, 1425 (CH_2 , CH_3); 1216 ($=C-N$); 1133 ($N-C(S)=S$); 1054 ($C=S$); 855 ($C-S$). NMR 1H spectra ($CDCl_3$), δ , ppm: 0.86 (t, 3H, CH_3 (decyl)); 1.24 (s, 16H, $2CH_3$ (isopentyl), $5CH_2$); 1.40 (t, 5H, CH , $2CH_2$); 1.66 (m, 4H, $2CH_2$); 3.08 (t, 2H, $S-CH_2$); 4.62 (q, 2H, $N-CH_2$). NMR ^{13}C spectra ($CDCl_3$), δ , ppm: 14.22 (CH_3 (decyl)); 22.77 ($2CH_3$ (isopentyl)); 24.45 (CH); 28.46, 28.99, 29.22, 29.40, 29.56, 29.67 ($8CH_2$); 31.98 ($N-CH_2-CH_2$); 36.01 ($S-CH_2$); 69.80 ($N-CH_2$); 215.33 ($C=S$).

3. Results and discussion

The synthesis of disodium isopentyl-bis(dithiocarbamate) and sodium isopentylidithiocarbamate was carried out by the interaction of isopentylamine with carbon disulfide (in a ratio of 1:2) in the presence of an alkali in alcohol at room temperature. As a result of isolation from the reaction mixture, disodium isopentyl-bis(carbamodithioate) (1) and sodium isopentylcarbamodithioate (2) were obtained in individual form with yields of 58 and 30% respectively (Fig. 1).

In order to synthesize potential flotation reagents, the conditions for the synthesis of long-chain alkyl and dialkyl thioesters of isopentylidithiocarbamates were optimized. The synthesis of alkyl and dialkyl thioesters was carried out by the alkylation reaction of disodium isopentyl-bis(dithiocarbamate) (or sodium isopentylidithiocarbamate) with alkyl bromides (hexyl, heptyl, octyl, nonyl and decyl) in acetone at room temperature. As a result, alkyl thioesters of

isopentylcarbomodithioate (yields of 75–91%) and dialkyl thioesters of isopentyl-bis(carbamodithioate) (yields of 76–98%) were synthesized (Fig. 1).

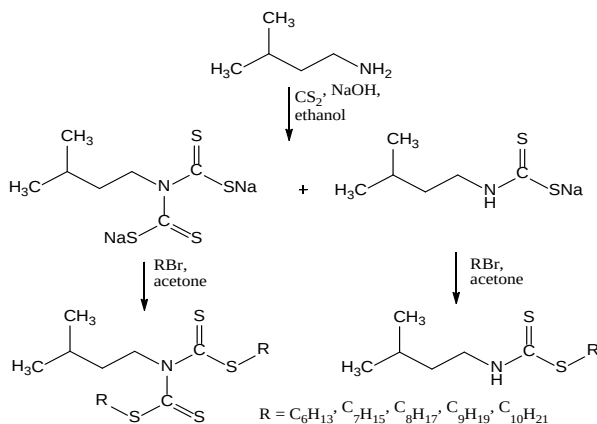


Figure 1 – Synthesis of isopentylthiocarbamates and their alkyl and dialkyl thioesters.

The composition and identity of the synthesized isopentylthiocarbamates (1,2) and their alkyl and dialkyl thioethers (3-12) were confirmed based on elemental analysis and IR spectroscopy.

The IR spectra of isopentylthiocarbamates (1,2) and their alkyl and dialkyl thioethers (3-12) exhibit characteristic absorption bands indicating the formation of dithiocarbamates and their alkyl thioethers. The band at 1216-1241 cm^{-1} corresponds to the stretching vibrations of the N–C= bond. The absorption at 1109-1145 cm^{-1} is due to the characteristic vibrations of the dithiocarbamate group N–C(S)=S. The absorption in the region of 966-1055 cm^{-1} is due to vibrations of the thiocarbonyl bond C=S, while the bands in the range of 853–893 cm^{-1} are characteristic for the C–S bond.

The IR spectrum of the monosubstituted isopentylthiocarbamate (2) contains an absorption band corresponding to the stretching vibrations of the NH group at 3369 cm^{-1} . The observed absorption bands confirm the formation of sodium dithiocarbamates based on isopentylamine.

Furthermore, the presence of long-chain alkyl substituents for alkyl and dialkyl thioethers (3-12) is confirmed by intense bands of stretching vibrations of the CH₂ and CH₃ groups in the region of 2854-2930 cm^{-1} , as well as deformation vibrations of methylene groups at 1425-1468 cm^{-1} .

The structure of isopentylthiocarbamates (1,2) and their alkyl and dialkyl thioethers (3-12) was established using ¹H and ¹³C NMR spectroscopy.

According to the ¹H and ¹³C NMR spectra, the signals of the isopentyl fragment and the dithiocarbamate group were identified for compounds (1) and (2). The N–CH₂ protons appear at δ 4.12 ppm for (1) and 4.35 ppm for (2), the remaining signals of the aliphatic fragment are in the range of δ 1.23–1.56 ppm. In the ¹³C spectra, the N–CH₂ carbon atom is characterized by signals at δ

53.06 and 53.08 ppm, respectively, and the carbons of the isopentyl substituent are in the range of δ 13.63–25.66 ppm. The presence of the dithiocarbamate group is confirmed by the signals of the thiocarbonyl carbon C=S at δ 205.05 ppm. for (1) and 204.28 ppm for (2). Thus, the spectral data confirm the formation of mono- and bis(dithiocarbamate) derivatives of isopentylamine.

Analysis of the ^1H and ^{13}C NMR spectra of the obtained dialkyl and alkyl isopentylthiocarbamate thioesters (3–12) revealed a consistent pattern of signals corresponding to their proposed structure. In the ^1H spectra, the signals of methyl protons of the alkyl radicals are located at δ 0.79–0.86 ppm, while methylene protons appear predominantly in the region of δ 1.20–1.66 ppm. With increasing alkyl chain length, the integrated intensity of these signals' increases. The isopentyl fragment is characterized by signals of methyl protons near δ 1.2–1.3 ppm and methine proton at δ 1.3–1.4 ppm. The signals of the S–CH₂ protons are observed at δ 3.08–3.25 ppm, while the N–CH₂ protons resonate downfield, at approximately δ 3.8–4.6 ppm.

In the ^{13}C spectra, the methyl groups of the alkyl chains give signals at δ 14.1–14.2 ppm, while the carbon atoms of isopentyl substituent methyl and methine groups give signals at approximately δ 22.6–22.8 and 24.5–26.1 ppm, respectively. The chemical shifts of the CH₂ groups of the alkyl chains are found in the δ 28–30 ppm region. The S–CH₂ carbon atom resonated at δ 36–37 ppm, and the N–CH₂ carbon atoms are observed in the δ 51–53 and 69.8 ppm region. The signals for thiocarbonyl carbon C=S are observed in the region of δ 196–215 ppm. The obtained spectral characteristics confirm the formation of alkyl and dialkyl isopentylthiocarbamate thioethers and are consistent with the change in the length of the alkyl substituents.

4. Conclusion

In this study, new dithiocarbamate derivatives based on isopentylamine were synthesized, including disodium isopentyl-bis(carbamodithioate) (1), sodium isopentylthiocarbamate (2), and their alkyl and dialkyl thioethers (3–12). The mono- and bis-isopentylthiocarbamates were synthesized in the interaction reaction of isopentylamine with carbon disulfide in an alkaline medium.

Using sodium salts (1) and (2), derivatives with linear alkyl substituents at C₆–C₁₀ were synthesized. The isolated compounds are characterized by satisfactory yields, demonstrating the applicability of this method to the preparation of a series of dithiocarbamate thioethers with varying hydrocarbon chain lengths.

The composition and structure of the synthesized compounds were confirmed by a combination of elemental analysis, IR, and NMR spectroscopy data. The spectral data are consistent with the proposed structures and allow the identification of signals from the isopentyl and alkyl fragments, as well as the characteristic N–CH₂, S–CH₂ and C=S signals.

The resulting series of compounds combines the dithiocarbamate functional moiety with alkyl chains of varying lengths, enabling the variation of their

hydrophobic and surface-active properties. Therefore, the synthesized alkyl and dialkyl thioethers are of interest as promising compounds for further study of their flotation activity and selectivity in the flotation enrichment of sulfide and other minerals.

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Conflict of Interest: All authors declare that they have no conflict of interest.

ИЗОПЕНТИЛДИТИОКАРБАМАТТАРДЫҢ АЛКИЛДІ ЖӘНЕ ДИАЛКИЛДІ ТИОЭФИРЛЕРІНІҢ СИНТЕЗІ ЖӘНЕ ҚҰРЫЛЫМЫ

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Түйіндеме. *Kіріспе.* Дитиокарбаматтар және олардың туындылары минералдық шикізатты флотациялық байытудағы флотореагенттер ретінде қолданылатын болашағы зор күкірткүрамды қосылыстар болып табылады. Көмірсутектік орынбасардың құрылымын өзгерту және қосымша функционалдық фрагменттерді енгізу олардың беттік қасиеттерін реттеуге мүмкіндік береді. *Зерттеудің мақсаты* – изопентилдитиокарбаматтар негізіндегі жаңа алкил- және диалкилді тиоэфирлерді синтездеу және олардың құрылымын ИҚ- және ЯМР-спектроскопиялық әдістерімен анықтау. *Нәтижелер және оларды талқылау.* Изопентиламиннің күкірт көміртегімен сілтілік ортада әрекеттесуі нәтижесінде сәйкесінше 58 және 30% шығыммен изопентил-бис(дитиокарбаматтың) динатрий тұзы және натрий изопентилдитиокарбаматы алынды. Тұздардың гексил, гептил, октил, нонил және децил бромидтерімен кейінгі реакциялық әрекеттесуі 75–98% шығыммен алкил- және диалкилді тиоэфирлер қатарын синтездеуге мүмкіндік берді. Синтезделген қосылыстардың құрамы мен құрылымы элементтік талдау, ИҚ-, ¹H және ¹³C ЯМР-спектроскопия әдістерімен дәлелденді. Спектрлік сипаттамалар дитиокарбамат фрагментінің, изопентил орынбасарының және әртүрлі ұзындықтағы алкил орынбасарларының бар екенін дәлелдейді. *Қорытынды.* Жаңа изопентилдитиокарбамат тиоэфирлерінің қатарын синтездеу шарттары жасалынды. Ұзындығы әртүрлі алкил фрагменттерімен синтезделген изопентилдитиокарбамат тиоэфирлері олардың флотациялық қасиеттерін және флотореагенттер ретінде қолдану мүмкіндігін одан әрі зерттеуге қызығушылық тудырады.

Түйінді сөздер: изопентилдитиокарбамат, алкил- және диалкилді тиоэфир, алкилдеу реакциясы, құрылым, ИҚ-спектроскопия, ¹H және ¹³C ЯМР-спектроскопиясы

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СИНТЕЗ И СТРУКТУРА АЛКИЛОВЫХ И ДИАЛКИЛОВЫХ ТИОЭФИРОВ ИЗОПЕНТИЛДИТИОКАРБАМАТОВ

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Резюме. Введение. Дитиокарбаматы и их производные являются перспективными серосодержащими соединениями, применяемыми в качестве флотореагентов при флотационном обогащении минерального сырья. Изменение строения углеводородного заместителя и введение дополнительных функциональных фрагментов позволяют регулировать их поверхностные свойства. Целью данного исследования являлся синтез новых алкиловых и диалкиловых тиоэфиров на основе изопентилдитиокарбаматов, и установление их структуры ИК и ЯМР спектральными методами. Результаты и обсуждение. В результате взаимодействия изопентиламина с сероуглеродом в щелочной среде получены динатриевая соль изопентил-бис(дитиокарбамата) и изопентилдитиокарбамат натрия с выходами 58 и 30%, соответственно. Последующая реакция солей с бромидами гексила, гептила, октила, нонила и децила позволила синтезировать серию алкиловых и диалкиловых тиоэфиров с выходами 75–98%. Состав и структура синтезированных соединений подтверждены методами элементного анализа, ИК-, ^1H и ^{13}C ЯМР-спектроскопии. Спектральные характеристики свидетельствуют о наличии дитиокарбаматного фрагмента, изопентильного заместителя и алкильных заместителей различной длины. Заключение. Разработаны условия синтеза серии новых изопентилдитиокарбаматных тиоэфиров. Синтезированные изопентилдитиокарбаматные тиоэфиры с варьируемой длиной алкильного фрагмента представляют интерес для дальнейшего изучения их флотационных свойств и возможности применения в качестве флотореагентов.

Ключевые слова: изопентилдитиокарбамат, алкил- и диалкиловый тиоэфир, реакция алкилирования, структура, ИК-спектроскопия, спектроскопия ЯМР ^1H и ^{13}C .

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REGENERATING SOLUTION COMPOSITION FOR SILICON REMOVAL AND ANION-EXCHANGE RESIN RESTORATION IN URANIUM EXTRACTION

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Abstract. The effect of the composition of regenerating solutions on the removal of silicon-containing and related impurities from anion exchange resins used for sorption extraction of uranium from productive solutions of in-situ leaching was investigated. The objects were technological solutions and regenerated resins from the Akdala and South Inkai deposits. The elemental composition was determined by atomic emission and X-ray fluorescence methods, and the phase composition of solid residues was determined by X-ray phase analysis. Screening of the NaOH–Na₂SO₄, H₂SO₄–NH₄HF₂ and HNO₃–NH₄HF₂ systems showed silicon removal at 90.2–97.9; 93.3–95.0 and 95.7–97.5%, respectively. The HNO₃–NH₄HF₂ system, despite its effectiveness, is excluded due to the high affinity of nitrate ions for the resin; NaOH–Na₂SO₄ and H₂SO₄–NH₄HF₂ were then studied. Increasing the concentrations of NaOH and Na₂SO₄ to 75 and 100 g/l increased silicon removal to 97.5–98.7% but could reduce the strength of the resin. A solution of 25 g/l of NaOH + 25 g/l of Na₂SO₄ removed 93.1% of Si, retained strength of 76.5%, increased hydrodynamic index by 30% and uranium capacity from 10.75 to 13.89 g/l; a solution of 150 g/l H₂SO₄ + 150 g/l NH₄HF₂ increased the capacity to 16.69 g/l. The choice of regenerating solution should consider not only the removal of silicon, but also the degree of purification, strength, hydrodynamic and sorption properties of the resin.

Keywords: uranium, anion exchange, resin, regeneration, silicon, in-situ leaching

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1. Introduction

In-situ recovery (ISR) is one of the principal methods used for the development of sandstone-hosted infiltration-type uranium deposits. The process involves mobilization of uranium directly within the ore-bearing horizon, followed by pumping of the uranium-bearing pregnant leach solution to the surface for subsequent recovery and concentration. Modern ISR flowsheets commonly employ ion-exchange sorption on strongly basic anion-exchange resins for uranium recovery from sulfate-bearing pregnant leach solutions. The continuing importance of ISR in uranium production has stimulated research aimed at improving both leaching performance and downstream processing of uranium-bearing solutions [1,7].

The efficiency of uranium sorption depends not only on the uranium concentration in the pregnant leach solution but also on the physicochemical state, functional groups, porosity, and mass-transfer characteristics of the ion-exchange material. Commercial anion-exchange resins can efficiently recover U(VI) from multicomponent sulfate solutions, while their sorption behavior is strongly influenced by solution composition and operating conditions [2,3]. The importance of resin chemistry is further demonstrated by studies of functionalized ion-exchange materials, in which the nature and arrangement of functional groups determine uranium affinity, selectivity, and adsorption mechanism [8].

Recent developments in uranium separation have also focused on alternative functional sorbents with enhanced affinity and selectivity toward U(VI). Amidoxime-based composite sorbents, polyamine-functionalized silica materials, metal-organic frameworks (MOFs), covalent-organic frameworks (COFs), and other functionalized porous materials have demonstrated high uranium uptake from complex aqueous media [10,13 - 15]. These studies indicate that both the chemical accessibility of active sites and the internal structure of the sorbent are critical factors governing uranium uptake. Nevertheless, for industrial ISR operations, conventional strongly basic anion-exchange resins remain particularly important because of their technological maturity, mechanical properties, and compatibility with continuous sorption-desorption circuits.

During long-term industrial operation, anion-exchange resins repeatedly undergo sorption, washing, desorption, and regeneration cycles. At the same time, non-target mineral and colloidal components present in pregnant leach solutions may accumulate on the bead surface and within the porous polymer matrix. Such deposits can progressively block accessible ion-exchange sites, alter mass transfer, and reduce uranium uptake. Deactivation of ion-exchange materials by inorganic and other contaminants has therefore been identified as an important factor affecting the long-term efficiency of uranium recovery [4]. Recent studies of strongly basic anion-exchange resins used in uranium hydrometallurgy have also shown that inorganic deposits, including Fe-containing contaminants, can be removed by appropriately selected chemical regeneration systems [9].

Among the inorganic impurities, silicon-containing compounds are of technological importance. Depending on concentration, solution acidity, ionic

composition, and residence time, silicic acid can undergo condensation and polymerization, forming progressively less soluble polysilicic species. In strongly basic anion-exchange resins, sorbed silicic acid may polymerize within the resin phase. Low-polymerized forms can be comparatively readily desorbed using alkaline solutions such as NaOH, whereas more extensively polymerized species are considerably more difficult to remove [5, 6].

The accumulation of silicon-containing species within the resin may reduce the accessible pore volume and hinder intraparticle mass transfer. Consequently, silicon removal should be considered not only as chemical purification of the ion exchanger but also as a means of restoring the accessibility of functional groups and the kinetic performance of the sorbent. This interpretation is consistent with broader studies of uranium sorption materials showing that pore accessibility, functional-group chemistry, and competing ions collectively determine uranium uptake from complex aqueous solutions [13 - 15].

2. Experimental part

2.1. Methods and tests

The study examined technological solutions and anion-exchange resins used to process uranium-bearing productive solutions from the Akdala and South Inkai deposits.

Productive, leaching, circulating, wash, and sorption mother solutions, as well as commercial desorbates, were analyzed.

Elemental composition was determined spectrometrically. Solid residues and suspended particles were analyzed by X-ray diffraction on a D8 Advance (Bruker) diffractometer with Cu radiation at 40 kV and 40 mA; diffractograms were processed in EVA, with phase identification using the PDF-2 database.

Elemental content in resin samples before and after regeneration was measured by X-ray fluorescence using an Olympus Vanta C analyzer.

Resin mechanical strength was determined with a Vibratory Ball Mill according to ST NAC 20-2017.

2.2. Rationale for the choice of silicon as the main controlled pollutant

In the productive solutions of the Akdala and South Inkai deposits, the concentration of silicon was 79.68 and 85.48 mg/l, respectively. Along with Si, Fe and Al were characterized by significant concentrations.

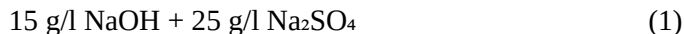
X-ray phase analysis of dry residues of productive solutions showed the presence of silicon dioxide and aluminosilicate phases. Thus, silicon was in the technological system not only in a dissolved form, but also as part of dispersed mineral formations.

The most important circumstance was the accumulation of Si directly in the exploited resin. In the original reclaimed resins, the silicon content was 11.391% for Akdala and 13.062% for South Inkai, significantly exceeding the content of other controlled impurities.

This was the basis for using the degree of Si removal as the main indicator of the efficiency of chemical regeneration.

2.3. Selection of regenerative solutions

Three chemical systems were selected for the initial screening:



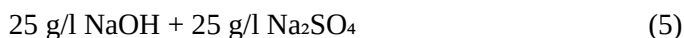
The alkaline system was chosen because NaOH converts silicon compounds into soluble forms, while Na₂SO₄ provides the required ionic medium.

Acid-fluoride systems were selected based on the possibility of chemical destruction of stable silicon-containing deposits when interacting with a fluorine-containing component.

At the laboratory stage, the ratio of solid to liquid phases was T:F = 1:25. Regeneration was carried out with continuous stirring for at least 180 minutes.

The efficiency of the process was evaluated by changing the content of Si, Ca, Fe and Re in the resin.

For subsequent enlarged laboratory experiments, alkaline solutions were studied:



and acid-fluoride solution:



In enlarged laboratory static experiments, the volume of resin was 3 liters, T:F = 1:5, the total volume of the regenerating solution was 15 liters, the duration of treatment was 180 minutes at room temperature.

3. Results and discussion

3.1. Composition of anion exchange resin contamination

The study of process solutions showed that the most significant non-target components were Fe, Al and Si. For Akdala, the content of Fe, Al and Si in the productive solution was 571.71, respectively; 356.16 and 79.68 mg/l, and for South Inkai - 1287.19; 836.09 and 85.48 mg/l.

Particular attention was given to the behavior of silicon. In the Akdala samples, its concentration decreased from 79.68 mg/l in the productive solution to 71.93 mg/l in the sorption mother liquor, indicating partial retention of silicon-containing compounds in the resin phase.

The presence of Si in commercial desorbates - 68.00 mg/l for Akdala and 53.13 mg/l for South Inkai - additionally indicated the accumulation of silicon-containing compounds in the resin during the technological cycle with subsequent partial removal during desorption.

X-ray phase analysis confirmed the complex nature of the silicon-containing component of productive solutions. SiO_2 and aluminosilicate phases were identified in the dry residues. After the solution passed through the sorption system, the content of several silicon-containing phases in the dry residue of the mother cell decreased, and free SiO_2 was not detected.

The combination of the results of elemental and phase analysis allows us to consider the accumulation of silicon as one of the factors in the deterioration of the anion exchange resin.

3.2. Initial selection of a chemical system for regeneration

The results of the initial comparative test of the three systems are presented in Table 1.

Table 1 – Efficiency of regenerating solutions in removing the main impurities from anion exchange resins

Regenerative System	Deposit	Removal of Si, %	Removal of Ca, %	Removal of Fe, %	Removal of Re, %
$\text{NaOH} + \text{Na}_2\text{SO}_4$	Akdala	90.2	49.0	27.0	23.0
$\text{NaOH} + \text{Na}_2\text{SO}_4$	South Inkai	97.9	20.0	—*	—*
$\text{H}_2\text{SO}_4 + \text{NH}_4\text{HF}_2$	Akdala	93.3	54.0	—*	17.4
$\text{H}_2\text{SO}_4 + \text{NH}_4\text{HF}_2$	South Inkai	95.0	100	100	23.3
$\text{HNO}_3 + \text{NH}_4\text{HF}_2$	Akdala	95.7	100	100	100
$\text{HNO}_3 + \text{NH}_4\text{HF}_2$	South Inkai	97.5	100	62.5	88.5

Note – The removal efficiency was not calculated because the measured content of the element after treatment exceeded that in the initial regenerated resin.

All three systems provided a high degree of silicon removal - at least 90%.

An alkaline solution of $\text{NaOH} - \text{Na}_2\text{SO}_4$ removed 90.2% Si from Akdala resin and 97.9% from South Inkai resin. This indicates the possibility of effective destruction or dissolution of a significant part of silicon-containing contaminants in an alkaline environment.

The $\text{H}_2\text{SO}_4 - \text{NH}_4\text{HF}_2$ solution provided removal of 93.3 and 95.0% Si, respectively. For the South Inkai resin, complete removal of the detectable compounds Ca and Fe was observed at the same time.

The maximum cumulative degree of impurity removal at the laboratory stage was provided by the $\text{HNO}_3 - \text{NH}_4\text{HF}_2$ solution. For Akdala, the removal of Si was 95.7%, and Ca, Fe and Re were 100%. For South Inkai, 97.5% Si, 100% Ca, 62.5% Fe, and 88.5% Re were removed. If only the chemical efficiency of treatment is evaluated, the $\text{HNO}_3 - \text{NH}_4\text{HF}_2$ system could be considered as the most effective. However, when choosing a regenerant, it is necessary to consider the subsequent state of the anion exchange resin. Nitrate ions are characterized by a high affinity for strongly basic anion exchange functional groups, because of which their subsequent displacement from the resin by sulfate solutions can complicate the technological cycle.

Therefore, the $\text{HNO}_3 - \text{NH}_4\text{HF}_2$ system was not selected for further optimization, despite the high degree of impurity removal.

According to the results of the first stage, two systems were left for enlarged laboratory research:



This approach is fundamentally important: the chemically most aggressive reagent is not necessarily the technologically optimal regenerant.

3.3. Effect of NaOH and Na₂SO₄ concentration on regeneration efficiency

The next step was to optimize the alkaline system. The main results are shown in Table 2.

Table 2 – Effect of the composition of the alkaline regenerating solution on the purification and mechanical strength of the resin

Solution composition, g/l	Resin	Removal of Si, %	Removal of Fe, %	Removal of Zn, %	Mechanical strength, %
25 NaOH + 25 Na ₂ SO ₄	Akdala	93.1	89.6	69.4	76.5
75 NaOH + 100 Na ₂ SO ₄	Akdala	97.5	Almost complete	90.2	60
75 NaOH + 100 Na ₂ SO ₄	South Inkai	98.7	50.0	91.7	-
75 NaOH + 100 Na ₂ SO ₄ , Dynamic Mode	Akdala	97.1	93.8	-	52

In the initial experimental materials for this experiment, two different values of mechanical strength are given - 82 and 63%.

At concentrations of 25 g/L NaOH and 25 g/L Na₂SO₄, the Si removal efficiency from the Akdala resin was 93.1%. At the same time, 89.6% of Fe and 69.4% of Zn were removed. The mechanical strength after treatment was 76.5%, remaining close to that of the initial regenerated resin.

Increasing the concentrations to 75 g/L NaOH and 100 g/L Na₂SO₄ increased Si removal to 97.5% for the Akdala resin. Thus, for the Akdala resin, increasing the regenerant concentration resulted in an additional 4.4 percentage points of Si removal compared with the 25 g/L NaOH + 25 g/L Na₂SO₄ solution. A high Si removal efficiency of 98.7% was also obtained for the South Inkai resin using 75 g/L NaOH + 100 g/L Na₂SO₄; however, a direct concentration-dependent comparison could not be made because the South Inkai resin was not tested with the 25 g/L NaOH + 25 g/L Na₂SO₄ solution under the same scaled-up laboratory conditions.

For the Akdala resin, the higher Si removal achieved with the more concentrated alkaline solution was accompanied by a decrease in mechanical strength. After static treatment, the mechanical strength decreased from 76.5% to 60%. This effect became more pronounced during the 36-h dynamic experiment:

although 97.1% of Si and 93.8% of Fe were removed, the mechanical strength decreased to 52%.

These results demonstrate that increasing Si removal alone cannot be considered sufficient for selecting regeneration conditions. The removal efficiency should be evaluated together with preservation of the mechanical integrity of the resin. For the Akdala resin, increasing Si removal from 93.1% to 97.5% was accompanied by a decrease in mechanical strength from 76.5% to 60%, while prolonged dynamic treatment resulted in a further decrease to 52%. Therefore, 25 g/L NaOH + 25 g/L Na₂SO₄ provided a more balanced combination of Si removal efficiency and mechanical strength for the Akdala resin.

3.4. Efficiency of the H₂SO₄ - NH₄HF₂ System

When using 150 g/L of H₂SO₄ + 150 g/L of NH₄HF₂, the Si removal rate was 89.0% for Akdala resin and 86.9% for South Inkai.

Table 3 – Results of treatment with a solution of 150 g/l H₂SO₄ + 150 g/l NH₄HF₂

Indicator	Akdala	South Inkai
Removal of Si, %	89.0	86.9
Removal of Fe, %	16.6	86.0
Removal of Zn, %	27.6	24.5
Removal of Ca, %	4.9	50.0
Mechanical strength, %	61.0	81.0

In terms of the degree of siliconization, this composition was inferior to optimized alkaline solutions. At the same time, its effect significantly depended on the origin of the resin.

For Akdala, an increase in NH₄HF₂ concentration was accompanied by a decrease in mechanical strength of up to 61%. For South Inkai, a value of 81% was recorded after treatment, meaning the result did not indicate a similar degradation of the material.

The difference in the behavior of the two industrial designs indicates that the effectiveness of a regenerant is determined not only by its chemical composition. The history of operation, the degree and nature of the resin contamination and, probably, the condition of its polymer matrix are significant.

Therefore, a universal choice of a reagent only by the Si removal index seems to be insufficiently substantiated.

3.5. Effect of regeneration on hydrodynamic characteristics

If the removal of silicon-containing deposits does free up the pore space of the resin, this should be manifested not only by a decrease in the Si content, but also by a change in the passage of the liquid through the sorbent bed.

Experimental verification confirmed this assumption.

Table 4 – Change in the hydrodynamic index after chemical regeneration

Sample	Volume flow, m ³ /h	Relative change, %
Akdala's Original Resin	0.180	–
Akdala, 150H ₂ SO ₄ + 150NH ₄ HF ₂	0.219	+21.67
South Inkai, 150H ₂ SO ₄ + 150NH ₄ HF ₂	0.223	+17.40
Akdala, 25NaOH + 25Na ₂ SO ₄	0.234	+30.00
Akdala, 75NaOH + 100Na ₂ SO ₄	0.225	+24.99

The maximum effect was obtained for the formulation of 25 g/l NaOH + 25 g/l Na₂SO₄: the hydrodynamic index increased by 30%.

For the more concentrated alkaline solution, the improvement was 24.99% despite the higher degree of Si removal.

Thus, the higher Si removal efficiency achieved with the more concentrated alkaline solution did not result in a corresponding improvement in the hydrodynamic characteristics of the resin.

H₂SO₄ - NH₄HF₂ treatment also improved fluid flow, with an increase of 21.67% for Akdala and 17.40% for South Inkai.

Consequently, chemical regeneration does change the state of the ion exchange resin layer and improve its hydrodynamic properties.

3.6. Restoration of the uranium sorption tank

A key criterion for evaluating the practical effectiveness of regeneration is the ability of the treated resin to recover uranium during subsequent sorption.

To evaluate this parameter, comparative sorption experiments were performed using the initial regenerated Akdala resin and resin samples treated with the two selected regenerating solutions.

Table 5 – Effect of regeneration on the uranium sorption capacity of the Akdala resin

Resin Condition	U content after sorption, g/l	Change relative to the original resin, %
Initial regenerated resin	10.75	–
After treatment with 25 g/L NaOH + 25 g/L Na ₂ SO ₄	13.89	+29
After treatment with 150 g/L H ₂ SO ₄ + 150 g/L NH ₄ HF ₂	16.69	+55

After treatment with the alkaline regenerating solution, the uranium sorption capacity increased from 10.75 to 13.89 g/L, corresponding to an increase of approximately 29%. Treatment with the H₂SO₄ - NH₄HF₂ solution resulted in a greater increase in uranium sorption capacity, reaching 16.69 g/L, approximately 55% higher than that of the initial regenerated resin.

These results demonstrate that chemical regeneration not only removes accumulated impurities but also improves the subsequent uranium sorption performance of the resin.

The solution containing 25 g/L NaOH + 25 g/L Na₂SO₄ provided the most balanced combination of properties for the Akdala resin: 93.1% Si removal, a

mechanical strength of 76.5%, a 30% improvement in hydrodynamic performance, and a 29% increase in uranium sorption capacity.

Treatment with 150 g/L H_2SO_4 + 150 g/L NH_4HF_2 resulted in the greatest increase in uranium sorption capacity, reaching 16.69 g/L, approximately 55% above that of the initial regenerated Akdala resin. However, the mechanical strength of the resin decreased to 61%.

Thus, the preferred regeneration conditions depend on the selected performance criterion. The acid–fluoride system provided the greatest restoration of uranium sorption capacity for the Akdala resin, whereas the moderately concentrated alkaline solution provided a more balanced combination of Si removal, mechanical strength, hydrodynamic performance, and uranium sorption capacity.

3.7. Comprehensive assessment and selection of the regenerating solution

Comparison of the results allows us to distinguish three consecutive levels of reagent selection.

At the first level, HNO_3 - NH_4HF_2 demonstrated the maximum removal of a number of impurities, but the technological features of the interaction of nitrate ions with the anion exchange resin limit the feasibility of its further use.

At the second level, an increase in the concentrations of NaOH and Na_2SO_4 made it possible to obtain the maximum degree of Si removal - up to 98.7%. However, for Akdala's resin, the increase in chemical action was accompanied by a significant decrease in mechanical strength.

At the third level, a set of operational characteristics was taken into account. This is where the formulation of 25 g/L NaOH + 25 g/L Na_2SO_4 showed the most balanced result.

Thus, it is advisable to formulate the criterion for selecting a regenerating solution not as the achievement of the maximum degree of Si removal, but as the achievement of a sufficient degree of silicon desilica with a minimum negative impact on the structure of the sorbent and the simultaneous restoration of its hydrodynamic and sorption characteristics.

From this point of view, for Akdala resin, the most rational of the studied alkaline formulations is 25 g/l of NaOH + 25 g/l of Na_2SO_4 .

The H_2SO_4 - NH_4HF_2 acid-fluoride system is also of practical interest, especially given the pronounced reduction of uranium capacity. However, the need to control its impact on mechanical strength requires further optimization of NH_4HF_2 concentration and processing time.

4. Conclusion

Chemical regeneration of anion-exchange resins from the Akdala and South Inkai uranium deposits was evaluated with respect to silicon removal and recovery of resin performance. Silicon contents in the regenerated industrial resins reached 11.4% for Akdala and 13.1% for South Inkai. The tested regenerants provided Si removal efficiencies of 90.2 - 97.9% for NaOH– Na_2SO_4 , 93.3 - 95.0% for H_2SO_4 - NH_4HF_2 , and 95.7 - 97.5% for HNO_3 - NH_4HF_2 . Despite

its high Si removal efficiency, the HNO_3 - NH_4HF_2 system was excluded from further optimization because nitrate ions have a high affinity for strongly basic anion-exchange resins, which may complicate their subsequent displacement during operation in sulfate-based uranium recovery circuits.

For the Akdala resin, 25 g/L NaOH + 25 g/L Na_2SO_4 provided the most balanced regeneration performance, achieving 93.1% Si removal while maintaining a mechanical strength of 76.5%, improving hydrodynamic performance by 30%, and increasing the uranium sorption capacity from 10.75 to 13.89 g/L. Increasing the concentrations to 75 g/L NaOH + 100 g/L Na_2SO_4 enhanced Si removal to 97.5%, but reduced the mechanical strength to 60% and, after prolonged dynamic treatment, to 52%; therefore, the more concentrated alkaline system is not recommended for prolonged treatment of the Akdala resin.

For the South Inkai resin, both alkaline and acid-fluoride regeneration showed high Si removal efficiency. The NaOH - Na_2SO_4 system provided up to 98.7% Si removal, whereas H_2SO_4 - NH_4HF_2 achieved 95.0% Si removal at the laboratory screening stage and simultaneously provided efficient removal of Fe and Ca. Thus, both systems can be considered for South Inkai resin, with the final selection depending on the required degree of impurity removal and preservation of resin mechanical properties.

Overall, the results demonstrate that regenerant selection should not be based solely on maximum Si removal. Resin mechanical strength, hydrodynamic behavior, and recovery of uranium sorption capacity should also be considered when selecting regeneration conditions for industrial application.

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УРАН ЭКСТРАКЦИЯСЫ КЕЗІНДЕ КРЕМНИЙДІ КЕТПУТЕ ЖӘНЕ АНИОН АЛМАСУ ШАЙЫРЫН ҚАЛПЫНА КЕЛТПУТЕ АРНАЛҒАН ЕРІТІНДІНІҢ РЕГЕНЕРАЦИЯЛЫҚ ҚҰРАМЫ

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Түйіндемe. Ұңғымалық жерасты шаймалау әдісімен алынатын уранқұрамды өнімді ерітінділерді өңдеу кезінде қолданылатын анионалмастырғыш шайырларды кремнийқұрамды және ілеспе қоспалардан тазартуға регенерациялаушы ерітінділер құрамының әсері зерттелді. Зерттеу нысандары ретінде Ақдала және Оңтүстік Инкай кен орындарында пайдаланылатын технологиялық ерітінділер мен регенерацияланған анионалмастырғыш шайырлар алынды. Үлгілердің элементтік құрамы атомдық-эмиссиялық және рентгенфлуоресценттік әдістермен, ал қатты қалдықтардың фазалық құрамы рентгенфазалық талдау әдісімен анықталды. NaOH - Na_2SO_4 , H_2SO_4 - NH_4HF_2 және HNO_3 - NH_4HF_2 негізіндегі регенерациялаушы жүйелерді сынау нәтижесінде кремнийді жою дәрежесі тиісінше 90,2 - 97,9; 93,3 - 95,0 және 95,7 - 97,5% құрады. HNO_3 - NH_4HF_2 жүйесі кремнийді жоюдың жоғары тиімділігін көрсеткенімен, нитрат-иондарының анионалмастырғыш шайырға жоғары сорбциялық бейімділігіне байланысты кейінгі зерттеулерден

алынып тасталды. Одан әрі NaOH - Na₂SO₄ және H₂SO₄ - NH₄HF₂ жүйелерінің тиімділігі зерттелді. NaOH және Na₂SO₄ концентрацияларын тиісінше 75 және 100 г/л-ге дейін арттыру кремнийдің жойылу дәрежесін 97,5 - 98,7%-ға дейін жоғарылатты, алайда шайырдың механикалық беріктігінің төмендеуіне әкелді. Құрамында 25 г/л NaOH және 25 г/л Na₂SO₄ бар ерітінді кремнийдің 93,1%-ын жоюды қамтамасыз етті, бұл ретте шайырдың механикалық беріктігі 76,5% деңгейінде сақталып, гидродинамикалық сипаттамалары 30%-ға жақсарды, ал уран бойынша сорбциялық сыйымдылығы 10,75-тен 13,89 г/л-ге дейін артты. 150 г/л H₂SO₄ және 150 г/л NH₄HF₂ ерітіндісімен өңдегеннен кейін шайырдың уран бойынша сорбциялық сыйымдылығы 16,69 г/л-ге дейін жоғарылады. Алынған нәтижелер регенерациялаушы ерітіндіні таңдауда кремнийді жою дәрежесімен қатар шайырдың механикалық беріктігін, гидродинамикалық сипаттамаларын және уран бойынша сорбциялық қасиеттерінің қалпына келуін кешенді түрде ескеру қажеттігін көрсетті.

Түйінді сөздер: уран, анион алмасу шайыры, регенерация, кремний, ұңғыманы шаймалау

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РЕГЕНЕРИРУЮЩИЙ СОСТАВ РАСТВОРА ДЛЯ УДАЛЕНИЯ КРЕМНИЯ И ВОССТАНОВЛЕНИЯ АНИОННО-ОБМЕННОЙ СМОЛЫ ПРИ ЭКСТРАКЦИИ УРАНА

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Резюме. Исследовано влияние состава регенерирующих растворов на удаление кремнийсодержащих и сопутствующих примесей из анионообменных смол, используемых для сорбционной экстракции урана из продукционных растворов скважинного подземного выщелачивания. Объектами исследования были технологические растворы и регенерированные смолы с месторождений Акдала и Южный Инкай. Элементный состав определяли атомно-эмиссионным и рентгенофлуоресцентным методами, а фазовый состав твердых остатков — рентгенофазовым анализом. При испытании систем NaOH–Na₂SO₄, H₂SO₄–NH₄HF₂ и HNO₃–NH₄HF₂ было установлено, что степень удаления кремния составляет 90,2–97,9; 93,3–95,0 и 95,7–97,5% соответственно. Система HNO₃–NH₄HF₂, несмотря на свою эффективность, была исключена из-за высокого сродства нитрат-ионов к смоле. Затем были изучены системы NaOH–Na₂SO₄ и H₂SO₄–NH₄HF₂. Повышение концентрации NaOH и Na₂SO₄ до 75 и 100 г/л увеличило степень удаления кремния до 97,5–98,7%, но могло снизить прочность смолы. Раствор с концентрацией 25 г/л NaOH + 25 г/л Na₂SO₄ удалил 93,1% Si, сохранил прочность на уровне 76,5%, повысил гидродинамический индекс на 30% и ёмкость по урану с 10,75 до 13,89 г/л; раствор с концентрацией 150 г/л H₂SO₄ + 150 г/л NH₄HF₂ повысил ёмкость до 16,69 г/л. При выборе регенерирующего раствора следует учитывать не только степень удаления кремния, но и степень очистки, прочность, гидродинамические и сорбционные свойства смолы.

Ключевые слова: уран, анионообменная смола, регенерация, кремний, скважинное выщелачивание

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CHEMICAL APPROACHES TO MONITORING AND EVALUATING THE BIOREMEDIATION OF OIL CONTAMINATED DESERT SOILS: A REVIEW OF MODERN METHODS

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Abstract. Oil spills in deserts and other arid regions, including Kuwait, the Arava Valley in Israel, and Western Kazakhstan, have created extensive areas of chronically contaminated soil whose remediation is constrained by low moisture, nutrient deficiency, salinity, temperature fluctuations, and the ageing of petroleum residues. The purpose of this review is to systematise modern chemical and physicochemical approaches to monitoring and evaluating the bioremediation of oil-contaminated desert soils and to identify indicators suitable for an integrated, risk-based assessment. The review considers the composition of crude oil as a multicomponent contaminant, including total petroleum hydrocarbons, polycyclic aromatic hydrocarbons, BTEX compounds, resins, and asphaltenes, as well as the soil properties that control their mobility, bioavailability, persistence, and toxicity. Natural attenuation, biostimulation, bioaugmentation, biopiling, and phytoremediation are compared with chemically enhanced treatments based on Fenton and persulfate oxidation, nanomaterials, electrokinetic processes, microwave heating, and bioelectrochemical systems. Particular attention is paid to combining chromatographic and spectroscopic determination of petroleum fractions with soil respiration, microbial and functional-gene indicators, ecotoxicological tests, and remote-sensing observations. Hyperspectral data and artificial-intelligence methods are discussed as tools for mapping contamination and tracking spatial changes during remediation. Sorbent materials, including shungite-based compositions relevant to Kazakhstan, are considered for the preliminary containment and removal of oil. The analysis shows that a decrease in total petroleum hydrocarbons alone is insufficient to demonstrate environmental recovery because persistent aromatic fractions and residual toxicity may remain.

Keywords: oil-contaminated desert soils; bioremediation; total petroleum hydrocarbons; polycyclic aromatic hydrocarbons; chemical oxidation; sorbents; environmental monitoring; remote sensing

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1. Introduction

Oil spills in deserts and other arid regions (for example, Kuwait, the Arava Valley in Israel, Western Kazakhstan) have led to extensive areas of chronically contaminated soil [1, 2]. Extreme environmental conditions act as a natural barrier to the microbial degradation of hydrocarbons, thereby limiting the potential applications of bioremediation. At the same time, many desert soils are inhabited by communities of microorganisms that are adapted not only to significant seasonal changes in temperature and salinity, but also to daily cycles of wetting and drying. These soils provide a habitat for indigenous microorganisms that degrade hydrocarbons. In addition, there are native plants which, when properly managed, possess the ability to oxidise oil.

From a chemical standpoint, petroleum contamination is not a single parameter but a complex multicomponent mixture of aliphatic, aromatic, resin-asphaltene fractions and heteroatomic compounds, each with its own resistance to degradation, toxicity, and mobility in the soil profile [3, 4]. This is precisely why a reliable assessment of remediation effectiveness cannot rely solely on the integral indicator of total petroleum hydrocarbons (TPH) - it requires a combination of:

- chemical indicators (total petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), BTEX, as well as functional groups recorded by IR and chromatography-mass spectrometry methods);
- biological indicators (abundance and composition of microorganisms, enzymatic activity, plant response);
- physical and remote-sensing methods (spectral indices, satellite mapping) [1, 5, 6];
- strategies for the bioremediation of desert oil spills (microbial remediation, phytoremediation, biopiling, as well as chemically enhanced and combined methods).

The purpose of this review is to systematise current knowledge on the chemical nature of petroleum contamination of desert soils, strategies for its biological and chemically enhanced remediation, and analytical approaches to environmental monitoring and assessment of remediation effectiveness - with an emphasis on the chemical component of each of the areas listed.

2. Chemical nature of petroleum contamination and physicochemical features of desert soils

2.1. Composition of crude oil as a contaminant

Crude oil is a mixture of saturated and unsaturated aliphatic hydrocarbons, mono- and polycyclic aromatic compounds (PAHs), as well as resins and asphaltenes containing oxygen, sulphur, and nitrogen. The ratio of these fractions determines the behaviour of the contaminant in the soil: light aliphatic and monoaromatic compounds (including BTEX - benzene, toluene, ethylbenzene, xylenes) evaporate and biodegrade relatively quickly, whereas high-molecular-weight PAHs and resin-asphaltene components have high sorption capacity, low

bioavailability, and can persist in soil for decades even after a substantial reduction in total hydrocarbon content [4, 6]. Petroleum contamination can alter not only the structure of the soil microbial community but also its metallome - the assemblage of mobile metal forms - which underscores the multifaceted nature of the chemical consequences of oil contamination and the need for a comprehensive rather than narrowly analytical assessment [7]. From an analytical perspective, the degradation kinetics of individual hydrocarbon fractions (including diesel fractions) are well described by models of bacterial growth and degradation, which allows the quantitative comparison of the effectiveness of different biopreparations and degrader strains [8].

2.2. Physicochemical characteristics of oil-contaminated desert soils

Desert and hyperarid soils are typically sandy or sandy-loam soils with low clay content, low water-holding capacity, and very low organic carbon content. In Kuwait, desert soils saturated with light crude oil can hold about 17.3% oil by mass [2, 9]. In such soils, hydrocarbons are retained in the upper layer, forming tar mats, oil lakes, or heavily contaminated horizons. Biodegradation is limited by the lack of nitrogen and phosphorus, moisture, and shade; however, indigenous hydrocarbon-degrading bacteria multiply rapidly once oil and moisture become available [2, 10–12]. Microbial diversity initially decreases and then shifts towards oil-degrading taxa such as Proteobacteria and certain Actinobacteria, accompanied by a strong long-term restructuring of the soil microbiome in contaminated arid soils [13]. Understanding these constraints and microbial dynamics is important for designing bioremediation measures and selecting appropriate monitoring indicators [2, 14, 15].

3. Bioremediation strategies for petroleum-contaminated desert soils: chemical and biological mechanisms

3.1. Microbial bioremediation and natural attenuation

A growing body of research from Kuwait and other arid regions demonstrates that indigenous microbial communities are able to remove substantial fractions of oil even from heavily contaminated soils. In desert soil saturated with 17.3% crude oil, natural bioremediation under open conditions (aeration and periodic moistening) removed 73-79% of the oil in about six months in model windrows (mini-piles); oil removal during the first month exceeded 50%. The number of indigenous degrader bacteria increased from $\sim 10^6$ CFU·g⁻¹ to $\sim 4.9 \times 10^8$ CFU·g⁻¹ during peak activity [2]. A subsequent study showed that self-cleaning proceeds effectively even at 20-30% oil contamination (super-saturated soils), with $\sim 70\%$ removal at 1-10% contamination and $\sim 50\%$ removal at 20-30% contamination over six months [10].

However, bioaugmentation with consortia of oil-degrading strains often fails to produce a significant improvement compared with indigenous communities. In the same microcosms of oil-contaminated desert soil (1.5% oil), a consortium of five strong hydrocarbon degraders did not significantly increase oil removal compared with untreated soil: $\sim 68.5\%$ removal versus 74.6%, respectively, after

six months, with no statistically significant difference [10]. Community analysis showed that indigenous species dominated in both treatment variants [10], i.e., well-adapted native bacteria are generally more effective than introduced consortia in desert soils [11, 12]. Thus, biostimulation (addition of nutrients and moisture) is generally more effective than bioaugmentation [11, 12, 15, 16].

3.2. Biopiling and biostimulation

Biopiling systems provide a controlled approach to treating excavated desert soil. A study of biopiles containing crude-oil-contaminated desert soil from Abu Dhabi compared four treatment variants: control, biostimulation (nutrients), bioaugmentation (commercial inoculant), and bioaugmentation + surfactant (Tween 80) [17]. After approximately 156 days, hydrocarbon removal reached 77% for the bioaugmentation + nutrients variant, ~55-56% for biopiles treated with surfactants, 23% for biostimulation without additives, and 4% in the control. Monitoring of CO₂ respiration showed increased activity in all treated biopiles, with faster peaks and earlier declines in the piles treated with surfactants owing to nitrogen depletion [17, 18]. Residual PAHs persisted in all treatment variants, indicating the presence of recalcitrant fractions and the need for long-term risk assessment [17].

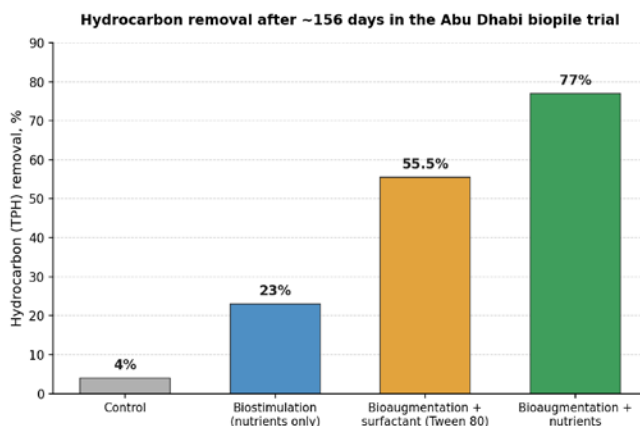


Figure 1 – Hydrocarbon (TPH) removal from crude-oil-contaminated desert soil in biopiles after approximately 156 days under four treatment regimens (Abu Dhabi biopile study) [17].

The chemical composition of the amendments applied significantly affects the outcome of biostimulation: the combined addition of nitrogen and phosphorus affects the biodegradation of different oil fractions differently, as confirmed by metatranscriptomic analysis of soil microbial communities [19]. The use of biochar as both a nutrient carrier and a sorbent simultaneously improves moisture retention and nitrogen/phosphorus bioavailability, enhancing hydrocarbon degradation and restoring soil microecological functions [19], and in some cases increases the resilience of plants growing in petrol-contaminated soils [20].

Large-scale studies at Middle Eastern desert sites show that soil excavation and biopiling (often combined with nutrient addition and irrigation) can remediate tens of thousands of cubic metres of soil to regulatory TPH thresholds within one to a few seasons [1, 14].

3.3. *Phytoremediation and plant-microbe interactions*

Desert and steppe environments are also favourable for phytoremediation using native or introduced plants. Resilient native desert plant species have been identified (for example, *Haloxylon salicornicum*, *Cyperus conglomeratus*, *Rhanterium epapposum*) that can establish on oil-contaminated sites, supporting the long-term restoration of natural vegetation. In Kuwait, the native shrub *Haloxylon salicornicum* survived and grew even in soils with 100% weathered-oil content in greenhouse experiments and showed comparable growth rates on contaminated and clean soils in field trials [21].

A field study in the Russian steppe (a low-precipitation region) compared natural and engineered phytoremediation at sites contaminated with oil (4.2-27.4 g TPH·kg⁻¹) [22]. Natural phytoremediation (spontaneous vegetation) reduced TPH content from ~13.0 g·kg⁻¹ to ~1.8 g·kg⁻¹ over five years, with decontamination exceeding 90% at some sites. Engineered phytoremediation (soil tillage, fertiliser application, and sowing of alfalfa and ryegrass) achieved a 72-90% reduction in total hydrocarbon content per year. Analysis of the root zone microflora reveals the presence of a diverse range of bacterial and fungal communities, including oil-degrading microorganisms (*Rhodococcus*, *Nocardia*, *Gordonia*, *Penicillium*), which highlights their key role in the plant root zone [12, 21].

3.4. *Chemically enhanced and combined remediation methods*

In addition to biological methods, in recent years methods have been developed that combine chemical treatment of the contaminant with subsequent or parallel microbiological degradation. Such methods are particularly relevant for persistent, weathered fractions of oil, including PAHs, which are difficult to treat using traditional biostimulation.

Pre-treatment of the soil with the Fenton reagent (Fe²⁺/H₂O₂) allows for the partial oxidation of the most stable components of weathered petroleum products, reducing their toxicity and increasing the bioavailability of the remaining fractions to the local microbiota. The effect of such combined treatment is manifested in an improvement in the soil's physico-chemical properties and a shift in the microbial community towards active degraders [23]. Following a similar principle, the use of sodium persulphate and other persulphate-based systems is demonstrated; these are capable of breaking down aromatic compounds and, when used in controlled doses, do not suppress but rather alter the functional activity of the soil microbiota. This enables further biological treatment to be carried out [24, 25].

Approaches based on the use of nanomaterials constitute a distinct field. Zinc oxide nanoparticles (nano-ZnO), applied together with plant-microbe systems (for example, involving soybean), can intensify rhizosphere metabolic processes and

accelerate the degradation of total petroleum hydrocarbons [26]. Quantum-chemical modelling (combining xTB, molecular dynamics, and density functional theory, DFT) of functionalised oxide surfaces (TiO₂, ZnO, CeO₂) makes it possible to predict, at the molecular level, their affinity for hydrocarbon molecules and their potential compatibility with microbial processes at low temperatures, opening the way to the rational selection of mineral amendments for cold desert winters [27].

Physical methods such as electrokinetic and microwave thermal treatment are also considered chemically significant tools for remediation intensification. Electrokinetic treatment combined with freeze-thaw cycles can redistribute and mobilise residual hydrocarbons in fine-grained soils, increasing the efficiency of their subsequent extraction or biodegradation [4]. Microwave thermal treatment allows selective heating of polar and conductive components of the contaminated matrix, accelerating desorption and subsequent hydrocarbon decomposition; a review of the factors and mechanisms involved highlights its promise for hard-to-reach or heavily contaminated sites [28]. Finally, bioelectrochemical systems (sediment microbial fuel cells) can simultaneously stimulate anaerobic hydrocarbon degradation and generate electrical energy, which is regarded as a low-carbon alternative to traditional means of intensifying biopiling [29]. The chemical nature of the biological intensifiers themselves is also important: novel biosurfactants (for example, trehalose tetraesters produced by *Rhodococcus erythropolis*) increase PAH bioavailability by reducing interfacial tension and emulsifying the oil phase, making them a promising addition to both biological and chemically enhanced clean-up schemes [30].

It is important to emphasise that the chemically enhanced methods listed above are generally applied not as a standalone replacement for bioremediation but as its complement - to "unlock" recalcitrant contaminant fractions and create conditions under which subsequent microbial or plant-based degradation becomes more effective.

Chemically enhanced removal also requires post-treatment verification. Fenton and persulfate oxidation may generate partially oxidised intermediates, including oxygenated aromatic compounds, aldehydes, ketones, and carboxylic acids, whose toxicity and biodegradability may differ from those of the parent hydrocarbons. Reagent addition can shift soil pH, increase electrical conductivity and sulfate or sodium loading, and alter nutrient availability; residual nanomaterials may likewise affect non-target soil organisms. Consequently, intermediate profiling, pH and salinity measurements, residual-oxidant checks, and plant or microbial toxicity assays should precede biological polishing and final acceptance of the treated soil [23–27].

4. Microbial community and molecular monitoring of bioremediation

Environmental assessment of bioremediation in desert soils increasingly relies on molecular and microbiological methods alongside chemical measurements of total hydrocarbon content.

In the hyperarid Evrona Nature Reserve (Arava Valley, Israel), high-throughput 16S rRNA sequencing [13] of soils from oil-spill sites (1975 and 2014) and nearby control plots revealed: (1) a significant long-term decrease in alpha diversity in contaminated soils compared with controls, with a stronger effect at the older (1975) spill site; (2) dominance of phyla associated with hydrocarbon degradation (Proteobacteria, Patescibacteria), and a reduction in the abundance of Actinobacteria, Chloroflexi, Gemmatimonadetes, and Planctomycetes; (3) strong shifts at the genus level, including enrichment of *Mycobacterium*, *Alkanindiges*, *Pseudoxanthomonas*, *Nocardioides*, and *Streptomyces*. These patterns suggest that long-term bioremediation monitoring in desert soils should include diversity metrics (Shannon index, OTU richness), indicator taxa of active degradation, and correlation of community changes with physicochemical soil parameters (moisture, electrical conductivity, nutrient availability) [2, 11, 13].

Studies from Kuwait show that indigenous microbial communities rapidly adapt to oil contamination and often outcompete introduced consortia: hydrocarbonoclastic communities converged over time towards highly tolerant taxa (*Dietzia* papillomatosus, *Nocardioides*, *Microbacterium*, *Alkanindiges*) regardless of dilution with other soils [2]. Bioaugmentation using microbial consortia caused a temporary change in the composition of the microbial community, but, compared with the natural microbiota, did not lead to a significant acceleration in oil degradation [10, 12]. Molecular monitoring (16S rRNA sequencing) played a key role in establishing that the introduced strains were not dominant, whilst the enrichment of rare native species contributed to bioremediation [10, 14]. These results highlight the importance of metagenomic analysis of the microbial community in environmental assessment processes: it helps to determine the stability of the introduced strains; the potential for enriching the population of native microorganisms capable of degrading substances; and the need to add nutrients [2, 11].

5. Chemical and ecotoxicological monitoring

5.1. Total petroleum hydrocarbons (TPH) and analysis of individual compounds

The main chemical parameter for assessing the effectiveness of bioremediation is the monitoring of total petroleum hydrocarbons (TPH). TPH content is measured using the gravimetric method or by IR-GC spectroscopy [12, 17, 18, 22]. In the Abu Dhabi biopile study, a 4-77% reduction in hydrocarbon content across the different treatment variants made it possible to assess the relative effectiveness of biostimulation, surfactant addition, and bioaugmentation [17]. Kinetic analysis of the degradation of individual diesel fuel fractions by indigenous strains shows that the rate and completeness of degradation depend substantially on the initial substrate concentration and strain adaptation, which allows the timing of achieving regulatory TPH values under given conditions to be predicted [8].

The comparability of TPH, PAH, and BTEX data depends strongly on sample preparation and on the analytical window of the method. Gravimetric or infrared TPH measurements provide an operationally defined bulk value, but co-extracted natural organic matter and the selected extraction solvent can reduce selectivity. Soxhlet extraction with acetone/hexane or methylene chloride/acetone is suitable for non-volatile and semivolatile hydrocarbons, whereas GC-FID resolves hydrocarbon ranges and GC-MS provides greater compound-level selectivity for PAHs. BTEX requires sealed sampling and purge-and-trap or headspace GC-MS to minimise volatile losses. Detection and reporting limits are matrix- and laboratory-dependent; therefore, studies should report the dry-mass basis, particle-size preparation, solvent composition and extraction time, cleanup procedure, surrogate and matrix-spike recoveries, calibration range, and method-specific LOD/LOQ. Results obtained with different extraction efficiencies, carbon-number windows, or detector responses should not be treated as directly interchangeable [18, 31–33].

A decrease in extractable soil concentration should not automatically be interpreted as biodegradation. Apparent removal may result from volatilization, vertical or lateral redistribution, leaching, sorption, or progressive formation of non-extractable residues. Where feasible, remediation studies should use dry-mass-normalized contaminant inventories, spatially representative replicate sampling, abiotic or untreated controls, extraction-recovery checks, and monitoring of deeper soil layers and leachate. Measurements of CO₂ evolution or other mineralization products can provide complementary evidence of biodegradation. Reporting both concentration changes and a documented mass balance prevents physical losses or reduced solvent extractability from being misclassified as biological destruction [2, 8, 17, 31–33].

Field tests under desert conditions typically use TPH threshold values (for example, 1 g·kg⁻¹) as clean-up targets in accordance with national or corporate guidelines [1, 14, 22]. However, total content alone is insufficient: residual PAHs [17] and weathered heavy fractions can persist for decades after the original spills even after a substantial reduction in TPH [13, 34]. Accordingly, monitoring of specific compounds (PAHs, BTEX, etc.) is recommended in cases where there is a risk to human health or sensitive ecosystems [1, 2, 6]; for example, in coastal sediments affected by petroleum product depots, the content of individual PAHs and the associated risks to humans and aquatic biota have been quantitatively assessed [6]. A comprehensive analysis of soil and groundwater quality in the oil-producing regions of Western Kazakhstan likewise demonstrates the need to combine chemical contaminant analysis with consideration of climatic factors when designing monitoring programmes [35]. A generalized approach to monitoring oil-contaminated soils involves a shift from the TPH method to a multi-parameter analysis of chemical and biological indicators. [36].

5.2. Soil respiration and biological activity

CO₂ release and associated parameters are widely used as criteria for evaluating bioremediation. In desert bio-piles, continuous monitoring of CO₂

revealed kinetic patterns of microbial activity: the addition of surfactants resulted in faster initial peaks; systems incorporating bio-enrichment demonstrated slower but more stable activity. [17, 18]. During the phytoremediation process, the abundance of the total number of heterotrophs and hydrocarbon-oxidising microorganisms increased as the plant cover grew, whilst the total hydrocarbon content decreased. A strong correlation was observed between plant cover, nitrogen availability and microbial abundance [12, 22]. The operational criteria that enable the optimisation of aeration, irrigation and nutrient dosing [17, 18] are respiratory rate and microbial biomass; these indicators show how effective the measures taken (such as the application of fertilisers) are [2, 11].

5.3. Ecotoxicological tests and bioassays

Bioremediation of desert soils contaminated with petroleum products not only reduces hydrocarbon levels but also restores their biological functions. For example, the germination rate of field bean (*Vicia faba*) seeds in oil-contaminated soil after six months of natural remediation was up to 96 per cent [2], and the seedlings reached maturity. Therefore, the inclusion of ecotoxicological tests (plant growth, earthworm survival) in monitoring systems [1, 14], combined with the analysis of petroleum products, is crucial for assessing the recovery of vegetation cover [2, 15].

5.4. Molecular and metabolomic markers of chemical transformation

In addition to classical chemical and microbiological indicators, molecular and metabolomic markers that directly link changes in contaminant chemical composition to ecosystem response are becoming increasingly important. It has been shown that petroleum contamination alters not only the structure of the microbial community but also its metallome - the assemblage of mobile soil metal forms - making metallome analysis an informative addition to conventional TPH and PAH monitoring [7]. Integrated mathematical and metabolomic approaches to assessing the spatial distribution of contamination make it possible to link chemical analysis data from samples to the nature and degree of toxicological impact at a specific site, improving the accuracy of identifying zones that require priority intervention [3].

6. Remote sensing, spectral analysis, and AI-assisted chemical indicators

6.1. Mapping of oil-contaminated soils and remediation progress

Given the vast spatial scale of desert oil contamination (for example, Kuwait's "oil lakes"), remote sensing has become a central element of environmental monitoring and assessment [1, 6, 34, 37]. In the Kuwait study, Landsat-5 images with a spatial resolution of 30 m and less than 5% cloud cover were used to represent extreme (1991), high (1992), and moderate (2002) contamination. Models based on Random Tree, support vector machine, and Random Forest algorithms were trained on 70% of 600 samples and tested on 180 independent points. Most model-data combinations yielded 97-100% correctly classified instances, whereas the indices-only SVM model for moderately contaminated soil achieved 78%; consequently, the highest accuracy values are

study-specific validation results rather than universal operational performance [34]. Such models allow retrospective mapping of historical contamination, evaluation of remediation outcomes (areas where spectral values approach pre-spill conditions), and prioritisation of remaining problem zones [1, 9, 34]. These approaches can be integrated with ground-based sampling for designing and monitoring bioremediation projects across large desert areas [1, 6].

6.2. Long-term spectral monitoring of vegetation response

Remote sensing is also useful for tracking vegetation stress and recovery in oil-affected desert landscapes. In Evrona (Israel), hyperspectral measurements in the 350-2500 nm range for four dominant shrub species at contaminated and control sites revealed changes in leaf reflectance and pigment composition years after the 2014 oil spill. Traditional vegetation indices were less sensitive to long-term contamination, but a new normalised blue-green stress index (NBGSI) effectively distinguished shrubs at contaminated versus clean sites (a significant correlation between contamination and pheophytin a content - a stress indicator) [37]. Machine-learning classifiers using full-spectrum reflectance data achieved high accuracy in separating shrubs at contaminated and control sites, demonstrating the potential of non-destructive spectral tools for ongoing bioremediation monitoring [1, 37].

6.3. Datasets for AI-based detection of onshore oil spills

A satellite-based database called ROSID was recently developed in Western Kazakhstan for the detection of onshore oil spills using Landsat imagery, aerial photography, and modern deep-learning models. Mask2Former and DeepLabV3+ produced the best results, with F-scores exceeding 80% and Intersection-over-Union values of approximately 67-73% for the oil class [38]. This high accuracy in identifying small spills and complex boundaries demonstrates that AI-based remote sensing can support operational monitoring of onshore oil contamination and remediation efforts. A similar principle applies to monitoring residual PAHs: combining remote sensors (including underwater drones) with knowledge-distillation methods makes it possible to predict the concentrations of individual PAH ring classes from indirect signals, substantially expanding the possibilities for operational chemical monitoring in hard-to-access environments [39]. For desert regions with developed oil infrastructure, such tools can be integrated into routine environmental monitoring and early-warning systems and can help verify the spatial effectiveness of bioremediation [1, 34, 38].

7. Sorbent materials and sustainability assessment of clean-up technologies

A separate area of chemical support for bioremediation involves the development and selection of sorbent materials for containing and partially removing oil before the biological clean-up stage begins. For Kazakhstan and neighbouring regions, natural carbonaceous minerals are of particular practical interest: carbonised shungite-based mixtures have been shown to have pronounced sorption capacity for oil, and artificial neural networks allow this capacity to be predicted with high accuracy depending on sorbent composition

and the carbonisation method, opening the way to the rational selection of low-cost local sorbents for the initial containment of spills prior to subsequent bioremediation [40].

In addition to the effectiveness of soil remediation, considerable attention is paid to the environmental and energy ‘costs’ associated with the technology itself. A life-cycle assessment (LCA) of various soil remediation schemes shows that, when choosing between biological, physico-chemical and combined methods, one should take into account not only the rate and completeness of decomposition, but also the associated greenhouse gas emissions, energy consumption and use of reagents [41]. This ‘green remediation’ approach is particularly relevant when selecting methods: for example, when choosing between intensive methods involving chemical enhancement (oxidation, electrokinetics, microwave heating) and less resource-intensive biological strategies.

The evidence base is not environmentally uniform. The electrokinetic study in [4] concerns cold-region soil, the field phytoremediation study in [22] was conducted in a temperate steppe, the PAH risk example in [6] concerns aquatic sediments, the microwave review [28] covers multiple soil and climate settings, [36] focuses on Arctic and sub-Arctic soils, and the underwater-drone example in [39] is an aquatic proof of concept. These studies support mechanisms or monitoring principles, but they do not directly validate performance in hyper-arid saline desert soils. Transfer therefore requires local testing under representative moisture, temperature, salinity, carbonate content, soil texture, contaminant ageing, and microbial-community conditions, together with desert-specific controls and endpoints.

8. An integrated framework for assessing the bioremediation of desert oil contamination

Based on the evidence presented above, an effective system for environmental monitoring and assessment of the bioremediation of oil-contaminated desert soils should include:

- baseline data and problem definition: initial mapping and classification of contamination (remote sensing, spectral indices) combined with ground-truthing (soil sampling and chemical analysis, micro- and molecular-biological analysis, soil toxicity bioassays);

- an informed choice of bioremediation strategy: for very high TPH content (>10-20% w/w), soil excavation followed by biopiling with biostimulation (nutrients, moisture, aeration) is applicable, if necessary with prior chemical treatment of recalcitrant fractions (oxidation, sorbents); for moderate or aged contamination and large areas, priority should be given to in-situ field work, monitored natural attenuation, and phytoremediation (natural or engineered) using tolerant native species; bioaugmentation should be applied only in specific situations and its effectiveness verified through microbiological and chemical monitoring;

– monitoring during remediation and after reclamation is completed: regular tracking of TPH, target compounds (PAHs, BTEX), soil respiration, microbial diversity, ecotoxicity, and, where applicable, remote spectral indicators, with comparison of results across stages and sites to ensure data comparability.

9. Conclusion

Research data from a Kuwait desert-soil windrow study show that, at an initial crude-oil content of 17.3% (w/w), open aeration and periodic moistening produced 73-79% removal over approximately six months, with more than 50% removed during the first month [2]. A separate six-month microcosm study reported approximately 70% removal at 1-10% oil contamination and approximately 50% removal at 20-30%, demonstrating the strong dependence of the reported efficiency on initial loading and treatment conditions [10].

Biostimulation and engineered systems (biopiles, landfarming) accelerate remediation and provide better control, whereas bioaugmentation often offers only limited additional benefit in removing recalcitrant compounds from soil. Chemically enhanced methods - oxidation with Fenton's reagent and persulfate, nanomaterial-based and electrokinetic approaches, microwave thermal treatment, and bioelectrochemical systems - represent a promising but as yet non-standardised toolkit for "unlocking" resistant, weathered contaminant fractions ahead of subsequent biological polishing.

Phytoremediation, whether natural or engineered, can achieve high rates of decontamination and vegetation restoration, particularly under moderate contamination, with native desert shrubs and grasses playing a key role. Environmental monitoring and assessment should integrate chemical, biological, and remote-sensing methods: measurements of total hydrocarbon and PAH content should be complemented by profiling of the microbial community and its metallome, soil respiration, plant-based indicators, toxicity tests, spectral monitoring, and, where economically justified, life-cycle assessment of the technology applied.

Key directions for further research and the implementation of arid-soil clean-up technologies should include:

1. stricter standardisation of chemical and biological monitoring protocols (combining TPH, PAHs, ecotoxicity, and microbial/metallomic indicators) adapted to desert conditions;
2. wider use of remote-sensing and artificial-intelligence tools for the operational monitoring of remediation, supported by open datasets such as ROSID;
3. systematic investigation of chemically enhanced and combined methods (oxidation, nanomaterials, electrokinetics, bioelectrochemistry) as means of increasing the bioavailability of recalcitrant oil fractions, including assessment of their compatibility with subsequent bioremediation and their associated environmental footprint (LCA);

4. long-term studies linking changes in microbial and plant diversity to ecosystem functioning and the resilience of reclaimed desert soils;

5. a shift from final endpoints based solely on total TPH content towards risk-based criteria that account for residual PAHs and their environmental significance.

Combining reliable, multifaceted chemical and biological monitoring of soil condition with bioremediation strategies tailored to the specific contamination can achieve effective clean-up and environmental restoration of oil-contaminated desert soils, while optimising costs and minimising the further impact of residual contaminants on fragile desert ecosystems.

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МҰНАЙМЕН ЛАСТАНҒАН ШӨЛ ТОПЫРАҚТАРЫН БИОРЕМЕДИАЦИЯЛАУДЫ ХИМИЯЛЫҚ ТҮРҒЫДАН БАҚЫЛАУ МЕН БАҒАЛАУ: ҚАЗІРГІ ЗАМАНҒЫ ӘДІСТЕРГЕ ШӨЛУ

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Түйіндеме. Шөлдер мен басқа да құрғақ аймақтарда, соның ішінде Кувейтте, Израильдегі Арава аңғарында және Батыс Қазақстанда болған мұнай төгінділері созылмалы түрде ластанған ауқымды топырақ аумақтарының қалыптасуына әкелді. Мұндай жерлерді қалпына келтіру ылғал мен қоректік элементтердің тапшылығына, тұздануға, температураның күрт ауытқуына және мұнай қалдықтарының ескіруіне байланысты қиындайды. Осы шөлудың мақсаты мұнаймен ластанған шөл топырақтарының биоремедиациясын бақылау мен бағалаудың қазіргі химиялық және физика-химиялық тәсілдерін жүйелеу, сондай-ақ кешенді тәуекелге негізделген бағалауға жарамды көрсеткіштерді анықтау болып табылады. Мұнайдың жалпы мұнай көмірсутектерін, полициклді ароматты көмірсутектерді, БТЭК қосылыстарын, шайырлар мен асфальтендерді қамтитын көпкомпонентті ластағыш ретіндегі құрамы және олардың қозғалғыштығын, биожетімділігін, тұрақтылығы мен уыттылығын айқындайтын топырақ қасиеттері қарастырылды. Табиғи ыдырау, биостимуляция, биоаугментация, биопайлинг және фиторемедиация Фентон реактиві мен персульфат арқылы тотығуға, наноматериалдарды қолдануға, электрокинетикалық үдерістерге, микротолқынды қыздыруға және биоэлектрохимиялық жүйелерге негізделген химиялық күшейтілген әдістермен салыстырылды. Мұнай фракцияларын хроматографиялық және спектроскопиялық анықтауды топырақ тынысымен, микробтық және функционалдық-гендік көрсеткіштермен, экотоксикологиялық сынақтармен және қашықтан зондаумен біріктіруге ерекше назар аударылды. Гиперспектрлік деректер мен жасанды интеллект әдістері ластануды картаға түсіру және биоремедиация кезіндегі кеңістіктік өзгерістерді бақылау құралдары ретінде талданды. Қазақстан үшін өзекті шунгит негізіндегі композицияларды қоса алғанда, сорбциялық материалдарды мұнайды бастапқы окшаулау және ішінара жою сатысында қолдану қарастырылды. Жалпы мұнай көмірсутектері мөлшерінің төмендеуі экологиялық қалпына келуді толық дәлелдемейтіні көрсетілді, өйткені тұрақты ароматты фракциялар мен қалдық уыттылық сақталуы мүмкін.

Түйінді сөздер: Мұнаймен ластанған шөл топырақтары; биоремедиация; мұнай көмірсутектерінің жалпы мөлшері; полициклді ароматты көмірсутектер; химиялық тотығу; сорбенттер; экологиялық мониторинг; қашықтықтан зондау

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ХИМИЧЕСКИЕ ПОДХОДЫ К МОНИТОРИНГУ И ОЦЕНКЕ БИОРЕМЕДИАЦИИ НЕФТЕЗАГРЯЗНЁННЫХ ПУСТЫННЫХ ПОЧВ: ОБЗОР СОВРЕМЕННЫХ МЕТОДОВ

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Резюме. Разливы нефти в пустынях и других засушливых регионах, включая Кувейт, долину Арава в Израиле и Западный Казахстан, привели к формированию обширных территорий с хронически загрязнёнными почвами, восстановление которых осложняется недостатком влаги и питательных элементов, засолением, резкими температурными колебаниями и старением нефтяных остатков. Цель обзора состоит в систематизации современных химических и физико-химических подходов к мониторингу и оценке биоремедиации нефтезагрязнённых пустынных почв, а также в определении показателей, пригодных для комплексной риск-ориентированной оценки. Рассмотрен состав нефти как многокомпонентного загрязнителя, включающего общее содержание нефтяных углеводородов, полициклические ароматические углеводороды, соединения БТЭК, смолы и асфальтены, а также свойства почв, определяющие их подвижность, биодоступность, устойчивость и токсичность. Естественное разложение, биостимуляция, биоаугментация, биоайлинг и фиторемедиация сопоставлены с химически усиленными методами на основе окисления реактивом Фентона и персульфатом, применения наноматериалов, электрокинетических процессов, микроволнового нагрева и биоэлектрохимических систем. Особое внимание уделено сочетанию хроматографического и спектроскопического определения нефтяных фракций с оценкой дыхания почвы, микробными и функционально-генными показателями, экотоксикологическими тестами и дистанционным зондированием. Гиперспектральные данные и методы искусственного интеллекта рассмотрены как инструменты картирования загрязнения и наблюдения за его пространственной динамикой. Проанализировано применение сорбционных материалов, включая шунгитовые композиции, актуальные для Казахстана, на стадии локализации и первичного удаления нефти. Показано, что снижение общего содержания нефтяных углеводородов само по себе не подтверждает экологическое восстановление, поскольку могут сохраняться устойчивые ароматические фракции и остаточная токсичность.

Ключевые слова: нефтезагрязнённые пустынные почвы; биоремедиация; общее содержание углеводородов нефти; полициклические ароматические углеводороды; химическое окисление; сорбенты; экологический мониторинг; дистанционное зондирование

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МАЗМҰНЫ

<i>А.М. Калиева, А.Е. Малмакова</i> ПОЛИМЕР ҚҰРАМЫ МЕН ТЕМПЕРАТУРАНЫҢ ХИТОЗАН-КАРБОКСИМЕТИЛЦЕЛЛЮЛОЗА ГИДРОГЕЛЬДЕРІНІҢ РЕОЛОГИЯЛЫҚ ҚАСИЕТТЕРІНЕ ӘСЕРІ	5
<i>М.К. Кылышканов, Б.Т. Алтайбаев, Ж.С. Кенжетасов, М.П. Копбаева, Р.Х. Шарипов, Г.К. Малдыбаев</i> ЖЕР АСТЫ ШАЙМАЛАУ ПРОЦЕСІНДЕГІ АНИОНАЛМАСТЫРҒЫШ ШАЙЫРЛАРДЫҢ КРЕМНИЙМЕН ЛАСТАНУЫ: ҚАЗІРГІ ТҮСІНІКТЕР ЖӘНЕ РЕГЕНЕРАЦИЯ ӘДІСТЕРІ	15
<i>М.А. Нұрбекова, М.М. Матаев, З.Б. Сарсенбаева, М.Р. Абдраймова, А.Қ. Көшікмбаева</i> SMMNO ₃ -LAMNO ₃ ПЕРОВСКИТТИ МАНГАНИТТИҢ СИНТЕЗІ, ҚҰРЫЛЫСЫ ЖӘНЕ МОРФОЛОГИЯСЫ.....	37
<i>Ә.Ж. Байзақ, Ж.Н. Кайнарбаева, Е.А. Тусупкалиев, А.А. Еспенбетов, Г.А. Усков, К.А. Кадирбеков, М.Т. Ошакбаев, Д. Турғалиев</i> "ӨЗЕНМҰНАЙГАЗ"АҚ МҰНАЙ ҚАЛДЫҚТАРЫН ПАЙДАЛЫ ӨНІМДЕРГЕ ӨНДЕУДІҢ ИННОВАЦИЯЛЫҚ ЖӘНЕ ЖЕТІЛДІРІЛГЕН ТЕХНОЛОГИЯСЫН ӨЗІРЛЕУ.....	48
<i>А.Н. Дюрягина, Т.В. Ширина, Ю.С. Бызова, К.А. Островной, А.А. Луценко</i> ҚАБЫҚ ТҮЗГІШТЕРДІҢ СУЛЫ ДИСПЕРСИЯЛАРЫНДАҒЫ ПОЛИЭЛЕКТРОЛИТ ӨЗАРА ӨРЕКЕТТЕСУІНІҢ ФИЗИКА-ХИМИЯЛЫҚ АСПЕКТІЛЕРІ.....	58
<i>А.Ю. Тен, В.К. Ю, С.Ш. Сафаров</i> ВОЛЬФРАМ МИНЕРАЛДАРЫНА АРНАЛҒАН ЗАМАНАУИ ФЛОТАЦИЯЛЫҚ ЖИНАҒЫШТАРҒА ШОЛУ: БИФУНКЦИОНАЛДЫ МОЛЕКУЛАЛАРДАН DFT НЕГІЗІНДЕГІ ЖОБАЛАУҒА ДЕЙІН (ШОЛУ).....	69
<i>Е.М. Ергалиева, В.В. Вадеев, А.Б. Узакова, Д.Б. Жусупова, М.А. Губенко, С.Б. Абеуова</i> АСТРАГАЛДАН АЛЫНҒАН ФИТОХИМИЯЛЫҚ ҚОСЫЛЫСТАРДЫ ГЛИКОГЕНСИНТАЗАКИНАЗА-3β-ҒА ҚАТЫСТЫ ДОКИНГТІК ЖӘНЕ АДМЕТ-БАҒАЛАУ.....	87
<i>К.А. Садыков, И.С. Хисамеденова, С.Б. Рыспаева, Ш.С. Ислам, А.Қ. Мекебаева</i> β-ЦИКЛОДЕКСТРИН МЕН СҮТ ҚЫШҚЫЛЫ НЕГІЗІНДЕГІ SUPRADES-тің АСФАЛЬТЕНДЕРДІҢ АГРЕГАЦИЯЛАНУ ПРОЦЕСТЕРІНЕ ӘСЕРІ.....	97
<i>С.Т. Ермуханова, С.С. Сатаева, Д.С. Назарова, А.Г. Абдрахманова, Е.Б. Казиев</i> МЫРЫШ ҚҰРАМДЫ ҚАЛДЫҚТАРДАН МЫРЫШ СУЛЬФАТЫНЫҢ МОНОГИДРАТЫН АЛУ ТЕХНОЛОГИЯСЫН ЗЕРТТЕУ.....	108
<i>А.З. Ғалымжан, С.С. Қожабеков, В.Г. Бондалетов, А. Қуанышев, А.К. Абдрасилова</i> ОКТАДЕЦИЛМЕТАКРИЛАТ ПЕН ВИНИЛИМИДАЗОЛДЫҢ СОПОЛИМЕРЛЕРІН ДИЗЕЛЬ ОТЫНЫНЫҢ ТӨМЕН ТЕМПЕРАТУРАЛЫҚ КӨРСЕТКІШТЕРІН ЖАҚСАРТАТЫН ҚОСПАЛАР РЕТІНДЕ СИНТЕЗДЕУ ЖӘНЕ ОЛАРДЫ БАҒАЛАУ.....	119
<i>Г.Е. Ерлан, Б.Б. Тюсюпова, С.М. Тажимаева, К.Б. Мусабеков, М.А. Муртаза</i> КӨПВАЛЕНТТІ ИОНДАР ЖӘНЕ МОДИФИКАЦИЯЛАНҒАН МОНТМОРИЛЛОНИТ НЕГІЗІНДЕ БИОКОМПОЗИТТЕРДІ ОҢТАЙЛАНДЫРУ.....	130
<i>М.А. Жолмаганбетова, С. Усманов, Г.Т. Омарова, Ш. Байбацаева, Э.Н. Рамазанова, Н.Н. Есеркеева, Р.У. Махмудов, Х.С. Усманов</i> МОНОМЕТИЛОЛМОЧЕВИНА, МЫС ПЕН МЫРЫШТЫҢ ФИТОҚОСЫЛЫСТАРЫ ЖӘНЕ МОНОЭТАНОЛАМИН КАЛЬЦИЙ ФОСФАТТАРЫ НЕГІЗІНДЕ ТҮЙІРІШКЕЛГЕН КОМПОЗИЦИЯ АЛУ ТЕХНОЛОГИЯСЫН ЗЕРТТЕУ	142
<i>Ә.Қ. Жаңабаева, Ә. Хамбарқызы, І.А. Темірғали, А.Қ. Өмірғали, А. Бердихалық, А.Х. Юсуф</i> ТЕХНОЛОГИЯЛЫҚ ЕРІТІНДІЛЕРДЕН КРЕМНИЙДІ ЖОЮДА ӘЛЕУЕТТІ ҚОЛДАНУ ҮШІН ХРИЗОТИЛ-АСБЕСТ ҚАЛДЫҚТАРЫНАН КЕУЕКТІ КРЕМНЕЗЕМҚҰРАМДЫ МАТРИЦА ҚАЛЫПТАСТЫРУ.....	151
<i>О.А. Нұркенов, Л. К. Абуляисова, С.Д. Фазылов, А.Қ. Сыздықов, А.Т. Қажмұратова, А.М. Тәжібай, А.Ө. Уайылда</i> МОРФОЛИН ЖӘНЕ АЛКАЛОИД ЦИТИЗИН НЕГІЗІНДЕГІ АМИНОФТАЛИДТЕРДІҢ СИНТЕЗІ	163

М.С. Муканова, Л.М. Ахметова, Е.С. Сычева ИЗОПЕНТИЛДИТИОКАРБАМАТТАРДЫҢ АЛКИЛДІ ЖӘНЕ ДИАЛКИЛДІ ТИОЭФИРЛЕРІНІҢ СИНТЕЗІ ЖӘНЕ ҚҰРЫЛЫМЫ	173
М.К. Кылышканов, Г.К. Малдыбаев, Р.Х. Шарипов, Б.Т. Алтайбаев, Л.К. Бекбаева, Ә.Қ. Жаңабаева, А.Х. Юсуф УРАН ЭКСТРАКЦИЯСЫ КЕЗІНДЕ КРЕМНИЙДІ КЕТПҮГЕ ЖӘНЕ АНИОН АЛМАСУ ШАЙЫРЫН ҚАЛПЫНА КЕЛТПҮГЕ АРНАЛҒАН ЕРІТІНДІНІҢ РЕГЕНЕРАЦИЯЛЫҚ ҚҰРАМЫ.....	184
Р.А. Нарманова, С.Ж. Қужамбердиева, Б.Г. Алимхан, С.А. Канжар, Н.О. Аппазов МҰНАЙМЕН ЛАСТАНҒАН ШӨЛ ТОПЫРАҚТАРЫН БИОРЕМЕДИАЦИЯЛАУДЫ ХИМИЯЛЫҚ ТҰРҒЫДАН БАҚЫЛАУ МЕН БАҒАЛАУ: ҚАЗІРГІ ЗАМАНҒЫ ӘДІСТЕРГЕ ШӨЛУ.....	197

СОДЕРЖАНИЕ

<i>А.М. Калиева, А.Е. Малмакова</i> ВЛИЯНИЕ СОСТАВА ПОЛИМЕРОВ И ТЕМПЕРАТУРЫ НА РЕОЛОГИЧЕСКИЕ СВОЙСТВА ХИТОЗАН-КАРБОКСИМЕТИЛЦЕЛЛЮЛОЗНЫХ ГИДРОГЕЛЕЙ.....	5
<i>М.К. Кылышканов, Б.Т. Алтайбаев, Ж.С. Кенжетеев, М.П. Копбаева, Р.Х. Шарипов, Г.К. Малдыбаев</i> ЗАГРЯЗНЕНИЕ АНИОНООБМЕННЫХ СМОЛ КРЕМНИЕМ В ПРОЦЕССЕ ПОДЗЕМНОГО ВЫЩЕЛАЧИВАНИЯ УРАНА: СОВРЕМЕННОЕ ПОНИМАНИЕ И ПОДХОДЫ К РЕГЕНЕРАЦИИ	15
<i>М.А. Нурбекова, М.М. Матаев, З.Б. Сарсенбаева, М.Р. Абдраймова, А.К. Көшікмбаева</i> СИНТЕЗ, СТРУКТУРА И МОРФОЛОГИЯ ПЕРОВСКИТНОГО КОМПОЗИТА $\text{SmMnO}_3\text{-LaMnO}_3$	37
<i>А.Ж. Байзак, Ж.Н. Кайнарбаева, Е.А. Тусупкалиев, А.А. Еспенбетов, Г.А. Усков, К.А. Кадирбеков, М.Т. Ошакбаев, Д. Турғалиев</i> РАЗРАБОТКА ИННОВАЦИОННОЙ И УЛУЧШЕННОЙ ТЕХНОЛОГИИ ПЕРЕРАБОТКИ НЕФТЕОТХОДОВ АО «ОЗЕНМУНАЙГАЗ» В ПОЛЕЗНЫЕ ПРОДУКТЫ.....	48
<i>А.Н. Дюрягина, Т.В. Ширина, Ю.С. Бызова, К.А. Островной, А.А. Луценко</i> ФИЗИКО-ХИМИЧЕСКИЕ АСПЕКТЫ ВЗАИМОДЕЙСТВИЯ ПОЛИЭЛЕКТРОЛИТА В ВОДНЫХ ДИСПЕРСИЯХ ПЛЕНКООБРАЗУЮЩИХ	58
<i>А.Ю. Тен, В.К. Ю, С.Ш. Сафаров</i> ОБЗОР СОВРЕМЕННЫХ ФЛОТАЦИОННЫХ КОЛЛЕКТОРОВ ДЛЯ ВОЛЬФРАМОВЫХ МИНЕРАЛОВ: ОТ БИФУНКЦИОНАЛЬНЫХ МОЛЕКУЛ ДО ПРОЕКТИРОВАНИЯ НА ОСНОВЕ DFT (ОБЗОР)	69
<i>Е.М. Ергалиева, В.В. Вазжев, А.Б. Узакова, Д.Б. Жусупова, М.А. Губенко, С.Б. Абеуова</i> ФИЗИКО-ХИМИЧЕСКИЕ АСПЕКТЫ ВЗАИМОДЕЙСТВИЯ ПОЛИЭЛЕКТРОЛИТА В ВОДНЫХ ДИСПЕРСИЯХ ПЛЕНКООБРАЗУЮЩИХ	87
<i>К.А. Садыков, И. С. Хисамеденова, С.Б. Рыспаева, Ш.С. Ислам, А.К. Мекебаева</i> ВЛИЯНИЕ SUPRADES НА ОСНОВЕ β -ЦИКЛОДЕКСТРИНА И МОЛОЧНОЙ КИСЛОТЫ НА ПРОЦЕССЫ АГРЕГАЦИИ АСФАЛЬТЕНОВ.....	97
<i>С.Т. Ермуханова, С.С. Сатаева, Д.С. Назарова, А.Г. Абдрахманова, Е.Б. Казиев</i> ИССЛЕДОВАНИЕ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ МОНОГИДРАТА СУЛЬФАТА ЦИНКА ИЗ ЦИНКСОДЕРЖАЩИХ ОТХОДОВ	108
<i>А.З. Гальмжан, С.С. Кожабекков, В.Г. Бондалетов, А. Куанышев, А.К. Абдрасилова</i> СИНТЕЗ И ОЦЕНКА СОПОЛИМЕРОВ ОКТАДЕЦИЛМЕТАКРИЛАТА И ВИНИЛИМИДАЗОЛА В КАЧЕСТВЕ ПРИСАДОК ДЛЯ УЛУЧШЕНИЯ НИЗКОТЕМПЕРАТУРНЫХ СВОЙСТВ ДИЗЕЛЬНОГО ТОПЛИВА.....	119
<i>Г.Е. Ерлан, Б.Б. Тюсюпова, С.М. Тажибаева, К.Б. Мусабеков, М.А. Муртаза</i> СТРУКТУРНАЯ ОПТИМИЗАЦИЯ БИОКОМПОЗИТОВ С ИСПОЛЬЗОВАНИЕМ МНГОВАЛЕНТНЫХ ИОНОВ И МОДИФИЦИРОВАННЫХ МОНТМОРИЛЛОНИТА.....	130
<i>М.А. Жолмаганбетова, С. Усманов, Г.Т. Омарова, Ш. Байбацаева, Э.Н. Рамазанова, Н.Н. Есеркеева, Р.У. Махмудов, Х.С. Усманов</i> ИССЛЕДОВАНИЕ ТЕХНОЛОГИИ ПОЛУЧЕНИЯ ГРАНУЛИРОВАННОЙ КОМПОЗИЦИИ НА ОСНОВЕ МОНОМЕТИЛОЛМОЧЕВИНЫ, ФИТОСОЕДИНЕНИИ МЕДИ И ЦИНКА, КАЛЬЦИЙФОСФАТОВ МОНОЭТАНОЛАМИНА.....	142
<i>А.К. Жанабаева, А. Хамбаркызы, И.А. Темиргали, А.К. Омиргали, А. Бердыхалык, А.Х. Юсуф</i> ФОРМИРОВАНИЕ ПОРИСТОЙ КРЕМНЕЗЕМСОДЕРЖАЩЕЙ МАТРИЦЫ ИЗ ОТХОДОВ ХРИЗОТИЛ-АСБЕСТА ДЛЯ ПОТЕНЦИАЛЬНОГО ПРИМЕНЕНИЯ ПРИ УДАЛЕНИИ КРЕМНИЯ ИЗ ТЕХНОЛОГИЧЕСКИХ РАСТВОРОВ	151
<i>О.А. Нуркенов, Л.К. Абулялисова, С.Д. Фазылов, А.К. Сыздыков, А.Т. Кажмуратова, А.М. Тажибай, А.О. Уайдильда</i> СИНТЕЗ АМИНОФТАЛИДОВ НА ОСНОВЕ МОРФОЛИНА И АЛКАЛОИДА ЦИТИЗИНА.....	163
<i>М.С. Муканова, Л.М. Ахметова, Е.С. Сычева</i> СИНТЕЗ И СТРУКТУРА АЛКИЛОВЫХ И ДИАЛКИЛОВЫХ ТИОЭФИРОВ ИЗОПЕНТИЛДИТИОКАРБАМАТОВ.....	173
<i>М.К. Кылышканов, Г.К. Малдыбаев, Р.Х. Шарипов, Б.Т. Алтайбаев, Л.К. Бекбаева, А.К. Жанабаев, А.Х. Юсуф</i> РЕГЕНЕРИРУЮЩИЙ СОСТАВ РАСТВОРА ДЛЯ УДАЛЕНИЯ	

КРЕМНИЯ И ВОССТАНОВЛЕНИЯ АНИОННО-ОБМЕННОЙ СМОЛЫ ПРИ ЭКСТРАКЦИИ УРАНА	184
<i>Р.А.Нарманова, С.Ж. Қужамбердиева, Б.Г.Алимхан , С.А. Канжар, Н.О.Аппазов</i> ХИМИЧЕСКИЕ ПОДХОДЫ К МОНИТОРИНГУ И ОЦЕНКЕ БИОРЕМЕДИАЦИИ НЕФТЕЗАГРЯЗНЁННЫХ ПУСТЫННЫХ ПОЧВ: ОБЗОР СОВРЕМЕННЫХ МЕТОДОВ.....	197

CONTENTS

A.M. Kaliyeva, A.E. Malmakova EFFECT OF POLYMER COMPOSITION AND TEMPERATURE ON THE RHEOLOGICAL PROPERTIES OF CHITOSAN-CARBOXYMETHYL CELLULOSE HYDROGELS	5
M.K. Kylyshkanov, B.T. Altaibayev, Zh. S. Kenzhetaev, M.P. Kopbaeva, R.H. Sharipov, G.K. Maldybayev SILICA FOULING OF ANION-EXCHANGE RESINS IN URANIUM IN-SITU RECOVERY: CURRENT UNDERSTANDING AND REGENERATION APPROACHES	15
M.A. Nurbekova, M.M. Mataev , Z.B. Sarsenbaeva, M.R. Abdraimova, A.K. Koshkimbayeva SYNTHESIS, STRUCTURE AND MORPHOLOGY OF SmMnO ₃ -LaMnO ₃ PEROVSKITE COMPOSITE.....	37
A.Zh. Bayzak, Zh.N. Kaynarbayeva, E.A. Tussupkaliyev, A.A. Espenbetov, G.A. Uskov, K.A. Kadirbekov, M.T. Oshakbayev, D.A. Turgaliyev DEVELOPMENT OF AN INNOVATIVE AND IMPROVED TECHNOLOGY FOR PROCESSING OIL WASTE FROM JSC “OZENMUNAYGAZ” INTO USEFUL PRODUCTS.....	48
A.N. Dyuryagina, T.V. Shirina, Yu.S. Byzova, K.A. Ostrovnoy, A.A. Lutsenko PHYSICOCHEMICAL ASPECTS OF POLYELECTROLYTE INTERACTIONS IN AQUEOUS FILM-FORMER DISPERSIONS	58
A.Yu. Ten, V.K. Yu, S.Sh. Safarov A REVIEW OF MODERN FLOTATION COLLECTORS FOR TUNGSTEN MINERALS: FROM BIFUNCTIONAL MOLECULES TO DFT-GUIDED DESIGN (REVIEW)	69
E.M. Yergaliyeva, V.V. Vazhev, A.B. Uzakova, D.B. Zhusupova, M.A. Gubenko , S.B. Abeuova DOCKING AND ADMET EVALUATION OF ASTRAGALUS-DERIVED PHYTOCHEMICALS AGAINST GLYCOGEN SYNTHASE KINASE-3β.....	87
K.A. Sadykov, I.S. Khisamedenova, S.B. Ryspayeva, Sh.S. Islam, A.K. Mekebaeva EFFECT OF β-CYCLODEXTRIN AND LACTIC ACID-BASED SUPRADES ON ASPHALTENE AGGREGATION PROCESSES.....	97
S.T. Yermukhanova, S.S. Satayeva, D.S. Nazarova, A.G. Abdrakhmanova, Ye.B. Kaziyeu RESEARCH ON THE TECHNOLOGY FOR PRODUCING ZINC SULFATE MONOHYDRATE FROM ZINC-CONTAINING WASTE.....	108
A. Galymzhan, S. Kozhabekov, V. Bondaletov, A. Kuanyshev, A. Abdrassilova SYNTHESIS AND EVALUATION OF OCTADECYL METHACRYLATE-VINYLMIDAZOLE COPOLYMERS AS COLD-FLOW IMPROVERS FOR DIESEL FUEL.....	119
G.Ye. Yerlan, B.B. Tyussypova, S.M. Tazhibayeva, K.B. Musabekov, M.A. Murtaza STRUCTURAL OPTIMIZATION OF BIOCOMPOSITES USING MULTIVALENT IONS AND MODIFIED MONTMORILLONITE	130
M.A. Zholmaganbetova, S. Usmanov, G.T. Omarova, Sh. Baibachshayeva, E.N. Ramazanova, N.N. Yesserkeyeva, R.U. Makhmudov, H.S. Usmanov RESEARCH OF THE TECHNOLOGY FOR PRODUCING A GRANULATED COMPOSITION BASED ON MONOMETHYLOLUREA, COPPER AND ZINC PHYTOCOMPOUNDS, CALCIUM PHOSPHATES OF MONOETHANOLAMINE.....	142
A.K. Zhangabayeva, A. Khambarkyzy, I.A. Temirgali, A.K. Omirgali, A. Berdykhalykh, A.H. Yusoff FORMATION OF A POROUS SILICA-RICH MATRIX FROM CHRYSOTILE-ASBESTOS WASTE FOR POTENTIAL APPLICATION IN SILICON REMOVAL FROM PROCESS SOLUTIONS.....	151
O.A. Nurkenov, L.K. Abulyaisova, S.D. Fazylov, A.K. Syzdykov , A.T. Kazhmutatova, A.M. Tazhibay, A.O. Uaidilda SYNTHESIS OF AMINOPHTHALIDES BASED ON MORPHOLINE AND CYTISINE ALKALOID	163
M.S. Mukanova, L.M. Akhmetova, Ye.S. Sycheva SYNTHESSES AND STRUCTURE OF ALKYL AND DIALKYL ISOPENTYLDITHIOCARBAMATE THIOETHERS.....	173
M.K. Kylyshkanov, G.K. Maldybayev, R.H. Sharipov, B.T. Altaibayev, L.K. Bekbayeva, A.K. Zhangabayeva, A.H. Yusoff REGENERATING SOLUTION COMPOSITION FOR SILICON REMOVAL AND ANION-EXCHANGE RESIN RESTORATION IN URANIUM EXTRACTION.....	184

R.A. Narmanova, S.Zh. Kuzhamberdieva, B.G. Alimkhan, S.A. Kanzhar, N.O. Appazov

A.H. CHEMICAL APPROACHES TO MONITORING AND EVALUATING THE
BIOREMEDIATION OF OIL CONTAMINATED DESERT SOILS: A REVIEW OF MODERN
METHODS.....

197

Правила оформления статей в журнале
«ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА»

1. ОБЩИЕ ПОЛОЖЕНИЯ

Журнал «Химический журнал Казахстана» (ISSN 1813-1107, eISSN 2710-1185) выпускается ордена Трудового Красного Знамени АО «Институтом химических наук им. А.Б. Бектурова» 4 раза в год и публикует работы по широкому кругу фундаментальных, прикладных и инновационных исследований в области химии и химической технологии.

Языки публикации: казахский, русский, английский. Журнал индексируется Казахстанской библиометрической системой и включен в Перечень изданий, рекомендуемых Комитетом по контролю в сфере образования и науки Министерства образования и науки Республики Казахстан для публикации основных результатов научной деятельности.

Издание имеет следующие рубрики:

1. Обзорные статьи до 20 печатных страниц
2. Оригинальные статьи (до 8–10 печатных страниц)
3. Краткие сообщения (до 4–5 печатных страниц)

2. ПРЕДСТАВЛЕНИЕ СТАТЕЙ

Редакция принимает статьи от казахстанских и зарубежных авторов. В целях популяризации Журнала, редакционной коллегией приветствуется прием статей на английском языке.

Для регистрации и публикации статьи материал статьи представляется в редакцию через систему электронной подачи статьи на сайте Журнала (<https://www.chemjournal.kz/>) в комплекте со следующими документами:

1. Электронная версия статьи в форматах Word и PDF со встроенными в текст таблицами, схемами, рисунками (файл должен быть назван по фамилии первого автора на английском языке).

2. Сопроводительное письмо, адресованное в Редакцию Химического журнала Казахстана от организации, в которой данное исследование выполнено, с утверждением, что материал рукописи нигде не публиковался, не находится на рассмотрении для опубликования в других журналах и в материалах статьи отсутствуют секретные данные. В сопроводительном письме указываются сведения об авторе для корреспонденции: Фамилия, имя и отчество автора, служебный адрес с указанием почтового индекса, адрес электронной почты, телефон и ORCID.

3. Все статьи, опубликованные в Химическом журнале Казахстана (ISSN 1813-1107, eISSN 2710-1185) публикуются в открытом доступе. Чтобы обеспечить свободный доступ читателям и покрыть расходы на экспертную оценку, редактирование, поддержание сайта журнала, долгосрочное архивирование и ведение журнала, взимается плата за обработку статьи. Правила оплаты за опубликование принятой к печати статьи находятся в отдельном документе на сайте Журнала «Оплата за опубликование».

4. Статье присваивается регистрационный номер, который сообщается авторам в течение недели после получения указанного перечня документов; на этот номер необходимо ссылаться при переписке.

5. Принятым к печати статьям присваивается цифровой идентификатор (DigitalObjectIdentifier – DOI).

6. Учитывая невозможность проводить статьи на казахском языке через систему антиплагиат, будут учитываться формулировки рецензентов и решение издательской коллегии.

7. Статьи должны быть оформлены согласно шаблону, который можно скачать в разделе «Отправка материалов» на сайте Химического Журнала Казахстана.

3. СТРУКТУРА ПУБЛИКАЦИЙ

3.1. В начале **обзоров, оригинальных статей и кратких сообщений** на первой строке указывается номер по Универсальной десятичной классификации (УДК или UDC), соответствующий заявленной теме. Дается прописными буквами в верхнем левом углу. Также на первой строке справа прописными буквами полужирным шрифтом № 14 указывается название журнала **ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА (ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ, CHEMICAL JOURNAL OF KAZAKHSTAN)**, год, номер.

3.2. Далее через строку приводится международный стандартный серийный номер журнала (ISSN 1813-1107, eISSN 2710-1185) и на следующей строке слева приводится DOI: который будет иметь значение после принятия статьи к печати.

3.3. Далее, после отступа строки указывается **заглавие статьи** прописными буквами, шрифт № 14 – полужирный, выравнивание текста по центру. Название должно максимально полно и точно описывать содержание статьи, включать ключевые слова, отражающие направление и/или основной результат исследования, но в то же время быть коротким и ясным и не содержать сокращений.

3.4. Далее, после отступа строки, указываются **инициалы и фамилии автора(-ов)** строчными буквами, шрифт № 12 полужирный, курсив, выравнивание текста по центру. Фамилия автора, с которым следует вести переписку, должна быть отмечена звездочкой (*): *С.С. Сатаева*, А.М. Джубаналиева.*

3.5. Через строку шрифтом № 12, строчными буквами, курсивом с выравниванием текста по центру следуют **наименование(я) организации(й)** с указанием части названия организации, которая относится к понятию юридического лица (в английском тексте необходимо указывать официально принятый перевод названия), город, страна. В английском варианте адресные сведения должны быть представлены на английском языке, в т.ч. город и страна.

Строки с фамилиями авторов и названиями организаций содержат надстрочные индексы (после фамилии и перед названием организации), указывающие на место работы авторов.

На следующей строке курсивным начертанием, шрифт № 12, с выравниванием текста по центру указывается электронный адрес для переписки.

3.6. **Резюме (Abstract, Түйіндеме)** состоит из краткого текста (не менее 150–250 слов, шрифт № 12) на языке статьи. **Abstract** публикуется в международных базах, данных в отрыве от основного текста. Резюме должно быть автономным, все вводимые обозначения и сокращения необходимо расшифровать здесь же.

Приветствуется структурированное резюме, повторяющее структуру статьи и включающее: *введение, цели и задачи, методы, результаты и обсуждение, заключение (выводы)*. В то же время, цели и задачи описываются, если они не ясны из заглавия статьи, методы следует описывать, если они отличаются новизной. В резюме включаются новые результаты, имеющие долгосрочное значение, важные

открытия, опровергающие существующие теории, а также данные, имеющие практическое значение. Следует использовать техническую (специальную) терминологию вашей дисциплины.

Резюме дается без абзацного отступа строчными буквами; оно не должно содержать номера соединений, экспериментальные данные и ссылки на литературу.

Резюме только одно – в начале текста.

3.7. Далее на языке статьи без абзацного отступа строчными буквами шрифтом № 12, выравнивание текста по левому краю приводятся **ключевые слова** (от 5 до 10 шт.), обеспечивающие наиболее полное раскрытие содержания статьи.

3.8. В **кратких сообщениях** приводится резюме (150–200 слов), ключевые слова, но деления на разделы не требуется. Дается текст краткого сообщения на одном из трех языков с выполнением требований к УДК, названию статьи, перечню авторов, наименований организаций, в которых они работают, указанию автора для переписки. В тексте краткого сообщения приводятся конкретные **существенно новые результаты, требующие закрепления приоритета** с необходимыми экспериментальными подробностями. Затем следуют: информация о финансировании, благодарности, сведения о конфликте интересов, информация об авторах и список литературы.

3.9. Статья начинается с **введения**, в котором формулируется цель и необходимость проведения исследования, кратко освещается состояние вопроса со ссылками на наиболее значимые публикации с избеганием ссылок на устаревшие результаты. Излагаются открытия, сделанные в ходе данного исследования. Указывается структура статьи.

3.10. **Экспериментальная часть** содержит описание хода и результатов эксперимента, характеристику полученных соединений. В начале экспериментальной части приводятся названия приборов, на которых зарегистрированы физико-химические характеристики веществ и указываются условия измерения; также указываются либо источники использованных нетривиальных реагентов (например, «коммерческие препараты, название фирмы»), либо даются ссылки на методики их получения.

Каждый параграф экспериментальной части, описывающий получение конкретного соединения, должен содержать его полное наименование по номенклатуре ИЮПАК и его порядковый номер в статье. В методиках обязательно указывать количества реагентов в мольных и массовых единицах (для катализаторов – массу и мольные проценты), объемы растворителей. Методика эксперимента излагается в *прошедшем* времени.

Для известных веществ, синтезированных опубликованным ранее методом, необходимо привести ссылку на литературные данные. Для известных веществ, полученных новыми или модифицированными методами, должны быть представлены их физические и спектральные характеристики, использованные для подтверждения идентичности структуры, метод синтеза и ссылка на литературные данные.

Для всех впервые синтезированных соединений необходимо привести доказательства приписываемого им строения и данные, позволяющие судить об их индивидуальности и степени чистоты. В частности, должны быть представлены данные элементного анализа или масс-спектры высокого разрешения, ИК спектры и спектры ЯМР ^1H и ^{13}C .

Данные рентгеноструктурного анализа представляются в виде **рисунков и таблиц**. Все **новые соединения**, данные PCA которых приводятся в статье, должны быть **зарегистрированы в Кембриджской базе структурных данных** и иметь соответствующие **CCDC номера**.

Если, по мнению рецензента или редактора, новые соединения не были удовлетворительно охарактеризованы, статья не будет принята к печати.

Пример методики: 3-(2-Amino-6-methylpyridino)-3-carbonyl-3,4-dihydrocoumarin (**12**). To the alcoholic solution of 2.18 g (0.01 mol) of 3-carbethoxycoumarin, 1.08 g (0.01 mol) of 2-amino-6-methylpyridine was added with stirring. The mixture was boiled for 10 h. The solution was cooled, the precipitate was filtered. Then it was washed with cold EtOH. After the drying and recrystallization of the residue from i-PrOH yield of the product **12** was 2.05 g (63%), mp 226–228 °C, Rf 0.82 (1/2, EtOAc/hexane as eluent). Calculated, %: C 68.56; H 4.32; N 9.99 for C₁₆H₁₂N₂O₃. Found, %: C 68.41; H 4.22; N 9.83. *Spectral data*.

Внимание! В статьях, посвященных синтезу новых соединений, допускается размещение **экспериментальной части** за разделом **Результаты и обсуждение**.

3.11. В разделе **Результаты и обсуждение**, который является наиболее важным, следует обсудить и объяснить полученные в работе **результаты**, проанализировать особенности синтеза, продемонстрировать и указать возможные ограничения. Провести сравнение полученных результатов с опубликованными ранее. Все новые соединения должны быть полностью охарактеризованы соответствующими спектральными и другими физико-химическими данными. В тексте обобщаются и разъясняются только те спектральные данные, которые используются для подтверждения структуры полученных соединений. Перечисление одних и тех же данных в тексте, таблицах и на рисунках не допускается. Для новых методов синтеза желательно обсудить механизм реакции. Для обобщения данных необходимо использовать понятные рисунки и таблицы. Представленные данные должны поддаваться интерпретации.

При обсуждении результатов следует придерживаться официальной терминологии IUPAC. Результаты рекомендуется излагать в прошедшем времени.

Обсуждение не должно повторять описание результатов исследования. В тексте должны быть использованы общепринятые в научной литературе сокращения. Нестандартные сокращения должны быть расшифрованы после первого появления в тексте. Единицы измерений должны быть указаны в Международной системе СИ.

3.12. Затем рекомендуется сформулировать **закключение**, в котором указать основные достижения, представленные в статье, и основной вывод, содержащий ответ на вопрос, поставленный во вводной части статьи, а также возможность использования материала статьи в фундаментальных или прикладных исследованиях.

3.13. Приводится информация о **финансировании** исследований.

3.14. Выражается **благодарность** тем, кто помог вам в подготовке вашей работы.

3.15. В рукописи должно быть заявлено о том, имеется ли **конфликт интересов**

3.16. В **информации об авторах** указываются: ученая степень, звание, должность, e-mail, ORCID.

3.17. Статья заканчивается **списком литературы** со ссылками на русском (или казахском) языке и ссылками на языке оригинала. Ссылки на литературные источники в тексте приводятся порядковыми арабскими цифрами в квадратных скобках по мере упоминания. Каждая ссылка должна содержать только одну литературную цитату. Список литературы должен быть представлен наиболее свежими и актуальными источниками без излишнего самоцитирования (не более 20 процентов). Для статей желателен список из не менее 10 ссылок со строками доступа в интернете.

3.18. Обязательна **информация об авторах**. В ней указываются: ученая степень, звание, должность, e-mail, ORCID, **фамилия, имя, отчество** полностью на трех языках.

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Список цитируемой литературы оформляется в соответствии с нижеприведенными образцами библиографических описаний (4.8.).

3.19. В конце статьи после списка литературы *дополнительно* приводится перевод **Резюме** на казахский (**Түйіндеме**) и на английский языки (**Abstract**). Слово **Резюме (Abstract, Түйіндеме)** дается по центру. На следующей строке с выравниванием по левому краю прописными буквами полужирным шрифтом № 12 приводится название статьи. Через строку без абзацного отступа курсивом, полужирным шрифтом № 11 даются инициалы и фамилии авторов.

На следующей строке без абзацного отступа курсивом, строчными буквами, шрифтом № 11 приводятся места работы авторов с надстрочными индексами (после фамилии и перед названием организации), указывающие на место работы авторов. Затем через строку с абзацного отступа с выравниванием текста по ширине идет текст резюме, набранный строчным шрифтом № 12.

Далее через строку с абзацным отступом строчными буквами шрифтом № 12, с выравниванием текста по ширине приводятся **ключевые слова** (от 5 до 10 шт.), обеспечивающие наиболее полное раскрытие содержания статьи.

3.20. Для статей, подаваемых на языке, отличном от английского (на казахском или русском языке), в конце статьи находится английский блок (**Abstract, Information about authors, References**).

3.21. Все страницы рукописи следует пронумеровать.

4. ТРЕБОВАНИЯ К ОФОРМЛЕНИЮ РУКОПИСЕЙ

4.1. Объем статьи, включая аннотацию и список литературы: до 8–10 страниц. Обзорные статьи могут быть до 20 страниц. Статья должна быть напечатана на одной стороне листа А4 шрифтом Times New Roman, размер кегля 14 пт; межстрочный интервал – одинарный и полями: верхнее – 2.0 см, нижнее – 2.0 см, левое – 3.0 см, правое – 1.5 см; расстановка переносов не допускается; абзацный отступ – 1.0 см; форматирование – по ширине. Должен быть использован текстовый редактор *Microsoft Word for Windows*, в виде *doc*-файла, версия 7.0 и более поздние.

Для краткости и наглядности обсуждения соединения, упоминаемые более одного раза, следует нумеровать **арабскими** цифрами в сочетании со строчными **латинскими** буквами (для обозначения соединений с переменным заместителем). При упоминании полного названия соединения шифр дается в скобках.

Стереохимические символы и приставки, характеризующие структурные особенности или положение заместителя в молекуле, следует набирать курсивом (*italic*): (*R*)-энантиомер, *трет*-бутил, *пара*-ксилол. Вместо громоздких названий неорганических и часто употребляемых органических соединений следует давать их формулы: NaBr, TsOH вместо бромид натрия и толуолсульфоновая кислота. При использовании терминов и обозначений, не имеющих широкого применения в литературе, их значения поясняются в тексте при первом употреблении: например, полиэтилентерефталат (ПЭТФ).

Для изображения структурных формул химических соединений необходимо использовать редактор химических формул **ChemDrawUltra**. Все надписи на схемах приводятся на английском языке. В схеме необходимо указывать все условия реакций: над стрелкой – реагенты, катализаторы, растворители, под

стрелкой – температура, время, выход. Если условия реакций сильно загружают схему, их можно перенести в конец схемы, расшифровывая буквенными индексами, например, *i*: HCl, H₂O, 80 °C, 5h. Такой же буквенный индекс должен быть указан над стрелкой соответствующей реакции.

4.2. Уравнения, схемы, таблицы, рисунки и ссылки на литературу нумеруются в порядке их упоминания в тексте и *должны быть вставлены в текст статьи* после первого упоминания. Таблицы и рисунки должны сопровождаться подписью; заголовки к схемам даются при необходимости.

4.3. По возможности следует готовить **рисунки** с помощью компьютера. Однотипные кривые должны быть выполнены в одинаковом масштабе на одном рисунке. Кривые на рисунках нумеруются арабскими цифрами, которые расшифровываются в подписях к рисункам. Для всех **рисунков** необходимо представить графические файлы в формате *jpeg* с минимальным разрешением 300 dpi. Надписи на рисунках должны быть на английском языке и по возможности заменены цифрами, расшифровка которых дается в подписи к рисунку.

Одиночные прямые, как правило, не приводят, а заменяют уравнением линии регрессии. Пересечение осей координат следует располагать в левом углу рисунка, стрелки на концах осей не ставятся, линии, ограничивающие поле рисунка не приводятся, масштабная сетка не наносится. Малоинформативные рисунки, не обсуждаемые в статье спектры, вольтамперограммы и другие зависимости не публикуются. **Рисунки спектров не должны быть выполнены от руки**. Все рисунки должны иметь нумерацию арабскими цифрами (если рисунок не один). Слово «Рисунок» и наименование помещают после пояснительных данных и располагают следующим образом: Рисунок 1 – Детали прибора.

4.4. Каждая **таблица** должна иметь тематический заголовок и порядковый арабский номер (без знака №), на который дается ссылка в тексте (таблица 1). Название таблицы располагается над таблицей слева без абзацного отступа в одну строку с ее номером через тире без точки после названия. Графы в таблице должны иметь краткие заголовки, отражающие параметры, численные значения которых приведены в таблице; они пишутся в именительном падеже единственного числа с прописной буквы и через запятую сопровождаются соответствующими единицами измерения (в сокращенной форме). Рисунки или структурные формулы в графах таблиц не допускаются. Пропуски в графах при отсутствии данных обозначают тремя точками, при отсутствии явления – знаком «тире». Примечания к таблицам индексируются арабскими цифрами и помещаются в границах таблицы под материалом таблицы. Слово «Примечание» следует печатать с прописной буквы с абзаца. Если примечание одно, то после слова «Примечание» ставится тире и примечание печатается с прописной буквы. Несколько примечаний нумеруют по порядку арабскими цифрами без проставления точки и печатают с абзаца. В таблицах используют тот же шрифт, что и в тексте статьи; допускается уменьшенный (не менее № 10 шрифт TimesNewRoman).

4.5. При выборе единиц измерения рекомендуется придерживаться системы СИ: г, мг, м, см, мкм (микромметр, микрон); нм (наномметр, миллимикрон); пм (пикомметр); Э (ангстрем); с (секунда); мин, ч (час), Гц (герц); МГц (мегагерц); Э (эрстед); Гс (гаусс); В (вольт); эВ (электронвольт); А (ампер); Ом, Па (паскаль); МПа (мегапаскаль); гПа (гектопаскаль); Дж (джоуль); К (кельвин), °C (градус Цельсия); Д (Дебай).

В десятичных дробях целая часть отделяется от дробной не запятой, а точкой.

Используются следующие сокращения: т.кип. и т.пл. (точки кипения и плавления) – перед цифрами; конц. (концентрированный перед формулой соединения); М – молекулярная масса); моль, кал, ккал, н. (нормальный), М. (молярный); концентрация растворов обозначается (г/см³, г/л, моль/л).

Для всех впервые синтезированных соединений обязательны данные элементного анализа либо масс-спектры высокого разрешения.

В *брутто-формулах* элементы располагаются в следующем порядке: С, Н и далее согласно латинскому алфавиту. Формулы молекулярных соединений и ониевых солей даются через точку (например, C₅H₅N.HCl). Пример записи констант и данных элементного анализа: т.кип. 78°C (100 мм рт. ст.), т.пл. 50°C (EtOH), d₄²⁰0.9809, n_D²⁰1.5256; Найдено, %: С 59.06; Н 7.05; I 21.00; N 8.01. C_aH_bI_cN_dO_e. Вычислено, %: С 59.02; Н 7.01; I 21.20; N 8.22.

ИК и УФ спектры. В экспериментальной части для ИК и УФ спектров должны быть указаны характеристические частоты полос, длины волн максимумов поглощения, коэффициенты экстинкции (или их логарифмы) и условия, при которых записан спектр.

Примеры записи: ИК спектр (тонкий слой), ν , см⁻¹: 1650 (C=N), 3200–3440 (O–H). УФ спектр (EtOH), $\lambda_{\max}$, нм (lgε): 242 (4.55), 380 (4.22).

Спектры ЯМР ¹H и ¹³C. Должны быть указаны рабочая частота прибора, использованный стандарт и растворитель. Протоны в составе сложных групп, к которым относится сигнал, следует подчеркнуть снизу – 3.17–3.55 (4H, м, N(CH₂CH₃)₂); для положения заместителей использовать обозначения 3-CH₃; для обозначения положения атомов – C-3, N-4 и т.д. Если какой-нибудь сигнал в спектре описывается как дублет, триплет или дублет дублетов и т.п. (а не синглет или мультиплет), необходимо привести соответствующие КССВ. Если проведены дополнительные исследования для установления строения или пространственных взаимодействий атомов, должны быть указаны использованные двумерные методы. В описании спектров ЯМР ¹³C отнесение конкретного сигнала к конкретному атому углерода приводится только тогда, когда определение проведено на основе двумерных экспериментов.

Примеры записи:

Спектр ЯМР¹H (400 МГц, CDCl₃), δ, м. д. (J, Гц): 0.97 (3H, т, J= 7.0, CH₃); 3.91 (2H, к, J= 7.0, COOCH₂); 4.46 (2H, д, J= 6.1, NCH₂); 7.10–7.55 (6H, м, H-6,7,8, NHCH₂C₆H₅); 7.80 (1H, с, HAr); 7.97 (1H, с, H-5'); 8.13 (1H, д. д, J= 8.2, J= 2.3, H-5); 11.13 (1H, с, NH).

Спектр ЯМР¹³C (100 МГц, DMSO-d₆), δ, м. д. (J, Гц): 36.3 (CH₂CH₃); 48.5 (C-5); 62.3 (CH₂CH₃); 123.0(CAr); 125.8 (д, ²J_{CF} = 26.1, C-3',5' Ar); 128.9 (CPh); 134.4 (C-5a); 168.3 (C=O).

Масс-спектры приводятся в виде числовых значений *m/z* и относительных значений ионного тока. Необходимо указывать метод и энергию ионизации, массовые числа характеристических ионов, их интенсивность по отношению к основному иону и по возможности их генезис. В случае химической ионизации при описании прибора необходимо указать газ-реагент. В масс-спектрах высокого разрешения найденные и вычисленные значения *m/z* приводятся с четырьмя

десятичными знаками; если найденное значение m/z соответствует не молекулярному иону, брутто-формула и вычисленное значение m/z также приводится для того же иона.

Пример записи данных масс-спектра: Масс-спектр (ЭУ, 70 эВ), m/z ($I_{\text{отн}}$, %): 386 $[M]^+$ (36), 368 $[M-H_2O]^+$ (100), 353 $[M-H_2O-CH_3]^+$ (23).

Масс-спектр (ХИ, 200 эВ), m/z ($I_{\text{отн}}$, %): 387 $[M+H]^+$ (100), 369 $[M+H-H_2O]^+$ (23).

Пример записи данных масс-спектра высокого разрешения:

Найдено, m/z : 282.1819 $[M+Na]^+$. $C_{17}H_{25}NNaO$.

Вычислено, m/z : 282.1828.

4.6. **Данные рентгеноструктурного исследования** следует предоставлять в виде рисунка молекулы с пронумерованными атомами, например, C(1), N(3) (по возможности в представлении атомов эллипсо и дамипетловых колебаний). Полные кристаллографические данные, таблицы координат атомов, длин связей и валентных углов, температурные факторы в журнале не публикуются, а депонируются в Кембриджском банке структурных данных (в статье указывается регистрационный номер депонента).

4.7. По требованиям международных баз данных Scopus, Clarivate Analytics, Springer Nature при оценке публикаций на языках, отличных от английского, библиографические списки должны даваться не только на языке оригинала, но и на латинице (романским алфавитом). Поэтому авторы статей, подаваемых на русском и казахском языке, должны предоставлять список литературы в двух вариантах: *один на языке оригинала (Список литературы)*, а другой — *в романском алфавите (References)*. Последний список входит в английский блок, который расположен в конце статьи.

Если в списке есть ссылки на иностранные публикации, они полностью повторяются в списке **References**. При цитировании русскоязычного журнала, переводимого за рубежом, в русскоязычной версии Списка литературы необходимо привести полную ссылку на русскоязычную версию, а в **References** — на международную.

Список источников в **References** должен быть написан только на романском алфавите- латинице (при этом он должен оставаться полным аналогом Списка литературы, в котором источники были представлены на оригинальном языке опубликования).

Для написания ссылок на русскоязычные источники (и источники на иных, не использующих романский алфавит, языках) следует использовать ОФИЦИАЛЬНЫЙ ПЕРЕВОД и ТРАНСЛИТЕРАЦИЮ (см. Требования к переводу и транслитерации).

В **References** требуется следующая структура библиографической ссылки из русскоязычных источников: авторы (транслитерация), перевод названия статьи или книги на английский язык, название источника (транслитерация — для тех изданий, которые не имеют установленного редакцией английского названия), выходные данные в цифровом формате, указание на язык статьи в скобках (in Russian или in Kazakh). Транслитерацию можно выполнить на сайте <http://www.translit.ru>.

Условные сокращения названий русскоязычных журналов и справочников приводятся в соответствии с сокращениями, принятыми в «Реферативном журнале Химия». англоязычных и других иностранных журналов — в соответствии с сокращениями, рекомендуемыми издательством «Springer and Business Media»:

<http://chemister.ru/Chemie/journal-abbreviations.htm>. Для статей на русском и казахском языках название журнала «Химический Журнал Казахстана» следует сокращать: «Хим. Журн. Каз.» и «Каз. Хим. Журн.» соответственно, а для статей на английском языке: «Chem. J. Kaz.». Приводятся фамилии и инициалы **всех авторов** (сокращения и *др.* и *et al* не допускаются).

В Списке литературы и в **References** все работы перечисляются **В ПОРЯДКЕ ЦИТИРОВАНИЯ**, а **НЕ** в алфавитном порядке.

DOI. Во всех случаях, когда у цитируемого материала есть цифровой идентификатор, его необходимо указывать в самом конце описания источника. Проверять наличие doi у источника следует на сайте <http://search.crossref.org> или <https://www.citethisforme.com>.

Для формирования списка литературы (всех без исключения ссылок) в Журнале принят библиографический стандарт без использования разделителя «//»:

Author A.A., Author B.B., Author C.C. Title of article. Title of Journal, **2005**, 10, No. 2, 49–53.

Для казахско- или русскоязычного источника:

Author A.A., Author B.B., Author C.C. Title of article. Title of Journal, **2005**, 10, No. 2, 49– 53. (In Kazakh or In Russian).

Ниже приведены образцы оформления различных видов документов, которых необходимо придерживаться авторам при оформлении романского списка **References**.

Описание статьи из журналов:

Zagurenko A.G., Korotovskikh V.A., Kolesnikov A.A., Timinov A.V., Kardymov D.V. Technical and economical optimization of hydrofracturing design. Neftyanoe khozyaistvo. Oil Industry, **2008**, No. 11, 54–57. (In Russian).

Описание статьи с DOI:

Zhang Z., Zhu D. Experimental Research on the localized electrochemical micromachining. *Rus. J. Electrochem.*, **2008**, 44, No. 8, 926–930. doi: 10.1134/S1023193508080077.

Описание Интернет-ресурса:

Kondrat'ev V.B. *Global'naya farmatsevticheskaya promyshlennost'* [The global pharmaceutical industry]. Available at: http://perspektivy.info/rus/ekob/globalnaja_farmacevticheskaja_promyshlennost_2011-07-18.html (Accessed 23.06.2013).

или

APA Style (2011). Available at: <http://www.apastyle.org/apa-style-help.aspx> (accessed 5 February 2011).

или

Pravila Tsitirovaniya Istochnikov (Rules for the Citing of Sources) Available at: <http://www.scribd.com/doc/1034528/> (Accessed 7 February 2011).

Описание статьи из электронного журнала:

Swaminatan V., Lepkoswka-White E., Pao B.P. Browsers or buyers in cyberspace? An investigation of electronic factors influencing electronic exchange. *Journal of Computer-Mediated Communication*, **1999**, 5, No. 2. Available at: <http://www.ascusc.org/jcmc/vol.5/issue2/> (Accessed 24 April 2011).

Описание статьи из продолжающегося издания (сборника трудов)

Astakhov M.V., Tagantsev T.V. Eksperimental'noe issledovanie prochnost soedinenii «stal'- kompozit» [Experimental study of the strength of joints «steel-

composite»]. Trudy MGTU

«*Matematicheskoe modelirovanie slozhnykh tekhnicheskikh sistem*» [Proc. Of the Bauman MSTU

«Mathematic Modeling of the Complex Technical Systems»], **2006**, No. 593, 125–130.

Описание материалов конференций:

Usmanov T.S., Gusmanov A.A., Mullagalin I.Z., Muhametshina R.Ju., Chervyakova A.N., Sveshnikov A.V. Features of the design of the field development with the use of hydraulic fracturing. *Trudy 6 Mezhdunarodnogo Simpoziuma «Novye resurso sberegayushchie tekhnologii nedropol'zovaniya i povysheniya neftegazootdachi»* [Proc. 6th Int. Symp. «New energy saving subsoil technologies and the increasing of the oil and gas impact»]. Moscow, **2007**, 267–272. (In Russ.)

Нежелательно оставлять одно переводное название конференции (в случае если нет переведенного на английский язык названия конференции), так как оно при попытке кем-либо найти эти материалы, идентифицируется с большим трудом.

Описание книги (монографии, сборника):

Nenashev M.F. *Poslednee pravitel'stvo SSSR* [Last government of the USSR]. Moscow, Krom Publ., **1993**, 221 p.

Описание переводной книги:

Timoshenko S.P., Young D.H., Weaver W. *Vibration problems in engineering*. 4th ed. New York, Wiley, 1974. 521 p. (Russ. ed.: Timoshenko S.P., Iang D.Kh., Uiver U. *Kolebaniia v inzhenernom dele*. Moscow, Mashinostroenie Publ., **1985**. 472 p.).

Brooking A., Jones P., Cox F. *Expert systems. Principles and cases studies*. Chapman and Hall, 1984. 231 p. (Russ. ed.: Bruking A., Dzhons P., Koks F. *Ekspertnye sistemy. Printsipy raboty i primery*. Moscow, Radioisviaz' Publ., **1987**. 224 p.).

Описание диссертации или автореферата диссертации:

Grigor'ev Yu. A. *Razrabotka nauchnykh osnov proektirovaniia arkhitektury raspredelennykh sistem obrabotki dannykh. Diss. Dokt. Tekhn. Nauk* [Development of scientific bases of architectural design of distributed data processing systems. Dr. tech. sci. diss.]. Moscow, Bauman MSTU Publ., **1996**. 243 p.

Описание ГОСТа:

GOST 8.596.5–2005. *Metodika vypolneniia izmerenii. Izmerenie raskhoda i kolichestva zhidkosti i gazov s pomoshch'iu standartnykh suzhaiushchikh ustroistv* [State Standard 8.586.5 – 2005. Method of measurement. Measurement of flow rate and volume of liquids and gases by means of orifice devices]. Moscow, Standartinform Publ., **2007**. 10 p.

или

State Standard 8.586.5 – 2005. Method of measurement. Measurement of flow rate and volume of liquids and gases by means of orifice devices. Moscow, Standartinform Publ., **2007**. 10 p. (In Russian).

Описание патента:

Patent RU 228590. *Sposob orientirovaniia po krenu letatel'nogo apparata s opticheskoi golovkoi samonavedeniia* [The way to orient on the roll of aircraft with optical homing head], Palkin M.V., Ivanov N.M., Gusev B.B., Petrov R.H., **2006**.

4.9. Пример англоязычного блока для представления статьи, написанной на языке, отличном от английского:

Abstract

DETERMINATION OF THE HAZARD CLASS OF OIL-CONTAMINATED AND NEUTRALIZED SOIL

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Introduction. Pollution by oil has a negative effect on chemical, physical, agrophysical, agrochemical and biological properties of soils. Sorption methods of cleaning the soil with the help of humic preparations from oil pollution are of great importance. *The purpose* of this work is to study the composition and properties of the contaminated and neutralized soil, the determination of the toxicity indexes of all components of oil waste, the calculation of the hazard class of waste according to their toxic-ecological parameters. *Methodology.* Samples of the contaminated and neutralized soil were treated with the use of humate-based energy-accumulating substances. The metal content in the contaminated soil was determined by spectrometry using an AA 240 instrument using the method of decomposing the sample with a mixture of nitric, hydrofluoric and perchloric acids until the sample was completely opened. *Results and discussion.* Fractional composition of oil products of all samples is stable: the content of complex acetylene hydrocarbons is ~ 70.0% of the total mass of oil products, the content of resins and paraffin-naphthenic group of hydrocarbons is 27.3%, the content of bitumens is 2.6%. In the neutralized soil, paraffin-naphthenic fractions, resins, bitumens and asphaltenes were mainly found; complex acetylene hydrocarbons are not present. *Conclusion.* It has been established that the contaminated soil belongs to the substances of the 3rd hazard class. Neutralized soil became less toxic and according to the total toxicity index, it was classified as hazard class 4 (low hazard). Neutralized soil can be used as construction and road materials, at the improvement of boreholes and at land reclamation.

Keywords: oil, contaminated soil, neutralized soil, humate-based energy storage substance, toxicity, radioactivity, hazard class.

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Ғылыми жарияланымның этикасы

«Қазақстанның химиялық журналы» (бұдан әрі – Журнал) баспасының алқасы мен бас редакторы «Жариялану этикасы жөніндегі комитет – (Committee on Publication Ethics – COPE)» (<http://publicationethics.org/about>), «Еуропалық ғылыми редакторлардың қауымдастығы» (European Association of Science Editors – EASE) (<http://www.ease.org.uk>) және Ғылыми жарияланым этикасының комитетінде (<http://publicet.org/code/>) қабылданылған халықаралық талаптарды ұстанады.

Баспа қызметіндегі әдепке сай емес іс - әрекеттерді (плагиат, жалған ақпарат және т.б.) болдырмауға және ғылыми жарияланымдардың жоғары сапасын қамтамасыз ету үшін, қол жеткізген ғылыми нәтижелерді жұртшылыққа жариялау мақсатында редакция алқасы, авторлар, рецензенттер, сондай-ақ баспа үдерісіне қатысатын мекемелер этикалық нормалар мен ережелерді сақтауға міндетті және олардың бұзылмауына барлық шараларды пайдалануы тиіс. Осы үдеріске қатысушылардың барлығының ғылыми жарияланымдар этикасының ережелерін сақтауы, авторлардың зияткерлік меншік объектілеріне құқықтарын қамтамасыз етуге, жарияланымдар сапасын арттыруға және авторлық құқықпен қорғалған материалдарды жеке тұлғалардың мүддесі үшін пайдалану мүмкіндігін жоюға көмектеседі.

Редакцияға жіберілген барлық ғылыми мақалалар міндетті түрде екі жақты құпия сараптамаға жіберіледі. Журналдың редакциялық алқасы мақаланың журнал тақырыбына және талаптарына сәйкестігін анықтайды, журналға тіркеу үшін оны алдын ала саралауға журналдың жауапты хатшысына жібереді. Ол қолжазбаның ғылыми құндылығын анықтап, мақала тақырыбына жақын ғылыми мамандықтары бар екі тәуелсіз сарапшыны анықтайды. Мақалаларды редакциялық алқа және редакциялық алқа мүшелері, сондай-ақ басқа елдерден шақырылған рецензенттер сараптайды. Мақаланы сараптау үшін рецензенттерді таңдау туралы шешімді бас редактор қабылдайды. Сараптау мерзімі 2-4 апта және рецензент өтініші бойынша оны 2 аптаға ұзартуға болады.

Редакция мен рецензент қарауға жіберілген жарияланбаған материалдардың құпиялылығына кепілдік береді. Жариялау туралы шешім журналдың редакциялық алқасы тексергеннен кейін қабылданады. Қажет болған жағдайда (редактор(лар) және/немесе рецензент(лер) тарапынан ескертулердің болуы) қолжазба авторларға қосымша түзетулерге жіберіледі, содан кейін ол қайта қаралады. Этика нормалары бұзылған жағдайда, мақаланы жариялаудан бас тарту құқығын Редакция өзіне қалдырады. Жауапты редактор мақалада плагиат деп есептеуге жеткілікті ақпарат болған жағдайда оны жариялауға рұқсат бермейді.

Авторлар редакцияға жіберілген материалдардың жаңа, бұрын жарияланбаған және түпнұсқа екендігіне кепілдік береді. Авторлар ғылыми нәтижелердің сенімділігі мен маңыздылығына, сондай-ақ ғылыми этика қағидаттарының сақталуына, атап айтқанда, ғылыми этиканы бұзылмауына (ғылыми деректерді қолдан жасау, зерттеу деректерін бұрмалауға әкелетін бұрмалау, плагиат және жалған бірлескен авторлық, қайталау, басқа адамдардың нәтижелерін иемдену және т.б.) тікелей жауапты.

Мақаланы редакцияға беру авторлардың мақаланы (түпнұсқада немесе басқа тілдерге немесе тілден аудармада) басқа журналға(ларға) жібермегенін және бұл материалдың бұрын жарияланбағанын білдіреді. Олай болмаған жағдайда мақала

авторларға «Авторлық құқықты бұзғаны үшін мақаланы жарияламау» деген шешіммен қайтарылады. Басқа автордың туындысының 10 пайыздан астамын, оның авторлығын және дереккөзге сілтемелерді көрсетпей сөзбе-сөз көшіруге жол берілмейді. Алынған үзінділер немесе мәлімдемелер автор мен дереккөзді міндетті түрде көрсете отырып ресімделуі керек. Шамадан тыс өзге материалдарды пайдалану, сондай-ақ кез келген нысандағы плагиат, соның ішінде дәйексіз дәйексөздер, басқа адамдардың зерттеулерінің нәтижелерін иемдену этикаға жатпайды және қабылданбайды. Зерттеу барысына қатынасқан барлық тұлғалардың үлесін мойындау қажет және мақалада зерттеуді жүргізуде маңызды болған жұмыстарға сілтемелер берілуі керек. Бірлескен авторлар арасында зерттеуге қатыспаған адамдарды көрсетуге жол берілмейді.

Автор(лар) жұмыстарында қателіктер байқалса, бұл туралы дереу редакторға хабарлап, түзету туралы ұсыныс беруі тиіс.

Қолжазбаны басып шығарудан бас тарту туралы шешім рецензенттердің ұсыныстарын ескере отырып, редакция алқасының отырысында қабылданады. Редакциялық алқаның шешімімен жариялауға ұсынылмаған мақала қайта қарауға қабылданбайды. Жариялаудан бас тарту туралы хабарлама авторға электрондық пошта арқылы жіберіледі.

Журналдың редакциялық алқасы мақаланы жариялауға рұқсат беру туралы шешім қабылдағаннан кейін редакциялық алқа бұл туралы авторға хабарлайды және жариялау шарттарын көрсетеді. Мақалаға берілген пікірлердің түпнұсқасы Журнал редакциясында 3 жыл сақталынады.

Этика научных публикаций

Редакционная коллегия и главный редактор научного журнала «Химический журнал Казахстана» (далее – Журнал) придерживаются принятых международных стандартов «Комитета этики по публикациям» (Committee on Publication Ethics – COPE) (<http://publicationethics.org/about>), «Европейской ассоциации научных редакторов» (European Association of Science Editors – EASE) (<http://www.ease.org.uk>) и «Комитета по этике научных публикаций» (<http://publicet.org/code/>).

Во избежание недобросовестной практики в публикационной деятельности (плагиат, изложение недостоверных сведений и др.) и в целях обеспечения высокого качества научных публикаций, признания общественностью, полученных автором научных результатов, члены редакционного совета, авторы, рецензенты, а также учреждения, участвующие в издательском процессе, обязаны соблюдать этические стандарты, нормы и правила и принимать все меры для предотвращения их нарушений. Соблюдение правил этики научных публикаций всеми участниками этого процесса способствует обеспечению прав авторов на интеллектуальную собственность, повышению качества издания и исключению возможности неправомерного использования авторских материалов в интересах отдельных лиц.

Все научные статьи, поступившие в редакцию, подлежат обязательному двойному слепому рецензированию. Редакция Журнала устанавливает соответствие статьи профилю Журнала, требованиям к оформлению и направляет ее на первое рассмотрение ответственному секретарю Журнала, который определяет научную ценность рукописи и назначает двух независимых рецензентов – специалистов, имеющих наиболее близкие к теме статьи научные специализации. Рецензирование статей осуществляется членами редакционного совета и редакционной коллегии, а также приглашенными рецензентами других стран. Решение о выборе того или иного рецензента для проведения экспертизы статьи принимает главный редактор. Срок рецензирования составляет 2-4 недели, но по просьбе рецензента он может быть продлен, но не более чем на 2 недели.

Редакция и рецензент гарантируют сохранение конфиденциальности неопубликованных материалов присланных на рассмотрение работ. Решение о публикации принимается редакционной коллегией Журнала после рецензирования. В случае необходимости (наличие замечаний редактора(-ов) и /или рецензента(-ов)) рукопись направляется авторам на доработку, после чего она повторно рецензируется. Редакция оставляет за собой право отклонить публикацию статьи в случае нарушения правил этики. Ответственный редактор не должен допускать к публикации информацию, если имеется достаточно оснований полагать, что она является плагиатом.

Авторы гарантируют, что представленные в редакцию материалы являются новыми, ранее неопубликованными и оригинальными. Авторы несут ответственность за достоверность и значимость научных результатов, а также соблюдение принципов научной этики, в частности, недопущение фактов нарушения научной этики (фабрикация научных данных, фальсификация, ведущая к искажению исследовательских данных, плагиат и ложное соавторство, дублирование, присвоение чужих результатов и др.)

Направление статьи в редакцию означает, что авторы не передавали статью (в оригинале или в переводе на другие языки или с других языков) в другой(-ие) журнал(ы) и что этот материал не был ранее опубликован. В противном случае статья немедленно возвращается авторам с формулировкой «Отклонить статью за нарушение авторских прав». Не допускается дословное копирование более 10 процентов работы другого автора без указания его авторства и ссылок на источник. Заимствованные фрагменты или утверждения должны быть оформлены с обязательным указанием автора и первоисточника. Чрезмерные заимствования, а также плагиат в любой форме, включая неоформленные цитаты, перефразирование или присвоение прав на результаты чужих исследований, неэтичны и неприемлемы. Необходимо признавать вклад всех лиц, так или иначе повлиявших на ход исследования, в частности, в статье должны быть представлены ссылки на работы, которые имели значение при проведении исследования. Среди соавторов недопустимо указывать лиц, не участвовавших в исследовании.

Если автором(-ами) обнаружена ошибка в работе, необходимо срочно уведомить редактора и вместе принять решение об исправлении.

Решение об отказе в публикации рукописи принимается на заседании редакционной коллегии с учетом рекомендаций рецензентов. Статья, не рекомендованная решением редакционной коллегии к публикации, к повторному рассмотрению не принимается. Сообщение об отказе в публикации направляется автору по электронной почте.

После принятия редколлегией Журнала решения о допуске статьи к публикации редакция информирует об этом автора и указывает сроки публикации. Оригиналы рецензий хранятся в редакции Журнала в течение 3 лет.

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The Editorial Board and Editor-in-Chief of the scientific journal the “Chemical Journal of Kazakhstan” (hereinafter referred to as the Journal) adhere to the accepted international standards of the “Committee on Publication Ethics” (Committee on Publication Ethics – COPE) (<http://publicationethics.org/about>), the “European Association of Science Editors” (European Association of Science Editors – EASE) (<http://www.ease.org.uk>) and the “Committee on Scientific Publication Ethics” (<http://publicet.org/code/>).

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