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Ophthalmic drug delivery system based on the complex of gellan and ofloxacin

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Complex formation between a natural polysaccharide – gellan and an antimicrobial drug – ofloxacin was studied in aqueous solution. Conductimetric and potentiometric titration curves revealed that gellan and ofloxacin forms a water-soluble complex of composition 2:1 mol/mol stabilized by ionic and hydrogen bonds. The formation of the gellan-ofloxacin complex was confirmed by FTIR spectroscopy, dynamic light scattering, zeta-potential and thermogravimetric analysis. The average hydrodynamic size of the complex was found 307±5 nm and its zeta-potential was negative and equal to -15 mV. Thin films of the gellan-ofloxacin complex, gelled in 0.3 wt.% of $CaCl_2$, were used to study the release kinetics of ofloxacin in distilled water and phosphate buffer. The drug release kinetics evaluated by UV-Vis spectroscopy at λ_{max} = 289 nm and calculated by the Ritger-Peppas model correspond to non-Fickian diffusion in distilled water and Case II transport (zero-order kinetics) in phosphate buffer. The cumulative release of ofloxacin from the gellan-ofloxacin films was equal to 96±2% and 36±2% in phosphate buffer and distilled water, respectively. It is expected that the gellan-ofloxacin complex is able to form *in situ* gel on the surface of the eye and to prolong the drug residence time in the tear fluid.

Keywords: gellan; ofloxacin; complexation; drug delivery.

Геллан және офлоксацин кешеніне негізделген офтальмологиялық дәрі-дәрмектерді жеткізу жүйесі

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Табиғи полисахарид – геллан мен микробқа қарсы препарат – офлоксациннің сулы ерітінділерінің арасындағы кешеннің түзілуі зерттелді. Кондуктометрлік және pH-метрлік титрлеу қисықтарының нәтижелері бойынша геллан офлоксацинмен иондық және сутектік байланыстар арқылы 2:1 моль/моль қатынаста кешен түзетіндігі анықталды. Кешеннің орташа гидродинамикалық өлшемі 307±5 нм, дзета-потенциалы теріс, яғни -15 мВ тең. Геллан-офлоксацин кешенінің түзілетінін ИК-Фурье спектроскопия, динамикалы жарықты шашыратқыш, дзета-потенциал және термогравиметриялық анализдермен расталды. Геллан-офлоксациннің өте жұқа пленкасы 0,3% $CaCl_2$ ерітіндісінің қатысында алынып, су және фосфат буферінің ерітіндісіне пленкадан офлоксациннің шығу кинетикасы зерттелді. Дәрілік заттың шығу кинетикасы УК-көрінетін спектроскопиясында $\lambda_{макс}$ = 289 нм толқын ұзындығында анықталып, Ритгер-Пеппас моделімен есептелді. Суда және фосфат буферінің ерітіндісінде дәрілік заттың шығу кинетикасы Фик заңына бағынбайды және аномальды (II жағдайда) диффузия байқалады. Геллан-офлоксацин пленкасынан офлоксациннің кумулятивті босап шығуы фосфат буферінде 96±2%, ал дистилденген суда 36±2% тең болды. Зерттеулерден күтетін нәтиже, геллан-офлоксацин кешені көз жасымен әрекеттескенде in situ гель түзіп, дәрілік заттың әсер ету мерзімін ұзартады.

Түйін сөздер: геллан; офлоксацин; кешен түзілу; дәрі-дәрмекті босату.

Офтальмологическая система доставки лекарств на основе комплекса геллан-офлоксацин

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Комплексообразование между природным полисахаридом – гелланом и антимикробным препаратом – офлоксацином изучено в водном растворе. Кривые кондуктометрического и pH-метрического титрования показали, что геллан образует с офлоксацином водорастворимый комплекс состава 2:1 моль/моль, стабилизированный ионными взаимодействиями и водородными связями. Среднегидродинамический размер комплекса составляет 307±5 нм, а его дзета-потенциал отрицателен и равен -15 мВ. Образование комплекса геллан-офлоксацин подтверждено данными ИК-Фурье спектроскопии, динамического светорассеяния, дзета-потенциала и термогравиметрического анализа. Тонкая пленка геллан-офлоксацин, приготовленная в 0,3% растворе $CaCl_2$ была использована для изучения кинетики выхода офлоксацина в воду и фосфатный буфер. Кинетика выхода лекарства, изученная методом УФ-видимой спектроскопии при $\lambda_{макс}$ = 289 нм и вычисленная по модели Ритгера-Пеппаса, в воду и фосфатный буфер соответствует нефиковской и аномальной (случай II) диффузии. Кумулятивное высвобождение офлоксацина из пленок геллан-офлоксацин соответственно равно 96±2% и 36±2% в фосфатном буфере и дистиллированной воде. Ожидается, что комплекс геллан-офлоксацин способен образовать in situ гель в слезной жидкости и пролонгировать время удержания лекарства.

Ключевые слова: геллан; офлоксацин; комплексообразование; высвобождение лекарства.

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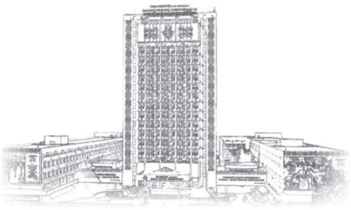

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Ophthalmic drug delivery system based on the complex of gellan and ofloxacin

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1. Introduction

Over the past few decades, microbial polysaccharides have attracted the attention of researchers due to their advantageous physicochemical properties. Currently, one of the most widely studied and comprehensively described member of this group is gellan – a linear polymer consisting of a tetrasaccharide repeating unit of 1,3-linked β-D-glucose, 1,4-linked β-D-glucuronic acid, 1,4-linked β-D-glucose, and 1,4-linked α-L-rhamnose produced by *Sphingomonas elodea* [1]. The fermentative production and manufacturing of gellan at industrial scale is described in many reviews [2,3].

Due to its unique structure and beneficial properties, gellan is currently described as a potent multifunctional additive for various pharmaceutical products. Its specific gelling properties in different media has led to the development of controlled release formulations based on gellan. Various formulations have been studied including oral, ophthalmic, nasal and other [4, 5]. A recent report [4] suggests that gellan-based materials can also be used in regenerative medicine, dentistry or gene delivery. Gellan gum-based hydrogels exhibit excellent *in vivo* and *in vitro* biocompatibility [6], tunable physical mechanical and injectable properties [7-9] for application in the regeneration of cartilage [7,8], tissue engineering [10], cell encapsulation [11], nucleus pulposes regeneration [12]. Recent progress in the design of multi-functional hydrogels based on gellan gum in the context of biomedical engineering and regenerative medicine is discussed and summarized in recent reviews [4,13-15].

Gellan-based systems for the sustained delivery of ophthalmic drugs are of great interest because the sol-gel transition of gellan in response to mono- (Na^+, K^+) and bivalent (Ca^{2+}, Mg^{2+}) cations present in tear fluid makes it suitable for ophthalmic formulations as a thickening or gelling component [14, 16]. Gellan is nontoxic and not harmful for human organisms and is therefore widely used as a viscosifying additive in the food industry [17]. The most popular ocular formulation based on gellan is Timoptic XE® which is administered topically to the eye and increases the drug bioavailability by 3-4 times, while it considerably decreases the unfavorable effect in comparison with the standard solution of timolol [18,19]. The systems consisting of the model drug Gatifloxacin (0.3%) and gellan or a mixture of gellan-sodium alginate-carboxymethylcellulose exhibit mucoadhesive properties. *In vivo* experiments on ocular delivery demonstrated that the drug retention was exceeding 12 h [20]. Combination of a Gerlite®:alginate containing matrix also shows the prolonged effect *in vivo*. The rheological measurements showed that such mixtures exhibit pseudoplastic character after contact with tear liquids [21]. The viscosity of a microemulsion system containing terbinafine hydrochloride in combination with mucin confirms the interaction of gellan and mucin justifying the possibility of adhesion to biosurfaces [22]. Gellan gum and its methacrylated derivatives were tested as in situ gelling mucoadhesive formulations of pilocarpine [23]. A recent review [24] highlights the stimuli-responsive in-situ gelling systems based on gellan gum studied using *in vivo* models for glaucoma and various ocular infections. In spite of the wide applications of gellan-drug combinations in medicine, pharmacy and biotechnology, the application of novel eye drops of prolonged action based on gellan and ofloxacin in ophthalmology was not described in the literature yet. Only one information that we have found is ofloxacin loaded gellan/poly(vinyl alcohol) nanofibers possessing gastroretentive/mucoadhesive drug delivery potential [25].

The present communication describes the complexation of gellan with ofloxacin to develop prolonged dosage eye drops by the immobilization of the antibacterial drug – ofloxacin within a matrix of biocompatible and biodegradable natural polymer – gellan in the form of thin film. It is expected that the eye drops consisting of gellan and ofloxacin will form a thin gel-like film on the eye surface due to the presence of inorganic ions in tear fluid and will provide delivery of ofloxacin for a definite time.

2. Experiment

2.1 Materials

Commercial low acyl gellan with the molecular weight in the range of $(1\text{-}5)\cdot10^5$ Da was purchased from "Zhejiang DSM Zhongken Biotechnology Co., Ltd.", China, and used without further purification. Antimicrobial drug – ofloxacin purchased from Sigma-Aldrich (UK) was used as received. Reagent grade phosphate buffer with pH 7.4 was purchased from Sigma-Aldrich (UK).

2.2 Methods

FTIR spectra of samples were recorded using Carry 660 (Agilent, USA) using dried samples. The thermal characteristics of samples were determined using TGA «Labsys EVO» Setaram (France). The average hydrodynamic sizes and ζ-potentials were measured using Malvern Zetasizer Nano ZS90 (UK). Absorption spectra were registered by UV-Vis spectroscopy (Specord 210 plus BU, Germany). Conductimetric and pH-metric titrations were carried out on Modular conductivity meter 856 Conductivity Module Metrohm and Automatic Titrator 905 Titrando Metrohm (Switzerland). Mini-magnetic stirrer IKA Topolino (Germany) was used for gentle stirring of the solution (around of 50 rpm) in order not to damage the hydrogel film.

2.3 Preparation of gellan-ofloxacin films

Gellan-ofloxacin films were prepared by mixing of a 10 mL 10^{-3} mol·L^{-1} gellan solution and 5 mL 10^{-3} mol·L^{-1} ofloxacin (2:1 mol/mol) and adding 1 mL 0.3 wt.% $CaCl_2$ to this mixture to achieve a uniform dispersion and gelation. Casting of the fluid gel into Petri dishes and allowing it to stand at room temperature and afterwards drying for 24 h, leads to the formation of an insoluble in water gellan-ofloxacin flexible film. Circular pieces of each film, 4.0±0.2 mm in diameter and 0.5±0.1 mm thick, were cut with a cork borer and were used for drug delivery studies. Each piece of weighed film was approximately equal to 10±1 mg.

2.4 Evaluation of release rate of ofloxacin from gellan-ofloxacin films

The release rate of ofloxacin from the gellan-ofloxacin films was studied as follows. Small pieces of gellan-ofloxacin films (d = 4.0±0.2 mm, h = 0.5±0.1 mm) were placed in glass vials at room temperature (25±1°C) and soaked in either 8 mL distilled water or phosphate buffer under gentle stirring (around of 50 rpm) in order not to damage the hydrogel film [26]. From time to time 2 mL of the solution were taken to measure the absorbance of ofloxacin at 289 nm. These experiments were performed under sink conditions and to keep the volume of the solution constant, the 2 mL solution taken for UV-Vis measurement were compensated by adding 2 mL of distilled water or phosphate buffer, respectively [25]. The accumulative release was calculated by formula [27]:

$$\text{Cumulative percentage release, \%} = \\ = \frac{\text{Volume of sample withdrawn, mL}}{\text{Bath volume, mL}} \cdot P_{t-1} + P_t,$$

where P_t is the percentage release at time t; P_{t-1} is the percentage release previous to "t"

and the results were shown as mean ± SD. The cumulative release of ofloxacin is the total amount (in percentage) of ofloxacin released from the gel matrix during the full time of experiments until the full or partly release of drug will be reached.

3. Results and Discussion

Addition of an aqueous solution of ofloxacin to an aqueous solution of gellan leads to the decrease in the electrical conductivity and pH of the system due to the formation of both ionic and hydrogen bonds between the two components (Figure 1). Partial neutralization of glucuronic acid of gellan by tertiary amine groups of ofloxacin and formation of hydrogen bonds with participation of carboxylic groups of drug and polymer chain is responsible for sharp decrease in conductivity and gradually decrease the pH of the solution. After formation of gellan-ofloxacin complex of definite composition, the excess of drug molecules significantly increases the conductivity and slightly decreases pH of the system. Such phenomenon is usually specific for interpolymer or polymer-drug complexes stabilized by ionic and hydrogen bonds or both [28,29]

The composition of gellan-ofloxacin determined from the minimum and the bend in the conductimetric and pH-metric titration curves was approximately equal to [gellan]:[ofloxacin] = 2:1 mol/mol. Taking into account that the molar composition of gellan-ofloxacin determined by the conductimetric and pH-metric titration curves is close to 2:1 mol/mol, the speculative structure of the complex can be represented as shown in Figure 2.

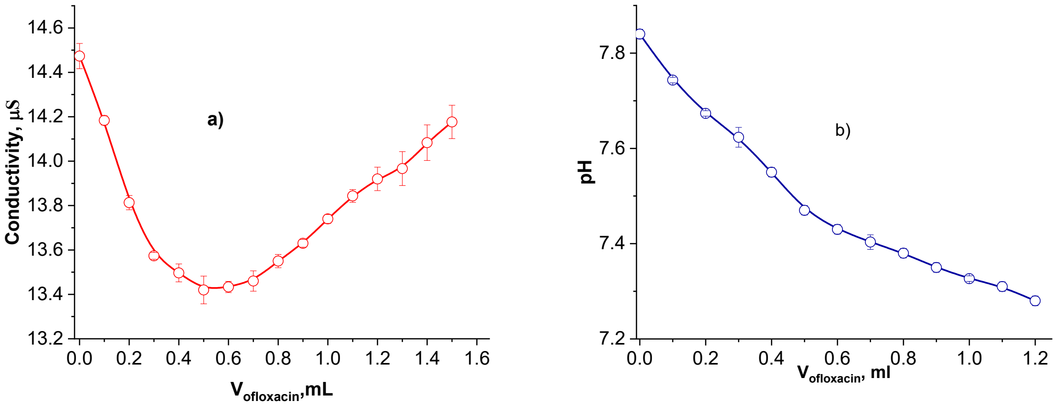

Figure 1 – Conductimetric (a) and pH-metric (b) titration curves of gellan with ofloxacin. [Gellan] = $1{\cdot}10^{-4}$ mol·L^{-1}, [Ofloxacin] = $1{\cdot}10^{-3}$ mol·L^{-1}. The volume of gellan solution used for the titration is 10 mL.

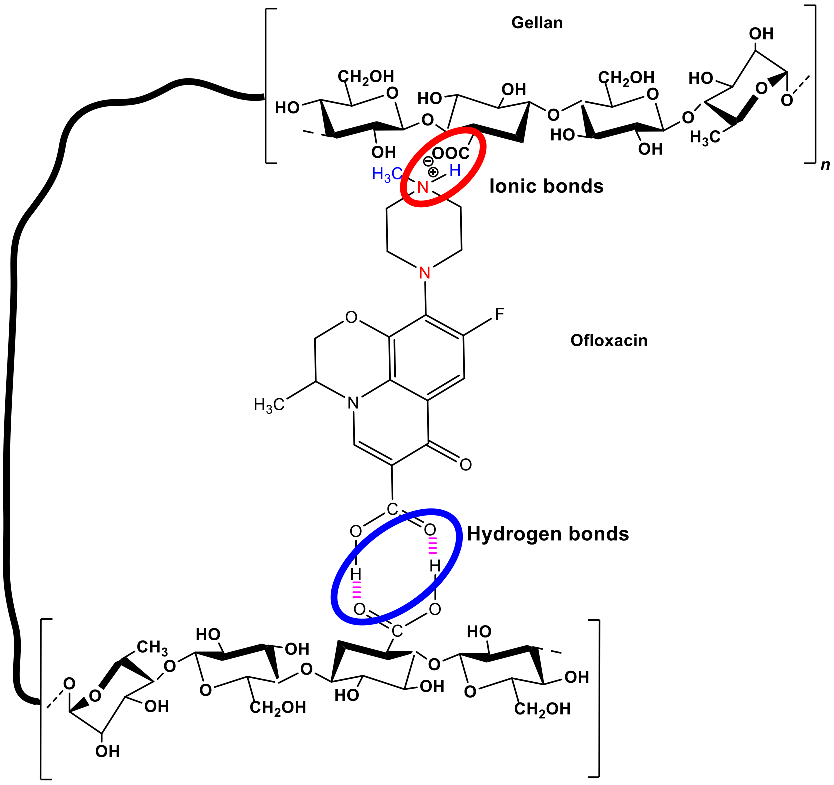

Figure 2 – Schematic representation of the intra-macromolecular gellan-ofloxacin complex of composition 2:1 mol/mol

It should be noted that ofloxacin can be involved into both intra-macromolecular and inter-macromolecular complexation with both hydroxyl and carboxyl groups of gellan. Formation of a gellan-ofloxacin complex of composition 2:1 mol/mol is also confirmed by DLS measurements (Table 1).

The minimal values of average hydrodynamic size and zeta-potential of the complex gellan-ofloxacin confirm the composition of 2:1 mol/mol. The negative charges of gellan, ofloxacin and the complex particles is due to the presence of carboxylic groups in the structure of all substances. The minimum value of zeta-potential (– 14.9 mV) in case of the gellan-ofloxacin complex 2:1 mol/mol is probably related to the partial neutralization of the carboxylic groups of gellan by the amine groups of ofloxacin and the involvement of the carboxylic groups of gellan and ofloxacin in the formation of hydrogen bonds as schematically shown in Figure 2.

Table 1 – The average hydrodynamic size and zeta-potential of gellan, ofloxacin and a mixture of gellan-ofloxacin of different composition

Composition of gellan-ofloxacin, mol/mol	Average hydrodynamic size, nm	Zeta-potential, mV
4:1	336±5	-43.0±2
2:1	307±5	-15.0±1
1:1	315±5	-40.0±2
1:2	338±4	-21.0±5
1:4	370±2	-25.0±5
Gellan	605±10	-41.0±2
Ofloxacin	187±3	1.0±3

The FTIR spectra of dry gellan, ofloxacin and the complex of gellan-ofloxacin (2:1 mol/mol) are shown in Figure 3 together with the identification of some characteristic bands (Table 2).

As revealed from the FTIR spectra, the intensive peak at 1712 cm^{-1} disappears in the complex of gellan-ofloxacin because of the hydrogen bonding of the carboxylic groups of ofloxacin with the hydroxyl or carboxyl groups of gellan. In addition, the C-N stretching vibration of ofloxacin at 1549 and 1522 cm^{-1} are shifted to 1537 cm^{-1} confirming the involvement of the amine groups of ofloxacin in the formation of ionic bonds.

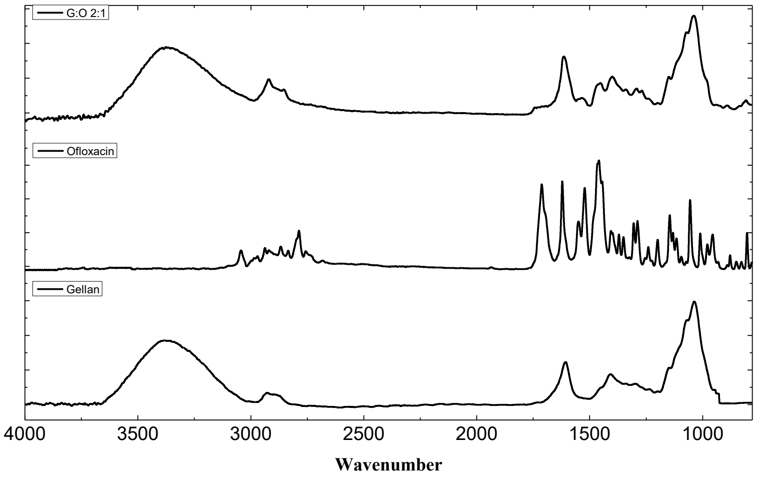

Figure 3 – FTIR spectra of dry gellan, ofloxacin and the gellan-ofloxacin complex of composition 2:1 mol/mol

Table 2 – Identification of the characteristic bands of gellan, ofloxacin and the gellan-ofloxacin complex (2:1 mol/mol)

Wavenumber, cm^{-1}			
Gellan	Ofloxacin	Gellan-ofloxacin complex (2:1 mol/mol)	Band assignments
3369	-	3376	OH stretching
2928	3044-2786	2920, 2857	CH stretching
-	1712	-	C=O stretching of COOH groups
1607	1621	1615	COO^{-} stretching
-	1549, 1522	1537	C-N stretching
	1459	1453	C-C stretching in benzene ring
1408	1406	1399	CH deformation
1037	-	1039	C-O-C stretching

DTA curves of the individual components and the complex are shown in Figure 4. Decomposition of the gellan backbone takes place between 200 and 300°C. The sharpest weight loss is observed at 249°C that coincides well with the literature [16] which reports the thermal decomposition of ofloxacin at 243°C. In the case of the gellan-ofloxacin complex (2:1 mol/mol) the decomposition peaks of the individual components (gellan and ofloxacin) fully disappear demonstrating a weight loss for the complex at 338 and 379°C. This is related to the formation of the gellan-ofloxacin complex as the sole compound.

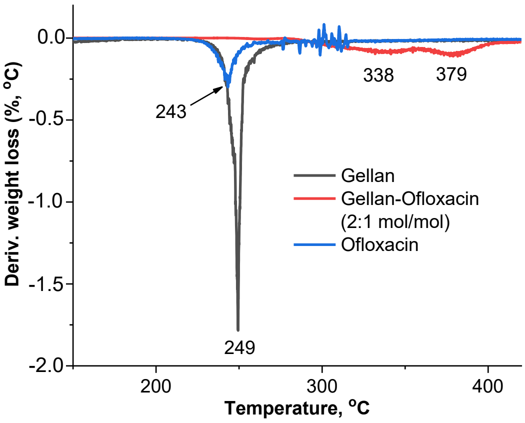

Figure 4 – DTA curves of gellan, ofloxacin and the gellan-ofloxacin (2:1 mol/mol) complex

The release kinetics of ofloxacin from the gellan-ofloxacin thin films, gelled by addition of 0.3 wt.% $CaCl_2$, were evaluated using UV-Vis spectroscopy by detecting the time dependent absorption spectra of ofloxacin at λ = 289 nm in distilled water and phosphate buffer at room temperature (Figure 5).

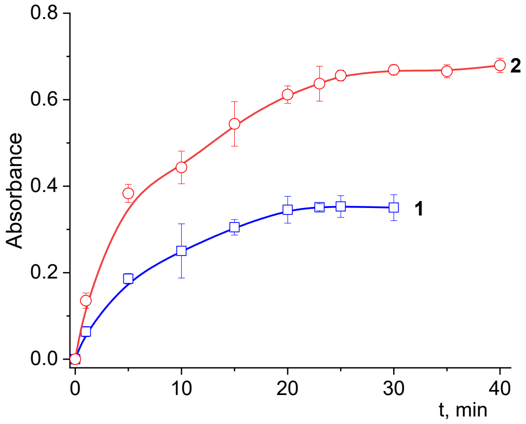

Figure 6 – Release kinetics of ofloxacin from the gellan-ofloxacin thin films, gelled by the addition of 0.3 wt.% $CaCl_2$, into distilled water (1) and phosphate buffer (2) at 25±1°C

As seen from Figure 6 the release kinetics of ofloxacin from the gellan-ofloxacin (2:1 mol/mol) thin films into distilled water and phosphate buffer is different. During 30-40 min, the release of ofloxacin in phosphate buffer is 2 times faster compared to that in distilled water; this is related to the presence of inorganic ions in the buffer solution that reduce the strength of the polymer-drug ionic bonds. Calculation of the release kinetics using the Ritger-Peppas model [30] expressed as $A_t/A_\infty = kt^n$ (where A_t is the absorbance of ofloxacin at time t, A_∞ is the absorbance of ofloxacin at infinite time t_∞, k is a structural/geometric constant for a gelled film, n is the release exponent representing the release mechanism) corresponds to non-Fickian diffusion (n = 0.59) in distilled water and Case II transport (n = 0.95) in phosphate buffer. The percentage release of ofloxacin into distilled water after 30 min and phosphate buffer after 40 min was leveled off at ≈ 12±1% and ≈ 4±0.5% respectively (Figure 7). The cumulative release of ofloxacin from the gellan-ofloxacin films calculated by procedure [27] is equal to 36±2% and 96±2% into distilled water and buffer solution respectively (Figure 8). In the case of distilled water, the release of ofloxacin may be influenced by the hydration and swelling of the gellan film, the penetration of water into the gel matrix

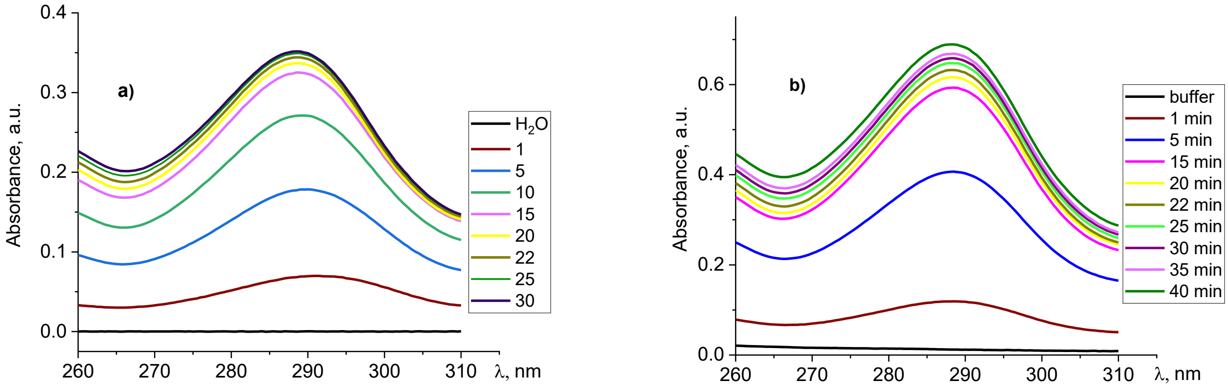

Figure 5 – Time-dependent absorbance of ofloxacin from the gellan-ofloxacin (2:1 mol/mol) thin films gelled by the addition of 0.3 wt.% $CaCl_2$ into distilled water (a) and phosphate buffer (b) at 25±1°C

resulting in the passive diffusion of ofloxacin from the gel matrix. The faster release of ofloxacin into the buffer solution was attributed to the destruction of the ionic bonds, formed between the carboxylic groups of gellan and the amine groups of ofloxacin, by the ionic species of the solution, which is accompanied by an enhanced diffusion of ofloxacin from the gel matrix.

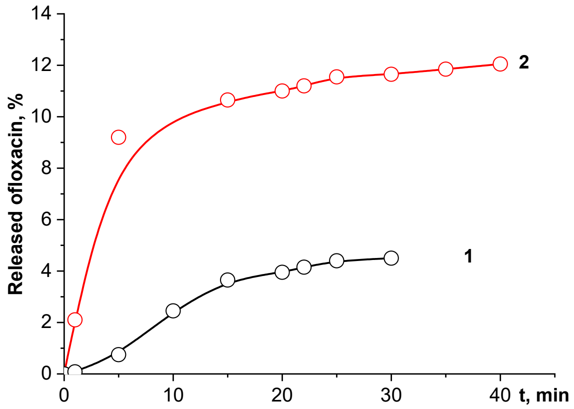

Figure 7 – Percentage of released ofloxacin into distilled water (1) and phosphate buffer (2) from the gellan-ofloxacin thin films, gelled by the addition of 0.3 wt.% $CaCl_2$ at 25±1°C

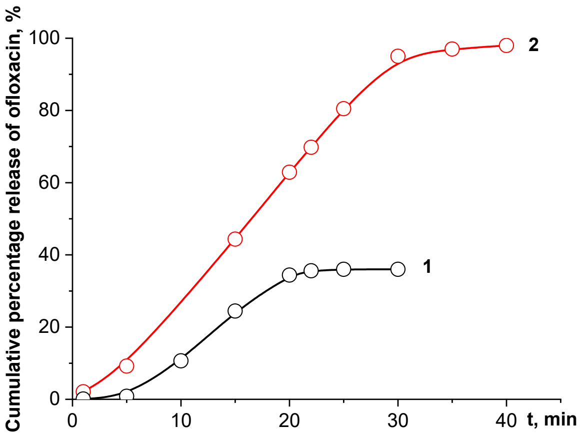

Figure 8 – Cumulative percentage release of ofloxacin from gellan gel matrix into distilled water (1) and phosphate buffer (2) from the gellan-ofloxacin thin films, gelled by the addition of 0.3 wt.% $CaCl_2$ at 25±1°C

Authors [31] have studied in vitro release of covalently bounded and physically incorporated methylprednisolone (MP) from the gellan film and found that approximately 75% and 95% of MP is released into phosphate buffer at 32°C during 24 h. The gellan-MP films exhibited zero-order (or Case II transport) release kinetics with n=0.93. Since the gellan-MP film contains esterified MP, its release involves penetration of water into the matrix, swelling of the matrix, hydrolysis of the covalent ester bonds and diffusion of the drug through the matrix. The gellan film with physically entrapped methylprednisolone exhibited anomalous release kinetics with n = 0.7. The release mechanism of physically entrapped MP from the gellan gel matrix is explained by hydration and swelling of the network, penetration of water and diffusion of drug to the outer solution. The behavior of the gellan-ofloxacin system studied by us is also similar to the results of above authors.

4. Conclusion

A water-soluble gellan-ofloxacin complex of composition 2:1 mol/mol is stabilized by both ionic and hydrogen bonds, formed by the carboxylic, hydroxyl and amine groups of the two interacting components. The formation of the gellan-ofloxacin complex is confirmed by conductimetric and potentiometric titrations, DLS and zeta-potential measurements in addition to FTIR spectroscopy and TG analysis. The gellan-ofloxacin complex is gelled upon addition of 0.3 wt.% $CaCl_2$ and forms thin gel films. The release kinetics of ofloxacin from the gellan-ofloxacin complex were described by the Ritger-Peppas model ($A_t/A_\infty = kt^n$) and corresponds to non-Fickian diffusion (n = 0.59) in distilled water and Case II transport (n = 0.95) in phosphate buffer. The amount of cumulative ofloxacin release from the gellan-ofloxacin films was 96±2% in phosphate buffer and 36±2% in distilled water. To assess the effectiveness of the gellan-ofloxacin system as a sustainable drug delivery system, experiments, both *in vitro* and *in vivo*, should be carried out in tear fluids at various temperatures, and pH values of the medium.

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References (GOST)

1 Morris E.R., Katsuyoshi N., Rinaudo M. Gelation of gellan. – A review // Food Hydrocolloids. – 2012. – Vol.28, Is.2. – P.373-411.
2 Bajaj I.B., Survase S.A., Saudagar P.S., Singhal R.S. Gellan gum: Fermentative production, downstream processing and applications // Food Technol Biotechnol. – 2007. – Vol.45, Is.4. – P.341-354.
3 Giavasis I., Harvey L.M., Neil Mc. B. Gellan gum // Critical Reviews in Biotechnology. – 2000. – Vol.20. – P.177-211.
4 Osmalek T., Froelich A., Tasarek S. Application of gellan

gum in pharmacy and medicine // International Journal of Pharmaceutics. – 2014. – Vol.466, Is.1-2. – P.328-340.

5 Gan L., Gan Y., Zhu X., Zhu J. Novel microemulsion in situ electrolyte–triggered system for ophthalmic delivery of lipophilic cyclosporine A: In vitro and in vivo results // International Journal of Pharmaceutics. – 2009. – Vol.365, Is.1-2. – P.143-149.

6 Correa S. J., Zavan B., Vindigni V., Silva T.H., Oliveira J.M., et al. Biocompatibility evaluation of ionic- and photo-crosslinked methacryalted gellan gum hydrogels: In vivo and in vitro study // Advanced Healthcare Materials. – 2013. – Vol.2, Is.4. – P.568-575.

7 Gong J., Wang C., Lai R.C., Su K., Zhang K., et al. An improved injectable polysaccharide hydrogel: Modified gellan gum for long–term cartilage regeneration in vitro // Journal of Materials Chemistry. – 2009. – Vol.19. – P.1968-1977.

8 Oliveira J.T., Gardel L.S., Rada T., Martins L., Gomes M.E., et al. Injectable gellan gum hydrogels with autologous cells for the treatment of rabbit articular cartilage defects // Journal of Orthopaedic Research. – 2010. – Vol.28, Is.9. – P.1193-1199.

9 Coutinho D.F., Sant S., Shin H., Oliveira J.T., et al. Modified gellan gum hydrogels with tunable physical and mechanical properties // Biomaterials. – 2010. – Vol.31, Is.2. – P.7494-7502.

10 Correa S.J., Oliveira J.M., Caridade S.G., Oliveira J.T., Sousa R.A., et al. Gellan gum–based hydrogels for intervertebral disc tissue engineering applications // Tissue Engineering and Regenerative Medicine. – 2011. – Vol.5, Is.6. – P.e97-e107.

11 Tsaryk R., Correia S. J., Oliveira J.M., Unger R.E., Landes C., et al. Biological performance of cell-encapsulated methacrylated gellan gum-based hydrogels for nucleus pulposes regeneration // Tissue Engineering and Regenerative Medicine. – 2017. – Vol.11, Is.3. – Vol.637-648.

12 Correa S. J., Goncalves M.V., Salgado A.J., Sousa N., Oliveira J.M., et al. Angiogenic potential of gellan-gum-based hydrogels for application nucleus pulposes regeneration: In vivo study // Tissue Engineering and Regenerative Medicine. Part A. – 2012. – Vol.18, Is.11-12. – P.1203-1212.

13 Hacker M.C., Nawaz H.A. Multi–functional macromers for hydrogel design in biomedical and regenerative medicine // International Journal of Molecular Sciences. – 2015. – Vol.16, Is.11. – P.27677-27706.

14 Tatykhanova G.S., Aseyev V.O., Kudaibergenov S.E. Mucoadhesive properties of gellan and its modified derivatives // Review Journal of Chemistry. – 2020, –Vol.10, Is.3-4. – P.140-157.

15 Kudaibergenov S.E., Nurakhmetova Zh.A., Tatykhanova G.S. Immobilized anticancer agents and metal nanoparticles in a matrix of gellan: achievements and prospects // Chemical Bulletin of Kazakh National University. – 2020. – Vol.99, Is.4. –P.32-41.

16 Lavikainen J., Dauletbekova M., Toleutay G., Kaliva M., Chatzinikolaidou M., et al. Poly(2–ethyl–2–oxazoline) grafted gellan gum for potential application in transmucosal drug delivery // Polymers for Advanced Technologies. – 2021. – Vol.32, Is.7. – P.2770-2780.

17 Singh S.R., Carreiro S.T., Chu J., Niesman M.R, Collette W.W., Younis H.S., Sartnurak S., Gukasyan H.J. L–Carnosine: multifunctional dipeptide buffer for sustained-duration topical ophthalmic formulations // Journal of Pharmacy and Pharmacology. – 2009. – Vol.61, Is.6. – P.733-742.

18 Rozier A., Mazuel C., Grove J., Plazonnet B. Gelrite: a novel, ion–activated, in situ gelling polymer for ophthalmic vehicles – effect on bioavailability of timolol // International Journal of Pharmaceutics. – 1989. – Vol.57. – P.163-168.

19 Arthur Sh.H., Laurence J., Barrish A., et al. Plasma timolol concentrations of timolol maleate: Timolol gel–forming solution (TIMOPTIC–XE(R)) once daily versus timolol maleate ophthalmic solution twice daily // Documenta Ophthalmologica. – 2001. – Vol.103, Is.1. – P.73-79.

20 Kesavan K., Nath G., Pandit J. K. Preparation and in vitro antibacterial evaluation of gatifloxacin mucoadhesive gellan system // DARU Journal of Pharmaceutical Sciences. – 2010. – Vol.18, Is.4. – P.237-246.

21 Liu Y., Liu J., Zhang X., et al. In situ gelling Gelrite/Alginate Formulations as Vehicles for ophthalmic drug delivery // AAPS Pharmscitech. – 2010. – Vol.11, Is.2. – P.610-620.

22 Tayel S.Ah., El-Nabarawi M.Ah., Tadros M.I., et al. Promising ion–sensitive in situ ocular nanoemulsion gels of terbinafine hydrochloride: Design, in vitro characterization and in vivo estimation of the ocular irritation and drug pharmacokinetics in the aqueous humor of rabbits // International Journal Pharmaceutics. – 2012. – Vol.443, Is.1-2. – P.293-305.

23 Agibayeva L.E., Kaldybekov D.B., Porfiryeva N.N., Garipova V.R., Mangazbayeva R. A., Moustafine R. I., Semina I. I., Mun G. A., Kudaibergenov S. E., Khutoryanskiy V. V. Gellan gum and its methacrylated derivatives as in situ gelling mucoadhesive formulations of pilocarpine // International Journal of Pharmaceutics. – 2020. – Vol.577. – P.119093.

24 Pandey M., Choudhury H., Azila binti Abd Aziz A., Bhattamisra S.K., Gorain B., Su J.S.T., Tan C.L., Chin W.Y., Yip K.Y. Potential of stimuli-responsive in situ gel system for sustained ocular drug delivery: Recent progress and contemporary research // Polymers. – 2021. –Vol.13. – P.1340.

25 Vashisth P., Raghuwanshi N., Srivastava A.K., Singh H., Nagar H., Pruthi V. Ofloxacin loaded gellan/PVA nanofibers – synthesis, characterization and evaluation of their gastroretentive/mucoadhesive drug delivery potential // Materials Science and Engineering: C. – 2017. –Vol.71. – P.611.

26 Zhu L., Ao J., Li P. A novel in situ gel base of deacetylase gellan gum for sustained ophthalmic drug delivery of ketotifen: in vitro and in vivo evaluation // Drug Design, Development and Therapy – 2015. – Vol.9. – P.3943-3949.

27 Chandrasekaran A. R., Jia Ch. Y., Theng Ch. Sh., Muniandy T., Muralidharan S., Dhanaraj S. A. In vitro studies and evaluation of metformin marketed tablets–Malaysia // Journal of Applied Pharmaceutical Science. –2011. – Vol.1, Is.5. – P.214-217.

28 Bekturov E.A., Bimendina L.A. Interpolymer Complexes // Adv. Polym. Sci. – 1981. – Vol.45. –P.1-119.

29 Bekturov E.A., Legkunetz R.E. Association of polymers with small molecules. – Nauka, Alma-Ata, 1982. – 207 pp.

30 Ritger P.L., Peppas N.A. A simple equation for description of solute release I. Fickian and non–fickian release from non–swellable devices in the form of slabs, spheres, cylinders or discs // Journal of Controlled Release. –1987. – Vol.5. – P.23-36.

31 Sanzgiri Y.D., Maschi S., Crescenzi V., Callegaro L., Topp E. M., Stella V.J. Gellan–based systems for ophthalmic sustained delivery of methylprednisolone // Journal of Controlled Release –1993. – Vol.26. – P.195-201.

References

1 Morris ER, Katsuyoshi N, Rinaudo M (2012) Food Hydrocolloids 28:373-411. *https://doi.org/10.1016/j.foodhyd.2012.01.004*

2 Bajaj IB, Survase SA, Saudagar PS, Singhal RS (2007) Food Technol Biotechnol 45:341-354.

3 Giavasis I, Harvey LM, Neil McB (2000) Crit Rev Biotechnol 20:177-211. *https://doi.org/10.1080/07388550008984169*

4 Osmalek T, Froelich A, Tasarek S (2014) Int J Pharm 466:328-340. *https://doi.org/10.1016/j.ijpharm.2014.03.038*

5 Gan L, Gan Y, Zhu X, Zhu J (2009) Int J Pharm 365:143-149. *https://doi.org/10.1016/j.ijpharm.2008.08.004*

6 Correa SJ, Zavan B, Vindigni V, Silva TH, Oliveira JM, et al (2013) Adv Healthc Mater 2:568-575. *https://doi.org/10.1002/adhm.201200256*

7 Gong J, Wang C, Lai RC, Su K, Zhang K, et al (2009) J Mater Chem 19:1968-1977. *https://doi.org/10.1039/b818090c*

8 Oliveira JT, Gardel LS, Rada T, Martins L, Gomes ME, Reis LR (2010) J Orthop Res 28:1193-1199. *https://doi.org/10.1002/jor.21114*

9 Coutinho DF, Sant S, Shin H, Oliveira JT, et al (2010) Biomaterials 31:7494-7502. *https://doi.org/10.1016/j.biomaterials.2010.06.035*

10 Correa SJ, Oliveira JM, Caridade SG, Oliveira JT, Sousa RA, et al (2011) J Tissue Eng Regen Med 5:e97-e107. *https://doi.org/10.1002/term.363*

11 Tsaryk R, Correia SJ, Oliveira JM, Unger RE, Landes C, et al (2017) J Tissue Eng Regen Med 11:637-648. *https://doi.org/10.1002/term.1959*

12 Correa SJ, Goncalves MV, Salgado AJ, Sousa N, Oliveira JM, et al (2012) Tissue Eng Part A 18:1203-1212. *https://doi.org/10.1089/ten.tea.2011.0632*

13 Hacker MC, Nawaz HA (2015) Int J Mol Sci 16:27677-27706. *https://doi.org/10.3390/ijms161126056*

14 Tatykhanova GS, Aseyev VO, Kudaibergenov SE (2020) Rev J Chem 10:140-157. *https://doi.org/10.1134/S207997802003005X*

15 Kudaibergenov SE, Nurakhmetova ZhA, Tatykhanova GS (2020) Chem Bull Kaz Nat Univ 99:32-41. *https://doi.org/10.15328/cb1169*

16 Lavikainen J, Dauletbekova M, Toleutay G, Kaliva M, Chatzinikolaidou M, et al (2021) Polym Adv Technol 32:2770-2780. *https://doi.org/10.1002/pat.5298*

17 Singh SR, Carreiro ST, Chu J, Niesman MR, Collette WW, et al (2009) J Pharmacy Pharmaco 61:733-742. *https://doi.org/10.1211/jpp.61.06.0005*

18 Rozier A, Mazuel C, Grove J, Plazonnet B (1989) Intern J Pharmaceutics 57:163-168.

19 Arthur ShH, Laurence J, Barrish A, et al (2001) Documenta Ophthalmologica 103:73-79. *https://doi.org/10.1023/A:1017962731813*

20 Kesavan K, Nath G, Pandit JK (2010) Daru J Pharm Scien18:237-246.

21 Liu Y, Liu J, Zhang X, et al (2010) AAPS Pharmscitech 11:610-620. *https://doi.org/10.1208/s12249-010-9413-0*

22 Tayel SAh, El-Nabarawi MAh, Tadros MI, Wessam HAE (2012) Int J Pharm 443:293-305. *https://doi.org/10.1016/j.ijpharm.2012.12.049*

23 Agibayeva LE, Kaldybekov DB, Porfiryeva NN, Garipova VR, Mangazbayeva RA, Moustafine RI, Semina II, Mun GA, Kudaibergenov SE, Khutoryanskiy VV (2020) Int J Pharm 577:119093. *https://doi.org/10.1016/j.ijpharm.2020.119093*

24 Pandey M, Choudhury H, Azila binti Abd Aziz A, Bhattamisra SK, Gorain B, Su JST, Tan CL, Chin WY, Yip KY (2021) Polym 13:1340. *https://doi.org/10.3390/polym13081340*

25 Vashisth P, Raghuwanshi N, Srivastava AK, Singh H, Nagar H, Pruthi V (2017) Mater Sci Eng C 71:611. *https://doi.org/10.1016/j.msec.2016.10.051*

26 Zhu L, Ao J, Li P (2015) Drug Design, Development and Therapy 9:3943. *https://doi.org/10.2147/DDDT.S87368*

27 Chandrasekaran AR, Jia CY, Theng Ch Sh, Muniandy T, Muralidharan S, Dhanaraj SA (2011) J Appl Pharm Sci 01:214 Corpus ID: 759716.

28 Bekturov EA, Bimendina LA (1981) Adv Polym Sci 45:1-119

29 Bekturov EA, Legkunetz RE (1982) Association of polymers with small molecules. Nauka, Alma-Ata, Kazakhstan.

30 Ritger PL, Peppas NA (1987) J Control Release 5:23-36.

31 Sanzgiri YD, Maschi S, Crescenzi V, Callegaro L, Topp EM, Stella VJ (1993) J Control Release 26:195-201. *https://doi.org/10.1016/0168-3659(93)90186-9*

Effect of food processing method on heavy metals content

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The problem of high content of heavy metals in food has spread broadly over the world. The presented study suggests the minimization of heavy metal content in processed food due to different applied techniques such as the frying, boiling, steaming and sous-vide. Three main food products were chosen for investigation – *Daucus carota subsp. Sativus* (carrot), *Solanum tuberosum* (potato) and *Allium cepa* (onion). The concentration of heavy metals (Zn, Pb, Mn, Cd, Cu) was determined in samples investigated by atomic-absorption spectrometer. The health risk index (HRI) was calculated based on obtained data. In all investigated samples, high concentration of lead was identified among the heavy metals. The highest concentration of zinc, lead and manganese was determined in boiled *Daucus carota subsp. Sativus,* cadmium – in sous - vide *Daucus carota subsp. Sativus,* copper – in steamed *Daucus carota subsp. Sativus.* HRI values of cadmium for *Solanum tuberosum* samples were ranged from 6.8 to 7.1 and for lead are ranged between 3.4 and 4.9.

Keywords: heavy metals; vegetable crops; food processing; atomic absorption spectrometry; health risk index.

Өңдеу әдісінің тамақ өнімдеріндегі ауыр металдардың мөлшеріне әсері

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Азық-түлік өнімдеріндегі ауыр металдардың көп болуы бүкіл әлемде кең таралған мәселе. Ұсынылған зерттеу жұмысы әртүрлі қолданылатын технологиялардың арқасында өңделген тағамдардағы ауыр металдардың мөлшерін азайтуды ұсынады. Олардың арасында қуыру, қайнату, бумен пісіру және су-вид түрлері бар. Зерттеу үшін Daucus carota subsp. *Sativus* (сәбіз), *Solanum tuberosum* (картоп) және *Allium cepa* (пияз) сияқты үш негізгі тамақ өнімдері таңдалды. Зерттелген үлгілердің құрамындағы ауыр металдардың (Zn, Pb, Mn, Cd, Cu) концентрациясы атомдық-абсорбциялық спектрометрдің көмегімен анықталды. Алынған мәліметтер негізінде денсаулыққа қауіп индексі есептелді. Барлық зерттелген үлгілерде қорғасынның концентрациясы жоғары екендігі анықталды. Мырыш, қорғасын және марганецтің ең жоғары концентрациясы қайнатылған *Daucus carota subsp. Sativus*-те, кадмий – су-вид әдісімен дайындалған *Daucus carota subsp. Sativus*-те, мыс – буға пісірілген *Daucus carota subsp. Sativus*-те анықталды. Барлық *Solanum tuberosum* үлгілеріндегі кадмий үшін денсаулыққа қауіп индексі 6,8 және 7,1 аралығында, ал қорғасын үшін 3,4 және 4,9 дейін болды.

Түйін сөздер: ауыр металдар; көкөніс дақылдары; тамақ дайындау; атомдық-абсорбциялық спектрометрия; денсаулыққа қауіп индексі.

Влияние способа обработки пищевых продуктов на содержание тяжелых металлов

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Повышенное содержание тяжелых металлов в продуктах питания является широко распространенной проблемой во всем мире, требующей детального изучения. Настоящее исследование предлагает минимизировать содержание тяжелых металлов в пищевых продуктах за счет метода приготовления, таких как обжаривание, отваривание, приготовление на пару и метод су-вид. Для исследования были выбраны три распространенных пищевых продукта, таких как *Daucus carota subsp. Sativu*s (морковь), *Solanum tuberosum* (картофель) и *Allium cepa* (лук). Концентрация тяжелых металлов (Zn, Pb, Mn, Cd, Cu) в исследуемых образцах была определена атомно-абсорбционной спектрометрией. На основании полученных данных был рассчитан индекс риска здоровью. Во всех исследованных образцах была установлена высокая концентрация свинца. Наибольшая концентрация цинка, свинца и марганца была определена в отварной *Daucus carota subsp. Sativus*, кадмия – в *Daucus carota subsp. Sativus,* приготовленной методом су-вид, меди – в приготовленном на пару *Daucus carota subsp. Sativus*. Значения индекса риска здоровью для кадмия во всех образцах *Solanum tuberosum* варьировались от 6,8 до 7,1, а для свинца – от 3,4 до 4,9.

Ключевые слова: тяжелые металлы; овощные культуры; приготовление продуктов питания; атомно-абсорбционная спектрометрия; индекс риска здоровью.

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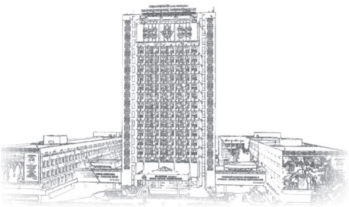

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Effect of food processing method on heavy metals content

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1. Introduction

Due to rapid industrialization and urbanization activities, heavy metals (HMs) pollution spread over the globe that leads to environmental problems, as well as health hazards to human being [1]. The presence of HMs in the environment can have a natural or industrial origin. Industry is the main emitter of HMs to the environment [2]. Concentration of heavy metals in different foods depends on the soil composition, water, nutrient balance, and metal permissibility, selectivity, and absorption ability of the species. In addition, direct foliar uptake of heavy metals from the atmosphere could also be possible during plant growth [3]. Heavy metals can accumulate in different plant species and living systems [4]. Through the food chain, heavy metals enter the human body, which leads to negative affect to human health. Information about heavy metals in food products are important for adequate food consumption data [5]. Iron, zinc, copper, chromium, cobalt and manganese are essential elements needed, while lead, cadmium, nickel and mercury are toxic at certain levels [6]. Effect of heavy metals on human health has been shown in several researches. In [7-10], it is reported, that cadmium and arsenic may cause kidney dysfunction, lung cancer and destructive influence on neurological system. Excessive amount of lead in blood causes toxic epidermal necrolysis and serious problems with neurologic and hematologic systems and the gastrointestinal tract [11-13]. High content of copper leads to changes in cellular activity, such as regulation of lipid metabolism, gene expression, neuronal activity, resistance of tumor cells to chemotherapeutic drugs, different abnormal mutations and the temporal and spatial distribution of copper in hepatocytes [14-16]. Special attention is required to consider the effect of heavy metals on the body of children and infants, because of some specific features of growing organisms [17]. Another difficulty about substances containing heavy metals is that they are hard crumbling in human body and slowly get out of human organism. This is the reason why heavy metals are considered as one of the most dangerous pollutants of food industry and their concentrations and influence must be controlled and studied thoroughly in complex with soil pollutions by heavy metals [18-21].

Three commonly used types of food product (*Daucus carota subsp. Sativus* – carrot, *Solanum tuberosum* – potato and *Allium cepa* – onion) were chosen as investigated samples. For determination of effect of food processing method on content of heavy metals in investigated samples, in this research, four most commonly used methods of food processing were chosen: frying, boiling, steaming and sous-vide. For evaluation of health risk index, concentration of heavy metals was determined by atomic-absorption spectrometer.

2. Experiment

2.1 Sample pretreatment

Samples were purchased in local market of Almaty, largest city of Kazakhstan and second in Central Asia. All samples were washed by distilled water.

Investigated samples were processed in four different ways: frying, boiling, steaming and sous-vide. Samples were crushed using ceramic knife. Boiling was performed during 30 min in deep teflon skillet. Frying was performed in the same Teflon skillet without application of oil. Samples were fried until the crust is formed. Steaming was performed during 30 min in stainless steel steam cooker through the porous piece of cloth in order to avoid contact between steel surface and samples. Sous-vide was performed during four hours in vacuum bags at 65°C. After cooking, all samples were cut into small pieces and dried in oven “VULCAN” type A-550 (Ney, USA) at 40°C till the constant mass.

In order to avoid contamination of food by metallic dishes and other tools, only teflon, glass and ceramic tools were used during whole process of sample preparation.

2.2 Determination of heavy metals

All reagents used for analysis were analytical grade and purchased in "LaborPharma", Almaty, Kazakhstan.

The certain mass of sample was placed in 250 mL Kjeldahl flask and fully oxidized by the mix of concentrated sulfuric (chemically pure, Russia) and nitric acids (chemically pure, Russia) in the ratio 1:1 at 180°C. The indicator of ending of oxidizing is the release of nitrogen dioxide gas. The content of the flask was quantitatively transferred into the 25 mL flask through paper filter and diluted by bi-distilled water. The samples were measured by atomic-absorption spectrometer (AA – 6200 Shimadzu, Japan) [22].

2.3 Health risk index

HRI was calculated for each sample by following equation [23]:

$$HRI = DIM/R_f,$$

where *DIM* is daily intake of heavy metal mg/person/day and R_f is the oral reference dose, mg kg^{-1} body weight d^{-1}. R_{fd} value for Zn, Pb, Cd, Mn and Cu is 1.5, 0.004, 0.001, 0.033, and 0.04, respectively [24].

The health risk index values greater than 1 for human health were not considered safe [23].

The *DIM* was calculated by following equation [19]:

$$DIM = C_m * C_f * D_{FI} / \text{body weight},$$

where C_m is concentration of heavy metal in sample, mg/kg; C_f is conversion factor, which convert the fresh vegetable weight to dry weight; D_{FI} is daily intake of vegetables/food, kg/d.

According to the food basket of Kazakhstan [25], each citizen of Kazakhstan consumes the following amounts of *Allium cepa* – 0.05 kg d^{-1}, *Daucus carota subsp. sativus* – 0.05 kg d^{-1}, *Solanum tuberosum* – 0.26 kg d^{-1}. Average adult weight for Kazakhstan was considered as 60 kg.

3. Results and Discussion

3.1 Content of heavy metals

Among the heavy metals, the highest concentration was identified for lead in differently processed *Daucus carota subsp. sativus*. The highest concentration of lead was determined in boiled *Daucus carota subsp. Sativus* and equal to 73.8 mg/kg, in comparison to the lowest concentration – sous- vide *Daucus carota subsp. Sativus*, it was 1.3 times higher.

According to the Figure 1, the lowest concentration among the heavy metals was determined for cadmium. In all differently processed *Daucus carota subsp. Sativus* samples the concentration of cadmium ranged from 19 to 22 mg/kg. In case of zinc and copper, the concentration of heavy metals did not change significantly depending on method of processing. For manganese, the highest concentration was determined for boiled *Daucus carota subsp. Sativus,* while in comparison to the lowest concentration was 1.4 times higher.

In investigated samples of *Solanum tuberosum,* the highest concentration of lead was determined in boiled sample according to Figure 2. Among the differently processed samples of *Solanum tuberosum,* the lowest concentration of lead was determined in fried sample, which was 1.4 times lower than in boiled sample. The lowest concentration among the heavy metals was for cadmium in *Solanum tuberosum* samples. The content of cadmium was around 19 mg/kg in all samples of *Solanum tuberosum* and did not depend from processing method. For copper, manganese and zinc, it can be stated from Figure 2, that concentration was fluctuated, however insignificantly changed depending on method of processing.

In case of *Allium cepa* samples, the highest concentration of lead was determined in comparison with other metals. Steamed and sous-vide samples of *Allium cepa* had highest concentration of lead which was equal to 66 mg/kg. Compared to the lowest concentration, it was 1.3 times higher. The lowest concentration among the heavy metals was determined for cadmium, manganese and copper. Meanwhile, for boiled and sous – vide *Allium cepa,* content of copper 2.4 times was lower than for fried sample. The content of zinc in fried and boiled

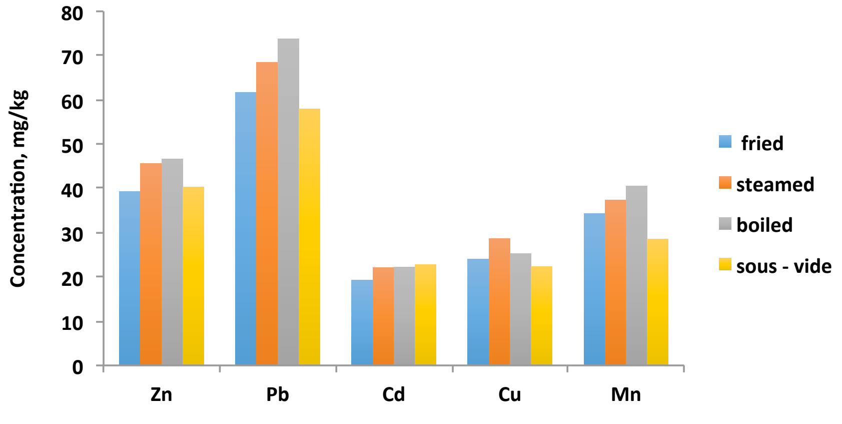

Figure 1 – Concentration of heavy metals in *Daucus carota subsp. sativus*

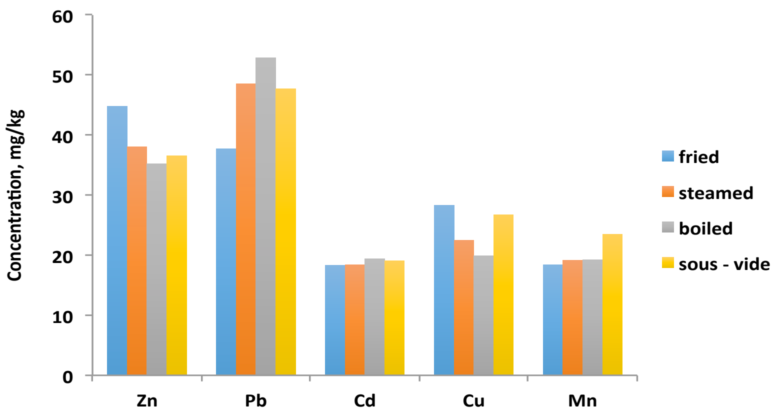

Figure 2 – Concentration of heavy metals in *Solanum tuberosum*

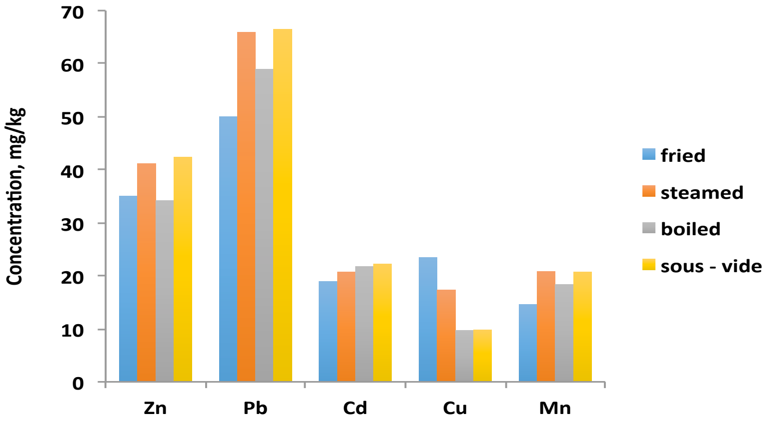

Figure 3 – Concentration of heavy metals in *Allium cepa*

sample of *Allium cepa* was equal, and 1.2 times lower comparing to steamed and sous – vide samples.

Out of all results, it can be concluded, that content of not all investigated heavy metals will depend on method of processing food. We can observe, weak correlation between content of lead, copper and manganese depending on method of processing of food.

3.2 Health Risk Index (HRI)

Risk assessment is helpful in estimating of possible health risk posed to human population which can be exposed by certain contaminants, including heavy metals, over a long period via daily dietary intake. Based on concentration of heavy metals in investigated samples, values of HRI were calculated.

In Table 1 it is seen that only two metals – lead and cadmium are exceeding of HRI value to dangerous values. In case of *Solanum tuberosum*, for all differently processed samples, HRI value of cadmium was significantly higher than 1. The same trend was seen for HRI value of lead for *Solanum tuberosum* samples. As a result, it indicated the possible health risk to human body in case of long period *Solanum tuberosum*

Table 1 – HRI of heavy metals

HRI	Zn	Pb	Cd	Cu	Mn
Daucus carota subsp. Sativus					
Fried	0	1.1	1.5	0	0
Steamed	0	1.3	1.7	0	0
Boiled	0	1.4	1.7	0	0
Sous-vide	0	1.1	1.1	0.2	0
Allium cepa					
Fried	0	1	1.4	0	0
Steamed	0	1.2	1.6	0	0
Boiled	0	1.1	1.7	0	0
Sous-vide	0	1.2	1.7	0	0
Solanum tuberosum					
Fried	0	3.4	6.8	0.2	0.2
Steamed	0	4.4	6.8	0.2	0.2
Boiled	0	4.9	7.1	0.1	0.2
Sous-vide	0	4.3	7.0	0.2	0.2

consumption. However, in case of HRI value of lead for *Solanum tuberosum*, the highest value was calculated for boiled samples, while the lowest value was indicated in fried ones, which means that, we can insignificantly reduce exposure of lead by choosing the method of processing food.

For *Daucus carota subsp. sativus* and *Allium cepa* samples, HRI value of cadmium and lead was slightly higher than 1. HRI value of zinc, copper and manganese for all investigated samples were less than 1, which indicates no health risk to human.

4. Conclusion

The high concentration of lead was determined in all investigated samples among the heavy metals. In *Solanum tuberosum* and *Daucus carota subsp. Sativus*, the high concentration of lead was determined for boiled samples; meanwhile for other samples of *Solanum tuberosum* and *Daucus carota subsp. Sativus* with different applied processing method the same value was slightly low.

HRI of cadmium and lead in *Solanum tuberosum* samples are significantly exceeding one. The highest value of HRI of lead was calculated for boiled *Solanum tuberosum*, while the lowest value was indicated in fried, which means that, we can insignificantly reduce exposure of lead by choosing the method of processing food.

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References (GOST)

1 Rai P.K., Lee S.S., Zhang M., Tsang Y.F., Kim K.H. Heavy metals in food crops: Health risks, fate, mechanisms, and management // Environment International. – 2019. – Vol.125. – P.365-385.

2 Pogrzeba M., Rusinowski S., Krzyżak J. Macroelements and heavy metals content in energy crops cultivated on contaminated soil under different fertilization—case studies on autumn harvest // Environmental Science and Pollution Research. – 2018. – Vol.25. – P.12096-12106.

3 Md. Saiful Islam, Md. Kawser Ahmed, Md. Habibullah-Al-Mamun. Heavy metals in cereals and pulses: Health implications in Bangladesh // Journal of Agricultural and Food Chemistry. – 2014. – Vol.62, Is.44. – P.10828-10835.

4 Sharma S., Kaur I., Nagpal A.K. Estimation of arsenic, manganese and iron in mustard seeds, maize grains, groundwater and associated human health risks in Ropar wetland, Punjab, India, and its adjoining areas // Environmental Monitoring and Assessment. – 2018. – Vol.190. – P.385.

5 Vincent O. Adimula, Percy C. Onianwa, Omolola Ilupeju, Eric Ayom, Alafara A. Baba. Assessment of heavy metals in foods and adult dietary intake estimates // African Journal of Science, Technology, Innovation and Development. – 2019. – Vol.11, Is.1. – P.1-8.

6 Onianwa P.C., Adeyemo A.O., Idowu O.E., Ogabiela E.E. Copper and zinc contents of nigerian foods and estimates of the adult dietary intakes // Food Chemistry. – 2001. – Vol.72. – P.89-95.

7 He K., Wang S., Zhang L. Blood lead levels of children and its trend in China // Science of The Total Environment. – 2009. – Vol.407, Is.13. – P.3986-3993.

8 Chiodo L.M., Jacobson S.W., Jacobson J.L. Neurodevelopmental effects of postnatal lead exposure at very low levels // Neurotoxicology and Teratology. – 2004. – Vol.26, Is.3. – P.359-371.

9 Koller K., Brown T., Spurgeon A., Levy L. Recent Developments in low-level lead exposure and intellectual impairment in children // Environmental Health Perspectives. – 2004. – Vol.112, Is.9. – P.987-994.

10 Waalkes M.P. Cadmium carcinogenesis // Mutation Research/Fundamental and Molecular Mechanisms of Mutagenesis. – 2003. – Vol.533, Is.1-2. – P.107-120.

11 Lestan D. Novel chelant-based washing method for soil contaminated with Pb and other metals: A pilot-scale study // Land Degradation and Devolopment. – 2017. – Vol.28, Is.8. – P.2585-2595.

12 Gardener H., Bowen J., Callan J.S. Lead and cadmium contamination in a large sample of United States infant formulas and baby foods // Science of The Total Environment. – 2019. – Vol.651. – P.822-827.

13 Chuang H.Y., Cheng W.C., Chen C.Y., Yang Y.H., Sung F.C., et al. A follow-up comparison of blood lead levels between foreign and native workers of battery manufacturing in Taiwan // Science of The Total Environment. – 2008. – Vol.394, Is.1. – P.52-56.

14 Zhou J., Liang J., Hu Y., Zhang W., Liu H., et al. Exposure risk of local residents to copper near the largest flash copper smelter in China // Science of The Total Environment. – 2018. – Vol.630. – P.453-461.

15 Cai L.M., Wang Q.S., Luo J., Chen L.G., Zhu R.L., et al. Heavy metal contamination and health risk assessment for children near a large Cu-smelter in central China // Science of The Total Environment. – 2019. – Vol.650. – P.725-733.

16 Gaetke L.M., Chow-Johnson H.S., Chow C.K. Copper: toxicological relevance and mechanisms // Archives of Toxicology volume. – 2014. – Vol.88. – P.1929-1938.

17 Cao S., Duan X., Zhao X., Wang B., Ma J., et al. Health risk assessment of various metal(loid)s via multiple exposure pathways on children living near a typical lead-acid battery plant, China // Environmental Pollution. – 2015. – Vol.200. – P.16-23.

18 Brunetti G., Ruta C., Traversa A., D'Ambruoso G., Tarraf W., et al. Remediation of a heavy metals contaminated soil using mycorrhized and non-mycorrhized Helichrysum italicum (Roth) Don // Land Degradation and Development. – 2018. – Vol.29. – P.91-104.

19 Jiang Y., Chao S., Liu J., Yang Y., Chen Y., Zhang A., Cao H. Source apportionment and health risk assessment of heavy metals in soil for a township in Jiangsu Province, China // Chemosphere. – 2017. – Vol.168. – P.1658-1668.

20 Wang Y., Wang R., Fan L., Chen T., Bai Y., et al. Assessment of multiple exposure to chemical elements and health risks among residents near Huodehong lead-zinc mining area in Yunnan, Southwest China // Chemosphere. – 2017. – Vol.174. – P.613-627.

21 Ayub H., Ahmad A. Physiochemical changes in sous-vide and conventionally cooked meat // International Journal of Gastronomy and Food Science. – 2019. – Vol.17. – P.100-145.

22 Ponomarenko O.I., Botvinkina M.A., Matveyeva I.A. Methods of control of natural objects and environmental monitoring: educational-methodological handbook. – Almaty: Kazakh University, 2014. – P.165.

23 Mehmood A., Raza W., Kim K., Raza N., Lee S.S., Zhang M., Lee H., Sarfraz M. Spatial distribution of heavy metals in crops in a wastewater irrigated zone and health risk assessment // Environmental Research. – 2018. – Vol.168. – P.382-388.

24 US-EPA IRIS // Database. *https://www.epa.gov/iris*

25 Web page (2018) Minimum consumer busket: defenition and composition [Minimal'naya potrebitel'skaya korzina: opredelenie i sostav]. *https://mojazarplata.kz/dohodyminimum/Prozhitochnyj_minimum/minimalnaja-potrebitelskaja-korzina*

References

1 Rai PK, Lee SS, Zhang M, Tsang YF, Kim KH (2019) Environ Int 125:365-385. *https://doi.org/10.1016/j.envint.2019.01.067*

2 Pogrzeba M, Rusinowski S, Krzyżak J (2018) Environ Sci Pollut R 12096-12106. *https://doi.org/10.1007/s11356-018-1490-8*

3 Islam MS, Ahmed MK, Habibullah-Al-Mamun M (2014) J Agr Food Chem 62(44):10828-10835. *https://doi.org/10.1021/jf502486q*

4 Sharma S, Kaur I, Nagpal AK (2018) Environ Monit Assess 190:385. *https://doi.org/10.1007/s10661-018-6763-7*

5 Adimula VO, Onianwa PC, Ilupeju O, Ayom E, Baba AA (2019) African Journal of Science, Technology, Innovation and Development 11:261-268. *https://doi.org/10.1080/20421338.2018.1556455*

6 Onianwa PC, Adeyemo AO, Idowu OE, Ogabiela EE (2001) Food Chem 72:89-95.

7 He K, Wang S, Zhang L (2009) Sci Total Environ 407:3986-3993. *https://doi.org/10.1016/j.scitotenv.2009.03.018*

8 Chiodo LM, Jacobson SW, Jacobson JL (2004) Neurotoxicol Teratol 26:359-371. *https://doi.org/10.1016/j.ntt.2004.01.010*

9 Koller K, Brown T, Spurgeon A, Levy L (2004) Environ Health Persp 112:987-994. *https://doi.org/10.1289/ehp.6941*

10 Waalkes MP (2003) Mutat Res-Fund Mol M 533:107-120. *https://doi.org/10.1016/j.mrfmmm.2003.07.011*

11 Lestan D (2017) Land Degrad Dev *https://doi.org/10.1002/ldr.2818*

12 Gardener H, Bowen J, Callan JS (2019) Sci Total Environ 651:822-827. *https://doi.org/10.1016/j.scitotenv.2018.09.026*

13 Chuang HY, Cheng WC, Chen CY, Yang YH, Sung FC, et al (2008) Sci Total Environ 394:52-56. *https://doi.org/10.1016/j.scitotenv.2008.01.032*

14 Zhou J, Liang J, Hu Y, Zhang W, Liu H, et al (2018) Sci Total Environ 630:453-461. *https://doi.org/10.1016/j.scitotenv.2018.02.211*

15 Cai LM, Wang QS, Luo J, Chen LG, Zhu RL, et al (2019) Sci Total Environ 650725-733. *https://doi.org/10.1016/j.scitotenv.2018.09.081*

16 Gaetke LM, Chow-Johnson HS, Chow CK (2014) Arch Toxicol 88:1929-1938. *https://doi.org/10.1007/s00204-014-1355-y*

17 Cao S, Duan X, Zhao X, Wang B, Ma J, et al (2015) Environ Pollut 200:16-23. *https://doi.org/10.1016/j.envpol.2015.02.010*

18 Brunetti G, Ruta C, Traversa A, D'Ambruoso G, Tarraf W, et al (2018) Land Degrad Dev 29:91-104. *https://doi.org/10.1002/ldr.2842*

19 Jiang Y, Chao S, Liu J, Yang Y, Chen Y, et al (2017) Chemosphere 168:1658-1668. *https://doi.org/10.1016/j.chemosphere.2016.11.088*

20 Wang Y, Wang R, Fan L, Chen T, Bai Y, et al (2017) Chemosphere 174:613-627. *https://doi.org/10.1016/j.chemosphere.2017.01.055*

21 Ayub H, Ahmad A (2019) International Journal of Gastronomy and Food Science 17:100-145. *https://doi.org/10.1016/j.ijgfs.2019.100145*

22 Ponomarenko OI, Botvinkina MA, Matveyeva IA (2014) Methods of control of natural objects and environmental monitoring: educational-methodological handbook. Kazakh University, Almaty. P.165. ISBN 978-601-04-1096-1

23 Mehmood A, Raza W, Kim K, Raza N, Lee SS, Zhang M, Lee H, Sarfraz M (2018) Environ Res 168: 382-388. *https://doi.org/10.1016/j.envres.2018.09.020*

24 US-EPA IRIS // Database. *https://www.epa.gov/iris*

25 Web page (2018) Minimum consumer busket: defenition and composition [Minimal'naya potrebitel'skaya korzina: opredelenie i sostav]. *https://mojazarplata.kz/dohodyminimum/Prozhitochnyj_minimum/minimalnaja-potrebitelskaja-korzina*

Synthesis of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide and its plant growth-stimulating activity assessment

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The aim of this study was to synthesize novel ionic compound – 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide – via the *N*-alkylation (in conventional conditions and using ultrasound activation), and investigate its influence on the plant growth-stimulating activity using of sweet sorghum seeds. The synthesized compound was fully characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. Regardless of the type of synthesis' methods, the isolated yield of the produced ionic compound is showed 79-81%, however, the reaction rate was significantly increased by using ultrasonic activation. For the assessment of the growth-stimulating activity of the synthesized ionic compound, parameters such as root length, shoot length, seed energy germination rate, and germination capacity were determined on 10 genotypes of sweet sorghum seeds. The results of samples with low concentration (0.001% vol. solution) were demonstrated the higher intensity for tested genotypes than control samples, especially for process of gemmogenesis and intensity of rhizogenesis. The results of this study can be used as basis for the further development of plant growth stimulants based on ionic compounds.

Keywords: tolperisone; ionic compound; ultrasound activation; sweet sorghum; germination; plant growth-stimulating activity.

1-Пропаргил-1-(2-метил-3-оксо-3-(п-толил)пропил)-пиперидин-1-иум бромидінің синтезі және оның өсімдіктердің өсу-белсенділігіне әсерін бағалау

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Берілген зерттеудің мақсаты жаңа иондық қосылыс - 1-пропаргил-1-(2-метил-3-оксо-3-(п-толил)пропил)-пиперидин-1-иум бромидті, *N*-алкилдеу арқылы синтездеу (қалыпты жағдайда және ультрадыбыстық белсендірумен) және тәтті жүгерінің дәндерін қолданып, оның өсімдіктердің өсу ынталандыру белсенділігіе әсерін зерттеу. Алынған қосылыс инфрақызыл спектроскопиясы (ИҚ) және ядролық-магнитті резонанс спектроскопиясы (ЯМР) арқылы сипатталынды. Алынған қосылыстың шығымы синтез әдісіне байланысты емес - 78-81%, бірақ қалаулы өнімнің құрылуы ультрадыбыстық белсендірумен әлдеқайда тезірек болады. Синтезделген иондық қосылыстың өсу ынталандыру белсенділігін тексеру кезінде тамыр ұзындығы, жапырақ ұзындығы, өну энергиясы және зертханалық өнгіштік сияқты параметрлер тәтті жүгері дәндерінің 10 генотипында өлшелінді. Қосылыстың ең кішкентай консентрациядағы ерітіндісі (0,001%) жақсы көрсеткіштер көрсетеді, әсіресе тамыр және жапырақ дамуының процессіне. Осы зерттеудің нәтижелері келесі әлеуетті экологиялық-қауіпсіз өсімдік өсу ынталандырғыштар үшін негіз ретінде қолданыла алады.

Түйін сөздер: толперизон; иондық қосылыс; ультрадыбыспен белсендіру; тәтті құмай; өну; өсуді ынталандыратын белсенділік.

Синтез 1-пропаргил-1-(2-метил-3-оксо-3-(*п*-толил)пропил)-пиперидин-1-иум бромида и оценка его ростстимулирующей активности

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Целью данного исследования было синтезировать новое ионное соединение –1-пропаргил-1-(2-метил-3-оксо-3-(п-толил)пропил)-пиперидин-1-иум бромид – с помощью N-алкилирования (в обычных условиях и с использованием ультразвуковой активации) и исследовать его влияние на ростостимулирующую активность растений с использованием семян сладкого сорго. Полученное соединение было охарактеризовано с помощью инфракрасной (ИК) спектроскопии и спектроскопии ядерно-магнитного резонанса (ЯМР). Выход полученного соединения составил 79–81% вне зависимости от метода синтеза, однако образование желаемого соединения происходит значительно быстрее при ультразвуковой активации. Для проверка ростостимулирующей активности синтезированного ионного соединения были измерены такие параметры как длина корня, длина листа, энергия прорастания и лабораторная всхожесть на 10 генотипах семян сладкого сорго. Раствор вещества с меньшей концентрацией (0,001%) показывает хорошие показатели, в особенно на процесс развития корней и листьев. Результаты этого исследования могут послужить базой для дальнейшей разработки стимуляторов роста растений на основе ионных соединений.

Ключевые слова: толперизон; ионное соединение; активация ультразвуком; сладкое сорго; прорастание; ростстимулирующая активность.

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Synthesis of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide and its plant growth-stimulating activity assessment

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1. Introduction

Sorghum (*Sorghum bicolor (L.)*) is a very important gain crop, it could produce a large yield and adapted under rough conditions such as heat and drought [1]. A substantial variation of sugar content makes sweet sorghum a potential source of biofuel [1]. It is used for animal feed [2], alcohol [1,4], syrups, glucose, modified starches, citric acid, etc. [3,5]. To stimulate the germination of sorghum different growth regulators are recommended [6]. Recently, *N*-methyl derivative of tolperisone was found practically harmless toward A. Fischeri [7], which makes other derivatives of tolperisone potentially promising environmentally friendly growth stimulants. In the present study, we describe the synthesis of a new ionic compound obtained via *N*-alkylation of tolperisone and its germination stimulating activity.

2. Experiment

2.1 Materials and research methods. Synthesis of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide

The melting point of ionic compound was measured in open capillary tube on an OptiMelt (Stanford Research System). IR spectra were recorded on Nicolet «5 700 FT-IR» spectrometer in a KBr tablet. ^{13}C NMR and ^{1}H spectra of synthesized compounds were recorded on «JNM-ECA Jeol 400» (100.53 and 399.78 MHz respectively) using $CDCl_3$ as solvent, the shooting temperature is 25°C. Control over the process of reactions and individuality of compounds was carried out by TLC on SiO_2 plates (Sigma Aldrich®, Germany) with mixture of diethyl ether:ethanol (4:1) as eluent and with iodine vapors development. Tolperisone freebase was obtained from Mydocalm® for synthesis at the room temperature and from corresponding hydrochloride (Shanghai Acmec Biochemical Technology Co, Ltd.) for synthesis with ultrasound activation. All reactants and solvents from Sigma Aldrich®. An ultrasonic probe from Cole Parmer (50-60Hz, 0-240 W) was used for the reaction. The separation and purification of the substances was carried out by recrystallization from appropriate solvents.

"Room temperature" method: In 15 ml acetonitrile, which contains 7.3 mmol tolperisone free-base, 5 ml of new acetonitrile with 8.03 mmol propargyl bromide was added. After mixing the reaction was carried in room temperature for 6 days. The precipitate was washed by cold acetonitrile and purified by recrystallization from diethyl ether: ethanol = 1:4. Product is beige crystals. Yield 81%. mp = 180°C. IR (KBr), cm^{-1}: 1670 (C=O), 1132 (C-N),3264 (≡C-H)

"Ultrasound activation" method: Tolperisone free-base (9.5 mmol) was dissolve in 15 ml acetonitrile and propargyl bromide (11.1 mmol) was added. Reaction was carried out with ultrasound activation (240 W, 30–50°C) for 5 hours, after precipitate was formed, it was washed by cold acetonitrile and purified by recrystallization from diethyl ether: ethanol = 2:3. Product is beige crystals. Yield 79%. mp = 177°C. IR (KBr), cm^{-1}: 1670 (C=O), 1132 (C-N), 3264 (≡C-H)

^{1}H NMR ($CDCl_3$) δ, ppm: 1.35 – 1.40 (C_{12}), 1.64 – 2.04 ($C_{2,3,4,9}$), 2.36 – 2.39 (C_{21}), 3.37 – 3.45 ($C_{1ax,5ax}$), 3.57 – 3.68 ($C_{1eq,5eq}$), 3.89 – 3.99 (C_{10ax}), 4.01 – 4.10 (C_{10eq}), 4.56 – 4.63 (C_{11}), 5.10 – 5.16 (C_7), 7.24 – 7.33 ($C_{17,19}$), 8.14 – 8.18 ($C_{16,20}$). ^{13}C NMR ($CDCl_3$) δ, ppm: 19.99 (C_{12}), 20.08 ($C_{2,4}$), 20.62 (C_3), 21.87 (C_{21}), 35,65 (C_{11}), 51.67 (C_7), 60.35 (C_{10}), 60.87 ($C_{1,5}$), 71.84 (C_8), 81.67 (C_9), 129.77 ($C_{17,19}$), 131.36 ($C_{16,20}$), 131.36 (C_{18}), 145.50 (C_{15}), 199.96 (C_{13}).

2.2 Assessment of plant grow-stimulating activity

The synthesized ionic compound was tested for germination energy and capacity with 10 sorghum genotypes (*KAZ-16 2013, Victoria-4 2013, Victoria-4 2014 (20 cm), Kiz-9 2015, Kiz-9 2014 (18.5 cm), Kiz-9 2013, Kiz-8 2015, Kiz-8 2014 (19.5 cm), Kiz-8 2013, Kiz-20 2013*). The experiment was performed with 2 solution of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide with different concentration – 0.01% (mass) and 0.001% (mass) and water was included as control. All dishes and experiment equipment were sterilized. Sorghum seeds were soaked in 90% ethanol for 6-7 minutes and after, were washed 3-4 times with distilled water. 20 seeds were placed in each Petri dish (10 Petri dishes for control, 50 – for each concentration of solution) on the filter paper, so they did not touch walls and each other. The filter paper was moisturized with the corresponding solution. The samples were placed in a light-proof cabinet, temperature: 22-25°C. Growth parameters including root length, shoot length and rate of the germination were determined after 4 and 9 days. For each batch of 100 seeds, the normally sprouted seeds are counted, considering the initial and final calculations. If the germination results of individual batches did not exceed the standard deviation, the batches were considered comparable. The result was the determination of the arithmetic mean with an accuracy of 1%.

3. Result and Discussion

Ultrasound activation - one of the best known non-conventional activation techniques at a laboratory scale. It is used by chemists to increase the reaction rate, speed up reaction time, and operate the reaction at more mild conditions [8]. Synthesis of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide (Figure 1) was carried out from obtained free-base [7] of tolperisone hydrochloride with *N*-alkylation under room temperature and with ultrasound activation (Table 1). The isolated yield of both methods is showed almost identical results; however, the reaction rate of the ultrasound activation method is 28 times faster.

During the assessment of the growth-stimulating activity of the synthesized ionic compound, the effect of the seed germination was studied on the 10 genotypes of sweet sorghum and growth parameters such as root length, shoot length, seed energy germination rate (after 4 days), and germination capacity (after 9 days) were determined. Experiments were carried out with solutions of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide (concentration 0.01% and 0.001%) and water were used as control. The mean value of the results on the effect of germination of sweet sorghum seeds, including standard deviation (SD) is presented in Tables 2-4.

The data of the gemmogenesis (Table 2) and the rhizogenesis (Table 3) presents that samples with low concentration (0.001% solution) is demonstrated the higher intensity for tested genotypes than control samples. 0.01% concentration of ionic compound shows better results (for root and shoot length) only for genotype *Victoria-4 20 cm 2014* after 9 days of germination (Figure 2) compared to control and lower concentration.

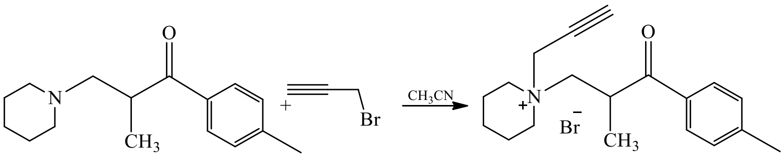

Figure 1 – The reaction of *N*-alkylation of tolperisone free-base with propargyl bromide to produce 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide

Table 1 – The yield and time of the reaction in respect with method of synthesis

Method of synthesis	Time	Yield, %	Solvents of recrystallization	Melting point
Room temperature	6 days	81	Et_2O:EtOH = 1:4	180°C
Ultrasound activation	5 h	79	Et_2O:EtOH = 2:3	177°C

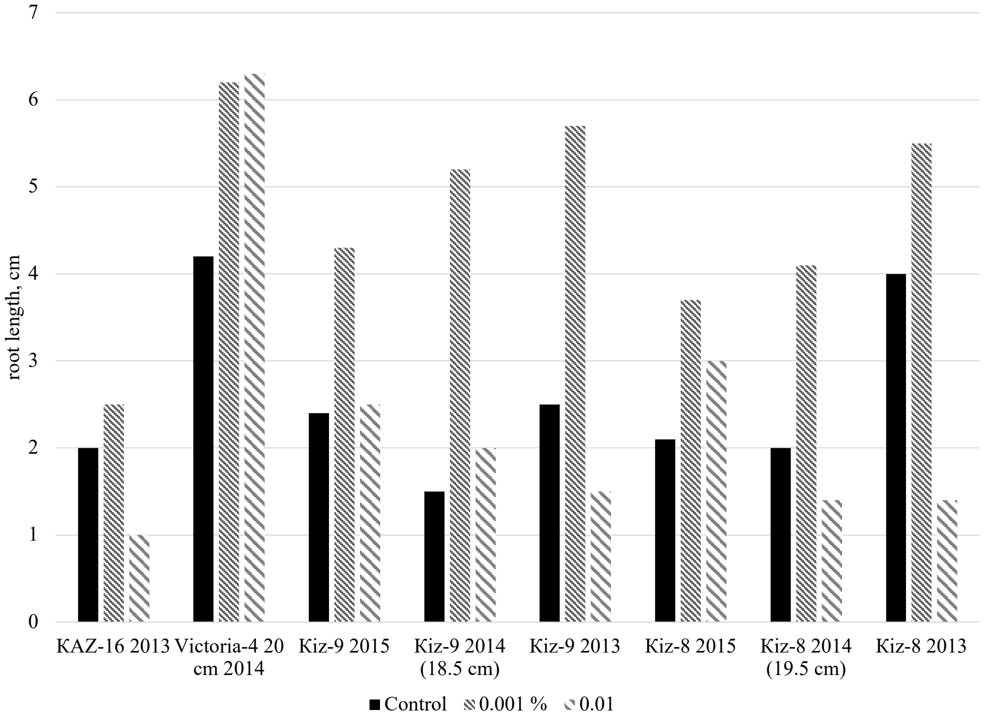

Figure 2 – Growth stimulant's effect on the root length (cm) of several genotypes of the sweet sorghum seeds after 9 days of germination

Table 2 – The result of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide's effect on the root length of sweet sorghum seeds

No.	Genotype	Germination after 4 days, cm (SD ±0.02)			Germination after 9 days, cm (SD ±0.3)		
		Control	0.01%	0.001%	Control	0.01%	0.001%
1	KAZ-16 2013	0.3	0.2	0.8	2.0	1.0	2.5
2	Victoria-4 2013	-	-	-	-	-	-
3	Victoria-4 20 cm 2014	1.2	1.5	1.8	4.2	6.3	6.2
4	Kiz-9 2015	0.1	0.2	0.1	2.4	2.5	4.3
5	Kiz-9 2014 (18.5 cm)	0.1	0.7	1.2	1.5	2.0	5.2
6	Kiz-9 2013	0.1	0.1	0.4	2.5	1.5	5.7
7	Kiz-8 2015	0.1	0.1	0.1	2.1	3.0	3.7
8	Kiz-8 2014 (19.5 cm)	-	0.1	0.1	2.0	1.4	4.1
9	Kiz-8 2013	0.1	0.1	0.1	4.0	1.4	5.5
10	Kiz-20 2013	-	-	-	-	-	-

Table 3 – The result of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide's effect on the shoot length of sweet sorghum seeds

No.	Genotype	Germination after 4 days, cm (SD ±0.01)			Germination after 9 days, cm (SD ±0.2)		
		Control	0.01%	0.001%	Control	0.01%	0.001%
1	KAZ-16 2013	0.5	0.1	1.0	2.5	2.0	4.5
2	Victoria-4 2013	-	-	-	-	-	-
3	Victoria-4 20 cm 2014	0.5	1.2	1.7	4.3	5.1	5.1
4	Kiz-9 2015	0.1	0.3	0.1	3.0	3.0	3.4
5	Kiz-9 2014 (18.5 cm)	0.1	0.4	0.5	3.0	3.5	4.5
6	Kiz-9 2013	0.1	0.2	0.3	3.3	2.0	4.7
7	Kiz-8 2015	0.1	0.1	0.1	3.2	4.2	5.0
8	Kiz-8 2014 (19.5 cm)	-	0.1	0.2	3.0	2.4	3.7
9	Kiz-8 2013	0.1	0.1	0.1	3.5	3.0	4.5
10	Kiz-20 2013	-	-	-	-	-	-

The result of seed energy germination rate (Table 4) varies depending on the genotype of sorghum. Samples with low concentration show a better result for *Kiz-9 2013, KAZ-16 2013, Kiz-8 2015* compared to control and higher concentrated solution. However higher concentrated solution is demonstrated by growth for 5-25% for such genotype as *Victoria-4 20 cm 2014, Kiz-9 2014 (18.5 cm)* and *Kiz-8 2014 (19.5 cm);* for genotype *Kiz-9 2015* and *Kiz-8 2013* water provides more effectiveness than solutions of ionic compounds. On the 9th day, we determined the germination capacity (Table 4), and it has been noticed that 4 genotypes (*KAZ-16 2013, Kiz-9 2014 (18.5 cm), Kiz-9 2013, Kiz-8 2015*) have maintained the same dependence of the result as seed energy germination rate. Nevertheless, *Kiz-9 2015, Kiz-8 2013, Victoria-4 20 cm 2014* presents the same rate of control and more concentrated solution of the ionic compound.

Table 4 – The result of 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide's effect on the germination energy and germination capacity of sweet sorghum seeds

No.	Genotype	Germination energy, % (SD ±3.2)			Germination capacity, % (SD ±2.5)		
		Control	0.01%	0.001%	Control	0.01%	0.001%
1	KAZ-16 2013	60	35	80	65	40	80
2	Victoria-4 2013	-	-	-	-	-	-
3	Victoria-4 20 cm 2014	75	80	65	80	80	70
4	Kiz-9 2015	30	20	15	25	25	20
5	Kiz-9 2014 (18.5 cm)	30	50	25	20	55	30
6	Kiz-9 2013	30	30	55	30	35	55
7	Kiz-8 2015	15	15	35	50	50	70
8	Kiz-8 2014 (19.5 cm)	-	25	20	10	30	35
9	Kiz-8 2013	35	15	30	50	50	40
10	Kiz-20 2013	-	-	-	-	-	-

4. Conclusion

Using ultrasound activation for the synthesis of ionic compound, 1-propargyl-1-(2-methyl-3-oxo-3-(*p*-tolyl)propyl)-piperidin-1-ium bromide was obtained with almost the same yield in a shorter time. The synthesized ionic compound's solution with control did not show any effect on the germination of 2 genotypes: *Victoria-4 2013 and Kiz-20 2013*. For other genotypes of sweet sorghum (*KAZ-16 2013, Kiz-9 2014 (18.5 cm), Kiz-9 2013, Kiz-8 2015, Kiz-8 2014 (19.5 cm)*), germination energy and capacity of seeds, processes of gemmogenesis and intensity of rhizogenesis were better affected by solution with low concentration, although the influence of ionic compound on germination capacity of *Kiz-9 2015*, *Kiz-8 2013, Victoria-4 20 cm 2014* presents the same or worst results compared to control.

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References (GOST)

1 Ali M.L., Rajewski J.F., Baenziger P.S., Gill K.S., Eskridge K.M., et al. Assessment of genetic diversity and relationship among a collection of US sweet sorghum germplasm BY ssr markers // Molecular Breeding. – 2007. – Vol.21, Is.4. – P.497-509.

2 Kleih U., Ravi S.B., Rao B.D., Yoganand B. Industrial Utilization of Sorghum in India // Monograph. International Crops Research Institute for the Semi-Arid Tropics. – 2000.

3 Somani R.B., Almodares A., Pandrangi R.B., Sepahi A. Potential of sweet sorghum in India and Iran for alcohol and sweetners production // First International Sweet Sorghum Conference, China. – 1997.

4 Ratnavathi C.V., Komala V.V., Lavanya U. Chapter 4 - Sorghum Uses—Ethanol. In: Ratnavathi C.V., Patil J.V., Chavan U.D. (Eds.) Sorghum Biochemistry. – Academic Press Elsevier, 2016. – P.181-252.

5 Ratnavathi C.V., Chavan U.D. Sorghum syrup and other by products // Sorghum Biochemistry. An Industrial Perspective. – 2016. – P.253-310.

6 Macedo W.R., Araújo D.K., Santos V.M., Castro P.R., Fernandes G.M. Plant growth regulators on sweet sorghum: Physiological and nutritional value analysis // Comunicata Scientiae. – 2017. – Vol.8, Is.1. – 170 p.

7 Giner B., Mergenbayeva S., Lomba L., Rafikova K., Dauletbakov A. et al. Synthesis and ecotoxicological studies of ionic compounds based on tolperisone, diphenhydramine and trimecaine // ChemistrySelect. – 2020. – Vol.5, Is.41. – P.12823-12828.

8 Lévêque J.M., Estager J., Draye M., Cravotto G., Boffa L., Bonrath W. Synthesis of ionic liquids using non conventional activation methods // An Overview. Monatshefte Für Chemie – Chemical Monthly. – 2007. – Vol.138, Is.11. – P.1103-1113.

References

1 Ali ML, Rajewski JF, Baenziger PS, Gill KS, Eskridge KM, et al (2007) Mol Breeding 21(4):497-509. *https://doi.org/10.1007/s11032-007-9149-z*

2 Kleih U, Ravi SB, Rao BD, Yoganand B (2000) Industrial Utilization of Sorghum in India. Monograph. International Crops Research Institute for the Semi-Arid Tropics.

3 Somani RB, Almodares A, Pandrangi RB, Sepahi A (1997) Potential of sweet sorghum in India and Iran for alcohol and sweetners production. First International Sweet Sorghum Conference, China.

4 Ratnavathi CV, Komala VV, Lavanya U (2016) Chapter 4 - Sorghum Uses—Ethanol. In: Ratnavathi CV, Patil JV, Chavan UD (Eds) Sorghum Biochemistry. An Industrial Perspective. Academic Press Elsevier, UK. P.181-252. *https://doi.org/10.1016/b978-0-12-803157-5.00004-6*

5 Ratnavathi CV, Chavan UD (2016) Sorghum Biochemistry 5:253-310. *https://doi.org/10.1016/b978-0-12-803157-5.00005-8*

6 Macedo WR, Araújo DK, Santos VM, Castro PR, Fernandes GM (2017) Comunicata Scientiae 8(1):170-175. *https://doi.org/10.14295/cs.v8i1.1315*

7 Giner B, Mergenbayeva S, Lomba L, Rafikova K, Dauletbakov A et al (2020) ChemistrySelect 41:12823-12828. *https://doi.org/10.1002/slct.202001771*

8 Lévêque JM, Estager J, Draye M, Cravotto G, Boffa L, Bonrath W (2007) Chemical Monthly 138(11):1103-1113. *https://doi.org/10.1007/s00706-007-0742-y*

Kinetic parameters of thermal destruction of the copolymer of polyethylene glycol fumarate with acrylic acid in inert medium

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Thermal decomposition of the copolymer of polyethylene glycol fumarate with acrylic acid (p-EGF:AA) of two different compositions synthesized earlier was studied in the present work. TG and DTG curves prove that decomposition takes place in several stages. According to thermogravimetric curves it has been found out that for the copolymer with higher content of acrylic acid the decomposition of the copolymer's sample is started at higher temperatures. It has been shown the shift of the temperature of decomposition's start to the higher area with the increase of heating rate which is necessary for the detorsion of macromolecular coil. Experimental data processed using graphical methods of Kissinger–Akahira–Sunose and Friedman allowed us to calculate the activation energy of the thermal decomposition process. It has been established that the copolymer with the composition of 21.03:78.97 mass.% has lower meaning of activation energy than the one with the composition of 68.96:31.04 mass.%. As a result of calculation one can see that the meanings found out using these methods depend slightly on conversion. Using Achar-Brindley-Sharp method and the method of invariant kinetic parameters the kinetic triplet of the decomposition process has been found which was used to build the calculated curve. The dependences of g(α) on α using these parameters showed a satisfactory agreement of calculated curves with the experimental ones. One can conclude that the decomposition process of the copolymer of polyethylene glycol fumarate with acrylic acid is well described with of D3 (three-dimensional diffusion) model.

Keywords: thermogravimetry; activation energy; copolymers; polyethylene glycol fumarate; acrylic acid.

Инертті ортада акрил қышқылымен полиэтиленгликолумарат сополимерінің термиялық деструкциясының кинетикалық параметрлері

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Бұл жұмыста бұрын синтезделген екі түрлі құрамдағы акрил қышқылымен полиэтиленгликольфумарат сополимерінің (п-ЭГФ:АҚ) термиялық ыдырауы зерттелген. TG және DTG қисықтары ыдырау процесі бірнеше сатыда жүретінін дәлелдейді. Термогравиметриялық қисық сызыққа сәйкес, құрамында акрил қышқылы көп сополимер үшін сополимер үлгісінің ыдырауы жоғары температурада басталатыны анықталды. Макромолекулалық шарларды айналдыру қажеттілігімен байланысты қыздыру жылдамдығының жоғарылауымен жоғары аймаққа ыдыраудың басталу температурасының өзгеруі көрсетілген. Фридман мен Киссинджер-Акахир-Сануздын графикалық әдістерімен өңделген эксперименттік мәліметтер термиялық ыдырау процесінің активтену энергиясын есептеуге мүмкіндік берді. 21.03:78.97 масс. % құрамының сополимері 68.96:31.04 масс. % -тен жоғары ыдырау активтендіру энергиясына ие екендігі анықталды. Есептеулер нәтижелері бойынша осы әдістермен табылған мәндер конверсияға қатты тәуелді емес екенін көруге болады. Ахар-Бриндли-Шарпа әдісін және инвариантты кинетикалық параметрлер әдісін қолдана отырып, есептелген қисық сызықты құру үшін қолданылатын ыдырау процесінің кинетикалық триплеті табылды. Осы параметрлерді қолдана отырып, g(α) α-ға тәуелділігі есептеу қисықтарының тәжірибелік қисықтармен қанағаттанарлық келісімін көрсетті. Акрил қышқылымен полиэтиленгликольфумарат сополимерінің ыдырау процесі D3 (үш өлшемді диффузия) моделімен жақсы сипатталған деп айта аламыз.

Түйін сөздер: термогравиметрия; активтендіру энергиясы; сополимерлер; полиэтиленгликольфумарат; акрил қышқылы.

Кинетические параметры термической деструкции сополимера полиэтиленгликольфумарата с акриловой кислотой в инертной среде

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В настоящей работе исследовано термическое разложение синтезированного ранее сополимера полиэтиленгликольфумарата с акриловой кислотой (п-ЭГФ:АК) двух различных составов. TG и DTG кривые доказывают, что процесс разложения происходит в несколько стадий. По термогравиметрическим кривым установлено, что для сополимера с большим содержанием акриловой кислоты разложение образца сополимера начинается при более высоких температурах. Показан сдвиг температуры начала разложения в более высокую область с ростом скорости нагрева, связанный с необходимостью раскручивания макромолекулярных клубков. Экспериментальные данные, обработанные графическими методами Фридмана и Киссинджера-Акахира-Сануза, позволили рассчитать энергии активации процесса термического разложения. Установлено, что сополимер с составом 21.03:78.97 масс, % имеет энергию активации разложения выше, чем 68.96:31.04 масс. %. По результатам расчетов можно увидеть, что значения, найденные данными методами, не сильно зависят от конверсии. Используя метод Ахара-Бриндли-Шарпа и метод инвариантных кинетических параметров, найден кинетический триплет процесса разложения, который использован для построения расчетной кривой. Зависимости g(α) от α с использованием данных параметров показали удовлетворительное согласие расчётных кривых с экспериментальными. Можно сказать, что процесс разложения сополимера полиэтиленгликольфумарата с акриловой кислотой хорошо описывается моделью D3 (трехмерная диффузия).

Ключевые слова: термогравиметрия; энергия активации; сополимеры; полиэтиленгликольфумарат; акриловая кислота.

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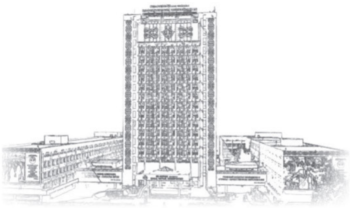

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Kinetic parameters of thermal destruction of the copolymer of polyethylene glycol fumarate with acrylic acid in inert medium

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1. Introduction

The study of the kinetics of thermal decomposition of the copolymers on the basis of unsaturated polyester resins is of great importance from the scientific point of view within the last decades as the study of physicochemical properties of such objects has vital role in modern industry [1].

Unsaturated polyesters are obtained by condensation polymerization of unsaturated dicarbon acids or their mixtures with saturated acids with polyhydric alcohols [2]. Compositional materials based on polyester resins have wide application as binding, film-forming, impregnated and filling compounds [3]. Besides, the ease of processing the unsaturated polyesters to the end-product makes actual the use of the copolymers on their basis for the number of industrial directions and therefore the question of the level of their thermal stability is of special importance [4,5].

Usually the thermogravimetry is used for the study of thermal destruction of polymers. Qualitative analysis of experimental data depends on reliable estimation of kinetic parameters $E_{a,}$ A and f(a), and in essence it gives mathematical explanation which is necessary for the extrapolation of the behavior of the decomposition reaction. In this regard there were worked out many different methods for the determination of kinetic parameters on the basis of experimental data of thermogravimetry [6,7].

At the beginning stage of the studies the main kinetic and thermodynamic parameters of decomposition of some copolymers on the basis of polyethylene glycol fumarate with acrylic acid have been determined with the help of differential and integral methods [8,9]. It was found that at different degrees of conversion, the activation energies are very close: E = 205-227 kJ/mol. And the copolymer is more thermally stable in a nitrogen atmosphere in accordance with the kinetic parameters. The result of the study has shown the practical value of this procedure.

The aim of this work is to make a comparative analysis of the kinetics of thermal decomposition of the samples of polyethylene glycol fumarate with acrylic acid of the composition of 21.03:78.97 and 68.96:31.04 mass.%.

2. Experiment

Study of thermal properties of p-EGF:AA copolymer in three parallel experiments was made with the help of device for simultaneous thermal analysis Labsys Evolution TG-DTA/DSC of «Setaram» brand in dynamic mode with temperature range of 30-600°C at heating in Al_2O_3 crucible with rate of 2.5, 5, 10 and 20°C/min in nitrogen atmosphere with stream rate of 30 mL/min. Calibration of device for thermogravimetric studies and heat flow rate was carried out three fold under the $CaCO_3$ standards and In respectively.

The kinetics of thermal decomposition is usually expressed by the following equation:

$$\frac{d\alpha}{dt} = k(T) \qquad (1)$$

where k is the rate constant, t is the reaction time, α is the conversion, which is described as:

$$\alpha = \frac{m_i - m_t}{m_i - m_f} \qquad (2)$$

where m_i, m_t, and m_f are the mass at the beginning, at time t, and at the end of the reaction.

The decomposition rate constant (k(T)) is a temperature-dependent function and is usually described by the Arrhenius equation.

Hence, the equation (1) can be written as follows:

$$\frac{d\alpha}{dt} = Aexp\left(\frac{-E}{RT}\right)f(\alpha) \tag{3}$$

where A is the pre-exponential factor, E is the activation energy, R is the universal gas constant (8,314 J·mol^{-1}), *f(α)* is the reaction model and T is the temperature (K).

Integral and differential methods were used to determine the activation energy (E_a).

The **Kissinger–Akahira–Sunose** method [10,11] is based on the following expression:

$$ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right) = Const - \left(\frac{E}{RT}\right) \tag{4}$$

where β_i is the heating rate (°C/min).

The activation energy can be obtained from a plot of $ln\left(\frac{\beta_i}{T_{\alpha,i}^2}\right)$ versus 1/T, for a given value of the degree of conversion, α, where the slope is equal to E_a /R.

The most common differential isoconversion method is that **Friedman** method [12]. The method is based on the equation:

$$ln\left[\beta_i\left(\frac{d\alpha}{dT}\right)_{\alpha,i}\right] = ln[f(\alpha)A_\alpha] - \frac{E_a}{RT_{\alpha,i}} \tag{5}$$

Eq. (5) is applicable to any temperature program. At each given a the value of E_a is determined from the slope of a plot of $ln(\beta_i{*}d\alpha/dt)_{\alpha,i}$ against $1/T_{\alpha,i}$. The index is introduced to denote various temperature programs.

To define the reaction model and pre-exponential factor, method of invariant kinetic parameters and model fitting method were used in this work. Differential method of Achar-Brindley-Sharp [13] was obtained as the result of equation logarithm (3):

$$ln\left(\frac{d\alpha/dt}{f(\alpha)}\right) = lnA - \frac{E}{RT} \tag{6}$$

Left part of equation (6) for this analytic form *f(α)* will be straight line, whose incline and crossing allow the estimation of activation energy and pre-exponential factor, respectively. Despite the fact that parameters are modified in wide range with *f(α)*, they all demonstrate the strong correlation, known as compensation effect:

$$lnA_i = a^*E_i + b^* \tag{7}$$

where a^* and b^* are the compensation parameters and the subscript i refers to a factor producing a change in the Arrhenius parameters(conversion, temperature program).

Using the ratio of apparent compensation effect, compensation parameters are defined for each heating rate. Thus, diagram a^* *vs* b^* represents the straight line, whose parameters allow estimating the invariant kinetic parameters [6]:

$$b^* = lnA + a^*E \tag{8}$$

3. Results and Discussion

At practical application of polymers, thermal stability in necessary temperature range plays a great role. Copolymers of unsaturated polyether resins with hydrophobial monomers, having the spatial linked structure, are distinct with thermal stability in wide range of temperatures and are widely described in the literature [14,15]. In the result of studies it was found that composition of unsaturated polyether and monomers used for linking influences significantly the thermal stability of copolymerization products, presence of aliphatic inclusions in copolymer decreases the thermal resistance. Increase of degree of unsaturation of polyether resin, as well as increase of polyether resin content compared to monomer leads to increase of thermal stability of copolymers. Results of thermogravimetric analysis showed that these copolymers are thermally resistant up to 250-300°C, and after this thermal destruction happens, that runs in several steps.

At the first time synthesized copolymers of polyglycolemaleanates with unsaturated carbonic acids have spatial linked structure as well [16,17], and it seemed interesting to study the influence of temperature on their behavior by thermogravimetry. In this work, is a previously synthesized copolymers p-EGF:AA of composition 21.03:78.97 and 68.96:31.04 mass.% is the object of research [18], which have proven themselves as «smart» systems. Thermogravimetric analysis was performed in dynamic conditions at four different heating rates. Figure 1a shows the dependence of sample weight from the temperature, and figure 1b shows the curves of the rate of decomposition.

As we see in Figure 1a, increase in the composition of acrylic acid leads to the offset of copolymer decomposition start to the area of higher temperatures. This concept is illustrated slower with DTG curve (Figure 1b): thus, maximum rate of copolymer decomposition is moved from 356 to 375ºC. Figure 1 shows that decomposition process is started at the temperature of ~150°C, and then there is step-by-step decreasing of sample weight with emission of volatile matters. The second stage of decomposition starts at the temperature of 265°C and is finished at 480°C, with a lower ratio of acrylic acid. With a ratio of 21.03:78.97 mass.%, start and final decomposition temperature moved to 280 and 500°C respectively. The same trend is observed in DTG curve. Residue weight at the end amounts approximately 15-17 percent of total sample weight.

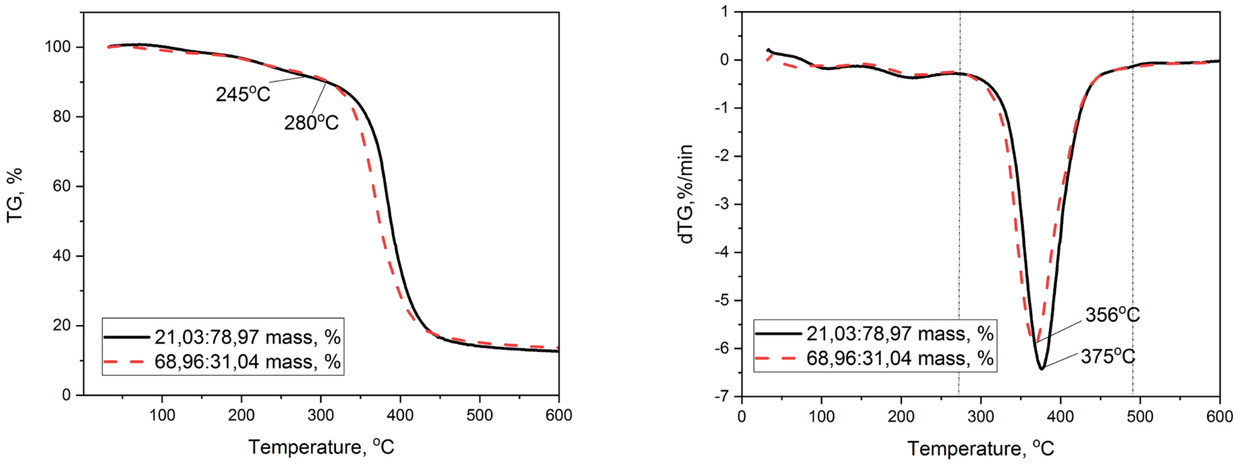

Figure 1 – TG (a) and DTG (b) curves of p-EGF:AA 21.03:78.97 and 68.96:31.04 mass.% at heating rate 5°C/min

To process the thermogravimetric curves at different heating rates, areas with highest weight loss are selected. Figure 2 shows the dependence of conversion degree and temperature.

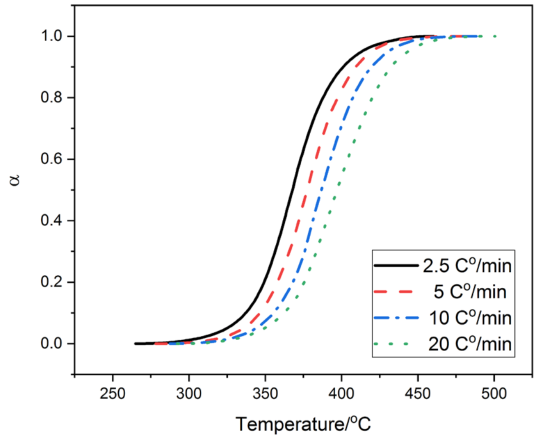

Figure 2 – Dependence of the conversion (α) of the copolymer p-EGF:AA 21.03:78.97 mass.% on the temperature at different heating rates

With the aim to estimate the thermodynamic stability subject to activation energy of copolymers, equations the Kissinger–Akahira–Sunose and the Friedman was applied. Selection of these methods was conditioned with the possibility to compare the activation energies obtained by integral and differential methods, which allow to estimate the legitimacy of allowances made at equation derivation. Dependence diagrams of equations are shown in the Figure 3 a, b, c and d.

As can be seen from the graphs, the points obtained by the Friedman differential method have a greater scatter (Figure 3) than in the Kissinger-Akahira-Sunose (KAS) method, and as a consequence, the latter are more parallel to each other. For all the obtained partial dependencies, activation parameters are calculated; their values are shown in Table 1.

As we see in Table 1, activation energies at different levels of conversion, have good convergence for both methods. At the primary stage of decomposition, activation energy values are changed in the range ~236 and 271 kJ/mol. Further we can observe stabilization and slight decrease. At value of α > 0.7 activation energy starts increasing gradually and reaches its maximum at α = 0.9. Increase of E_a is mainly connected to intensive decomposition of copolymer p-EGF:AA at high temperatures in inert media. As well, high values of activation energy in the beginning of the process witness the complex processes, happened at thermal destruction, related to breaking of unsaturated double bonds in copolymer structure.

Using equation 6, thirteen values of E_i and $\ln A_i$ were obtained for respective reaction models. Since for invariant kinetic parameters method it is necessary for E_a not to depend strongly on level of transformation, the range 0.1-0.9 was selected.

Figure 4a shows that for the ratio 21.03:78.97, the points lie on the same straight line and have a high degree of correlation, and for the ratio 68.96:31.04, the degree of correlation is slightly lower (Figure 4b). In inclination and crossing of the diagram, invariant kinetic parameters of copolymer decomposition were found, E_a = 240 kJ/mol and lnA = 38 for a copolymer with a lower ratio of polyester resin and E_a = 248 kJ/mol and lnA = 40 with a higher ratio. Activation energy conforms with values obtained by isoconversion methods.

When both parameters are defined, we can numerically reconstruct the reaction models in any integral or differential

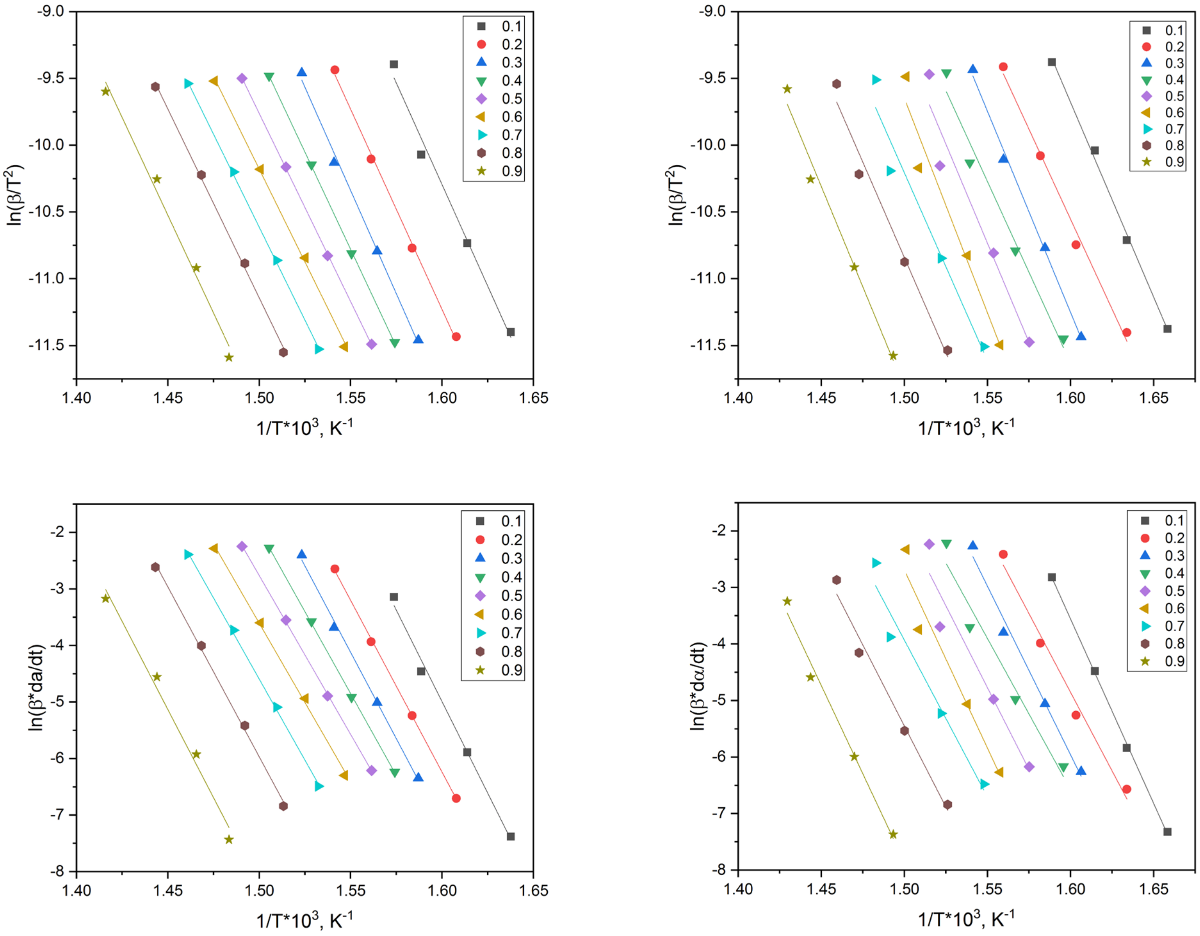

Figure 3 – Kissinger-Akahira-Sunose (a,b) and Friedman (c,d) plots of p-EGF:AA 21.03:78.97 and 68.96:31.04 mass.%

Table 1 – Kinetic parameters according to, Kissinger-Akahira-Sunose and Friedman

α, %	Kissinger-Akahira-Sunose				Friedman			
	21.03:78.97		68.96:31.04		21.03:78.97		68.96:31.04	
	E_a, kJ/mol	R^2	E_a, kJ/mol	R^2	E_a, kJ/mol	R^2	E_a, kJ/mol	R^2
0.1	236.21	0.9881	242.51	0.9967	248.26	0.9936	271.19	0.9993
0.2	232.57	0.9979	223.95	0.9919	244.16	0.9996	231.25	0.9859
0.3	240.42	0.9961	250.39	0.9966	237.38	0.9975	247.91	0.9885
0.4	233.72	0.9998	226.02	0.9766	232.53	0.9997	222.04	0.9608
0.5	225.87	0.9999	246.61	0.9438	225.28	0.9997	240.61	0.9303
0.6	222.79	0.9986	267.16	0.9555	224.76	0.9981	261.84	0.9486
0.7	223.12	0.9995	234.02	0.9558	230.13	0.9990	230.68	0.9582
0.8	226.84	0.9983	237.56	0.9790	237.48	0.9980	238.34	0.9829
0.9	235.11	0.9884	250.03	0.9849	242.70	0.9853	259.55	0.9880
Mean	**230.74**	**0.9963**	**242.03**	**0.9756**	**235.85**	**0.9967**	**244.82**	**0.9714**

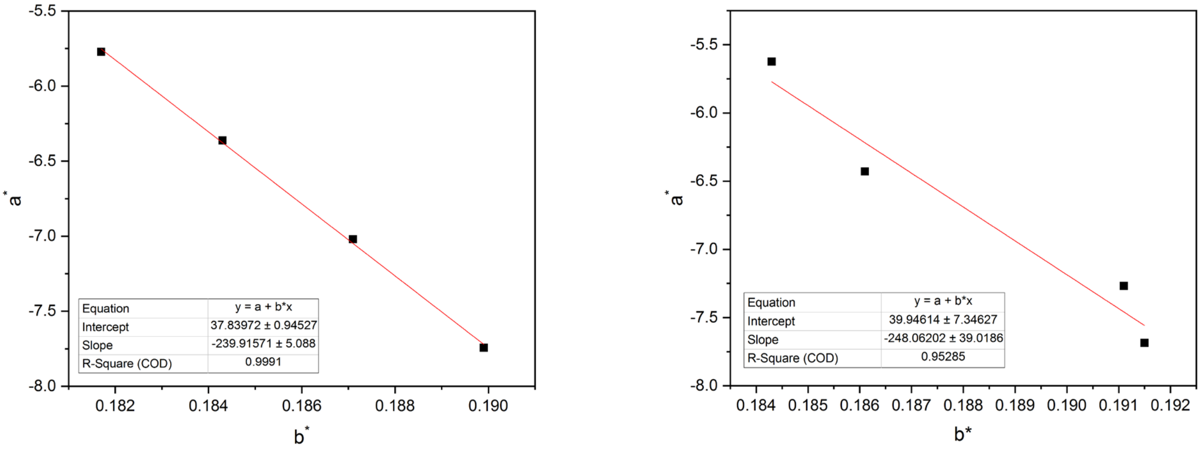

Figure 4 – Plot of the supercorrelation ratio (a* vs b*) of p-EGF:AA 21.03:78.97 mass.% (a) and 68.96:31.04 mass.% (b)

Table 2 – Some of the kinetic models used in the solid-state kinetics

#	Reaction model	Code	*f(α)*	*g(α)*
1	Power law	P4	$4\ \alpha^{3/4}$	$\alpha^{1/4}$
2	Power law	P3	$3\ \alpha^{2/3}$	$\alpha^{1/3}$
3	Power law	P2	$2\ \alpha^{1/2}$	$\alpha^{1/2}$
4	Power law	P2/3	$2/3\ \alpha^{-1/2}$	$\alpha^{3/2}$
5	One-dimensional diffusion Mampel (first	D1	$1/2\ \alpha^{-1}$	α^{2}
6	order)	F1	$1-\alpha$	$-\ln(1-\alpha)$
7	Avrami–Erofeev	A4	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$	$[-\ln(1-\alpha)]^{1/4}$
8	Avrami–Erofeev	A3	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$	$[-\ln(1-\alpha)]^{1/3}$
9	Avrami–Erofeev	A2	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$	$[-\ln(1-\alpha)]^{1/2}$
10	Three-dimensional diffusion Contracting	D3	$3/2(1-\alpha)^{2/3}[1-(1-\alpha)]^{1/3}]^{-1}$	$[1-(1-\alpha)]^{1/3}]^{2}$
11	sphere	R3	$3(1-\alpha)$	$1-(1-\alpha)^{1/3}$
12	Contracting cylinder	R2	$2(1-\alpha)$	$1-(1-\alpha)^{1/2}$
13	Two-dimensional diffusion	D2	$[-\ln(1-\alpha)]^{-1}$	$(1-\alpha)\ln(1-\alpha)+\alpha$

form. The models used in this study have been summarized in Table 2. Integral form might be reconstructed by value substitution of E_a and A to the equation [19]:

$$g(\alpha) = \frac{A}{\beta}\int_0^{T_\alpha} exp\left(\frac{-E}{RT}\right) dT \qquad (9)$$

With the help of equation 9, the set of numeric values g(α) for different conversion levels was obtained. With the aim to check the correctness of obtained data, we made the attempt to compare the experimental curves with calculated ones.

The dependence graph of the reaction model on the conversion degree has a profile reminiscent of an accelerating reaction (F1, D1, R3, etc.). Therefore, the calculated data were compared to the previously selected theoretical graphs g(α). As seen in Figure 8, a good conformity was found for the D3 model, the same situation is peculiar for other values of heating rate.

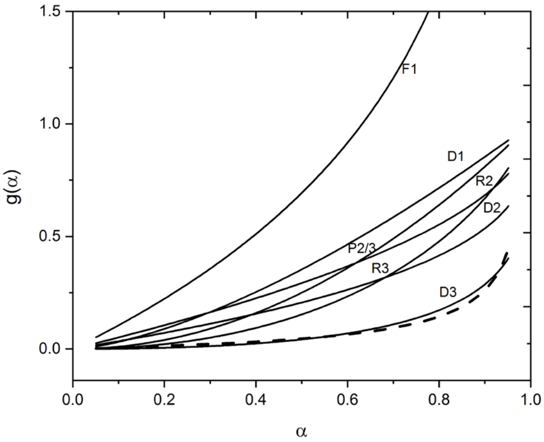

Figure 5 – Theoretical g(α) plots as a function of conversion a for several kinetic models and experimental plot for kinetic model D3 (dotted lines)

4. Conclusion

Thermal decomposition of copolymer p-EGF:AA at different heating rates was studied, and it showed that growth of the latter moves the decomposition start temperature to higher area. Comparative analysis showed that the more heat-resistant is that the copolymer with a lower content of polyester resin. Activation parameters of decomposition reaction are calculated with isoconversion methods of Friedman and Kissinger-Akahira-Sunose, which have high converging.

Combining different methods, kinetic triplet was obtained, corresponding to $E_a \approx 240$ kJ/mol, $A \approx 3{,}19 \cdot 10^{16}$ min^{-1} for a copolymer of composition 21.03:78.97 mass.% and $E_a \approx 248$ kJ/mol, $A \approx 2{,}35 \cdot 10^{17}$ min^{-1} for a copolymer of composition 68.96:31.04 mass.%. Using the integrated Arrhenius equation, calculated curves of thermogravimetric analysis are composed, which have slight divergence with experimental ones. Thus, we may say that p-EGF:AA copolymer decomposition processes fully described with D3 model $g(\alpha) = [1-(1-\alpha)]^{1/3}]^2$.

Conflicts of interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgment

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References (GOST)

1 Kandelbauer A., Tondi G., Zaske O.C., Goodman S.H. In Handbook of Thermoset Plastics, 3rd ed. – San Diego: William Andrew, 2014. – P.111

2 Boenig H.V. Unsaturated Polyesters: Structure and Properties. – Amsterdam: Elsevier, 1964.

3 Tang Au-Chin, Yao Kuo-Sui Mechanism of hydrogen ion catalysis in esterification. II. Studies on the kinetics of polyesterification reactions between dibasic acids and glycols // Journal of Polymer Science. – 1959. – Vol.35. – P.219-233.

4 Gordon M., Grieveson B.M., McMillan I.D. Monomer reactivity ratios in a model unsaturated polyester system // Journal of Polymer Science. – 1955. – Vol.18. – P.497.

5 Fidanovski B.Z., Spasojevic P.M., Panic V.V., Seslija S.I., Spasojevic J.P., Popovic I.G. Synthesis and characterization of fully bio-based unsaturated polyester resins // Journal of Materials Science. – 2017. – Vol.53, Is.6. – P.4635-4644.

6 Vyazovkin S., Burnhnam A.K., Criado J.M., Perez-Maqueda L.A., Popescu C., Sbirrazzuolli N. ICTAC Kinetic Committee recommendation for performing kinetic computations on thermal analysis data // Thermochimica Acta. – 2011. – Vol.520, Is.1-2. – P.1-19.

7 Lesnikovich A.I., Levchik S.V. A method of finding invariant values of kinetic parameters // Journal of thermal analysis. – 1983. – Vol.27. – P.89-93.

8 Burkeev M.Zh., Sarsenbekova A.Zh., Bolatbay A.N. et al. The use of differential calculation methods for the destruction of copolymers of polyethylene glycol fumarate with the acrylic acid // Bulletin of the University of Karahganda. Chemistry. – 2020. – Vol.99, Is.3. – P.4-10.

9 Burkeev M.Zh., Bolatbay A.N., Sarsenbekova A.Zh., Davrenbekov S.Zh., Nasikhatuly E. Integral ways of calculating the destruction of copolymers of polyethylene glycol fumarate with acrylic acid // Russian Journal of Physical Chemistry A. – 2021. – Vol.95, Is.10. – P.2009-2013.

10 Kissinger H.E. Reaction kinetics in differential thermal analysis // Anaytical Chemistry. – 1957. – Vol.29, Is.11. – P.1702-1706.

11 Akahira T., Sunose T. Method of determining activation deterioration constant of electrical insulating materials // SciTechnol – 1971. – Vol.16. – P.22-31.

12 Friedman H.L. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic // Journal of Polymer Science. – 1964. – Vol.6. – P.183-185.

13 Achar B.B., Brindley G.W., Sharp J.H. Kinetics and mechanism of dehydroxylation processes, III. Applications and limitations of dynamic methods, in: L. Heller, A. Weiss Eds. // Proc. Int. Clay Conf. Jerusalem, Israel Prog. Sci. Transl., Jerusalem, Israel, 1966. – P.67-73.

14 Vinogradova S.V., Korstak V.V., Ulchitski V.I. Thermal stability of unsaturated polyesters and copolymers based on them // Polymer Science U.S.S.R. – 1968. – Vol.7. – P.1757-1764.

15 Ewa K.W. Kinetics of thermal decomposition of unsaturated polyester resins with reduced flammability // Journal of Applied Polymer Science. – 2003. – Vol.88. – P.2851-2857.

16 Burkeev M.Z., Kudaibergen G.K., Burkeeva G.K. et al. New Polyampholyte polymers based on polypropylene glycol fumarate with acrylic acid and dimethylaminoethyl methacrylate // Russian Journal of Applied Chemistry. – 2018. – Vol.91. – P.1145-1152.

17 Burkeev M.Zh., Kudaibergen G.K., Tazhbayev Ye.M., Hranicek J., Burkeyeva G.K., Sarsenbekova A.Zh. Synthesis and investigation of copolymer properties on the basis of poly(ethylene glycol)fumarate and methacrylic acid // Bulletin of the University of Karaganda. Chemistry. – 2019. – Vol.93. – P.32-38.

18 Kudaibergen G.K., Burkeyeva G.K., Tazhbayev Y.M., Burkeyev M.Zh., Omasheva A.V., Yesentayeva N.A. Constants and parameters of radical copolymerization of poly(ethylene glycol fumarate) with acrylic acid // Chemical Journal of Kazakhstan. – 2018. – Vol.61. – P.216-222.

19 Sbirrazzuolli N. Determination of pre-exponential factors and of the mathematical functions *f(α)* or *G(α)* that describe the reaction mechanism in a model-free way // Thermochimica Acta – 2013. – Vol.564. – P.59-69.

References

1 Kandelbauer A, Tondi G, Zaske OC, Goodman SH (2014) In Handbook of Thermoset Plastics, 3rd ed. William Andrew, San Diego, USA. P.111. ISBN: 9781455731077

2 Boenig HV (1964) Unsaturated Polyesters: Structure and Properties. Elsevier, Amsterdam, Netderlands. ISBN: 9780444400611

3 Tang Au-Chin, Yao Kuo-Sui (1959) J Polym Sci 35:219-233. *https://doi.org/10.1002/pol.1959.1203512818*

4 Gordon M, Grieveson BM, McMillan ID (1955) J Polym Sci 18:497. *https://doi.org/10.1002/pol.1955.120189006*

5 Fidanovski BZ, Spasojevic PM, Panic VV, Seslija SI, Spasojevic JP, Popovic IG (2017) J Mater Sci 53:4635-4644. *https://doi.org/10.1007/s10853-017-1822-y*

6 Vyazovkin S, Burnhnam AK, Criado JM, Perez-Maqueda LA, Popescu C, Sbirrazzuolli N (2011) Thermochim Acta 520:1-19. *https://doi.org/10.1016/j.tca.2011.03.034*

7 Lesnikovich AI, Levchik SV (1983) J Therm Anal 27:89-93. *https://doi.org/10.1007/BF01907324*

8 Burkeev MZ, Sarsenbekova AZ, Bolatbay AN et al (2020) Bulletin of the University of Karahganda. Chemistry 99:4-10. *https://doi.org/10.31489/2020ch3/4-10*

9 Burkeev MZ, Bolatbay AN, Sarsenbekova AZ, Davrenbekov SZ, Nasikhatuly E (2021) Russ J Phys Chem A 95:2009-2013. *https://doi.org/10.1134/S0036024421100034*

10 Kissinger HE (1957) Anaytical Chemistry 29:1702-1706. *http://doi.org/10.1021/ac60131a045*

11 Akahira T, Sunose T (1971) SciTechnol 16:22-31. *https://doi.org/10.17221/115/2016-RAE*

12 Friedman HL (1964) J Polym Sci 6:183-185. *https://doi.org/10.1002/polc.5070060121*

13 Achar BB, Brindley GW, Sharp JH (1966) Kinetics and mechanism of dehydroxylation processes, III. Applications and limitations of dynamic methods, in: L. Heller, A. Weiss Eds. Proc. lnt. Clay Conf. Jerusalem, Israel Prog. Sci. Transl., Jerusalem, Israel. P.67–73.

14 Vinogradova SV, Korstak VV, Ulchitski VI (1968) Polymer Science USSR 7:1757-1764. *https://doi.org/10.1016/0032-3950(68)90368-7*

15 Ewa KW (2003) J Appl Polym Sci 88:2851-2857. *https://doi.org/10.1002/app.11723*

16 Burkeev MZ, Kudaibergen GK, Burkeeva GK et al (2018) Russ J Appl Chem 91:1145-1152. *https://doi.org/10.1134/S1070427218070121*

17 Burkeev MZ, Kudaibergen GK, Tazhbayev YeM, Hranicek J, Burkeyeva GK, Sarsenbekova AZh (2019) Bulletin of the University of Karaganda. Chemistry 93:32-38. *https://doi.org/10.31489/2019Ch1/32-38*

18 Kudaibergen GK, Burkeyeva GK, Tazhbayev YM, Burkeyev MZ, Omasheva AV, Yesentayeva NA (2018) Chemical Journal of Kazakhstan 61:216-222. *https://doi.org/10.31489/2019Ch1/25-31*

19 Sbirrazzuolli N (2013) Thermochimica Acta 564:59-69. *https://doi.org/10.1016/j.tca.2013.04.015*

Chemical composition and biological activity of *Zosima absinthifolia* (*apiaceae*)

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Zosima absinthifolia (Vent.) Link is a perennial herb and is found in Iran, Turkey, Iraq and different countries of the Caucasus, Middle East and Central Asia. It is the only member of *Zosima* genus growing in Azerbaijan. It has been used as a medicinal plant since ancient time in Iran, Turkey and Pakistan. The fruits are used as a food flavoring and as a food spice in Iran. The knowledge of *Z. absinthifolia* organs containing a great number of bioactive compounds is of high importance. The aim of this study is to sum up literature data on the results of experimental studies of the chemical composition and biological activity of *Z. absinthifolia*. The results of the chemical study of *Z. absinthifolia* show that fruits, roots, seeds, flowers and other aboveground parts of plants are rich in various biologically active substances such as coumarins, furocoumarins, pyranocoumarins, flavonoids, monoterpenes, sesquiterpenes and etc. Chemical components that isolated from different organs of *Z. absinthifolia* have allelopathic, high antibacterial, antifungal, antioxidant, anti-inflammatory and other properties. Some of the chemical constituents have substantial pharmacological properties. It is clear that *Z. absinthifolia* has significant potential for useful natural supplements in many contemporary diseases.

Keywords: *Zosima* a*bsinthifolia;* chemical composition; biological activity; essential oil; coumarin.

Zosima absinthifolia *(apiaceae)* химиялық құрамы және биологиялық қызметі

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Zosima absinthifolia (Vent.) Link – Иранда, Түркияда, Иракта және Кавказ, Таяу Шығыс пен Орта Азияның түрлі елдерінде кездесетін көпжылдық шөп. Бұл Әзірбайжанда өсетін *Zosima* тұқымының жалғыз өкілі. Ол ежелгі дәуірден бастап Иран, Түркия және Пәкістанда дәрілік өсімдік ретінде қолданылған. Жемістер Иранда тағамдық хош иістендіргіш және тағамдық дәмдеуіш ретінде қолданылады. Көптеген биоактивті қосылыстары бар *Z. absinthifolia* ағзаларын білу үлкен маңызға ие. Бұл жұмыстың мақсаты – *Z. absinthifolia* химиялық құрамы мен биологиялық белсенділігін эксперименттік зерттеу нәтижелері бойынша әдеби деректерді жалпылау болып табылады. *Z. absinthifoli*a химиялық зерттеу нәтижелері өсімдіктердің жемістері, тамырлары, тұқымдары, гүлдері және басқа да жер үсті бөліктері кумариндер, фурокумариндер, пиранокумариндер, флавоноидтар, монотерпендер, сесквитерпендер және т.б. сияқты әртүрлі биологиялық белсенді заттарға бай екенін көрсетеді. Химиялық компоненттер әртүрлі *Z. absinthifolia* мүшелерінен оқшауланған, аллопатикалық, жоғары антибактериалды, саңырауқұлаққа қарсы, антиоксиданттты, қабынуға қарсы және басқа да қасиеттерге ие. Кейбір химиялық компоненттер айтарлықтай фармакологиялық қасиеттерге ие. *Z. absinthifolia* қазіргі кезеңдегі көп таралған сырқаттарда пайдалы табиғи қоспалар ретінде айтарлықтай потенциалға ие екені анық.

Түйін сөздер: *Zosima* жусан жапырағы; химиялық құрам; биологиялық белсенділік; эфир майы; кумарин.

Химический состав и биологическая активность *Zosima absinthifolia (apiaceae)*

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Zosima absinthifolia (Vent.) Link — многолетнее травянистое растение, встречается в Иране, Турции, Ираке и различных странах Кавказа, Ближнего Востока и Средней Азии. Это единственный представитель рода *Zosima*, произрастающий в Азербайджане. Он использовался как лекарственное растение с древних времен в Иране, Турции и Пакистане. Плоды используются в качестве пищевого ароматизатора и пищевой приправы в Иране. Большое значение имеет знание органов *Z. absinthifolia*, содержащих большое количество биоактивных соединений. Целью настоящей работы является обобщение литературных данных по результатам экспериментальных исследований химического состава и биологической активности *Z. absinthifolia.* Результаты химического изучения *Z. absinthifolia* показывают, что плоды, корни, семена, цветки и другие надземные части растений богаты различными биологически активными веществами, такими как кумарины, фурокумарины, пиранокумарины, флавоноиды, монотерпены, сесквитерпены и др. Химические компоненты выделенные из различных органов *Z. absinthifolia*, обладают аллелопатичными, высокими антибактериальными, противогрибковыми, антиоксидантными, противовоспалительными и другими свойствами. Некоторые из химических компонентов обладают существенными фармакологическими свойствами. Ясно, что *Z. absinthifolia* обладает значительным потенциалом в качестве полезных натуральных добавок при многих современных заболеваниях.

Ключевые слова: *Zosima* полыннолистная; химический состав; биологическая активность; эфирное масло; кумарин.

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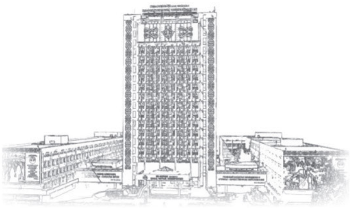

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Chemical composition and biological activity of *Zosima absinthifolia* (*apiaceae*)

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1. Introduction

Zosima absinthifolia (Vent.) Link belongs to *Zosima* Hoffm. genus of the *Apiaceae* family and is a perennial dense deciduous plant. The genus includes 10 species distributed from Arabia to Baluchistan (Pakistan) in the Caucasus, Central Asia, and Asia Minor. In the Caucasus and Azerbaijan, genus is represented by a species of *Z. absinthifolia*. It as an ordinary plant is distributed in various botanical-geographical regions of Azerbaijan (Absheron, Gobustan, Khazar lowland, Kur-Araz lowland, central, South Caucasus, Nakhchivan, Diabar), from lowland to middle mountainous areas. It is often found in wormwood semi-deserts, dry clay soils, dry rocky and rocky slopes [1-3]

Z. absinthifolia is known as a medicinal plant in Iran, Turkey, Pakistan, etc. since ancient times. In folk medicine, fruits, flowers, and aerial parts of plants are used. In Turkish folk medicine, the mixture made from the leaves is used in the treatment of diabetes [4-6]. In the Kalat and Khudzar districts of Pakistan's Balochistan province, the plant seed extract has an effective effect against coughs and other sore throats in children, and from the aerial parts against gastrointestinal, cough and other diseases [7-9]. Aqueous infusion of the flowers of the plant is used as a hemostatic agent in internal bleeding [10]. Another factor is the use of *Z. absinthifolia* fruits and aerial parts as a sedative in traditional medicine [11].

The medicinal and nutritional features of *Z. absinthifolia* are due to the presence of various groups of compounds-flavonoids, coumarins, mono-, sesquiterpenes, various groups of biologically active substances, essential oils in it.

A number of literature data show that the chemical components isolated from *Z. absinthifolia* have antibacterial, antioxidant, anti-inflammatory, allergic, antifungal and other biological properties. Biological activity and use of various organs of *Z. absinthifolia* in traditional medicine mainly depend on the quantity of different groups of biologically active components in plant.

2. Main part. Chemical composition of *Z. absinthifolia*

Z. absinthifolia plant material collected from different places contains essential oil, flavonoids, coumarin, etc. have been found to contain biologically active substances such as.

2.1 Essential oil

Many biological features of *Z. absinthifolia* are associated with the presence of essential oil in various organs. Quantitative composition of essential oil was in terms of dry raw materials in flowers – 0.11%, in the aerial parts during flowering – 0.26%, in leaves – 0.08%, in the green parts of stems – 0.037%, in green leaves – 0.08%, in small green fruits – 0.55%, 1.4-1.8% in immature large fruits, 1.3% and 0,9-1,6% in ripe fruits and 0.72% in dried fruits [12,45].

The oil obtained from the fruits of samples taken from Azerbaijan had a multi-component composition, the main components of which was octyl alcohol, octyl butyrate and octyl acetate [12,13].

An analysis of the literature on the amount and composition of essential oils shows that it depends on plant growth and soil-climatic conditions.

A study of the composition of the essential oil in different areas shows that both the main and the minor components quantity change significantly (Table 1).

In the essential oil obtained from the fruits distilled by hydro-distillation of samples collected from Turkey, octyl acetate (38.4%), octyl hexanate (31.9%), octanol (12.9%), nonane – 27.1%, α-pinene 12.7% and germacrene B-10.3%. were dominant [14]. Another group of scientists in Turkey studied the composition of the essential oil and determined

Table 1 – Component composition of essential oil of *Z. absinthifolia* in different areals

Components	Content in essential oil				
	Turkey, %	Cyprus, %	Iran, %	Azerbaijan, %	References
1	2	3	4	5	6
Octylbutyrate	2.0	1.0	0.27	5.1, 0.97, 9.47	[12, 14, 16, 19, 41, 42]
Octyl acetate	38.4, 1.0, 19.9, 81.6	63.2	3.8, 87.48, 7.52, 10.5, 59.72, 66.82, 69.69	79.7, 89.44, 44.76	[12, 14-19, 41, 42]
Octyl hexanoate	31.9, 0.6, 0.2	19.8	4.5	0.06, 0.12	[14-17, 41, 42]
Octanol	12.9, 2.8, 4.6, 3.2	2.2	9.6, 2.16, 3.12, 7.62, 14.22, 17.06	19.1	[12-17, 19]
α-pinene	0.2, 1.3, 2.2, 0.1		1.1, 7.08, 2.23, 1.38, 0.11	0.08, 0.22	[14-17, 19, 41, 42]
β-pinene	8.9		0.1, 5.32, 2.12, 0.31, 0.21	0.02	[15, 17, 19, 41]
p-cymene	2.2, 0.1		0.99, 0.37		[15, 16, 19]
β-bourbonene	0.2, 0.1, 0.3		2.95, 0.69, 0.45	0.05, 0.72	[14-16, 19, 41, 42]
Linalool	0.4, 0.4, 0.2		1.8, 0.19, 0.17		[14, 15, 17, 19]
Limonen	2.7, 1.5, 0.1		3.28, 0.7		[15, 19]
Octanal	1.0, 2.5, 0.2	0.3	0.2, 1.27, 0.8	0.68, 1.29	[14-17, 19, 41, 42]
Germacren-d	0.2, 2.0, 0.5	0.1	13.42, 4.14, 1.59, 0.38	4.54	[14-17, 19, 42]
Octyl octanoate	6.0, 0.8, 0.9	9.2	5.03		[14-16, 18]
Germakren B	10,3				[14]
2-Nonanon	2.6				[15]
Hexadecanoic acid	0.3, 1.3, 0.5	0.4	0.8, 0.15, 0.52		[14-17, 19]
Ostol	1.5		0.4		[14, 17]
Camphene	0.1		0.2, 2.99, 1.66, 0.92, 0.9, 0.1		[15, 17, 19]
Sabinene	0.1		0.1, 3.43, 1.26, 0.31, 0.2, 0.1		[15, 17, 19]
Myrcene	3.0, 1.3		0.9		[15, 17]
β-phellandrene	0.4, 0.7, 0.1		1.1		[15, 17]
(Z) -4-octenyl acetate	0.5, 5.1	0.5			[15, 16]
Bornyl acetate	0.3, 1.3, 0.2		1.5, 1.54, 0.62, 1.06, 1.36, 0.53	1.07, 0.67	[15, 17, 19, 41, 42]
β-caryophyllene	0.2, 1.0, 0.2	0.5	13.9, 7.84, 5.47, 2.57, 0.77	0.26	[15-17, 19, 41]
Myrtenal	1.5		0.2		[15]
(E)-2-Decenal	26.7, 0.1		0.1, 0.34		[15, 17]
trans-pinocarvyl acetate	1.4, 0.1, 26.7				[15, 17, 19]
trans piperitol	0.4				[15]
Myrtenyl acetate	0.9				[15]
α-terpineol	0.3		0.1, 0.41, 0.28	0.05	[15, 17, 19, 41]
cis-piperitol	0.5				[15]
Citronellol	0.4				[15]
(E, E) -2,4-decadienal	0.9				[15]
Myrtenol	0.6				[15]
Cuparene	0.6, 0.1				[15]
(Z) -4-octenyl hexanoate	0.7	0.1			[15, 16]
Geranyl acetone	1.4, 0.1				[15]
2,5-dimethoxy-p-cymene	3.6				[15]
Caryophyllene oxide	0.8, 0.4, 0.1	0.2	5.7, 1.10, 5.87, 1.85, 0.5		[15-17, 19]
Spatulenol	0.5, 0.1	0.1	2.46, 2.68, 2.63, 1.05	0.71	[15, 16, 19, 42]
α-cadinol	0.6				[15]

Table 1 – Component composition of essential oil of *Z. absinthifolia* in different areals (Continued)

1	2	3	4	5	6
(2E, 6E) – Farnesyl acetate	2.3		0.15, 0.52, 0.8, 0.15, 0.52		[15, 17, 19]
(2E, 6E) –Farnesal	0.4				[15]
Tricosan	0.7	0.4	0.4		[15-17]
(2E, 6E) –Farnesol	1.7			0.38	[15, 43]
Heptacosan	0.5				[15]
Dodecanoic acid	0.2	0.7			[15, 16]
Phytol	0.5			0.22	[15, 42]
Tetradecanoic acid	1.0	0.8			[15, 16]
Bicyclogermacrene		0.1	2.3		[16, 17]
Octyl heptanoate		18.6			[16]
Geranial			2.0		[17]
δ-elemene			0.1, 2.49, 1.15, 0.95, 0.43		[17, 19]
Geranyl butyrate			1.5		[17]
Caryophylla-4 (14), 8 (15) diene-5β-ol			0.6		[17]
geranyl valerate			9.6		[17]
(E)–sesquilavandulyl acetate			1.9		[17]
3-methyl nonane			6.07, 2.65		[19]
Cineole			0.36	0.52	[19, 41]
β-ocimene	0.4		0.4, 4.82, 1.06, 0.28	0.12	[15, 17, 19, 41]
Myrcene			2.64, 1.21		[19]
1-hexyl-3-methyl cyclopentane			2.92, 1.15		[19]
3-methylundecane			4.71, 1.11, 0.1, 0.18, 0.1		[19]
Camphor			35.24		[19]
Borneol			2.76		[19]
(4)-Decen-1-ol			1.89, 0.34		[19]
Hexyl Hexanoate			0.52, 0.7, 0.78		[19]
Geranyl acetate			0.31		[19]
Decenyl acetate			0.59, 5.02, 4.4, 0.31		[19]
N-octyl 2-methylbutyrate			0.41, 0.92, 0.4, 0.68, 0.71		[19]
β-Selinene			1.73, 1.37		[19]
β-Eudesmol			0.71, 1.84		[19]
α-Bisabolol oxide B			1.45		[19]
Octadecanal			0.1, 2.12, 4.06, 6.09		[19]
α-bisabolol			0.85, 0.57, 0.38		[19]
Meta-cymene				0.02	[41]
Cyclopropane, pentyl				4.79, 13.88	[41, 42]
L-4-terpineol				0.04	[41]
Decanal				0.08	[41]
α-copaene				0.05, 0.58	[41, 42]
β-copaene				0.03, 0.27	[41, 42]
Eicosane				0.08, 0.04	[41, 42]
γ-terpinene				0.06	[42]

Table 1 – Component composition of essential oil of *Z. absinthifolia* in different areals (Continued)

1	2	3	4	5	6
β-elemene					[42]
γ-pironene				3.03	[42]
α-Cubebene				0.06	[43]
β-Cubebene				0.24	[43]
Ylangene				0.06	[43]
β-Yglanene				5.32	[43]
Cedrene				2.45	[43]
α-Muurolene				0.21	[43]
γ-cadinene				0.89	[43]
α-Amorphene				1.3	[43]
γ -Muurolene				0.82	[43]
Allo-Aromadendrene				1.3	[43]

that the main components of this oil are octyl acetate – 81.6% and trans-pinocarvil acetate – 26.7% [15].

Some components were identified in the essential oil obtained by hydrodistillation from the dried fruits of *Z. absinthifolia* collected from two various areas of Northern Cyprus. Of these, octylacetate (63.2-59.5%), octylhexanate (19.8-18.6%), octyllocanaate (9.9-9.2%), octanol (7.1-2.2%) are major components in composition [16]. Cavidnia and co-authors show that, octylbutyrate 19.2%, β-caryophylline 13.9%, octanol 9.6%, geranilvalerate 9.6%, caryophylline oxide 5.7%, octanol 2.37% were dominant groups in the essential oil obtained from plant fruits [17].

In 2013, the composition of the essential oil of fruits was analyzed and it was determined that the main components are octyl acetate (87.48%) and octyllocanoate (5.03%) [18].

When studying the composition of essential oils in various organs, it was determined that the maximum amount of essential oil is in ripe seeds (0.88%), and the lowest amount is in the leaves (0.31%). Also, octyl acetate and 1-octanol are the main constituents of seeds [19].

The essential oil in different phenological stages of *Z. absinthifolia* seeds were studied by different authors. Some components as α-pinene, n-octanol, germacrene-D, β-caryophyllene, octyl acetate, caryophyllene oxide were the main components of the essential oil in different stages of seed growth [20].

Literature data on the component composition of *Z. absinthifolia* in different areas show that there are quantitative and qualitative differences between essential oil.

It depends on geographical and climatic factors in the area where the plant grows. Thus, the number of components in the obtained essential oil, their percentage varies. Summarizing all this, we can say that the composition of the essential oil is different in different areas, but all of them have a high content of compounds belonging to the group of octylacetate and other ethers.

2.2 Flavonoids and coumarins

The results of the literature show that biologically active substances such as some flavonoids, alkaloids and different coumarin have been found and identified in various organs of *Z. absinthifolia.* [21-23]. Also, various coumarins, furo-, piranocoumarins were obtained individually from the roots, fruits, seeds and aerial parts of plant. Imperatorin and two coumarins, 7-preniloxicoumarin and aurapten were obtained from the plant seeds and were identificated by UV, ^{1}H and ^{13}C NMR data [18,21]. A number of studies have analyzed the deltoin and columbianadin content of coumarins in the aerial parts and root of the plant and found that the amount of deltoin in the plant over the amount of columbianadine [24,25]. Numerous studies show that these coumarine derivatives posses a variety of biological properties including anti-cancer, anti-inflammatory, antioxidant, enzyme inhibitory, antitubercular, antifungal, antibacterial, anticonvulsant and etc. activity [26-32]. Furthermore, bergapten, imperatorin, pimpinellin, and umbelliferon were isolated of the roots from *Z. absinthifolia* [15]. Two pyrano-coumarins, aegelinol and agacillin, were also been identificated in dichloromethane extract of plant roots by Razavi S.M. [18]. Besides, two compenents- zozimin and marmesin were identified in the roots of the plant in Absheron [33]. In addition, the fruit contains zozimin, deltoin, bergapten, imperatorin, isobergapten, isopimpinellin, pimpinellin, sfondin, umbelliferon and others. coumarin substances were found [46,47].

2.3 Fatty acids

The fact that the plant has various beneficial therapeutic properties may also be due to the presence in it of fatty acids, which are part of the lipid components. During a number of studies, fatty acids were found in various parts of *Z. absinthifolia*.

During the initial research, 20.1% fat was found in the seeds of the plant [48]. In Azerbaijan, 1.2% capric acid was found in the fruits of *Z. absinthifolia* [13]. As a result of research conducted in Iran, only caprylic and palmitic acid were detected in the plant. Their amounts were 1.69 and 0.15% in the leaf, respectively, and 3.47 and 0.52% in the early stages of seed development [19]. S. Karakaya and colleagues identified caprylic (0.1%), lauric (0.2%) and myristic (0.8), aerial parts (4.1%), root (1.3%) and palmitic fatty acid in the fruits of the plant [15]. In addition, 0.8% palmitic acid [17] and 1.3% capric acid has been identified in the *Z. absinthifolia* aerial parts [34].Chromatographic analysis of the oil obtained from plant fruits was determined 14 fatty acids- caproic, caprylic, capric, lauric, myristic, myristoleic, palmitic, palmitoleic, stearic, oleic, linolenic, linoleic, arachidic and behenic. The main component of *Z. absinthifolia* fruit oil is oleic acid (74.36%). Small amounts of caprylic and palmitic acids were also found to be 8.9% and 5.39%, respectively. The lowest percentage is palmitinoleic acid (0.07%) [44].

2.4 Antibacterial activity

Zosima absinthifolia, like other species belonging to the family *Apiaceae*, contains coumarins, furocoumarins, pyranocoumarins, flavonoids, terpene compounds-mono-, sesquiterpenes, etc. The various biologically active components isolated from *Z. absinthifolia*, have anti-inflammatory, highly antibacterial, phytotoxic, antifungal, antioxidant and other biological properties.

A study conducted in Iran found antibacterial activity of three coumarin derivatives derived from the fruit of the plant - imperatorin, aurapten and 7-preiloxicumarin and essential oil [35]. In numerous studies are also known other biological properties of the imperatorin [36-37]. In addition some pyranocoumarins (aegelinol, agacillin) derived from the plant roots also have moderate antibacterial activity [18]. A group of researchers found that the essential oil of the fruit has a high antibacterial effect against *Bacillus subtilis* and *Bacillus pumilus* [35]. At the same time, the ethanol extract of the aerial parts of *Z. absinthifolia* has antimycobacterial activity [38]. The methanol extract was found to have a important antibacterial avtivity against *Bacillus cereus* and *Staphylococcus epidermidis* [35]. Antimicrobial properties of the essential oils of the species *Z. absinthifolia* has been studied as well as it was as certained that essaential oils can be used as antifungal means [41].

2.5 Antioxidant activity

According to some studies, the methanol extract of the plant fruit has significant antioxidant activity [39]. Ethyl acetate extracts of *Z. absinthifolia* also have high antioxidant potential [40]. The highest antioxidant activity of the plant is characterized in dichloromethane extract of essential oil from fruits and flowers. For this reason, the flowers and fruits of plant may be a new potential source of natural antioxidant and anticholinesterase compounds [15]. In addition, the results of biological studies show that acetone extract and seeds (in the early stages of development) have high antioxidant properties [19]. Plant methanol extract showed that high antioxidant feature with an RC50 value of 143.5 µg mL^{-1} [35].

2.6 Anti-inflammatory and alleopathic activity

Some researchers have reported that alleopathic activity of some components-aurapten and 7-preniloxicumarin derived from *Z. absinthifolia* fruits [35]. Razavi and co authers found that the essential oil obtained from the fruit of the plant has an alleopathic effect against bacteria and fungi from the middle to the top [35]. The imperatorin, isolated from the plant and belonging to coumarins, also plays an alleopathic role for the plant and can protect the plant from various pathogens [21]. In addition, a number of studies have found that the imperatorin has anti-inflammatory activity [31]. Also, *Z. absinthifolia* aerial part extract exhibited significant anti-inflammatory activity in 75 mg/kg dose [24, 25].

2.7 Antifungal and cytotoxic activity

Biologically active substances isolated from the seeds and roots of *Z. absinthifolia*, in particular imperatorin, have antifungal activity against the fungus *Sclerotinia sclerotiorum* [21]. Pirano-coumarins derived from the root of the plant - aegelinol and agacillin also have antifungal activity [21]. According to research, the cytotoxic properties are manifested in acetone extracts of flowers [19] and methanol extract [39].

4. Conclusion

Different types of chemical constituents of *Z. absinthifolia* and their biological activities are reflected in the article. Many chemical compounds were isolated from the selected plant and identified. Among them, mono-, sesquiterpens, coumarins are the main bioactive components in *Z. absinthifolia.* Also, many components in the chemical composition were evaluated for their biological activity. Some of the chemical constituents have substantial pharmacological properties. It is clear that, a number of component obtained from *Z. absinthifolia* has significant potential as useful natural supplements in numerous diseases and can be used in various fields of medicine in the future.

References (GOST)

1 Askerova R.K., Akhundov G.F., Isaev Y.M., Karyagin I.I., Irilipko L.I., Sofieva R.M. Flora of Azerbaijan [Flora Azerbaydzhana]. – Publishing house of the Academy of Sciences of the Azerbaijan SSR, Baku, Azerbaijan. 1955. – P.540. (In Russian)

2 Askerov A.M. Higher plants of Azerbaijan. Abstract of the flora of Azerbaijan. – Publishing House “Elm”, Baku, Azerbaijan, 2006. – Vol.2. – P.188-189.

3 Ibadullayeva S.C. (2004) Apiaceae of the Azerbaijan flora. – Publishing House “Elm”, Baku, Azerbaijan, 2004. – P.374.

4 Ozturk M., Altay V., Altundag E., Ibadullayeva S.C., Aslanipour B., Gönenc T.B. Herbals in Iğdır (Turkey), Nakhchivan

(Azerbaijan), and Tabriz (Iran) // Plant and Human Health. – 2018. – Vol.1. – P.197-266.

5 Sarikaya S., Öner Hidayet Harput Ü.Ş. Medicinal plants used for the treatment of diabetes in Turkey // Journal of Faculty of Pharmacy of Ankara University. – 2010. Vol.39, Is.4. – P.317-342.

6 Arıtuluk Z.C., Ezer N. Plants used against diabetes among people // Hacettepe University Faculty of Pharmacy Journal. – 2012. – Vol.32, Is.2. – P.179-208.

7 Pashtana S.J., Sadia B., Yousaf A., Naz N., Rehmat N., et al. Ethnobotanical study of flora of Gulistan, district Killa Abdullah, Balochistan, Pakistan // Pure and Applied Biology. – 2016. – Vol.5, Is.2. – P.361-368.

8 Goodman S.M., Ghafoor A. The Ethnobotany of Southern Balochistan, Pakistan, with Particular Reference to Medicinal Plants // Fieldiana Botany. – 1992. – Vol.31. – P.1-84.

9 Haq J.U., Muhammad S., Kanwal A., Muhammad G., Arsalan M., et al. Evaluation, hepatoprotective effects and the determination of safty and efficacy of Zosima absinthifolia // Indo American Journal of Pharmaceutical Sciences. – 2018. – Vol.5, Is.10. – P.10892-10901.

10 Damirov I.F., Prilipko L.I., Shukurov D.Z., Kerimov Y.B. Medicinal plants of Azerbaijan [Lekarstvennyye rasteniya Azerbaydzhana]. – Publishing house of the Academy of Sciences of the Azerbaijan SSR, Baku, Azerbaijan, 1982. – P.320. (In Russian)

11 Karakaya S., Oral D.Y., Kilic C.S., Gur S. Umbelliferone isolated from Zosima absinthifolia roots partially restored erectile dysfunction in streptozotocin-induced diabetic rats // Medicinal Chemistry Research. – 2019. – Vol.28. – P.1161-1167.

12 Gurvich N.L., Gadzhiev I.Y. Essential oil Zozimia absinthifolia // Proceedings of the Botanical Institute. Baku: AzFAN. – 1938. – Is.3. – P.167-173. (In Russian)

13 Gurvich N.L., Gadzhiev I.Y. Wild growing ethereal of the high-mountainous part of the Abrakunis district of Nakh. LSSR [Dikorastushchiye efirno mayelichnyyevysoko-gornoy chasti Abrakunisskogo rayona Nakh. LSSR] // Proceedings of BIN AZFAN. Baku: AZFAN. – 1938. – Is.3. – P.137-165. (In Russian)

14 Başer K. H., Özek T., Demirci B., Kurkcuoglu M., Aytac Z., Duman H. Composition of the essential oils of Zosima absinthifolia (Vent.) Link and Ferula elaeochytris Korovin from Turkey // Flavour and Fragrance Journal. – 2000. – Vol.15. – P.371-372.

15 Karakaya S., Koca M., Yılmaz S.V., Yıldırım K., Pınar N.M., et al. Molecular Docking Studies of Coumarins Isolated from Extracts and Essential Oils of Zosima absinthifolia Link as Potential Inhibitors for Alzheimer’s Disease // Molecules. – 2019 – Vol.24, Is.4. – P.722.

16 Baser K., Aburwais O., Demirci B. Essential oil composition of Zosima absinthifolia (Vent.) Link. from Northern Cyprus // Natural Volatiles & Essential Oils. – 2018. – Vol.5, Is.2. – P.19-23.

17 Javidnia K., Miri R., Soltani M., Khosravi A.R. Constituents of the Oil of Zosimia absinthifolia(Vent.) Link. from Iran // Journal of Essential Oil Research. – 2011. – Vol.20, Is.2. – P.114-116.

18 Razavi S.M. Phytochemicals from the fruits of Zosima absinthifolia, an edible and medicinal plant // Journal of Ege University Faculty of Agriculture. – 2013. – Vol.2. – P.513-517.

19 Mollaei S., Hazrati S., Lotfizadeh V., Dastan D., Asgharian P. Phytochemical variation and biological activities of Zosima absinthifolia during various stages of growth // International Journal of Food Properties. – 2020. – Vol.23. – P.1556-1567.

20 Amiri H. Quantitative and qualitative changes of essential oil of Zosimia absinthifolia (Vent.) Link. in different phenological stages // Iranian Journal of Medicinal and Aromatic Plants. – 202. – Vol.24, Is.2. – P.217-224.

21 Razavi S., Imanzadeh G., Davari M. Coumarins from Zosima absinthifolia seeds, with allelopatic effects // Eurasian Journal of Biosciences. – 2010. – Vol.4, Is.1. – P.17-22.

22 Nikonov G.K., Baranauskaite D.I. Lactones of Zosimia absinthifolia (Vent.) Link. // Chemistry of Natural Compounds. – 1965. – Vol.1, Is.1. – P.169-170.

23 Crowden R.K., Harborne J.B., Heywood V.H. Chemosystematics of the umbelliferae- a general survey // Phytochemistry. – 1969. – Vol.8, Is.10. – P.1963-1984

24 Bahadir O., Gulcin C.S., Hanefi O. Evaluation of anti-inflammatory effect of Zosima absinthifolia and deltoin // Journal of Medicinal Plants Research. – 2010. – Vol.4, Is.10. – P.909-914.

25 Bahadir O., Gulcin C.S., Hanefi O. Anti-inflammatory and hepatoprotective activities of Zosima absinthifolia // Proceedings of the Fifth Conference on Medicinal and Aromatic Plants of Southeast European Countries. – Brno, Czech Republic, 2-5 September, 2008. – P.67.

26 Thakur A., Singla R., Jaitak V. Coumarins as anticancer agents: A review on synthetic strategies, mechanism of action and SAR studies // European Journal of Medicinal Chemistry. – 2015. – Vol.101. – P.476-495.

27 Poumale H.M., Rebecca H., Zang Y., Shiono Y., Kuete V. 8 - Coumarins and Related Compounds from the Medicinal Plants of Africa. In: Kuete V (Ed.), Medicinal Plant Research in Africa: Pharmacology and Chemistry. –2013. – P.261-300.

28 Rohini K. , Srikumar P.S. Therapeutic Role of Coumarins and Coumarin-Related Compounds // Journal of Thermodynamics & Catalysis. – 2014. – Vol.5, Is.2. – P.2-3.

29 Luo D., Zhang J., Peng Y., Liu J., Han D., et al. Imperatorin improves in vitro porcine embryo development by reducing oxidative stress and autophagy // Theriogenology. – 2020 – Vol.146. – P.145-151.

30 Widelski J., Popova M., Graikou K., Glowniak K., Chinou I. Coumarins from Angelica Lucida L. Antibacterial Activities // Molecules. – 2009. – Vol.14, Is.8. – P.2729-2734.

31 Mao D., Long X., Li Z., Liaon Y., Liu L., Li X. Imperatorin: A review of its pharmacology, toxicity and pharmacokinetics // European Journal of Pharmacology. – 2020. – Vol.879. – P.173124.

32 Pelkonen O., Raunio H., Rautio A., Pasanen M., Lang M.A. The Metabolism of Coumarin. In: Richard O’Kennedy, Richard O’Kennedy (Eds.), Coumarins: Biology, Applications and Mode of Action. – John Wiley & Sons Chichester, UK, 1997. – P.67-92.

33 Kerimov Y.B., Abisov A.Z., Mustafayeva Kh.N. Coumarins Zosimia absinthifolia [Kumariny Zosimia absinthifolia] // Azerbaijan Pharmaceutical Journal [Azerbaydzhanskiy Farmatsevticheskiy Zhurnal]. – 2002. – Vol.2, Is.2. – P.26-28. (In Russian)

34 Shafaghat A. Comparison of chemical composition of essential oil and n-hexane extracts of Zosimia absinthifolia (Vent.) Link // Journal of Essential Oil Bearing Plants. – 2011. – Vol.14, Is.4. – P.490-493.

35 Razavi S.M., Nejad-Ebrahimi S. Chemical composition, allelopatic and antimicrobial potentials of the essential oil of Zosima absinthifolia (Vent.) Link. fruits from Iran // Natural Product Research. – 2009. – Vol.24. – P.1125-1130.

36 Hearm R.M.R., Kerr A.C., Rahim K.F., Ferguson J., Dawe R.S. Incidence of skin cancers in 3867 patients treated with narrow-band ultraviolet B phototerapy // British Journal of Dermatology. – 2008. – Vol.159, Is.4. – P.931-935.

37 Anand P., Singh B., Singh N.A. Review on coumarins as acedyecnoeenesterase inhibitors for Alzheimer's disease // Bioorganic & Medicinal Chemistry. – 2012. – Vol.20, Is.3. – P.1175-1180.

38 Al-Shamma A., Mitscher L.A. Comprehensive Survey of Indigenous Iraqı Plants for Potential Economic Value, 1. Screening Results of 327 Species for Alkaloids and Antimicrobial Agents // Journal of Natural Products. – 1979. – Vol.42, Is.6. – P.633-642.

39 Razavi S.M., Ghasemiyan A., Salehi S., Zahri F. Screening of biological activity of Zosima absinthifolia fruits extracts // Eurasian Journal of Biosciences. – 2009. – Vol.3, Is.1. – P.25-28.

40 Onder A., Cınar A.S., Gencaslan G., Coban T. Antioxidant potentials of the extracts from 14 selected medicinal plants // Journal of Medicinal Herbs and Ethnomedicine. – 2020. – Vol.6. – P.17-20.

41 Zulfuqarova P.V., Gasımov H.Z. Antimicrobial features of essential oils of some species in Apiaceae family // SEAB2-Symposium on EuroAsian Biodiversity. – Antalya Turkey, 2016. – P.234.

42 Alikhanova N.S., Novruzov E.N. GC-MS analysis of compounds in essential oils of Zosima absinthifolia (Vent.) Link fruits // Actual Problems of Science and Technology Collection of scientific articles based on materials of the VI - International Scientific and Practical Conference. – Ufa, Russia, 2021. – P.41-44.

43 Alikhanova N.S., Novruzov E. N., Zeynalova S.A., Chemical composition of the essential oil extracted from the aerial parts of Zosima absinthifolia Link. // Plant and Fungal Research Journal. – 2021. – Vol.4, Is.2. – P.56-60.

44 Alikhanova N.S., Novruzov E.N., Physical-Chemical Constants and Fatty Acid Composition of Zosima absinthifolia Link Fruit Oil // Bulletin of Science and Practice. – 2022. – Is.1. – P.43-49.

45 Goryaev M.I. Essential oils of the flora of the USSR [Efirnyye masla flory SSSR]. – Academy of Sciences of the Kazakh SSR, Alma-Ata, USSR, 1952. – P.378. (In Russian)

46 Kuznetsova G.A. Natural Coumarins and Furocoumarins [Prirodnyye kumariny i furokumariny]. – Nauka, Leningrad, USSR, 1967. – P.243. (In Russian)

47 Pimenov M.G. List of plants - sources of coumarin compounds [Perechen' rasteniy - istochnikov kumarinovykh soyedineniy]. – Nauka, Leningrad, USSR, 1971. – P.189. (In Russian)

48 Larin I.V. Fodder plants of the USSR [Kormovyye rasteniya SSSR] // Plant raw materials of the USSR [Rastitel'noye syr'ye SSSR]. – 1957. – Is.2. – P.152-325. (In Russian)

References

1 Askerova RK, Akhundov GF, Isaev YM, Karyagin II, Irilipko LI, Sofieva RM (1955) Flora of Azerbaijan [Flora Azerbaydzhana]. Publishing house of the Academy of Sciences of the Azerbaijan SSR, Baku, Azerbaijan. P.540 (In Russian)

2 Askerov AM (2006) Higher plants of Azerbaijan. Abstract of the flora of Azerbaijan. Publishing House "Elm", Baku, Azerbaijan. Vol.2. P.188-189.

3 Ibadullayeva SC (2004) Apiaceae of the Azerbaijan flora. Publishing House "Elm", Baku, Azerbaijan. P.374.

4 Ozturk M, Altay V, Altundag E, Ibadullayeva SC, Aslanipour B, Gönenc TB (2018) Plant and Human Health 1:197-266. *https://doi.org/10.1007/978-3-319-93997-1_6*

5 Sarikaya S, Öner Hidayet Harput ÜŞ (2010) Journal of Faculty of Pharmacy of Ankara University 39(4):317-342. *https://doi.org/10.1501/Eczfak_0000000572*

6 Arıtuluk ZC, Ezer N (2012) Hacettepe University Faculty of Pharmacy Journal 32(2):179-208.

7 Pashtana SJ, Sadia B, Yousaf A, Naz N, Rehmat N, et al (2016) Pure and Applied Biology 5(2):361-368. *http://doi.org/10.19045/bspab.2016.50047*

8 Goodman SM, Ghafoor A (1992) Fieldiana Botany 31:1-84.

9 Haq JU, Muhammad S, Kanwal A, Muhammad G, Arsalan M, et al (2018) Indo American Journal of Pharmaceutical Sciences 5(10):10892-10901. *http://doi.org/10.5281/zenodo.1472782*

10 Damirov IF, Prilipko LI, Shukurov DZ, Kerimov YB (1982) Medicinal plants of Azerbaijan [Lekarstvennyye rasteniya Azerbaydzhana]. Publishing house of the Academy of Sciences of the Azerbaijan SSR, Baku, Azerbaijan. P.320. (In Russian)

11 Karakaya S, Oral DY, Kilic CS, Gur S (2019) Med Chem Res 28:1161-1167. *https://doi.org/10.1007/s00044-019-02359-9*

12 Gurvich NL, Gadzhiev IY (1938) Proceedings of the Botanical Institute. Baku: AzFAN 3:167-173. (In Russian)

13 Gurvich NL, Gadzhiev IY (1938) Proceedings of BIN AZFAN. Baku: AZFAN 3:137-165. (In Russian)

14 Başer KH, Özek T, Demirci B, Kurkcuoglu M, Aytac Z, et al (2000) Flavour Frag J 15:371-372. *https://doi.org/10.1002/1099-1026(200011/12)15:6<371::AID-FFJ919>3.0.CO;2-Z*

15 Karakaya S, Koca M, Yılmaz SV, Yıldırım K, Pınar NM, et al (2019) Molecules 24(4):722. *https://doi.org/10.3390/molecules24040722*

16 Baser K, Aburwais O, Demirci B (2018) Natural Volatiles & Essential Oils 5(2):19-23.

17 Javidnia K, Miri R, Soltani M, Khosravi AR (2011) J Essent Oil Res 20(2):114-116. *https://doi.org/10.1080/10412905.2008.9699968*

18 Razavi SM (2013) Journal of Ege University Faculty of Agriculture 2:513-517.

19 Mollaei S, Hazrati S, Lotfizadeh V, Dastan D, Asgharian P (2020) Int J Food Prop 23:1556-1567. *https://doi.org/10.1080/10942912.2020.1818778*

20 Amiri H (2020) Iranian Journal of Medicinal and Aromatic Plants 24(2):217-224.

21 Razavi S, Imanzadeh G, Davari M (2010) Eurasian Journal of Biosciences 4(1):17-22. *https://doi.org/10.5053/ejobios.2010.4.0.3*

22 Nikonov GK, Baranauskaite DI (1965) Chemistry of Natural Compounds 1(1):169-170.

23 Crowden RK, Harborne JB, Heywood VH (1969) Phytochemistry 8(10):1963-1984. *https://doi.org/10.1016/S0031-9422(00)88084-X*

24 Bahadir O, Gulcin CS, Hanefi O (2010) Journal of Medicinal Plants Research 4(10):909-914. *https://doi.org/10.5897/JMPR10.106*

25 Bahadir O, Gulcin CS, Hanefi O (2008) Proceedings of the Fifth Conference on Medicinal and Aromatic Plants of Southeast European Countries. Brno, Czech Republic, 2-5 September, 2008. P.67.

26 Thakur A, Singla R, Jaitak V (2015) Eur J Med Chem 101:476-495. *https://doi.org/10.1016/j.ejmech.2015.07.010*

27 Poumale HMP, Hamm R, Zang Y, Shiono Y, Kuete V (2013) 8 - Coumarins and Related Compounds from the Medicinal Plants of Africa. In: Kuete V (Ed.), Medicinal Plant Research in Africa: Pharmacology and Chemistry. P.261-300. *https://doi.org/10.1016/B978-0-12-405927-6.00008-4*

28 Rohini K, Srikumar PS (2014) Journal of Thermodynamics & Catalysis 5(2):2-3. *https://doi.org/10.4172/2157-7544.1000130*

29 Luo D, Zhang J, Peng Y, Liu JB, Han D, et al (2020) Theriogenology 146:145-151. *https://doi.org/10.1016/j.theriogenology.2019.11.029*

30 Widelski J, Popova M, Graikou K, Glowniak K, Chinou I (2009) Molecules 14(8):2729-2734. *https://doi.org/10.3390/molecules14082729*

31 Mao D, Long X, Li Z, Liaon Y, Liu L, Li X (2020) Eur J Pharmac 879:173124. *https://doi.org/10.1016/j.ejphar.2020.173124*

32 Pelkonen O, Raunio H, Rautio A, Pasanen M, Lang MA (1997) The Metabolism of Coumarin. In: Richard O'Kennedy, Richard O'Kennedy (Eds.), Coumarins: Biology, Applications and Mode of Action. John Wiley & Sons Chichester,UK. P.67-92.

33 Kerimov YB, Abisov AZ, Mustafayeva KhN (2002) Azerbaijan Pharmaceutical Journal [Azerbaydzhanskiy Farmatsevticheskiy Zhurnal] 2(2):26-28. (In Russian)

34 Shafaghat A (2011) J Essent Oil Bear Pl 14(4):490-493. *https://doi.org/10.1080/0972060X.2011.10643606*

35 Razavi SM, Nejad-Ebrahimi S (2009) Nat Prod Res 24:1125-1130. *https://doi.org/10.1080/14786410902726142*

36 Hearm RMR, Kerr AC, Rahim KF, Ferguson J, Dawe RS (2008) Brit J Dermatol 159(4):931-935. *https://doi.org/10.1111/j.1365-2133.2008.08776.x*

37 Anand P, Singh B, Singh N (2012) Bioorgan Med Chem 20(3):1175-1180. *https://doi.org/10.1016/j.bmc.2011.12.042*

38 Al-Shamma A, Mitscher LA (1979) J Nat Prod 42(6):633-642. *https://doi.org/10.1021/np50006a009*

39 Razavi SM, Ghasemiyan A, Salehi S, Zahri F (2009) Eurasian Journal of Biosciences 3(1):25-28.

40 Onder A, Cınar AS, Gencaslan G, Coban T (2020) Journal of Medicinal Herbs and Ethnomedicine 6:17-20. *https://doi.org/10.25081/jmhe.2020.v6.6060*

41 Zulfuqarova PV, Gasımov HZ (2016) Antimicrobial features of essential oils of some species in Apiaceae family. SEAB2-Symposium on EuroAsian Biodiversity, Antalya, Turkey. P.234.

42 Alikhanova NS, Novruzov EN (2021) GC-MS analysis of compounds in essential oils of Zosima absinthifolia (Vent.) Link fruits. Actual Problems of Science and Technology Collection of scientific articles based on materials of the VI - International Scientific and Practical Conference, Ufa, Russia. P.41-44.

43 Alikhanova NS, Novruzov EN, Zeynalova SA (2021) Plant and Fungal Research Journal 4(2):56-60. *https://doi.org/10.30546/2664-5297.2021.4.2.7*

44 Alikhanova NS, Novruzov EN (2022) Bulletin of Science and Practice 1:43-49. *https://doi.org/10.33619/2414-2948/74/05*

45 Goryaev MI (1952) Essential oils of the flora of the USSR [Efirnyye masla flory SSSR]. Academy of Sciences of the Kazakh SSR, Alma-Ata, USSR. P.378. (In Russian)

46 Kuznetsova GA (1967) Natural Coumarins and Furocoumarins [Prirodnyye kumariny i furokumariny]. Nauka, Leningrad, USSR. P.243. (In Russian)

47 Pimenov MG (1971) List of plants - sources of coumarin compounds [Perechen' rasteniy - istochnikov kumarinovykh soyedineniy]. Nauka, Leningrad, USSR. P.189. (In Russian)

48 Larin IV (1957) Plant raw materials of the USSR [Rastitel'noye syr'ye SSSR] 2:152-325. (In Russian)

Применение сорбентов на основе природного цеолита и шамотной глины для извлечения ионов натрия и калия из соленой воды: предварительное исследование

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В данной работе были получены сорбенты на основе природного цеолита (Ц) и шамотной глины (ШГ), обработанные растворами NaCl и HNO$_3$, для извлечения ионов Na$^+$ и K$^+$ из соленой воды. Были исследованы физико-химические характеристики полученных сорбентов методами СЭМ, EDAX и БЭТ. Выявлено, что последовательная обработка растворами NaCl и HNO$_3$ положительно влияет на сорбционные свойства исследуемых материалов. Максимальное увеличение удельной поверхности с 4,5 м^2/г до 39,3 м^2/г наблюдается для Ц, обработанного кислотой, а удельная поверхность ШГ также повышается почти в 2 раза с 8,4 м^2/г до 15,3 м^2/г. Ионы Na$^+$ и K$^+$ извлекаются из воды за счет ионного обмена с катионами Ц и ШГ. В результате определения катионообменной емкости (КОЕ) исследуемых сорбентов, было установлено, что обработка раствором NaCl улучшает ионообменные свойства сорбента и приводит к образованию «гомоионной» формы алюмосиликатов, благодаря чему сорбенты легче вступают в реакции ионного обмена. Авторами установлена сорбционная активность полученных материалов на основе природного цеолита и шамота по отношению к катионам Na$^+$ и K$^+$. Максимальная степень извлечения составляет 28,45% для ионов Na$^+$ сорбентом ШГ-Na-H и 76,28% для ионов K$^+$ сорбентом ШГ-Na. Среди сорбентов на основе Ц наиболее эффективными формами являются Ц-Na-H (15,44% извлечения Na$^+$) и Ц-Na (60,47% извлечения K$^+$).

Ключевые слова: цеолит; шамотная глина; модификация; характеристики; сорбция; извлечение; опреснение; ионы Na$^+$ и K$^+$.

Тұзды судан натрий мен калий иондарын алу үшін табиғи цеолит пен шамот сазына негізделген сорбенттерді қолдану: алдын-ала зерттеу

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Бұл жұмыста тұзды судан Na$^+$ және K$^+$ иондарын бөліп алу үшін NaCl және HNO$_3$ ерітінділерімен өңделген табиғи цеолит (Ц) және шамот сазы (ШС) негізіндегі сорбенттер алынды. Алынған сорбенттердің физика-химиялық сипаттамалары СЭМ, EDAX, БЭТ әдістерімен зерттелді. NaCl және HNO$_3$ тізбектей өңдеу зерттелетін материалдардың сорбциялық қасиеттеріне оң әсер ететіні анықталды. Қышқылмен өңделген Ц меншікті бетінің максималды ұлғаюы 4,5 м^2/г-дан 39,3 м^2/г-ға дейін жоғарылауы байқалады, ал ШС меншікті беті 8,4 м^2/г-дан 15,3 м^2/г-ға дейін 2 есе артады. Ц және ШС катиондарымен ион алмасу нәтижесінде судан Na$^+$ және K$^+$ иондары бөліп алынады. Зерттелетін сорбенттердің катион алмасу сыйымдылығын (КАС) анықтау нәтижесінде NaCl ерітіндісімен өңдеу сорбенттің ионалмастырғыштық қасиетін жақсартып, алюмосиликаттардың «гомоиондық» түрінің түзілуіне әкелетіні анықталды. Осының арқасында сорбенттер иондық алмасу реакцияларына оңай түседі. Жұмыс авторларымен Na$^+$ және K$^+$ катиондарына қатысты табиғи цеолит пен шамот негізінде алынған материалдардың сорбциялық белсенділігін анықталынды. Ең жоғары бөліп алу ШС-Na-H сорбентімен Na$^+$ иондары үшін 28,45% және ШГ-Na сорбентімен K$^+$ иондары үшін 76,28% құрайды. Ц негізіндегі сорбенттер арасында Ц-Na-H (Na$^+$ алудың 15,44%) және Ц-Na (K$^+$ алудың 60,47%) неғұрлым тиімді нысандары болып табылады.

Түйін сөздер: цеолит; шамот сазы; түрлендіру; сипаттамалар; сорбция; бөліп алу; тұщыландыру; Na$^+$ және K$^+$ иондары.

The use of natural zeolite and chamotte clay-based sorbents for the extraction of sodium and potassium ions from saline water: a preliminary study

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In this work, sorbents based on natural zeolite (Z) and chamotte clay (ChC) treated with NaCl and HNO$_3$ solutions were obtained to extract Na$^+$ and K$^+$ ions from saline water. The physicochemical characteristics of the obtained sorbents were studied by SEM, EDAX, and BET methods. It was found that successive treatment with NaCl and HNO$_3$ solutions has a positive effect on the sorption properties of the studied materials. The maximum increase in the specific surface area from 4.5 m^2/g to 39.3 m^2/g is observed for acid-treated Z, and the specific surface area of ChC also increases almost 2-fold from 8.4 m^2/g to 15.3 m^2/g. Na$^+$ and K$^+$ ions are extracted from water due to ion exchange with Z and ChC cations. As a result of determining the cation exchange capacity (CEC) of the studied sorbents, it was found that treatment with a NaCl solution improves the ion exchange properties of the sorbent and leads to the formation of a “homoionic” form of aluminosilicates. Due to that the sorbents more easily enter ion exchange reactions. The authors established the sorption activity of the obtained materials based on natural Z and ChC with respect to Na$^+$ and K$^+$ cations. The maximum recovery rate is 28.45% for Na$^+$ ions with the ChC-Na-H sorbent and 76.28% for K$^+$ ions with the ChC-Na sorbent. Among Z-based sorbents, the most effective forms are Z-Na-H (15.44% Na$^+$ recovery) and Z-Na (60.47% K$^+$ recovery).

Keywords: zeolite; chamotte clay; modification; characteristics; sorption; extraction; desalination; Na$^+$ and K$^+$ ions.

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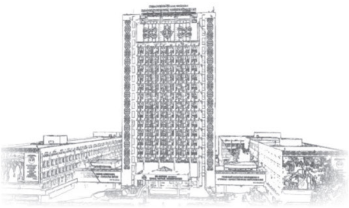

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Применение сорбентов на основе природного цеолита и шамотной глины для извлечения ионов натрия и калия из соленой воды: предварительное исследование

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1. Введение

По данным ООН, уже сейчас более 1,2 млрд людей живут в условиях постоянного дефицита пресной воды, около 2 млрд страдают от него регулярно. По прогнозам ФАО, к середине третьего десятилетия XXI в. численность живущих при перманентной нехватке воды превысит 4 млрд человек [1]. По прогнозам министерства экологии РК в Казахстане случится дефицит воды в 2040 году. 97% мировых запасов воды – соленые. С ростом численности населения планеты, а также развитием промышленности и технологий, также растет потребность в пресной воде. Учитывая вышеизложенное, возникает необходимость разработки способа опреснения соленой воды, который будет характеризоваться высокой эффективностью и низкой себестоимостью. Ряд стран, которые уже настиг водный кризис, вынуждены прибегать к использованию альтернативных водных источников, в том числе к использованию морских вод, подвергнутых предварительному опреснению. На сегодняшний день выделяют два наиболее распространённых метода опреснения солёной воды для её использования в качестве питьевой: многоступенчатая дистилляция и обратный осмос [2]. Многоступенчатая дистилляция относится к термическим методам опреснения и является достаточно простой и эффективной, но требует больших энергетических затрат, которые обуславливаются необходимостью постоянного поддержания высокой температуры в дистилляционном аппарате [3]. Обратный осмос – один из видов мембранной технологии – является наиболее распространённым методом опреснения. Данная технология является менее энергоёмкой и имеет большую эффективность по сравнению с термической, но имеет значительные недостатки, связанные со сложностью эксплуатации, высокой стоимостью самой осмотической установки и сменных мембран [4].

Сорбционный метод является перспективным в использовании в процессе опреснения соленой воды. Как известно, сорбенты представляют из себя материалы с развитой структурой, на поверхности или в объёме которых происходит концентрирование поглощаемого вещества. Сорбционный метод опреснения заключается в поглощении сорбентом засоляющих ионов из воды, которыми преимущественно являются Na^+, K^+ и Cl^- [5].

Согласно [6], адсорбционный метод относится к методам, в котором реализуется механизм, характеризующийся короткодействующим взаимодействием объекта с сорбционным материалом. Данный метод, в основном, используется для опреснения воды со средним или низким значением солености. Для опреснения воды с более высокой соленостью адсорбция является экономически не самым рациональным способом, так как требует достаточно большого объема сорбентов, которые необходимо предварительно синтезировать. Однако, несмотря на имеющиеся недостатки и ограничения, многие научные группы дальнего и ближнего зарубежья, как показывает обзор литературы, активно развивают сорбционные методы в опреснении: предлагают новые сорбенты, новые способы модифицирования, оптимальные условия опреснения на основе анализа влияния различных факторов на исследуемые процессы.

Так, популярны сорбенты на основе природного минерального сырья, которые характеризуются сорбционной активностью по отношению к ионам металлов, содержащихся в соленой воде. Необходимо отметить, что по сравнению с синтетическими сорбентами, использование природных материалов более выгодно с экономической и экологической точек зрения. Для улучшения сорбционных характеристик исходных объектов используются различные методы их модификации [5].

Природные цеолиты и глины достаточно эффективные, дешевые и распространенные материалы, обладающие высокой сорбционной активностью по отношению к веществам различной природы [7,8].

Из литературы известно, что природные цеолиты достаточно эффективны в процессах опреснения соленой воды. Так, в работе [9] природный цеолит Индонезии был термически активирован и использован для опреснения морской воды, тем самым уменьшив содержание соли на 9,4%. Учеными из Канады [10,11] также был использован природный цеолит, подвергшийся термической активации с последующей обработкой хлоридом натрия и кислотой. Данный вид обработки оказался более эффективным, уменьшив содержание ионов Na^+, K^+ и Cl^- на 90-96%. Также в данной работе отмечено, что перспективным направлением для исследований будет применение использованного цеолита как источник калия для растений.

В исследовании [12] для опреснения морской воды было использовано два вида природного цеолита, а также глинистый материал *layered-double hydroxide (*слоистый двойной гидроксид). Солесодержание уменьшилось до 2,09% после обработки морской воды природным цеолитом, и до 0,70% - глиной. Обработанная вода была использована для орошения семян редиса, что привело к прорастанию семян. То есть, опресненная вода оказалась благоприятной для использования в агрокультуре.

Большой интерес представляет работа [13], в которой исследован процесс гиперфильтрации соленых грунтовых вод проницаемыми отложениями глины. Было установлено, что наибольший вклад в механизм опреснения грунтовых вод вносит ионный обмен. В процессе фильтрации ионы кальция и магния на поверхности глины замещаются ионами натрия из воды, тем самым снижая солесодержание.

В качестве ионообменных материалов широко используются природные минералы как, например, цеолиты, обладающие адсорбционными свойствами по отношению к различным ионам металлов и органических соединений. Цеолиты участвуют в реакциях катионного обмена [6], т.е. способны замещать свои катионы на ионы, в частности, Na^+ и K^+. Так, в работе [14] цеолиты, богатые кальцием были использованы для извлечения ионов Na^+. Известно, что селективность ионов Na^+ и K^+ выше, чем Ca^{2+} и Mg^{2+} [15]. Поэтому использование цеолита, в качестве сорбционной матрицы в процессах опреснения, является целесообразным.

В связи с этим, в данной статье представлены результаты по разработке агентов-опреснителей на основе цеолита и шамотной глины, изучению их физико-химических характеристик, а также по оценке их сорбционной активности в процессах извлечения ионов Na^+ и K^+.

Новизной данного исследования является применение цеолита и шамотной глины Казахстанского происхождения для получения агентов-опреснителей соленой воды. Природные цеолит и шамотная глина были модифицированы растворами NaCl и HNO_3 для улучшения их адсорбционных свойств. Были предложены новые сорбционные агенты для извлечения ионов Na^+ и K^+ из соленой воды.

2. Эксперимент

Объектами исследования являются сорбенты на основе природного цеолита месторождения Шанканай (Алматинская область), а также шамотной глины компании «Теплосвет Инжиниринг».

В ходе работы использованы следующие физико-химические методы анализа: атомно-абсорбционная спектроскопия (АА-6200 Shimadzu), сканирующая электронная микроскопия (СЭМ, FEI 400 Magellan), энергодисперсионная рентгеновская спектроскопия (EDAX, FEI 400 Magellan), БЭТ (анализатор удельной поверхности и пористости Quantachrome Nova 4200e).

2.1 Определение катионообменной емкости сорбентов

Катионообменная емкость материалов определена согласно стандартной методике, описанной в [16,17]:

1 г сорбента смешивали с 100 мл 1 М раствора NH_4Cl. Суспензии перемешивались в течение 24 ч и центрифугировались. Далее были определены концентрации ионов Ca^{2+}, Mg^{2+}, Na^+ и K^+ в растворе при помощи атомно-абсорбционного спектрометра. КОЕ были рассчитаны как сумма концентраций высвобожденных катионов и выраженную в мэкв/100 г, используя следующее уравнение:

$$M_{\text{мэкв/100г}} = C/(Э \times 10), \tag{1}$$

где $M_{мэкв/100\,г}$ – это концентрация высвобожденных катионов, мэкв/100 г;

C – это концентрация высвобожденных катионов, мг/л;

Э – это эквивалентная масса высвобожденных катионов – атомная масса, умноженная на его фактор эквивалентности.

2.2 Получение сорбентов

В работе использованы 4 серии сорбентов на основе цеолита (Ц) и шамотной глины (ШГ):

1 серия: исходные минералы – Ц и ШГ;

2 серия: Ц и ШГ, обработанные NaCl;

3 серия: Ц и ШГ, обработанные HNO_3;

4 серия: Ц и ШГ, последовательно обработанные NaCl и HNO_3.

Сорбенты были получены следующим образом:

Для 1 серии сорбентов исходные Ц и ШГ промывались дистиллированной водой в соотношении 100 мл воды на 1 г минерала. После промытые минералы были высушены при температуре 100°С в течение 1 ч, далее на воздухе в течение 24 ч. Высушенные минералы измельчались до мелкодисперсного состояния, затем просеивались через сито для удаления механических примесей и крупных частей.

Для получения 2 и 3 серии сорбентов 15 г промытого Ц и ШГ обрабатывались 1 М раствором NaCl или HNO_3 в соотношении тв:ж 1:5. Суспензия перемешивалась на магнитной мешалке в течение 6 ч при частоте 200 об./мин. Суспензия отфильтровывалась, обработанный минерал промывался дистиллированной водой до полного удаления ионов Cl^- (при обработке NaCl; контроль проводился 0,1 М раствором $AgNO_3$) и до достижения постоянного уровня pH (при обработке $HNO)_3$. Промытый обработанный минерал высушивался при температуре 100°С в течение 4 ч, затем на воздухе в течение 12 ч.

4 серия сорбентов получалась путем дальнейшей обработки сорбентов 2 серии 1 М раствором HNO_3 (по методике получения 3 серии сорбентов).

2.3 Адсорбция ионов Na^+ и K^+

Определение адсорбционных характеристик исследуемых материалов проводили по отношению к ионам Na^+ и K^+ с использованием модельных растворов в статическом режиме при комнатной температуре:

– раствор NaCl, концентрация ионов натрия 50 мг/л;

– раствор KCl, концентрация ионов калия 50 мг/л.

Для проведения адсорбции ионов Na^+ и K^+ отбирали навеску сорбентов массой 0,5 г и помещали их в химические пробирки объемом 50 мл. В пробирки с сорбентами заливали по 30 мл модельного раствора. Содержимое пробирок тщательно перемешивалось в течение 6-12 ч при 200 об./мин. Затем растворы отделялись от сорбентов в центрифуге при 3000 об./мин. Образцы анализировали на содержание ионов металлов на атомно-абсорбционном спектрометре. Для получения воспроизводимых результатов все эксперименты по проведению адсорбции ионов Na^+ и K^+ проводились три раза.

Величину степени извлечения металла рассчитывали по уравнению:

$$E = \frac{c_0 - c_e}{c_0} * 100\%, \qquad (2)$$

где c_0 и c_e – начальная и равновесная концентрации сорбата соответственно, мг/л.

Величину адсорбции для всех сорбентов рассчитывали по уравнению:

$$A = \frac{c_0 - c_e}{m} * V, \qquad (3)$$

где c_0 и c_e – начальная и равновесная концентрация сорбата соответственно, мг/л;

V – объем раствора сорбата, л;

m – масса сорбента, г.

3. Результаты и обсуждение

3.1 Физико-химические характеристики сорбентов

На основе анализа экспериментальных данных устновлено, что цеолит (Ц) Шанканайского месторождения относится к минералу клиноптиллолитового типа. Клиноптиллолит является наиболее распространенным типом природных цеолитов и относится к цеолитам типа гейландита [18].

Для гейландитов характерна трехмерная алюмосиликатная кристаллическая решетка, состоящая в основном из слоев структурных единиц 4-4-1-1: двух 4-членных колец тетраэдров, соединенных двумя дополнительными тетраэдрами. Звенья 4-4-1-1 образуют слои (010), каналы из 10-12-членных колец.

Шамотная глина – белая термообработанная каолиновая глина со свойствами камня, устойчивая к агрессивным средам, содержащая высокодисперсные гидроалюмосиликаты. Глина не требует дополнительной очистки после вторичного использования. Она может быть использована в промышленности в больших количествах.

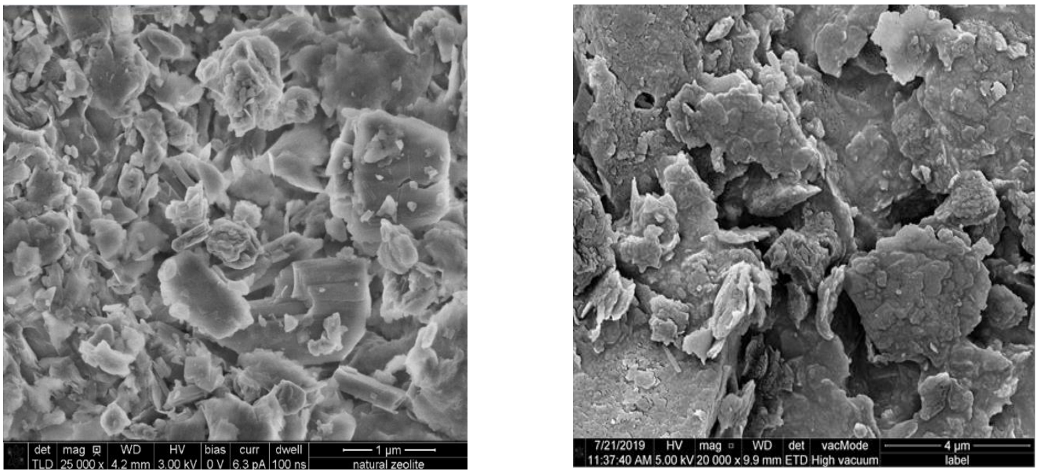
В состав ШГ входят такие элементы, как оксиды кремния, алюминия, кальциты, оксиды магния, оксиды активных металлов, соединения железа и другие. В стандарте, добываемом в карьерах, огнеупор ШГ содержит более 5% воды. Огнеупор ШГ можно эксплуатировать не выше диапазона температур от 1520 до 1820°С, этот показатель зависит от состава огнеупорной глины. Средний размер гранул ШГ составляет от 1,5 до 2,5 мм.

На рисунке 1 представлены СЭМ-изображения объектов исследования.

Морфология природного Ц (рисунок 1А) характеризуется плотными агломератами различной формы с некоторым пространством между ними (порами). Распределение частиц по размерам охватывает широкий диапазон от 0,1 до 100 мкм со средним размером (1,223 ± 0,788) мкм^2. Частицы исходной ШГ (рисунок 1Б) имеют чешуйчатую форму различных размеров. Средний размер частиц исходной глины составляет (1,29 ± 1,61) мкм^2.

Результаты элементного анализа, полученные методом энергодисперсионной спектрометрии (EDAX), представлены в таблице 1.

Исходный Ц содержит в основном Si, O и Al, а также небольшое количество таких металлов, как Na, Mg, K, Ca и Fe. Примечательно, что после обработки Ц 1 М раствором NaCl содержание натрия увеличивается с 0,45 до 1,97%, а содержание остальных металлов уменьшается: Mg с 1,49 до 0,35%, K с 0,60 до 0,45%, Fe с 2,70 до 0,45%, 0,69%. Вероятно, это связано с замещением ионов указанных металлов ионами натрия.



А) Ц **Б) ШГ**

Рисунок 1 – СЭМ-изображения образцов: А) частицы природного цеолита (Ц) с плотными агломератами различной формы с некоторым пространством между ними (порами); Б) частицы исходной шамотной глины (ШГ) с чешуйчатой формой различных размеров

Исходная ШГ содержит в основном Si, O и Al, а также небольшие количества металлов, таких как Na, Mg, K, Ca и Fe. Примечательно, что после обработки ШГ 1 М раствором NaCl содержание Na также увеличивается с 0,44 до 0,62%, содержание Mg практически не меняется с 0,50 до 0,52%, содержание К увеличивается с 0,86 до 0,92%. Скорее всего, это связано с замещением ионов металлов ионами натрия.

Таким образом, поскольку все металлы в структуре Ц и ШГ являются потенциальными центрами катионного обмена, их содержание изменяется после их обработки раствором NaCl.

Представляет интерес соотношение Si/Al, определяющее сорбционные свойства Ц и ШГ. Целью кислотной обработки является увеличение отношения Si/Al, которое для природных цеолитов варьируется от 2 до 10. Высококремнистые цеолиты имеют большую удельную поверхность и объем пор [19].

При низких значениях данного соотношения поверхность цеолитов и глин является гидрофильной, в то время как высокие значения приводят к ее гидрофобности [20]. Значения соотношения Si/Al для исследуемых объектов являются достаточно низкими, что свидетельствует о гидрофильности поверхности сорбентов и благоприятно для адсорбции неорганических ионов. После обработки Ц кислотой значение Si/Al практически не изменилось, а после обработки хлоридом натрия уменьшилось с 4,43 до 2,93. Это может говорить о повышении гидрофильности поверхности и увеличении сорбционной активности по отношению к неорганическим ионам. В случае ШГ наблюдается обратный эффект – увеличение соотношения после обработки солью от 1,19 до 1,45 и уменьшение до 0,88 после обработки кислотой. Вероятно, в случае ШГ более эффективной формой в процессах опреснения будет ШГ-Н.

Таблица 1 – Результаты элементного анализа сорбентов, полученные методом энергодисперсионной спектрометрии

Образец	С, вес.%	O, вес.%	Al, вес.%	Si, вес.%	Na, вес.%	K, вес.%	Mg, вес.%	Ca, вес.%	Fe, вес.%	Si/Al
Ц	13,92	52,07	4,85	21,48	0,45	0,60	1,49	2,84	2,30	4,43
	±2,47	±1,15	±1,02	±2,56	±0,19	±0,06	±0,30	±0,88	±0,38	±2,51
Ц-Na	12,34	47,07	8,64	25,34	1,97	0,45	0,35	3,11	0,69	2,93
	±4,75	±2,65	±1,43	±1,5	±0,07	±0,91	±0,71	±0,49	±0,07	±1,01
Ц-Н	28,10	44,02	3,56	15,99	1,05	0,92	1,86	1,80	2,70	4,49
	±9,14	±4,72	±0,73	±1,68	±0,53	±0,42	±1,48	±0,38	±0,89	±2,30
ШГ	6,71	43,22	22,40	26,62	0,44	0,86	0,50	-	-	1,19
	±1,98	±1,27	±1,72	±2,37	±0,09	±0,21	±0,24			±1,28
ШГ-Na	24,70	38,18	11,78	17,11	0,62	0,92	0,52	-	-	1,45
	±3,45	±1,83	±1,01	±1,25	±0,11	±0,76	±0,38			±2,03
ШГ-Н	20,47	30,03	19,30	16,97	0,33	1,61	0,54	-	-	0,88
	±4,01	±2,15	±0,86	±1,13	±0,28	±0,84	±0,66			±1,34

Одной из важнейших характеристик для описания сорбентов является удельная поверхность и размер пор, которые можно получить методом Брунауэра-Эммета-Теллера (БЭТ). Результаты оценки адсорбционной активности исследуемых материалов, полученные методом БЭТ, представлены в таблице 2.

Сравнительный анализ данных таблицы 2 указывает на то, что исходный цеолит имеет довольно низкую удельную площадь поверхности, равную 4,5 м^2/г. Модификация хлоридом натрия приводит к повышению удельной площади поверхности до 6,2 м^2/г. Наибольший эффект соответствует кислотной обработке цеолита, в результате которой данная характеристика увеличивается до 39,3 м^2/г.

Таблица 2 – Результаты БЭТ

Образцы	Удельная площадь поверхности, м^2/г	Общий объем пор, $*10^3$ см^3/г
Ц	4,50 ± 0,09	2,00 ± 0,04
Ц-Na	6,20 ± 0,13	2,00 ± 0,04
Ц-H	39,30 ± 0,94	5,00 ± 0,09
ШГ	8,40 ± 0,22	2,90 ± 0,03
ШГ-Na	10,90 ± 0,23	3,90 ± 0,04
ШГ-H	15,30 ± 0,38	4,00 ± 0,06

Удельная поверхность ШГ составляет 8,4 м^2/г. Обработка солью приводит к увеличению данной величины до 10,9 м^2/г, сопровождающееся повышением объема пор с 0,029 до 0,039 см^3/г. Объем пор после кислотной обработки ШГ практически такой же, как и после обработки солью. Удельная поверхность ШГ после кислотной обработки характеризуется заметным ее увеличением с 8,4 до 15,3 м^2/г. Таким образом, ШГ, обработанная кислотой, будет более эффективна в сорбционных процессах, которые характеризуются физическим взаимодействием реагентов.

Катионообменная емкость (КОЕ) является важной характеристикой для количественной оценки способности минералов вступать в реакции ионного обмена. В таблице 3 представлены значения КОЕ для исследуемых материалов, КОЕ природных цеолитов и глин колеблется от 200 до 400 мэкв/100 г [21]. Как видно из данных таблицы 3, КОЕ необработанного Ц довольно высока, в частности, для ионов кальция, поэтому можно сделать вывод, что Ц содержит больше кальция, чем других обменных катионов. Обработка Ц хлоридом натрия (NaCl) позволило увеличить КОЕ исходного минерала с 616,0 до 624,4 мэкв/100 г. Кислотная обработка приводит к значительному снижению КОЕ цеолита до 129,2 мэкв/100 г за счет выщелачивания ионообменных элементов.

Следует отметить, что общее значение КОЕ для Ц после обработки натрием повысилось незначительно. Однако следует обратить внимание на КОЕ по отдельным ионам: КОЕ (Na^+) повысилась от 116,8 до 230,1, в то время как КОЕ по Ca^{2+} и Mg^{2+} уменьшились от 441,2 до 348,4 и от 42,3 до 29,3, соответственно. В то же время КОЕ по K^+ практически не изменилась. Отсюда можно сделать вывод, что в результате обработки солью происходит увеличение содержания ионов натрия в цеолите за счет ионообменных процессов преимущественно с ионами кальция и магния. Насыщение поверхности цеолитов и глин ионами натрия приводит к образованию «гомоионной» формы алюмосиликата и улучшает ионообменные свойства материала, так как ионы натрия легче вступают в реакции ионного обмена [22,23].

КОЕ исходной шамотной глины составляла 291,3 мэкв/100 г, что является средним значением для глинистых материалов. В результате обработки хлоридом натрия значение КОЕ глины повысилось до 353,9 мэкв/100 г. При кислотной обработке вследствие выщелачивания обменных катионов КОЕ исходного материала уменьшилось до 129,3 мэкв/100 г. В случае ШГ-Na также заметно увеличение КОЕ по ионам натрия и значительное уменьшение по ионам кальция и магния, что также свидетельствует о насыщении поверхности глины ионами натрия за счет ионного обмена преимущественно с кальцием и магнием.

Таким образом, получены материалы на основе цеолита и шамотной глины, обработанные хлоридом натрия и азотной кислотой, изучены физико-химические характеристики, которые позволяют их использовать в сорбционных процессах.

Таблица 3 – Катионообменная емкость исследуемых объектов

Образцы	КОЕ, мэкв/100 г				
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Суммарное значение
Ц	116,80±3,45	15,70±1,61	441,20±10,53	42,30±1,12	616,00±16,71
Ц-Na	230,10±5,98	16,70±2,03	348,40±8,08	29,20±0,57	624,40±16,66
Ц-H	86,60±2,01	10,30±0,67	28,20±0,97	4,20±0,04	129,20±3,69
ШГ	166,90±5,78	11,30±2,16	5,70±0,81	50,20±1,89	291,30±10,64
ШГ-Na	239,80±6,34	8,70±0,74	1,90±0,03	35,60±1,53	353,90±8,64
ШГ-H	95,80±2,47	7,50±0,38	0,30±0,01	0,70±0,02	129,30±2,88

Сорбенты на основе Ц и ШГ были исследованы в процессах опреснения соленой воды, в частности, для извлечения ионов натрия и калия (таблицы 4-5).

Следует отметить, что для исходных Ц/ШГ, а также обработанных солью форм Ц-Na/ШГ-Na наблюдается небольшое увеличение содержания ионов натрия в растворе после контакта с сорбентом. Это может быть обусловлено тем, что в данных формах сорбентов содержится значительное количество натрия, который в процессе взаимодействия с соленой водой выделяется в раствор, т.е. происходит десорбция. Таким образом, данные формы сорбентов являются неэффективными в процессах опреснения. Однако, обработка натрием является важной ступенью получения сорбента, способного извлекать ионы натрия из водных растворов. Из [11] известно, что предварительная обработка цеолита Na^+ в результате последующей кислотной обработки приводит к более полному замещению обменных катионов на протоны. Авторами было установлено, что без предварительной обработки ионами натрия перевод цеолита в гомоионную Н-форму был менее полным. Также, предварительная обработка натрием уменьшает разрушение структуры минерала и деалюминирование при обработке кислотой [24].

Как видно из таблицы 4, наилучшие показатели достигаются у сорбентов, полученных путем последовательной обработки Ц и ШГ хлоридом натрия и кислотой (Ц-Na-H и ШГ-Na-H), которые составляют 15,44% и 28,45% соответственно.

Таблица 4 – Результаты извлечения ионов Na^+ из модельных растворов

Образцы	C(Na^+), мг/л	E, %	A, мг/г
NaCl (модельный раствор)	24,96±1,50	-	-
Ц	29,25±2,01	десорбция	десорбция
Ц-Na	34,61±2,25	десорбция	десорбция
Ц-H	22,31±1,34	11,90±0,84	0,16±0,01
Ц-Na-H	21,62±1,47	15,44±0,95	0,20±0,01
ШГ	31,09±2,74	десорбция	десорбция
ШГ-Na	25,45±1,54	десорбция	десорбция
ШГ-H	22,20±1,42	12,43±0,81	0,17±0,01
ШГ-Na-H	19,43±1,34	28,45±1,83	0,33±0,02

В таблице 5 приведены результаты извлечения ионов K^+ сорбентами на основе Ц и ШГ. Сорбенты на основе ШГ демонстрируют более высокие значения степени извлечения в пределах 67,96-76,28%. Это, вероятно, связано с тем, что ШГ содержит в своем составе, в основном, ионы Na^+, которые максимально замещают ионы K^+, содержащиеся в модельном растворе. Результаты извлечения ионов K^+ сорбентами на основе Ц ниже по сравнению с сорбентами на основе ШГ. Возможно, это связано с тем, что в составе Ц содержатся ионы и Na^+ и K^+, поэтому при извлечении ионов K^+ из модельных растворов, ионообменным процессам подвергаются только ионы натрия.

Анализ результатов, представленных в таблице 5, указывает на относительно высокие сорбционные характеристики для Ц и ШГ, обработанных хлоридом натрия, что, вероятно, обусловлено переводом исходных материалов в гомоионную Na-форму.

Таблица 5 – Результаты извлечения ионов K^+ из модельных растворов

Образцы	C(K^+), мг/л	E, %	A, мг/л
KCl (модельный раствор)	49,54±2,98	-	-
Ц	33,23±2,01	32,93±2,05	0,98±0,06
Ц-Na	19,58±1,27	60,47±3,83	1,80±0,11
Ц-H	36,92±2,39	25,49±1,55	0,76±0,05
Ц-Na-H	36,95±2,28	25,40±1,71	0,76±0,04
ШГ	15,22±1,03	69,28±4,41	2,10±0,13
ШГ-Na	11,75±0,79	76,28±4,71	2,27±0,14
ШГ-H	15,87±1,02	67,96±4,08	2,02±0,13
ШГ-Na-H	15,50±0,98	68,70±4,25	2,04±0,12

Однако, в данном случае эффективность обработанных хлоридом натрия форм сорбентов являются спорными при опреснении, так как может происходить замещение одного засоляющего иона на другой – калия на натрий. При этом степень солености раствора может не уменьшаться. Но данная форма обработки алюмосиликатов может иметь практический интерес в других сферах, где необходимо концентрирование и извлечение ионов калия. Например, Ц и ШГ после извлечения ионов калия могут применяться в качестве удобрений как источник калия, который является важными микроэлементом для растений [25].

Таким образом, в процессах опреснения лучше использовать обработанные кислотой, либо последовательно солью и кислотой формы сорбентов.

3.2 Сравнение эффективности полученных сорбентов с известными из литературы данными

Известно, что сорбенты на основе углерода, такие как активированный уголь, углеродные нанотрубки и графены, обладают значительными адсорбционными свойствами по отношению к различным органическим и неорганическим соединениям [6]. Так, в работе [26] использована активированная углеродная ткань для извлечения ионов Na^+ и K^+ из воды. Было установлено, что извлечение ионов Na^+ углеродным сорбентом составило 9%, а ионов K^+ – 50%.

В работе [27], для извлечения ионов Na^+ из воды использовали тонкую пленку аморфного углерода, в результате которого степень извлечения ионов Na+ составила 45%. Авторами [28] исследована эффективность альгинатного геля для адсорбции ионов натрия, степень извлечения которого составила 16,8%. В работах [15,29] представлены результаты по опреснению с использованием цеолита. Так, в работе [29] установлено, что степень извлечения ионов K+ цеолитом, обработанного раствором NaCl, составила 50%. В работе [15] исследовано извлечение ионов Na+ сорбентом на основе природного цеолита, обработанного раствором серной кислоты, степень извлечения равна 88%. Сравнительный анализ сорбционных материалов указывает на то, что многие из них являются достаточно дорогостоящими, синтезируемыми в ходе многоступенчатых процессов. Следует отметить, что полученные в настоящем исследовании сорбенты характеризуются сравнительно невысокими значениями степени извлечения ионов натрия и калия, однако являются доступными в финансовом отношении, представляют минеральное сырье Казахстана.

4. Заключение

В работе были получены сорбенты на основе природного цеолита и шамотной глины и исследованы их адсорбционные свойства по отношению к ионам Na^+ и K^+ для опреснения соленой воды. В результате обработки природного цеолита и шамотной глины хлоридом натрия и азотной кислотой были получены 4 серии сорбентов. Исследованы физико-химические характеристики полученных сорбентов методами СЭМ, EDAX и БЭТ. В результате кислотной обработки происходит значительное увеличение удельной поверхности Ц и ШГ с 4,5 $м^2$/г до 39,3 $м^2$/г и с 8,4 $м^2$/г, г до 15,3 $м^2$/г, соответственно. Катионообменная емкость (КОЕ) повышается в результате обработки хлоридом натрия, численные значения с 616,0 до 624,4 мэкв/100 г и с 291,3 до 352,9 мэкв/100 г для Ц и ШГ, соответственно. Это объясняется образованием «гомоионной» формы алюмосиликата, в результате чего сорбенты легче вступают в реакции ионного обмена. Установлено, что сорбенты на основе ШГ показывают большие степени извлечения ионов по сравнению с сорбентами на основе Ц. Сорбент ШГ-Na-H характеризуется более высокой степенью извлечения ионов Na^+ (E = 28,45%), а сорбент ШГ-Na эффективен для связывания ионов K^+ (E = 76,28%) из модельных растворов. Среди сорбентов на основе Ц наиболее эффективными формами являются Ц-Na-H (15,44% извлечения Na^+) и Ц-Na (60,47% извлечения K^+). В результате предварительной оценки исследуемых материалов для извлечения ионов Na^+ и K^+, проведенной в рамках данного исследования установлено, что Ц и ШГ имеют потенциал для применения в процессах опреснения соленой воды.

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Литература

1 Данилов-Данильян В.И. Глобальная проблема пресной воды // Век Глобализации. – 2008. – №1. – P.45-56.

2 du Plessis A. Global Water Scarcity and Possible Conflicts. In: Freshwater Challenges of South Africa and its Upper Vaal River. – Springer Cham, 2017. – P.45-62.

3 Abdulstar A.R., Altemimi A., Al–Hilphy A.R.S., Watson D.G., Lakhssassi N. Water distillation using an ohmic heating apparatus // International Journal of Ambient Energy. – 2020. – P.1-11.

4 Franzsen S., Sheridan C., Simate G.S. Process for high recovery treatment of brackish water reverse osmosis concentrate // Desalination. – 2021. – Vol.498. – P.114792.

5 Godage N.H., Gionfriddo E. Use of natural sorbents as alternative and green extractive materials: A critical review // Analytica Chimica Acta. – 2020. – Vol.1125. – P.187-200.

6 Alaei Shahmirzadi M.A., Hosseini S.S., Luo J., Ortiz I. Significance, evolution and recent advances in adsorption technology, materials and processes for desalination, water softening and salt removal // Journal of environmental management. – 2018. – Vol.215. – P.324-344.

7 Reeve P.J., Fallowfield H.J. Natural and surfactant modified zeolites: A review of their applications for water remediation with a focus on surfactant desorption and toxicity towards microorganisms // Journal of Environmental Management. – 2018. – Vol.205. – P.253-261.

8 Uddin M.K. A review on the adsorption of heavy metals by clay minerals, with special focus on the past decade // Chemical Engineering Journal. – 2017. – Vol.308. – P.438-462.

9 Wibowo E., Sutisna, Rokhmat M., Murniati R., Khairurrijal, et al. Utilization of natural zeolite as sorbent material for seawater desalination // Procedia Engineering. – 2017. – Vol.170. – P.8-13.

10 Gibb N.P., Dynes J.J., Chang W. Synergistic desalination of potash brine-impacted groundwater using a dual adsorbent // Science of the Total Environment. – 2017. – Vol.593-594. – P.99-108.

11 Gibb N.P., Dynes J.J., Chang W. A recyclable adsorbent for salinized groundwater: Dual–adsorbent desalination and potassium–exchanged zeolite production // Chemosphere. – 2018. – Vol.209. – P.721-729.

12 Sekihata F., Wajima T. Preparation of desalination agent from ca-type clay minerals // International Journal of GEOMATE. – 2020. – Vol.19, Is.71. – P.123-129.

13 Wibowo E., Rokhmat M., Sutisna, Murniati R., Khairurrijal, Abdullah M. Thermally activated clay to compete zeolite for seawater desalination // Advanced Materials Research. – 2015. – Vol.1112. – P.154-157.

14 Ganjegunte G.K., Vance G.F., Gregory R.W., Urynowicz M.A., Surdam R.C. Improving saline-sodic coalbed natural gas water quality using natural zeolites // Journal of Environmental Quality. – 2011. – Vol.40, Is.1. – P.57-66.

15 Paul B., Dynes J.J., Chang W. Modified zeolite adsorbents for the remediation of potash brine-impacted groundwater: Built–in dual functions for desalination and pH neutralization // Desalination. – 2017. – Vol.419. – P.141-151.

16 Kragović M., Pašalić S., Marković M., Petrović M., Nedeljković B., Momčilović M., Stojmenović M. Natural and modified zeolite—alginate composites. Application for removal of heavy metal cations from contaminated water solutions // Minerals. – 2018. – Vol.8, Is.1. – P.11.

17 Rakhym A.B., Seilkhanova G.A., Mastai Y. Physicochemical evaluation of the effect of natural zeolite modification with didodecyldimethylammonium bromide on the adsorption of Bisphenol–A and Propranolol Hydrochloride // Microporous and Mesoporous Materials. – 2021. – Vol.318. – P.111020.

18 Moshoeshoe M., Nadiye–Tabbiruka M.S., Obuseng V. A review of the chemistry, structure, properties and applications of zeolites // American Journal of Materials Science. – 2017. – Vol.7, Is.5. – P.196-221.

19 Wang C., Leng S., Guo H., Yu J., Li W., Cao L., Huang J. Quantitative arrangement of Si/Al ratio of natural zeolite using acid treatment // Applied Surface Science. – 2019. – Vol.498. – P.143874.

20 Jiang N., Shang R., Heijman S.G.J., Rietveld L.C. High–silica zeolites for adsorption of organic micro–pollutants in water treatment: A review // Water Research. – 2018. – Vol.144. – P.145-161.

21 Noori M., Zendehdel M., Ahmadi A. Using natural zeolite for the improvement of soil salinity and crop yield // Toxicological and Environmental Chemistry. – 2006. – Vol.88, Is.1. – P.77-84.

22 Fard R.F., Aminabad M.S., Hadi M., Gholami M., Mirzaei N. Sorption of acid dye by surfactant modificated natural zeolites // Journal of the Taiwan Institute of Chemical Engineers. – 2015. – Vol.59. – P.186-194.

23 Peng S., Tang Z., Jiang W., Wu D., Hong S., Xing B. Mechanism and performance for adsorption of 2-chlorophenol onto zeolite with surfactant by one-step process from aqueous phase // Science of the Total Environment. – 2017. – Vol.581-582. – P.550-558.

24 Siemens A.M., Dynes J.J., Chang W. Sodium adsorption by reusable zeolite adsorbents: Integrated adsorption cycles for salinized groundwater treatment // Environmental Technology. – 2020. – Vol.42, Is.20. – P.3083-3094.

25 Naidu G., Jeong S., Choi Y., Song M.H., Oyunchuluun U., Vigneswaran S. Valuable rubidium extraction from potassium reduced seawater brine // Journal of Cleaner Production. – 2018. – Vol.174. – P.1079-1088.

26 Laxman K., Myint M.T.Z., Al Abri M., Sathe P., Dobretsov S., Dutta J. Desalination and disinfection of inland brackish ground water in a capacitive deionization cell using nanoporous activated carbon cloth electrodes // Desalination. – 2015. – Vol.362. – P.126-132.

27 Fathy M., Mousa M.A., Moghny T.A., Awadallah A.E. Characterization and evaluation of amorphous carbon thin film (ACTF) for sodium ion adsorption // Applied Water Science. – 2017. – Vol.7, Is.8. – P.4427-4435.

28 Pearce M., Brennan F. Novel findings in desalination // Desalination. – 2015. – Vol.360. – P.13-18.

29 Guo X.-F., Ji Z.-Y., Yuan J.-S., Zhao Y.-Y., Liu J. Recovery of K^+ from concentrates from brackish and seawater desalination with modified clinoptilolite // Desalination and Water Treatment. – 2016. – Vol.57, Is.15. – P.6829-6837.

References

1 Danilov-Danil’yan VI (2008) The Age of Globalization [Vek Globalizatsii] 1:45-56. (In Russian)

2 du Plessis A (2017) Global Water Scarcity and Possible Conflicts. In: Freshwater Challenges of South Africa and its Upper Vaal River. Springer Cham. P.45-62. *https://doi.org/10.1007/978-3-319-49502-6_3*

3 Abdulstar AR, Altemimi A, Al-Hilphy ARS, Watson DG, Lakhssassi N (2020) Int J Ambient Energy 1-11.

4 Franzsen S, Sheridan C, Simate GS (2021) Desalination 498:114792. *https://doi.org/10.1016/j.desal.2020.114792*

5 Godage NH, Gionfriddo E (2020) Anal Chim Acta 1125:187-200. *https://doi.org/10.1016/j.aca.2020.05.045*

6 Alaei Shahmirzadi MA, Hosseini SS, Luo J, Ortiz I (2018) J Environ Manage 215:324-344. *https://doi.org/10.1016/j.jenvman.2018.03.040*

7 Reeve PJ, Fallowfield HJ (2018) J Environ Manage 205:253-261. *https://doi.org/10.1016/j.jenvman.2017.09.077*

8 Uddin MK (2017) Chem Eng J 308:438-462. *https://doi.org/10.1016/j.cej.2016.09.029*

9 Wibowo E, Sutisna, Rokhmat M, Murniati R, Khairurrijal, Abdullah M (2017) Procedia Eng 170:8-13. *https://doi.org/10.1016/j.proeng.2017.03.002*

10 Gibb NP, Dynes JJ, Chang W (2017) Sci Total Environ 593-594:99-108. *https://doi.org/10.1016/j.scitotenv.2017.03.139*

11 Gibb NP, Dynes JJ, Chang W (2018) Chemosphere 209:721-729. *https://doi.org/10.1016/j.chemosphere.2018.06.130*

12 Sekihata F, Wajima T (2020) Int J GEOMATE 19:123-129. *https://doi.org/10.21660/2020.71.9325*

13 Wibowo E, Rokhmat M, Sutisna, Murniati R, Khairurrijal, Abdullah M (2015) Adv Mater Res 1112:154-157. *https://doi.org/10.4028/www.scientific.net/amr.1112.154*

14 Ganjegunte GK, Vance GF, Gregory RW, Urynowicz MA, Surdam RC (2011) J Environ Qual 40:57-66. *https://doi.org/10.2134/jeq2010.0219*

15 Paul B, Dynes JJ, Chang W (2017) Desalination 419:141-151. *https://doi.org/10.1016/j.desal.2017.06.009*

16 Kragović M, Pašalić S, Marković M, Petrović M, Nedeljković

B, Momčilović M, et al (2018) Minerals 8:11. https://doi.org/10.3390/min8010011

17 Rakhym AB, Seilkhanova GA, Mastai Y (2021) Microporous Mesoporous Mater 318:111020. https://doi.org/10.1016/j.micromeso.2021.111020

18 Moshoeshoe M, Nadiye-Tabbiruka MS, Obuseng V (2017) Am J Mater Sci 7:196-221.

19 Wang C, Leng S, Guo H, Yu J, Li W, Cao L, et al (2019) Appl Surf Sci 498:143874. https://doi.org/10.1016/j.apsusc.2019.143874

20 Jiang N, Shang R, Heijman SGJ, Rietveld LC (2018) Water Res 144:145-161. https://doi.org/10.1016/j.watres.2018.07.017

21 Noori M, Zendehdel M, Ahmadi A (2006) Toxicol Environ Chem 88:77-84. https://doi.org/10.1080/02772240500457928

22 Fard RF, Aminabad MS, Hadi M, Gholami M, Mirzaei N (2015) J Taiwan Inst Chem Eng 59:186-194. https://doi.org/10.1016/j.jtice.2015.07.010

23 Peng S, Tang Z, Jiang W, Wu D, Hong S, Xing B (2017) Sci Total Environ 581-582:550-558. https://doi.org/10.1016/j.scitotenv.2016.12.163

24 Siemens AM, Dynes JJ, Chang W (2020) Environ Technol 0:1-41. https://doi.org/10.1080/09593330.2020.1721567

25 Naidu G, Jeong S, Choi Y, Song MH, Oyunchuluun U, Vigneswaran S (2018) J Clean Prod 174:1079-1088. https://doi.org/10.1016/j.jclepro.2017.11.042

26 Laxman K, Myint MTZ, Al Abri M, Sathe P, Dobretsov S, Dutta J (2015) Desalination 362:126-132. https://doi.org/10.1016/j.desal.2015.02.010

27 Fathy M, Mousa MA, Moghny TA, Awadallah AE (2017) Appl Water Sci 7:4427-4435. https://doi.org/10.1007/s13201-017-0588-3

28 Pearce M, Brennan F (2015) Desalination 360:13-18. https://doi.org/10.1016/j.desal.2014.12.020

29 Guo X-F, Ji Z-Y, Yuan J-S, Zhao Y-Y, Liu J (2016) Desalin Water Treat 57:6829-6837. https://doi.org/10.1080/19443994.2015.1010590

МАЗМҰНЫ – СОДЕРЖАНИЕ

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