

INVESTIGATION OF THE SORPTION CAPACITY OF POLYVINYLPIRROLIDONE COPOLYMERS AS THE BASIS OF HYDROGEL COSMETIC MASKS WITH PLANT BIOMASS EXTRACTS

Sofiia Suberlyak¹, ✉, Romana Petrina¹, Oleksandr Grytsenko¹,
Nataliia Baran¹, Andriy Komar¹, Bohdan Berezhnyy¹

<https://doi.org/10.23939/chcht16.04.555>

Abstract. The possibility of using hydrogels based on copolymers of polyvinylpyrrolidone with 2-hydroxyethylmethacrylate to saturate them with plant extracts was established. Hydrogel materials were obtained with extracts of *Calendula officinalis* and *Arnica montana*. The sorption capacity of the hydrogels regarding the extract data was determined. The bactericidal and fungicidal activity of the obtained hydrogel materials with extracts of *Calendula officinalis* and *Arnica montana* on bacterial strains of *Escherichia coli*, *Staphylococcus aureus* and fungal strains of *Candida tenuis*, *Aspergillus niger* were investigated.

Keywords: hydrogels, polyvinylpyrrolidone, 2-hydroxyethylmethacrylate, swelling, cosmetic masks, flavonoids, antibacterial activity, antifungal activity.

1. Introduction

Nowadays cosmetics based on natural raw materials are popular in Ukraine and around the world. Hydrogel masks and eye patches deserve special attention.¹ Natural and synthetic hydrogel products are proposed as bases, which must be compatible with biological systems that are stable in the aquatic environment, must have the ability to absorb and retain moisture and release the filler in a controlled manner. It is also necessary to take into account the technological features of hydrogel production and the formation of a film product based on it. The possible fillers can be extracts of medicinal plants that contain a complex of biologically active substances, namely flavonoids, carotenoids, vitamins, *etc.*, which affect the activity,

namely anti-inflammatory, wound healing, antibacterial, antioxidant and others.²⁻⁴ Hydrogels are currently used to make various implants, contact lens materials, bandages for the treatment of wounds and burns, controlled release of drugs, *etc.*⁵⁻¹⁰

The use of polymeric hydrogel materials (mainly in film form) as transdermal long-acting therapeutics is widespread.¹¹⁻¹³ The use of film hydrogel therapies is applied due to the prolonged active action because of the controlled diffusion of drugs from the film volume. This property of the films provides a reduction in a single therapeutic dose. In addition, hydrogel films are permeable to air moisture and oxygen, which prevents the formation of bedsores on the diseased surface of the body.

Due to the ability to prolong the action, natural and synthetic hydrogels are used as materials for various cosmetics productions.^{14,15} Cosmetic masks based on hydrogels are currently popular in Korea and Japan, but there is low production of such masks in Ukraine. This mask maintains the optimal hydrolipid level of the epidermis, prevents the evaporation of moisture, has a hygienic, therapeutic and cosmetic effect. Polymer hydrogels are promising for use as cosmetic masks due to their unique porous structure, which in combination with the presence of hydrophilic functional groups, provides swelling of the polymer matrix in water and other polar solvents, resulting in high permeability to dissolve low molecular weight substances.¹⁶⁻¹⁸ The sorption capacity, osmotic permeability, as well as selective sorption and desorption capacity of film hydrogel agents are considerable values.¹⁹⁻²¹ Sorption capacity and selective permeability significantly depend on the chemical structure of the hydrogel polymer matrix, as well as the degree of crosslinking of its macromolecules. The level of sorption and desorption of active components may also depend on the pH value of the environment during saturation of the polymer matrix and during desorption when the saturated film comes into contact with the environment.¹⁶

¹ Lviv Polytechnic National University, 12, S.Bandery St., Lviv, 79013, Ukraine

✉ sophiia.a.suberliak@lpnu.ua

© Suberlyak S., Petrina R., Grytsenko O., Baran N., Komar A., Berezhnyy B., 2022

Materials that can be the basis of cosmetic masks should be characterized by the ability to swell in water and alcohol solutions, high permeability to biologically active substances from extracts, as well as high strength and elasticity. If taken into consideration the daily use, especially on sensitive areas of the face, hydrogel cosmetics, above all, should be non-toxic and should not cause allergies. At the same time, it is necessary to take into account the technological features of hydrogel production and the formation of a film product based on it.

Hydrogels are obtained both from natural organic raw materials²²⁻²⁴ and from synthetic polymers.²⁵⁻²⁹ Hydrogels based on poly-2-hydroxyethyl methacrylate (pHEMA)³⁰ and its copolymers^{31,32} are distinguished from a wide range of synthetic highly hydrophilic polymers. pHEMA and its copolymers are characterized by a high degree of water absorption, the ability to absorb low molecular weight substances, high biocompatibility, and low thrombogenicity.³⁰

Grafted copolymers of polyvinylpyrrolidone (PVP) with hydroxymethacrylates, for example, copolymers of PVP with HEMA (pHEMA-gr-PVP) are of special attention. pHEMA-gr-PVP copolymers are obtained *via* grafted radical or ion-radical copolymerization, which is carried out in bulk or in an aqueous medium.^{16,33-36} PVP has attracted much attention due to its impressive properties, such as biocompatibility, nontoxicity, solubility in water and many organic solvents, pH stability, affinity to complex both hydrophobic and hydrophilic substances, and chemically inert status in physiological reactions.³⁷ The use of PVP opens additional opportunities for the synthesis and stabilization of metal nanopowders, modification of various substances and materials, improvement of modern technologies, production of new functional materials, and the respective expansion of their fields of use.³⁸⁻⁴²

Preliminary research has established the prospects for the use of materials based on pHEMA-gr-PVP copolymers⁴³⁻⁴⁸ in the biomedical field, which is possible due to their high sorption capacity, elasticity, stability of form in solvents, and biotolerance. These characteristics make it possible to saturate pHEMA-gr-PVP copolymers with medicinal plant extracts and obtain materials that can be used for prolonged enrichment of the skin with biologically active components. The use of *C. officinalis* and *A. montana* extracts for this purpose will allow developing the hydrogel cosmetic masks with antioxidant, antimicrobial, antitumor, and anti-inflammatory properties to maintain skin health or for irritation, inflammation, or certain diseases. At the same time, one of the main tasks in the process of developing the obtaining technology of cosmetic film products with predictable content of therapeutic extracts is a knowledge of the principles of pHEMA-gr-PVP copolymers sorption in water and water-

ethanol solutions. Therefore, the aim of this work was to investigate the sorption capacity of pHEMA-gr-PVP copolymers in relation to water and water-ethanol solutions and to obtain on their basis cosmetic film products with extracts of *C. officinalis* and *A. montana*.

2. Experimental

2.1. Materials

To obtain the hydrogel matrix we used 2-hydroxyethyl methacrylate (Sigma Chemical Co), purified and distilled in a vacuum (residual pressure 130 N/m², $T_{\text{boiling}} = 351$ K); PVP (AppliChem GmbH) of high purity with MM 12000, previously dried at 338 K in vacuum for 2–3 hours; iron(II) sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (Sigma Chemical Co); seeds and meristems of *Arnica montana* and *Calendula officinalis* plants collected and harvested on the slopes of Hryniava Mountain (Hryniava Range, Ivano-Frankivsk Region) in June 2019 and June 2020.

2.2. Methods

The synthesis of pHEMA-gr-PVP copolymers was carried out in the presence of FeSO_4 at a temperature of 293–298 K in the air for 0.3–1 h (depending on the composition).³³ In order to combine the synthesis stages of the hydrophilic polymer and its subsequent swelling, the polymerization was performed in water. The calculated amounts of PVP and FeSO_4 were weighed according to the given recipe, HEMA and distilled water were dosed by volume. The required amount of PVP was dissolved in HEMA. Stirring of PVP was carried out at room temperature until its complete dissolution with the formation of a homogeneous mixture, without insoluble agglomerates and mechanical inclusions. An aqueous solution of iron(II) sulfate was prepared separately and mixed with the resulting mixture. The obtained starting composition was dosed into a cylindrical shape of the centrifugal unit. Films based on pHEMA-gr-PVP copolymers were obtained with a thickness of 0.5–1.5 mm by centrifugal molding.

For sterilization, the obtained films were irradiated with ultraviolet for 0.25 h (Portable UV sterilizer W81, $\lambda = 253.7$ nm); washed in 1.5 % sodium bicarbonate solution at a temperature of 318–323 K and washed at the same temperature in distilled water. Before use, the prepared film must be hydrated in distilled water for at least 2 h. The films were stored in distilled water in a hermetic container until used as a polymer matrix for saturation with therapeutic alcohol extract, antimicrobial and antiseptic drugs.

First, the plant material was washed with tap water for 10 min. Then sterilization was performed according to

the following protocol: 70 % ethanol (30 s), 10 % – 15 % – 20 % solutions of sodium hypochlorite (“Bleach”) (10 min, 15 min, 20 min) were washed in sterile distilled water for 20 min. Plant biomass was obtained using a biotechnological method of tissue culture on agar medium Murashige-Skuga with growth regulators of naphthylacetic (NAA), indoleacetic (IAA) acids and kinetin (K). Plant biomass was obtained *in vitro* at a temperature of 298 K, illumination of 2000 lux, and photoperiod 16/8. Extracts of *C. officinalis* and *A. montana* were obtained by infusing biomass in ethanol for 7 days with the ratio of raw materials : extractant = 1:10 at room temperature.

Samples in the form of disks with a diameter of 10 mm and thickness of 1.2 mm were cut from the obtained films, which later were saturated with water, water-ethanol solutions and water-ethanol plant extracts: extraction ratio hydrogel film : extract = 1:5 (w/wt). 70 % ethanol solution was used as a control.

The kinetics of swelling and drying were determined using the degree of water absorption α , g(H₂O)/g(p) and the degree of drying D , g(H₂O)/g(p). α and D at time t were determined, respectively, by the ratio of the liquid mass absorbed by the polymer during swelling and the liquid mass lost by the polymer during drying to the mass of dry polymer (m_0):

$$\alpha_t = (m_{t(s)} - m_0) / m_0 \quad (1)$$

$$D_t = (m_{t(d)} - m_0) / m_0 \quad (2)$$

where $m_{t(s)}$ is the mass of the swollen sample at time t , g;

$m_{t(d)}$ is the mass of the dried sample at time t , g;

Boundary water absorption (W , %) was determined by weight method as a difference between dry (m_0 , g) and swollen (m_s , g) samples:

$$W = \frac{m_s - m_0}{m_s} \cdot 100 \quad (3)$$

Hydrogel swelling coefficient was determined as a ratio of sizes of dry (d_0 , mm) and swollen (d_s , mm) samples:

$$k = \frac{d_s}{d_0} \quad (4)$$

The conditional porosity of the hydrogel materials P , % was determined by the formula:

$$P = (m_s - m_0) / V_s \cdot \rho_{H_2O} \quad (5)$$

where V_s is the volume of the swollen sample; ρ_{H_2O} is a solvent density (water).

Medical ethanol (70 %) and ethanol diluted with distilled water to 40 % concentration were used to study the process of saturation of the hydrogel film with a water-ethanol mixture. Samples of the same shape and size were cut out of the hydrogel film, which was equally swollen in water. The research was carried out by the

weight method. Weighing accuracy was $\pm 5 \cdot 10^{-5}$ g. The obtained samples were weighed before the study. Saturated sample weight was denoted as m_s , (g). The degree of swelling (α_{et}) in alcohol was determined by the alcohol content:

$$\alpha_{et} = \frac{m_{et} - m_s}{m_{et}} \cdot 100\% \quad (6)$$

where m_{et} is the mass of the sample after swelling in water-ethanol solution for 120 min.

Samples dried for 30 min at temperatures of 308 K and 318 K were also used for the research. Weight of dried samples, respectively, were denoted as m_d^{308} and m_d^{318} . The prepared samples were placed in an alcoholic solution at room temperature and incubated for $\tau = 30$ min, $\tau = 60$ min and $\tau = 120$ min. After exposure, the samples were weighed and the following values were obtained: m_{et}^{30} , m_{et}^{60} та m_{et}^{120} .

$$\alpha_{et}^\tau = \frac{m_{et}^\tau - m_d^{308(318)}}{m_{et}^\tau} \cdot 100\% \quad (7)$$

The total content of flavonoids in water-ethanol plant extracts was determined on the basis of the formation of a flavonoid-aluminum complex. 0.5 mL of 2 % ethanol AlCl₃ solution was added to 0.5 mL of extract solution and maintained for 1 h at room temperature. The optical density was measured at 420 nm in a cuvette with a layer thickness of 10 mm on a spectrophotometer Ulab108UV. In parallel, the optical density of a standard quercetin sample solution was measured on a spectrophotometer under the same conditions. The yellow color of the investigated solutions indicated that the extracts contained flavonoids, the total content of which was calculated from the concentration of quercetin (mg · g⁻¹), using the equation based on the calibration curve.

3. Results and Discussion

The prerequisite for the developing technology of obtaining cosmetic products based on pHEMA-gr-PVP copolymers and their hydrogels with plant extracts are the high reactivity of HEMA/PVP compositions and the implementability of polymerization in the presence of solvent with the achievement of high porosity of the polymer matrix, which provides ideal conditions for sorption of plant extracts. Copolymers of pHEMA-gr-PVP are characterized by a spatially cross-linked structure formed by blocks of HEMA grafted on PVP, and contain hydrophilic groups: hydroxyl and carbonyl HEMA and carbonyl of pyrrolidone PVP cycle. The number of such groups in the structure of the copolymer, as well as the

porosity of the hydrogel, determine its sorption capacity.⁴⁹ The porous structure promotes the rapid sorption of the solvent due to capillary forces, which causes swelling of pHEMA-gr-PVP copolymers.

The duration of the swelling and drying processes is one of the main technological parameters of obtaining hydrogel cosmetic masks saturated with plant extracts. Swelling time is a technological characteristic that affects the productivity of the technological process of obtaining cosmetic masks, namely, the stage of the hydrogel with plant extracts saturation, which is the longest one. Drying time is an operational characteristic that determines the service life of a product.

Fig. 1 shows the change in time of the degree of water absorption and the degree of drying of pHEMA-gr-PVP copolymers depending on the formulation of the

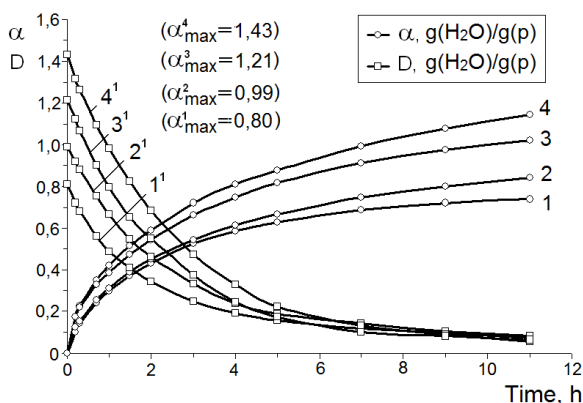


Fig. 1. Effect of the original composition on the kinetics of changes in the degree of swelling α (curves 1-4) and drying D (curves 1¹-4¹) for pHEMA-gr-PVP copolymers. T = 298 K.

Composition formulation of HEMA:PVP, mass parts:
1, 1¹ – 90:10; 2, 2¹ – 80:20; 3, 3¹ – 70:30; 4, 4¹ – 60:40

In some cases, the task is to quickly remove moisture from the hydrogel volume, in others – it is necessary to ensure the longest possible stay of the material in the swollen state. The nature of the kinetics of moisture loss of hydrogel material is similar to the rate of water sorption, which depends on the PVP content in the original composition (Fig. 1, curves 1¹-4¹), namely, on the content of pores remaining after washing in the hydrogel volume. If for maximum water absorption, samples with different composition formulation need 12–24 h, then during drying even at 298 K a significant part of moisture is lost after 7–8 h.

As the results show (Table 1), with increasing PVP content in the original composition, water absorption, swelling coefficient and conditional porosity of the synthesized pHEMA-gr-PVP copolymers increase as well. Temperature has an ambiguous influence on the kinetics of swelling and drying of hydrogels (Fig. 2). At the initial stages of water sorption, the rate of water absorption

original composition. Samples with a thickness of 1.3 ± 0.1 mm were used for research. According to research results, the degree of swelling naturally increases with increasing PVP content in the original composition, *i.e.*, with an increasing number of hydrophilic groups in the copolymer structure (Fig. 1, curves 1-4). In addition, the degree of swelling depends on the effectiveness of PVP grafting – non-grafted PVP is washed away during hydration; this forms cavities and improves the solvent sorption.⁵⁰ The maximum degree of swelling (α_{max}) of the samples with different compositions under normal conditions occurs after 24 h.

Along with the ability to swell, the rate of solvent release, in this case – water, is an important technological parameter in the processes of forming products from hydrogel materials.

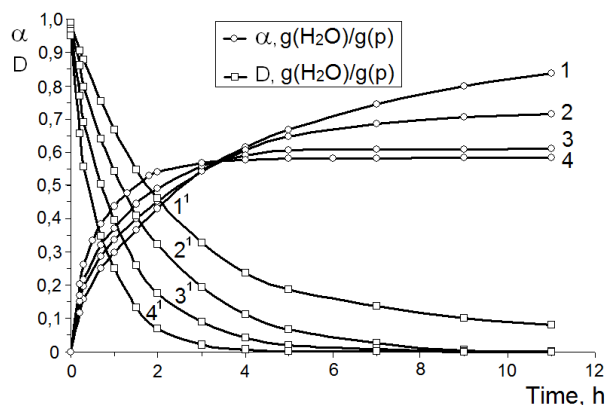


Fig. 2. Effect of temperature on the kinetics of changes in the degree of swelling (α) and drying (D) for copolymers (HEMA:PVP=80:20, mass parts): 1, 1¹ – 298 K; 2, 2¹ – 313 K; 3, 3¹ – 333 K; 4, 4¹ – 353 K

increases with increasing temperature and, naturally, the duration of the limiting swelling and the limiting degree of swelling decrease. The energy of macromolecules physical interaction with solvent molecules is much less than the energy of macromolecules interaction with each other. As the temperature increases, the binding of water decreases due to the increase in the kinetic energy, which causes the compression of the hydrogel.

Therefore, in the process of obtaining film hydrogel cosmetic products, swelling of the copolymers must be carried out at room temperature, which will provide the maximum possible degree of water absorption. During the drying of swollen hydrogels, the increase in temperature increases the rate of water loss (Fig. 2, curves 1¹, 2¹, 3¹, 4¹). There are two types of water in the copolymer structure – free and physically bound. During the increasing temperature, the intensity of drying is affected specifically by the evaporation rate of free water.

Table 1. Effect of the original composition formulation on the swelling ability for pHEMA-gr-PVP copolymers ($T = 298 \text{ K}$, $[\text{FeSO}_4] = 0.01 \%$; composition : $\text{H}_2\text{O} = 1 : 1$)

Composition formulation, mass parts		$W, \%$	k	$P, \%$
HEMA	PVP			
90	10	48	1.19	53
80	20	52	1.28	66
70	30	63	1.34	76
60	40	69	1.35	84

Notes: W is a water content; k is a swelling coefficient; P is a conditional porosity

It is important from a technological point of view to study the kinetics of water absorption and drying depending on the thickness of the hydrogel sample (Fig. 3). With the knowledge of the dependence of the change in the kinetics of swelling (drying) per 1 mm of product thickness, it is possible to calculate in advance the duration of hydration and drying of products with different thicknesses.

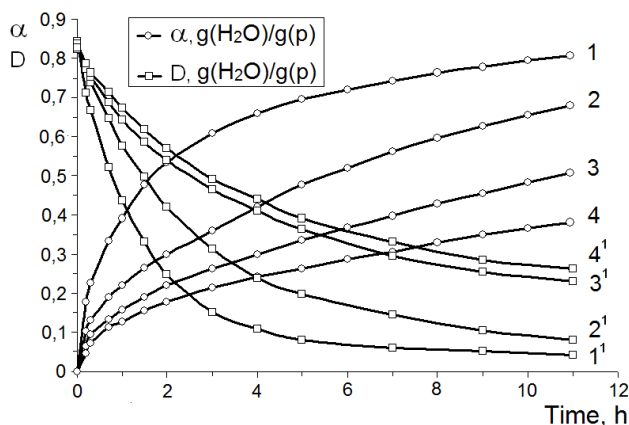


Fig. 3. Effect of hydrogel sample thickness on kinetics of change in degree of swelling (α) and drying (D) for copolymers (HEMA:PVP=80:20, mass parts): 1, 1¹ – 1 mm; 2, 2¹ – 2 mm; 3, 3¹ – 3 mm; 4, 4¹ – 4 mm

In order to the hydrogel film attain its healing properties, it is often saturated with medicinal plants extracts or synthetic drugs solutions. These agents are dissolved in ethanol or in water-ethanol solutions. It is important in this regard to establish the technological conditions for the implementation of the saturation stage. Extracts are prepared using ethanol of various concentrations. Solutions of medicinal substances can also be of different concentrations. As a result, it is important to determine how the concentration of alcohol affects the saturation of the hydrogel. In addition, the sorption of extracts will be affected by the degree of saturation of the hydrogel with water. The hydrogel sample may be equilibrium swollen in water or partially saturated when dried. Therefore, the conditions of sample preparation

before saturation with ethanol solution are important in technological terms.

Copolymers of PVP with HEMA are characterized by different amounts of sorption and osmotic permeability for organic substances, depending on their structure.¹⁶ This value is less than the sorption of water-soluble low molecular weight inorganic substances. The difference in the sorption of organic and inorganic substances is due to the physical binding of organic compounds directly with the surface of the hydrogel. Thus, when replacing water with ethanol, not even fully, the degree of hydrogel swelling increases from 1.2 to 1.6.⁵¹ The interaction of ethanol molecules with macromolecules of the polymer network is accompanied by the blocking of polar groups in the polymer units and, consequently, distancing the chains of the network among each other, which will naturally promote the increase in the diffusion of ethanol-dissolved organic compounds in the hydrogel volume, hence increasing the sorption value.

The water-ethanol mixtures with an alcohol concentration of 40 % and 70 % were used for the research. Three types of hydrogel films were used for saturation: 1 – equilibrium swelled in water; 2 – dried for 30 min at a temperature of 308 K; 3 – dried for 30 min at a temperature 318 K. The solution temperature of $\sim 291 \text{ K}$ for saturation was maintained the same in all experiments. Saturation was performed for 30 min, 60 min and 120 min. In all cases, the amount of absorption of the water-ethanol mixture was determined in comparison with the equilibrium swelled samples in water. The average values of the absorption of the water-ethanol solution according to the results of three experiments are shown in Fig. 4. These values of absorption characterize the degree of hydrogels swelling and indicate their high rate of swelling in alcoholic solutions.

Studies have shown that equilibrium saturated in water hydrogel additionally absorbs more than 41 wt. % of ethanol solution, even if a solution with an ethanol low concentration is used. This is the result of the higher energy of the alcohol interaction with the matrix, due to which there is a straightening of the polymer matrix chains with increasing distance among their individual fragments. In addition, it should be considered that the interaction of alcohol molecules with polar groups of the copolymer such as $-\text{C}=\text{O}$ and $-\text{OH}$ occurs. As a result of

this interaction, the polar groups are blocked, which causes the weakening of intermacromolecular physical bonds in the polymer matrix.

In the case of drying the hydrogel at a temperature of 318 K, there is a decrease in the absorption of the water-ethanol mixture. Rapid evaporation of water at elevated temperatures leads to the formation of a dense surface crust, which becomes less permeable to alcohol solution. This phenomenon is more pronounced at lower concentrations of ethanol.

To create hydrogel cosmeceutical masks based on hydrogel-plant extract complexes, it is necessary to use as a matrix hydrogel material and ethanol extracts of *Arnica montana* and *Calendula officinalis* biomass with different concentrations of ethanol. As a result, it is important to determine how the alcohol concentration affects the hydrogel saturation.

Biomass of *Arnica montana* and *Calendula officinalis* was obtained by standard methods *in vitro* on Murasige-Skuga medium. The composition and ratio of growth regulators were optimized for maximum biomass production, namely 1.0 mg / indoleacetic acid (IAA), 0.2 mg / naphthylacetic acid (NAA) and 0.5 mg / kinetyn for *Arnica montana* and 3.0 mg / IAA, 0.5 mg / NAA and 0.1 mg / kinetyn for *Calendula officinalis* (Table 2). The increase in biomass was 35 g of dry material per 1 L of nutrient medium for 42 days of cultivation for *Arnica montana* and 56 g of dry material per 1 L of nutrient

medium for 30 days of cultivation for *Calendula officinalis*.

Plant biomass obtained *in vitro* was used to obtain water-ethanol extracts. 20 %, 40 %, 70 % and 96 % ethanol solutions were used as extractants; biomass: extractant ratio was 1:10; extraction was carried out by infusion for 7 days at room temperature. The dependence of extract content in the hydrogel-plant complex and swelling coefficients on the ethanol concentration are shown in Table 3.

As can be seen from the results, the absorption of water-ethanol extracts is higher than the absorption of water (Table 1, Fig. 4). The extract content and the coefficient of swelling in water-ethanol extracts are higher than in studies of copolymers with water. *C. officinalis* extract is better absorbed by the pHEMA-gr-PVP copolymer than *A. montana* extract.

Also, from the conducted researches it is possible to draw a conclusion that the highest content of an extract in the hydrogel is received when using 70 % of ethanol: for *Arnica montana* – 58 %, for *Calendula officinalis* – 64 %. There are also the highest coefficients of swelling: for *Arnica montana* – 1.33, for *Calendula officinalis* – 1.35. For further studies, 70 % water-ethanol plant extracts were used and the dry material content was determined, which was 82.63 and 105.27 mg OE/g of dry mass of flavonoids in terms of quartcetin for *C. officinalis* extract and *A. montana* extract, respectively.

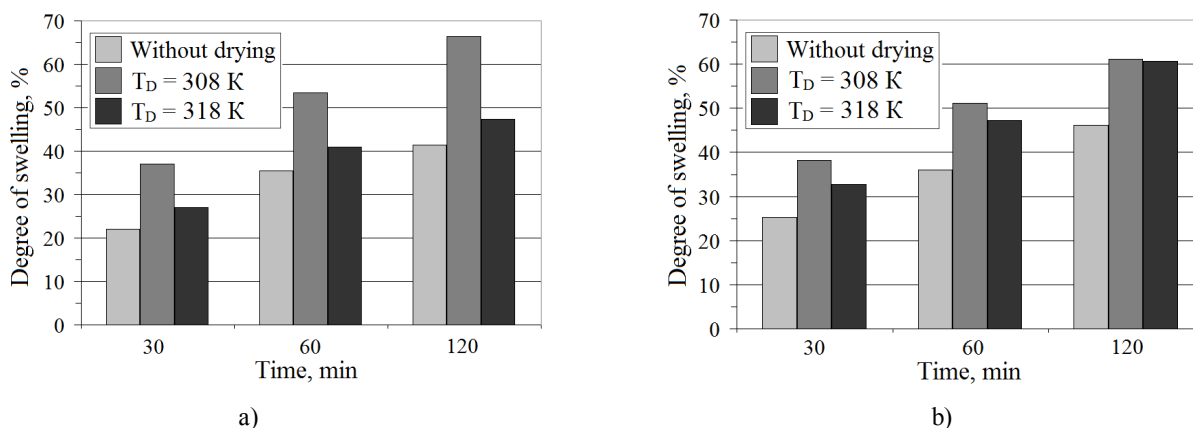


Fig. 4. Dependence of hydrogels swelling degree in the water-ethanol solutions on the swelling conditions (HEMA : PVP = 80:20, mass parts, drying time $\tau_D = 30$ min)
Alcohol content in water-ethanol solution: a – 40 %; b – 70 %

Table 2. Composition and concentration of phytohormones at the stage of obtaining callus biomass

Objects of research	Concentration of phytohormones, mg/L		
	NAA	IAA	kinetyn
<i>Arnica montana</i>	0.2	1.0	0.5
<i>Calendula officinalis</i>	0.5	3.0	0.1

Table 3. Dependence of extracts content and swelling coefficients in hydrogel materials on ethanol concentration and plant species (HEMA : PVP = 80:20 mass parts)

Sample	Plant species	Ethanol concentration, %	W_{e_2} , %	k
1	<i>Arnica montana</i>	20	36	1.20
2		40	42	1.26
3		70	58	1.33
4		96	26	1.12
5	<i>Calendula officinalis</i>	20	48	1.25
6		40	52	1.32
7		70	64	1.35
8		96	32	1.18

Notes: W_e is an extract content; k is a swelling coefficient

Table 4. Diametrical proportions of bacterial and fungal strains lysis zones on extracts and hydrogels saturated with plant extracts

Solutions	Diameter of the zone of growth inhibition, mm			
	<i>E. coli</i>	<i>St. aureus</i>	<i>A. niger</i>	<i>C. tenuis</i>
Extract <i>Calendula officinalis</i> *	8.5	5.2	8.0	3.0
pHEMA-gr-PVP/ <i>Calendula officinalis</i> **	19.0	17.5	19.2	15.2
Extract <i>Arnica montana</i> *	10.2	17.8	9.5	12.8
pHEMA-gr-PVP/ <i>Arnica montana</i> **	22.0	28.4	20.0	25.0

* The disk-diffusion method.

** The method of wells in the agar medium.

Water-ethanol extracts of *Arnica montana* and *Calendula officinalis* have bactericidal and fungicidal properties, therefore the obtained hydrogel-extract complexes were investigated for bactericidal and fungicidal activity. The bactericidal effect was investigated using the disk-diffusion method, where hydrogel composites saturated with plant extracts were used as disks. And for comparison, the bactericidal effect of the same extracts was determined using the method of wells in an agar medium. It was established that the obtained complexes are characterized by higher bactericidal activity than the plant extracts themselves. The zones of growth retardation of cultures of *St. aureus* and *E. coli* bacteria in comparison with the samples saturated with *A. montana* extract, are slightly less noticeable with the *C. officinalis* extract sample and fungi *C. tenuis*. The most detectable effect was observed for bacteria of the genus *St. aureus*, with significant areas of growth retardation ($d = 28.4$ mm for *A. montana* and $d = 17.5$ mm for *C. officinalis*). In comparison, in the study of extracts that were not included in the complex with the hydrogel, we obtained only slight growth retardation of *E. coli* and *St. aureus* (for *A. montana* 70% extract $d = 10.2$ mm and 17.8 mm, respectively, for *C. officinalis* 70% extract $d = 8.5$ mm and 5.2 mm, respectively).

The results of bactericidal and fungicidal activity are shown in Table 4.

The research results show that the obtained hydrogel-extract complexes of *C. officinalis* and *A. montana* plants enhance the bactericidal action of the

extracts. It was found that used hydrogel materials have antibacterial and fungicidal properties; high sensitivity of microorganisms to the recommended hydrogel materials based on pHEMA-gr-PVP copolymers and plant extracts retain in all test-cultural areas. The results obtained in a comparative study showed that the activity of the complexes is not inferior, and in some cases exceeds the activity of the *C. officinalis* and *A. montana* extracts.

4. Conclusions

Studies have shown that copolymers of 2-hydroxyethylmethacrylate with polyvinylpyrrolidone by their structural characteristics, ability to absorb water and water-ethanol solutions, as well as permeability to low molecular weight substances, can be used for sorption of plant extracts and the creation the hydrogel cosmetic film products on their basis. It was investigated that macroporous polymer hydrogels based on pHEMA-gr-PVP copolymers are characterized by high values of equilibrium swelling and conditional porosity. It was shown that by changing the ratio of components in the original HEMA/PVP composition and its solvent content, there is a possibility to change the porosity of hydrogels, as well as the rate of sorption of water and water-ethanol solutions.

Saturation of pHEMA-gr-PVP copolymers with extracts of *C. officinalis* and *A. montana* provided the possibility of obtaining hydrogel materials with antimicrobial and fungicidal activity, which was confirmed

by testing with the bacteria *Escherichia coli*, *Staphylococcus aureus* and fungi *Candida tenuis*, *Aspergillus niger*.

References

- [1] Nilforoushzadeh, M.A.; Amirkhani, M.A.; Zarrintaj, P.; Moghaddam, A.S.; Mehrabi, T.; Alavi, S.; Sisakht, M.M. Skin Care and Rejuvenation by Cosmeceutical Facial Mask. *J. Cosmet. Dermatol.* **2018**, *17*(5), 693–702. <https://doi.org/10.1111/jocd.12730>
- [2] Konechna, R.; Khropot, O.; Petrina, R.; Kurka, M.; Gubriy, Z.; Novikov, V. Research of Antioxidant Properties of Extracts of the Plants and the Callus Biomass. *Asian J. Pharm. Clin. Res.* **2017**, *10*(7), 182–184. <https://doi.org/10.22159/ajpcr.2017.v10i7.18408>
- [3] Krvavych, A.S.; Konechna, R.T.; Mylianych, A.O.; Petrina, R.O.; Fedoryshyn, O.M.; Mykytyuk, O.M.; Semenyshyn, Ye.M.; Atamaniuk, V.M.; Novikov, V.P. Kinetics and Mechanism of the Extraction of Biologically Active Substances from Wild Species *G. Imbricatus*. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2018**, *5*, 111–115.
- [4] Konechna, R.T.; Konechniy, Y.T.; Petrina, R.O.; Shykula, R.H.; Wiczorek, P.; Jasicka-Misiak, I.; Novikov, V.P. Obtaining and research of callus mass of *Gentiana lutea* L. roots. *Res. J. Pharm. Biol. Chem. Sci.* **2015**, *6*(4), 1490–1495.
- [5] Pal, K.; Banthia, A.K.; Majumdar, D.K. Polymeric Hydrogels: Characterization and Biomedical Applications. *Des. Monomers Polym.* **2009**, *12*(3), 197–200. <https://doi.org/10.1163/156855509X436030>
- [6] Samaryk, V.; Varvarenko, S.; Nosova, N.; Fihurka, N.; Musyanovych, A.; Landfester, K.; Popadyuk, N.; Voronov, S. Optical Properties of Hydrogels Filled with Dispersed Nanoparticles. *Chem. Chem. Technol.* **2017**, *11*(4), 449–453. <https://doi.org/10.23939/chcht11.04.449>
- [7] Hoffman, A.S. Hydrogels for Biomedical Applications. *Adv. Drug Deliv. Rev.* **2012**, *64*, 18–23. <https://doi.org/10.1016/j.addr.2012.09.010>
- [8] Slaughter, B.V.; Khurshid, S.S.; Fisher, O.Z.; Khademhosseini, A.; Peppas, N.A. Hydrogels in Regenerative Medicine. *Adv. Mater.* **2009**, *21*(32–33), 3307–3329. <https://doi.org/10.1002/adma.200802106>
- [9] Hoare, T.R.; Kohane, D.S. Hydrogels in Drug Delivery: Progress and Challenges. *Polymer* **2008**, *49*(8), 1993–2007. <https://doi.org/10.1016/j.polymer.2008.01.027>
- [10] Varvarenko, S.; Voronov, A.; Samaryk, V.; Tarnavchyk, I.; Nosova, N.; Kohut, A.; Voronov, S. Covalent Grafting of Polyacrylamide-Based Hydrogels to a Polypropylene Surface Activated with Functional Polyperoxide. *React. Funct. Polym.* **2010**, *70*(9), 647–655. <https://doi.org/10.1016/j.reactfunctpolym.2010.05.014>
- [11] Lu, H.; Yuan, L.; Yu, X.; Wu, Ch.; He, D.; Deng, J. Recent Advances of on-Demand Dissolution of Hydrogel Dressings. *Burns Trauma* **2018**, *6*(35), 1–13. <https://doi.org/10.1186/s41038-018-0138-8>
- [12] Larrañeta, E.; Stewart, S.; Ervine, M.; Al-Kasasbeh, R.; Donnelly, R. Hydrogels for Hydrophobic Drug Delivery. Classification, Synthesis and Applications. *J. Funct. Biomater.* **2018**, *9*(1), 13–33. <https://doi.org/10.3390/jfb9010013>
- [13] Hennink, W. E.; Kim, S. W.; Feijen, J. Inhibition of Surface Induced Coagulation by Preadsorption of Albumin-Heparin Conjugates. *J. Biomed. Mat. Res.* **1984**, *18*(8), 911–926. <https://doi.org/10.1002/jbm.820180806>
- [14] Perugini, P.; Blevé, M.; Redondi, R.; Cortinovis, F.; Colpani, A. *In vivo* Evaluation of the Effectiveness of Biocellulose Facial Masks as Active Delivery Systems to Skin. *J. Cosmet. Dermatol.* **2019**, *19*(3), 725–735. <https://doi.org/10.1111/jocd.13051>
- [15] Pacheco, G.; De Mello, C.V.; Chiari-Andréo, B.G.; Isaac, V.L.B.; Ribeiro, S.J.L.; Pecoraro, É.; Trovatti, E. Bacterial Cellulose Skin Masks-Properties and Sensory Tests. *J. Cosmet. Dermatol.* **2018**, *17*(5), 840–847. <https://doi.org/10.1111/jocd.12441>
- [16] Suberlyak, O.; Skorokhoda, V. Hydrogels Based on Polyvinylpyrrolidone Copolymers. In *Hydrogels*. Haider, S.; Haider, A., Eds.; IntechOpen; London, 2018; pp 136–214. <https://doi.org/10.5772/intechopen.72082>
- [17] Ahmed, E.M. Hydrogel: Preparation, Characterization, and Applications. *J. Adv. Res.* **2015**, *6*(2), 105–121. <https://doi.org/10.1016/j.jare.2013.07.006>
- [18] Jumadilov, T.; Kondaurov, R.; Imangazy, A.; Myrzakhmetova, N.; Saparbekova, I. Phenomenon of Remote Interaction and Sorption Ability of Rare Cross-Linked Hydrogels of Polymethacrylic Acid and Poly-4-vinylpyridine in Relation to Erbium Ions. *Chem. Chem. Technol.* **2019**, *13*(4), 451–458. <https://doi.org/10.23939/chcht13.04.451>
- [19] Suberlyak, O.; Melnyk, J.; Baran, N. High-Hydrophilic Membranes for Dialysis and Hemodialysis. *Engineering Biomaterials* **2007**, *63*, 18–19.
- [20] Skorokhoda, V.; Semenyuk, V.; Melnyk, Y.; Suberlyak, O. Hydrogels Penetration and Sorption Properties on the Substances Release Controlled Processes. *Chem. Chem. Technol.* **2009**, *3*(2), 117–121. <https://doi.org/10.23939/chcht03.02.117>
- [21] Maikovych, O.; Nosova, N.; Yakoviv, M.; Dron, I.; Stasiuk, A.; Samaryk, V.; Varvarenko, S.; Voronov, S. Composite Materials Based on Polyacrylamide and Gelatin Reinforced with Polypropylene Microfiber. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2021**, *1*, 45–54. <https://doi.org/10.32434/0321-4095-2021-134-1-45-54>
- [22] Popadyuk, N.; Zhlobko, O.; Donchak, V.; Harhay, Kh.; Budishevska, O.; Voronov, A.; Kohut, A.; Voronov, S. Ionically and Covalently Crosslinked Hydrogel Particles Based on Chitosan and Poly(ethylene glycol). *Chem. Chem. Technol.* **2014**, *8*(2), 171–176. <https://doi.org/10.23939/chcht08.02.171>
- [23] Barman, A.; Das, M. Cellulose-Based Hydrogels for Pharmaceutical and Biomedical Applications. In *Cellulose-Based Superabsorbent Hydrogels*. Polymers and Polymeric Composites: A Reference Series. Mondal, M., Ed.; Springer; Cham, 2018, 1103–130. https://doi.org/10.1007/978-3-319-76573-0_37-1
- [24] La Gatta, A.; Salzillo, R.; Catalano, C.; D'Agostino, A.; Pirozzi, A.V.A.; De Rosa, M.; Schiraldi, C. Hyaluronan-based hydrogels as dermal fillers: The Biophysical Properties That Translate into a "Volumetric" Effect. *PLoS ONE* **2019**, *14*(6), e0218287. <https://doi.org/10.1371/journal.pone.0218287>
- [25] Gibas, I.; Janik, H. Review: Synthetic Polymer Hydrogels for Biomedical Applications. *Chem. Chem. Technol.* **2010**, *4*(4), 297–304. <https://doi.org/10.23939/chcht04.04.297>
- [26] Nosova, N.G.; Samaryk, V.J.; Varvarenko, S.M.; Ferens, M.V.; Voronovska, A.V.; Nagomyak, M.I.; Khomyak, S.V.; Nadashkevych, Z.J.; Voronov, S.A. Porous Polyacrylamide Hydrogels: Preparation and Properties. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2016**, *5–6*, 78–86.
- [27] Jumadilov, T.; Abilov, Z.; Grazulevicius, J.; Zhunusbekova, N.; Kondaurov, R.; Agibayeva, L.; Akimov, A. Mutual Activation and Sorption Ability of Rare Cross-Linked Networks in Intergel System Based on Polymethacrylic Acid and Poly-4-vinylpyridine Hydrogels in Relation to Lanthanum Ions. *Chem. Chem. Technol.* **2017**, *11*(2), 188–194. <https://doi.org/10.23939/chcht11.02.188>
- [28] Yevchuk, I.; Demchyna, O.; Kochubey, V.; Romaniuk, H.; Koval, Z. Synthesis and Characterization of Organic-Inorganic Membranes Containing Sulphogroups. *Chem. Chem. Technol.* **2013**, *7*(1), 89–93. <https://doi.org/10.23939/chcht07.01.089>
- [29] Jumadilov, T.; Abilov, Z.; Kondaurov, R.; Himersen, H.; Yeskaliyeva, G.; Akylybekova, M.; Akimov, A. Influence of Hydrogels Initial State on Their Electrochemical and Volume-Gravimetric Properties in Intergel System Polyacrylic Acid Hydrogel and Poly-4-

- vinylpyridine Hydrogel. *Chem. Chem. Technol.* **2015**, *9(4)*, 459–462. <https://doi.org/10.23939/chcht09.04.459>
- [30] Montheard, J.-P.; Chatzopoulos, M.; Chappard, D. 2-Hydroxyethyl Methacrylate (HEMA): Chemical Properties and Applications in Biomedical Fields. *J. Macromol. Sci. C* **1992**, *32(1)*, 1–34. <https://doi.org/10.1080/15321799208018377>
- [31] Malesic, N.; Rusmirovic, J.; Jovasevic, J.; Perisic, M.; Dimitrijevic-Brankovic, S.; Filipovic, J.; Tomic, S. Antimicrobial Hydrogels Based on 2-Hydroxyethyl Methacrylate and Itaconic Acid Containing Silver(I) Ion. *Tehnika* **2014**, *69(4)*, 563–568. <https://doi.org/10.5937/tehnika1404563M>
- [32] Wang, J.; Wu, W. Swelling Behaviors, Tensile Properties and Thermodynamic Studies of Water Sorption of 2-Hydroxyethyl Methacrylate/Epoxy Methacrylate Copolymeric Hydrogels. *Eur. Polym. J.* **2005**, *41(5)*, 1143–1151. <https://doi.org/10.1016/j.eurpolymj.2004.11.034>
- [33] Grytsenko, O.; Dulebova, L.; Suberlyak, O.; Skorokhoda, V.; Spišák, E.; Gajdos, I. Features of Structure and Properties of pHEMA-gr-PVP Block Copolymers, Obtained in the Presence of Fe²⁺. *Materials* **2020**, *13(20)*, 4580–4594. <https://doi.org/10.3390/ma13204580>
- [34] Grytsenko, O.; Pukach, P.; Suberlyak, O.; Moravskiy, V.; Kovalchuk, R.; Berezhnyy, B. Using the Scheffe's Method in the Study of Mathematical Model of Optimization of Polymeric Hydrogels Composite Structures. *Math. Model. Comput.* **2019**, *6(2)*, 258–267. <https://doi.org/10.23939/mmcc2019.02.258>
- [35] Skorokhoda, V. Matrix Polymerization of 2-Hydroxyethylmethacrylate in the Presence of Polyvinylpyrrolidone in Permanent Magnetic Field. *Chem. Chem. Technol.* **2010**, *4(3)*, 191–196. <https://doi.org/10.23939/chcht04.03.191>
- [36] Suberlyak, O.V.; Baran, N.M.; Melnyk, Y.Y.; Grytsenko, O.M.; Yatsulchak, G.V. Regularities of Strengthening of Film Hydrogel Membranes Based on 2-Hydroxyethylmethacrylate Copolymers and Polyvinylpyrrolidone. *Funct. Mater.* **2020**, *27(2)*, 329–333. <https://doi.org/10.15407/fm27.02.329>
- [37] Teodorescu, M.; Bercea, M. Poly(vinylpyrrolidone) – a Versatile Polymer for Biomedical and beyond Medical Applications. *Polym. Plast. Technol. Eng.* **2015**, *54(9)*, 923–943. <https://doi.org/10.1080/03602559.2014.979506>
- [38] Grytsenko, O.M.; Suberlyak, O.V.; Moravskiy, V.S.; Gayduk, A.V. Investigation of Nickel Chemical Precipitation Kinetics. *Eastern European J. Enterp. Technol.* **2016**, *1(6)*, 26–31. <https://doi.org/10.15587/1729-4061.2016.59506>
- [39] Krasinskyi, V.; Suberlyak, O.; Dulebova, L.; Antoniuk, V. Nanocomposites on the Basis of Thermoplastics and Montmorillonite Modified by Polyvinylpyrrolidone. *Key Eng. Mater.* **2017**, *756*, 3–10. <https://doi.org/10.4028/www.scientific.net/KEM.756.3>
- [40] Grytsenko, O.; Naumenko, O.; Suberlyak, O.; Dulebova, L.; Berezhnyy, B. V. The Technological Parameters Optimization of the Graft Copolymerization 2-Hydroxyethyl Methacrylate with Polyvinylpyrrolidone for Nickel Deposition from Salts. *Vopr. Khimii i Khimicheskoi Tekhnologii* **2020**, *1*, 25–32. <https://doi.org/10.32434/0321-4095-2020-128-1-25-32>
- [41] Krasinskyi, V.; Suberlyak, O.; Zemke, V.; Klym, Y.; Gaidos, I. The Role of Polyvinylpyrrolidone in the Formation of Nanocomposites Based on Acompatible Polycaproamide and Polypropylene. *Chem. Chem. Technol.* **2019**, *13(1)*, 59–63. <https://doi.org/10.23939/chcht13.01.059>
- [42] Suberlyak, O.V.; Baran, N.M.; Melnyk, Y.Y.; Grytsenko, O.M.; Yatsulchak, H.V. Influence of the Molecular Weight of Polyvinylpyrrolidone on the Physicomechanical Properties of Composite Polyamide Hydrogel Membranes. *Mater. Sci.* **2020**, *55(5)*, 758–764. <https://doi.org/10.1007/s11003-020-00368-3>
- [43] Tang, Q.; Yu, J.-R.; Chen, L.; Zhu, J.; Hu, Z.-M. Preparation and Properties of Morphology Controlled Poly(2-hydroxyethyl methacrylate)/Poly(N-vinyl pyrrolidone) Double Networks for Biomedical Use. *Curr. Appl. Phys.* **2010**, *10(3)*, 766–770. <https://doi.org/10.1016/j.cap.2009.09.012>
- [44] Grytsenko, O.; Pukach, P.; Suberlyak, O.; Shakhovska, N.; Karović, V. Usage of Mathematical Modeling and Optimization in Development of Hydrogel Medical Dressings Production. *Electronics* **2021**, *10(5)*, 620. <https://doi.org/10.3390/electronics10050620>
- [45] Suberlyak, O.; Skorokhoda, V.; Kozlova, N.; Melnyk, Y.; Semenyuk, N.; Chopyk, N. The Polyvinylpyrrolidone Graft Copolymers and Soft Contact Lenses on Their Basis. *ScienceRise* **2014**, *5(3)*, 52–57. <https://doi.org/10.15587/2313-8416.2014.33235>
- [46] Suberlyak, O.; Grytsenko, O.; Baran, N.; Yatsulchak, G.; Berezhnyy, B. Formation Features of Tubular Products on the Basis of Composite Hydrogels. *Chem. Chem. Technol.* **2020**, *14(3)*, 312–317. <https://doi.org/10.23939/chcht14.03.312>
- [47] Jovašević, J.; Dimitrijević, S.; Filipović, J.; Tomić, S.; Mičić, M.; Suljovrujić E. Swelling, Mechanical and Antimicrobial Studies of Ag/P(HEMA/IA)/PVP Semi-IPN Hybrid Hydrogels. *Acta Phys. Pol. A* **2011**, *120*, 279–283. <https://doi.org/10.12693/APhysPolA.120.279>
- [48] Grytsenko, O.; Pukach, P.; Suberlyak, O.; Gaydos, I.; Kushnirchuk, M.; Berezhnyy, B. Mathematical Modeling and Optimization of Technological Parameters of the Obtaining Process of Hydrogel Medical Dressings. Books of Abstracts, 3rd International Conference on Informatics and Data-Driven Medicine, IDDM 2020, Vaxjo, November 19–21, 2020, CEUR Workshop Proceedings, 2753, 170–177.
- [49] Bashty, Y.; Fechan, A.; Grytsenko, O.; Hotra, Z.; Kremer, I.; Suberlyak, O.; Aksimentyeva, O.; Horbenko, Y.; Kotsarenko M. Electrical Elements of the Optical Systems Based on Hydrogel-Electrochromic Polymer Composites. *Mol. Cryst. Liq. Cryst.* **2019**, *672*, 150–158. <https://doi.org/10.1080/15421406.2018.1550546>
- [50] Suberlyak, O.; Hrytsenko, O.; Hishchak, Kh. Influence of the Metal Surface of Powder Filler on the Structure and Properties of Composite Materials Based on the Copolymers of Methacrylates with Polyvinylpyrrolidone. *Mater. Sci.* **2016**, *52*, 155–164. <https://doi.org/10.1007/s11003-016-9938-9>
- [51] Suberlyak, O.; Grytsenko, O. Fundamentals of Technology for Obtaining Metal-Filled Hydrogel Composites. *Rastr-7, Lviv* **2020**, 316.

Received: January 14, 2022 / Revised: February 18, 2022 / Accepted: May 10, 2022

ДОСЛІДЖЕННЯ СОРБЦІЙНОЇ ЗДАТНОСТІ КОПОЛІМЕРІВ ПОЛІВІНІЛПІРОЛІДОНУ ЯК ОСНОВИ ГІДРОГЕЛЕВИХ КОСМЕТИЧНИХ МАСОК З ЕКСТРАКТАМИ БІОМАСИ РОСЛИН

Анотація. Встановлена можливість використання гідрогелів на основі кополімерів полівинілпіролідону з 2-гідроксіетилметакрилатом для насичення їх рослинними екстрактами. Одержано гідрогелеві матеріали з екстрактами *Calendula officinalis* і *Arnica montana*. Визначено сорбційну здатність гідрогелів щодо даних екстрактів та кінетику виходу екстракту (за флавоноїдами). Досліджено бактерицидну та фунгіцидну активність одержаних гідрогелевих матеріалів з екстрактами *Calendula officinalis* і *Arnica montana* на бактерійних штамах *Escherichia coli*, *Staphylococcus aureus* та грибових штамах *Candida tenuis*, *Aspergillus niger*.

Ключові слова: гідрогелі, полівинілпіролідон, 2-гідроксіетилметакрилат, набрякання, косметичні маски, флавоноїди, антибактеріальна активність, антифунгальна активність.