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Study of Hybrid Modification with Humic Acids of Environmentally Safe Biodegradable Hydrogel Films Based on Hydroxypropyl Methylcellulose

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Abstract: The possibility of increasing the complexity of the operational properties of environmentally safe biodegradable polymer hydrogel materials based on hydroxypropyl methylcellulose due to modification by humic acids from lignite is considered. As a result of this research, environmentally safe hybrid hydrogel films with antibacterial properties were received. In the framework of physicochemical studies, it was determined by IR spectroscopy that hydroxypropyl methylcellulose modified with humic acids hybridmaterials are received by the mechanism of matrix synthesis, which is accompanied by hydroxypropyl methylcellulose crosslinking through multipoint interaction with the carboxyl group of humic acids. Regularities in terms of changes in water absorption, gelation time, and mold emergence time regarding the environmentally safe biodegradable polymer hydrogel materials based on hydroxypropyl methylcellulose depending on the humic acid content were revealed. It was established that the optimal humic acid content in environmentally safe biodegradable hydrogel films with bactericidal properties based on hydroxypropyl methylcellulose is 15% by mass. It was also established that the hybrid modification of hydroxypropyl methylcellulose with humic acids allows them to preserve their biodegradation properties while giving them antibacterial properties. The environmentally safe biodegradable hydrogel films with bactericidal properties based on hydroxypropyl methylcellulose and humic acids are superior in their operational characteristics to known similar biodegradable hydrogel films based on natural biopolymers.

Keywords: environmentally safe; biodegradable; hydrogel films; hydroxypropyl methylcellulose; bactericidal properties; humic acids; hybrid; modification

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1. Introduction

Plastics and synthetic polymers, which are primarily made from petroleum or petroleum derivatives, have become more common over the years. Their attractive properties, such as their durability, lightness, low cost, and plasticity have contributed to the mass production of plastics in various configurations and their wide application in various industries [1,2]. Plastic is both a blessing and a curse because, despite its properties, plastic persists in the environment for a long time and is easily transported into the biosphere. In 2020, end users in Europe, Norway, Switzerland, and Great Britain threw 29.5 million tons of plastic away, with about 23% of this plastic waste being sent to landfills [3].

Plastics are degraded by sunlight, oxygen, heat, mechanical stress, and/or enzymes into smaller particles such as microplastics and nanoplastics through abiotic and/or biotic degradation [4]. This plastic waste is much more toxic compared to macroplastics.

Numerous studies have reported the role of microplastics as carriers of chemical pollutants, including heavy metals, pesticides, persistent organic pollutants, and persistent bioaccumulative and toxic substances, etc. [5]. Plastic in the soil negatively changes its physical, chemical, and biological properties. Microplastics in the soil can change its porosity, bulk density, and water-holding capacity. The accumulation of microplastics in the soil can also change its biological properties, such as its organic carbon and nitrogen cycling, nutrient transport, and microbial activity [6]. That is why the most relevant direction in industrial polymer materials science today is the receiving of various biodegradable polymers, materials, and composites based on them. Such biodegradable polymers can be broken down abiotically and/or biologically into carbon dioxide, methane, water, and biomass. Such transformations are called biodegradability [7]. Today, there are a large number of biodegradable polymers that implement the principle of "zero waste" during their entire life cycle: «production-use-disposal» [8,9]. The use of a large assortment of environmentally safe biodegradable polymer matrices allows for the obtaining of materials with sufficient strength and heat resistance, which can be processed into various products and parts for various industries. Composite biodegradable materials obtained due to the interaction of chemically different components, most often inorganic and organic, which form a spatial crystal structure that differs from the structures of the original reagents but often inherits the properties of the original components, are called hybrids [10]. Receiving such biodegradable polymer materials and composites allows for a synergistic effect of useful properties for chemically different components in the finished hybrid which leads to area of such materials application expansion.

Several works have shown [11,12] the potential of modifying biodegradable polymer hydrogel materials (BPHMs) with coal, carbon, and graphene oxide derivatives due to their resulting fluorescent ability, photostability, biocompatibility, and large surface areas. Such modified BPHMs are used to receive effective transdermal systems in biomedical applications [13–17]. The most effective modern hydropolymeric microneedle patches are made up of hydroxypropylmethylcellulose [18], hyaluronic acid [19], carboxymethyl cellulose [20], polyvinylpyrrolidone [21], and polylactic glycolic acid [22]. In our opinion, there is great potential for BPHM functional modification based on hydroxypropyl methylcellulose with coal derivatives—humic acids, graphite, graphene, and others. In our previous works, environmentally safe hybrid biodegradable polymer materials based on gelatin [23], polyvinyl alcohol [24], and hydroxypropyl methylcellulose [25], which were modified with humic acids from Ukrainian brown coal [26], were designed and researched. In these works, the antibacterial effect of humic acids in the researched polymers was also established. However, the modification mechanism of hydroxypropyl methylcellulose with humic acids and its impact on the operational characteristics of environmentally safe biodegradable materials with antibacterial action based on them was not determined.

That is why this article studies the hybrid modification of environmentally safe biodegradable hydrogel films based on hydroxypropyl methylcellulose with humic acids. The tasks of this research was to:

- research the physicochemical features resulting from the hybrid modification of environmentally safe biodegradable hydrogels based on hydroxypropyl methylcellulose with humic acids;
- detect the effect of modification with humic acids on a set of strength-based and operational properties regarding environmentally safe, biodegradable hybrid hydrogel films based on hydroxypropyl methylcellulose.

2. Materials and Methods

2.1. Materials and Reagents

The hydroxypropyl methylcellulose brand was Walocel™, produced by Dow Corning (Dow Corning Inc., Midland, MI, USA). Hydroxypropyl methylcellulose is a natural polymer that dissolves easily and quickly in hot or cold water, forming solutions with different viscosity levels.

The sodium alginate was produced by Qingdao Yingfei Chemical Co (Qingdao Yingfei Chemical Co. Ltd., Shandong, Qingdao, China). Sodium alginate is a linear polysaccharide derivative of alginic acid comprised of 1,4-β-d-mannuronic (M) and α-l-guluronic (G) acids. Humic acids obtained during the extraction of lignite with an alkaline solution of sodium pyrophosphate followed by extraction with a 1% solution of sodium hydroxide and precipitation with mineral acid were used as hybrid modifiers. Table 1 shows the characteristics of the humic acids.

Table 1. Proximate analysis of lignite *.

Proximate Analysis, % wt.			
W^a (%)	A^d (%)	S^d_t (S^{daf}_t) (%)	V^{daf} (V^d) (%)
16.8	48.7	2.08 (2.50)	56.7 (29.1)

* W^a—moisture in the analytical state; A^d—ash content in a dry state; S^d_t (S^{daf}_t)—total sulfur content in a dry state (per organic mass); V^{daf} (V^d)—yield of volatile substances per organic mass (in a dry state).

2.2. Samples Preparation

Environmentally safe, biodegradable hybrid hydrogel materials based on hydroxypropyl methylcellulose (HESBHM based on hydroxypropyl methylcellulose) were received using the watering method with hydroxypropyl methylcellulose solutions at a concentration of 8% wt. by dissolving the polymer in a mass ratio of 8:100 hydroxypropyl methylcellulose: distilled water heated to 90–100 °C. After that, a defined amount of sodium alginate (2.5% wt.) was added to the previously prepared hydroxypropyl methylcellulose (8% wt.) solution and allowed to mix homogeneously on a magnetic stirrer (magnetic stirrer MM-7P). To analyze the properties of the HESBHM based on hydroxypropyl methylcellulose, solutions of hydroxypropyl methylcellulose and sodium alginate were received at different concentrations of humic acids (5, 10, 15% wt.). A total of 20 parallel experiments were carried out for each composition of HESBHM.

2.3. Characterization

IR spectra were obtained on an IR spectrophotometer SPECORD 75 UR at 20–25 °C in the frequency range 4000–500 cm^{-1} under the following conditions: slit—3, recording time—13.2 min., time constant—1 s.

Conductometric studies of polyvinyl alcohol solutions were carried out on a combined TDS-meter HM digital COM-100 (HM Digital Inc., Redondo Beach, CA, USA), scale range:

- Specific conductivity: from 0 to 9990 mkS/cm;
- Temperatures: from 0 to 55 °C;
- Error: ±2%.

Microscopic studies were carried out using the electron microscope Digital Microscope HD color CMOS Sensor (Shenzhen Huahai Hong Communication Technology Co. Ltd., Changzhou, Jiangsu, China).

The viscosity was determined according to ISO 2431. The method is based on determining the viscosity of a solution, with the free flow being taken as the time of continuous flow in seconds of a volume of 50 mL of the test material through a calibrated nozzle with a 4 mm diameter and a VZ-246 viscometer at a certain temperature.

The gelation time was determined by the loss of stickiness time [27].

The water absorption of hydrogel film samples in cold water was carried out according to ISO 62:2008.

Antibacterial properties were determined by the inhibition time of the active growth zones of *Aspergillus niger* (*A. niger*) molds on the surface of HESBHM in a nutrient medium using an electronic microscope, the Digital Microscope HD color CMOS Sensor.

The method described in ISO 846:1997 was used to measure the degree of biodegradation.

3. Results and Discussion

3.1. Rheological and Physical Studies of the Mechanism of Hybrid Modification of Hydroxypropyl Methylcellulose Hydrogels with Humic Acids

The HESBHM conditional viscosity and conductivity dependence of hydroxypropyl methylcellulose on different humic acid contents is shown in Figure 1.

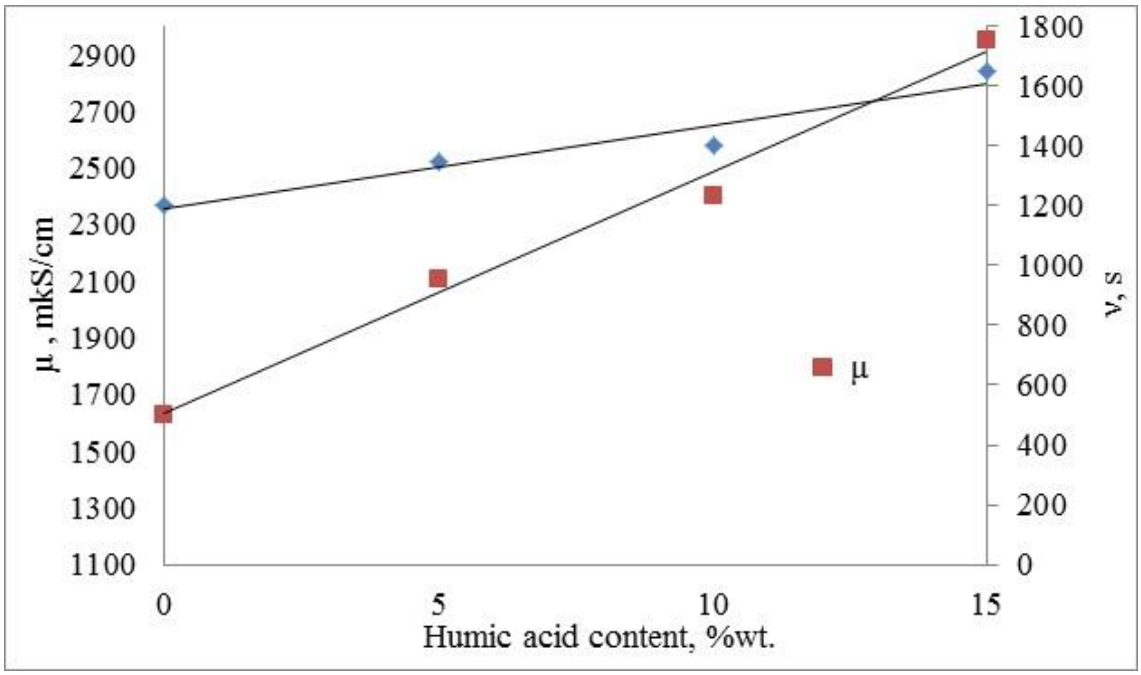

Figure 1. The HESBHM conditional viscosity (ν, s), conductivity dependence, and conductivity (μ, mkS/cm) of hydroxypropyl methylcellulose on the different humic acid contents.

From the data in the Figure 1 it can be seen that there is an increasing HESBHM conditional viscosity and specific electrical conductivity with an increase in humic acid content: from 1200 to 1650 s and from 1630 to 2950 mkS/cm, respectively. Such changes indicate the following effects in terms of modification by humic acids on the structure formation processes of HESBHM:

- more density and rigid network in terms of HESBHM, because an increase in viscosity is actually a measure of the density [28] and stiffness of the network formation in water-soluble polymeric hydrogel materials [29,30];
- the formation of a larger number of agglomerates in HESBHM due more intensive hydration process by a high-density and rigid network of HESBHM, because an increase in specific electrical conductivity is actually a measure of the hydration level by the high-density and rigid network in water-soluble polymeric hydrogel materials [31,32].

The formation of a larger number of agglomerates in the HESBHM is clearly visible from the microscopic studies results (Figure 2): unmodified hydroxypropyl cellulose-sodium alginate systems are homogeneous solutions without visible streaks and inhomogeneities both on the surface and in the volume. At the same time, with an increase in humic acid content, the appearance of visible streaks and inhomogeneities both on the surface and in the volume in the HESBHM occurs.

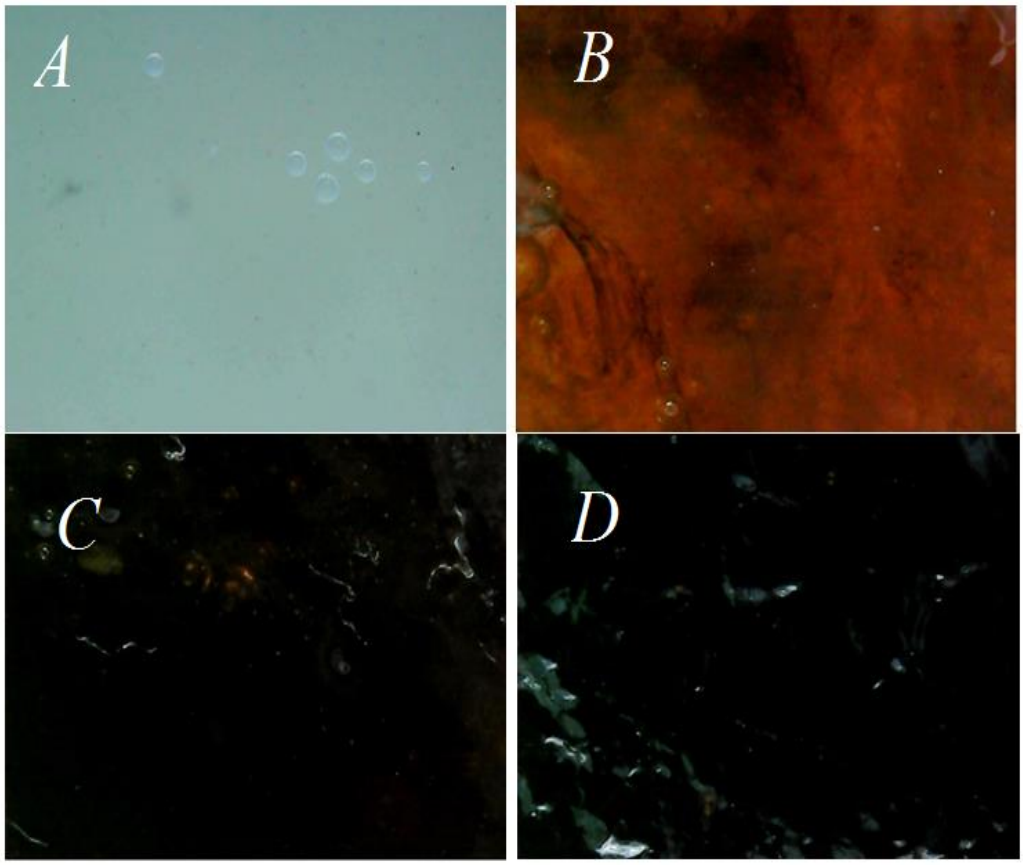

Figure 2. Microscopic studies of HESBHM: (**A**) pure hydroxypropyl methylcellulose and sodium alginate hydrogel; (**B**) hydroxypropyl methylcellulose and sodium alginate hydrogel + 5% wt. of humic acid; (**C**) hydroxypropyl methylcellulose and sodium alginate hydrogel + 10% wt. of humic acid; (**D**) hydroxypropyl methylcellulose and sodium alginate hydrogel + 15% wt. of humic acid.

Furthermore, the IR spectra of the original humic acid, original hydroxypropyl methylcellulose, and hydroxypropyl methylcellulose systems (5% by mass) were investigated by IR analysis (Figure 3 and Table 2). It was found that these functional groups determine the humic acid's ability to act as a hybrid modifier in relation to hydroxypropyl methylcellulose. Among the most characteristic humic acid spectral bands are: phenolic –OH hydroxyl groups at 3380–3400 cm^{-1}, aliphatic bands C–H at 2920–2940 cm^{-1}, symmetric νCOO– carboxyl and νCO (phenolic), and νOH (aliphatic) at 1100 cm^{-1}. The IR spectra of the hydroxypropyl methylcellulose–5% wt. of humic acid, characteristic bands from hydroxypropyl methylcellulose and humic acid are clearly observed, for example, a hydroxyl band at 3100–3600 cm^{-1}, a methyl band at 2750–2900 cm^{-1}, an aromatic C–C band at 1400 and 1600 cm^{-1}, a carboxyl band at approximately 1500–1650 cm^{-1}, and the C–O band at 1000–1150 cm^{-1} [29]. Compared with the IR spectra of hydroxypropyl methylcellulose and humic acid, there was a significant difference in the IR spectrum of the hydroxypropyl methylcellulose–5 wt%. system of humic acid: a band of carboxyl groups of hydroxypropyl methylcellulose systems–5% by mass of humic acid at 1595 cm^{-1} shifts to wave numbers 1625–1650 cm^{-1}. Additionally, it can be seen that there were increases in the formation of hydrogen bonds due to modification, as evidenced by the shift of the hydroxyl band at 3100–3600 cm^{-1} and C–O band at 1000–1150 cm^{-1} to the side by 50–100 cm^{-1}.

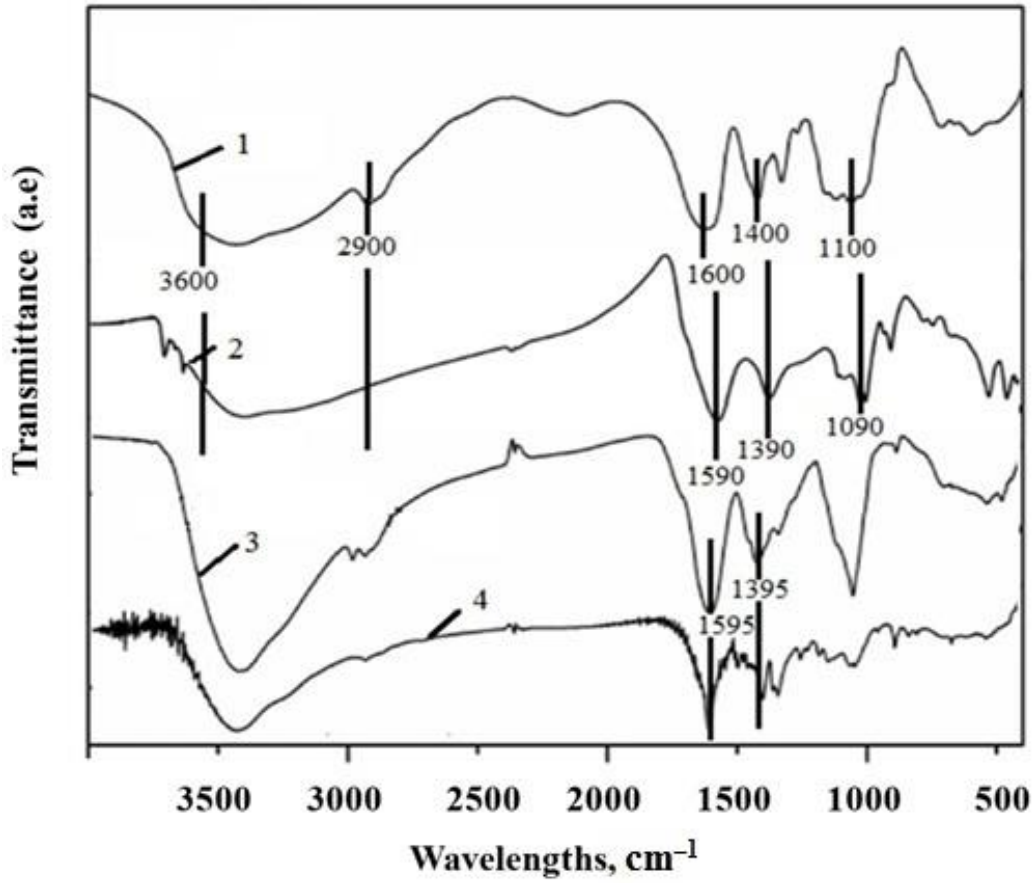

Figure 3. IR spectra of humic acids, hydroxypropyl methylcellulose, and hydroxypropyl methylcellulose–humic acids system: 1—hydroxypropyl methylcellulose; 2—humic acids; 3—hydroxypropyl methylcellulose +5% wt. humic acids, 4: hydroxypropyl methylcellulose +10% wt. humic acids.

Table 2. IR spectral characteristics of humic acids, hydroxypropyl methylcellulose, and hydroxypropyl methylcellulose–humic acids system.

Range (cm^{-1})	Functional Groups
3380–3400	phenolic −OH hydroxyl groups
2920–2940	aliphatic bands C–H
2750–2900	$–CH_3$
1650–1660	fluctuation νC=O
1540–1580	asymmetric νCOO– carboxyl
1400, 1600	C–C
1380–1400	symmetric νCOO– carboxyl
1100	νCO (phenolic), νOH (aliphatic)
1040	νC–N
1005	νCO
910	out-of-phase δCH (aromatic)

Such changes in the IR spectra are evidence that humic acids react with hydroxypropyl methylcellulose through the multipoint interaction of their carboxyl groups with the hydroxyl groups of the polymer, with the formation of such a structure (Figure 4) [18].

Based on the research described above, a general scheme and mechanism for the formation in systems of hydroxypropylcellulose-sodium alginate hybrid modification with humic acids due to the formation of a more rigid network, the enhancement of agglomeration processes, additional supramolecular interactions between functional groups, and an increase in the number of hydrogen bonds are proposed. In fact, the given structure of the hydroxypropyl

methylcellulose–humic acid system indicates that it is formed by the mechanism of matrix synthesis within the framework of the hybrid modification of the polymer.

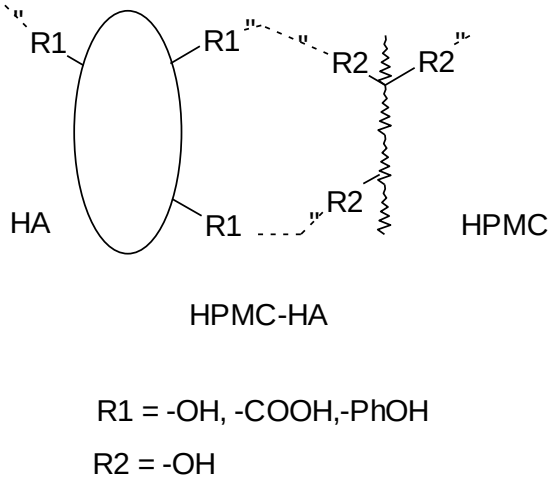

Figure 4. The structure of the hydroxypropyl methylcellulose–humic acid system, which is formed by the mechanism of matrix synthesis: HA—humic acids, HPMC—hydroxypropyl methylcellulose.

3.2. Study of the Effect of Hybrid Modification of Hydroxypropyl Methylcellulose with Humic Acids on a Set of Characteristics of Biodegradable Hydrogel Films

We have determined that hybrid modification by humic acid changes the most important characteristics of HESBHM: water absorption, gelation time, time of mold appearance, and degree of biodegradability. The graphical dependence of these indicators HESBHM based on hydroxypropyl methylcellulose and the humic acid content of humic acids is shown in Figure 5.

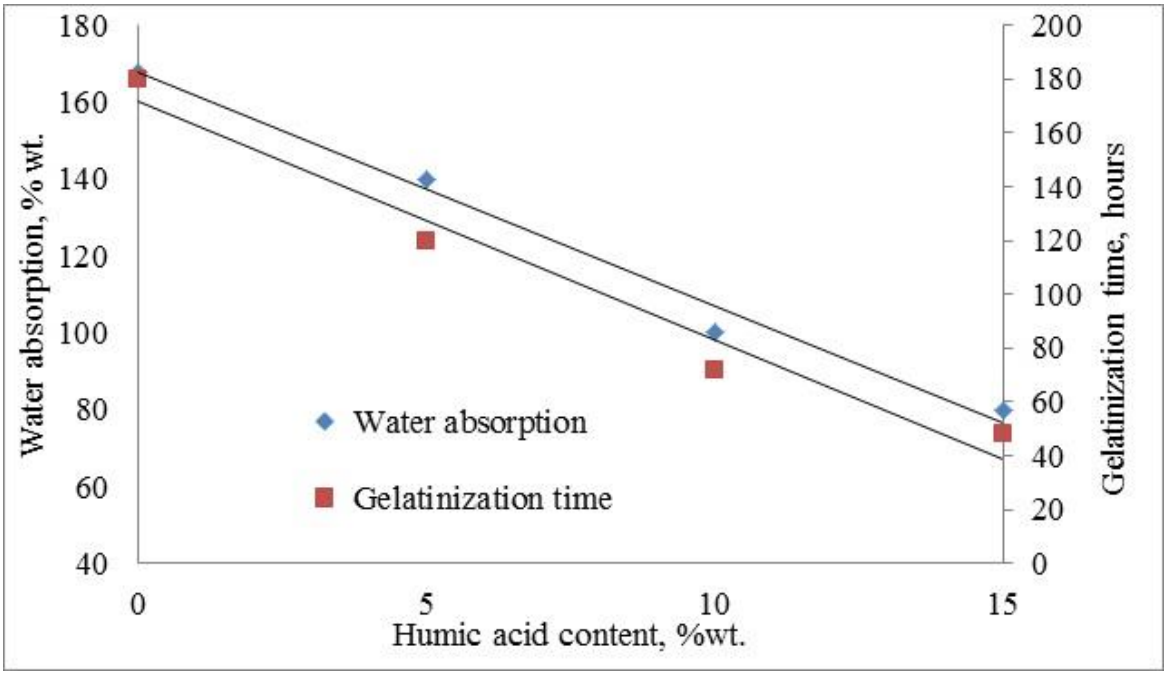

Figure 5. Graphical dependence of water absorption and gelation time of HESBHM based on hydroxypropyl methylcellulose and the humic acid content.

From Figure 4, it can be seen that the hybrid modification of hydroxypropyl methylcellulose with humic acids by mechanism matrix synthesis when receiving biodegradable hydrogel films allows for a reduction in their water absorption by reducing the time of gelation.

The mold appearance time and the degree of biodegradation of HESBHM based on hydroxypropyl methylcellulose and the humic acid content are shown in Table 3.

Table 3. Characterization of the mold appearance time and the degree of biodegradation of HESBHM based on hydroxypropyl methylcellulose and the humic acid content.

Sample	Humic Acid Content, % wt.	Degree of Biodegradation, %	Mold Appearance Time (Hours)
Pure hydroxypropyl methylcellulose and sodium alginate hydrogel	0	99	120
Humic acid	5	98	350
	10	97	does not appear
	15	95	does not appear

In general, it was found that the hybrid modification with humic acids according to the mechanism of matrix synthesis of biodegradable hydrogel films based on hydroxypropyl methylcellulose allows for a reduction in their water absorption and gives them antibacterial properties, which is confirmed by the data on the mold appearance time in the films, while preserving their biodegradation properties. It is important to note that the optimal humic substances content for hydroxypropyl cellulose–sodium alginate systems is no more than 15% wt. With this content in terms of humic acids, good antibacterial properties are achieved, due to the complete inhibition of mold formation and sufficiently high levels of water absorption, and the gelation time of hydrogel films are ensured due to an additional supramolecular multipoint interaction occurring between functional groups in addition to hydrogen bonds.

4. Conclusions

Environmentally safe hybrid hydrogel films with antibacterial properties were received based on hydroxypropyl methylcellulose modified with humic acids.

Using IR spectroscopy, it was determined that the hydroxypropyl methylcellulose, modified with humic acids, are received by the mechanism of matrix synthesis, which is accompanied by the crosslinking of hydroxypropyl methylcellulose through a multipoint interaction with the carboxyl group in humic acids.

Environmentally safe hybrid hydrogel films based on hydroxypropyl methylcellulose with humic acids (15% wt. content) exhibit antibacterial properties, which are achieved due to the complete inhibition of mold formation, sufficiently high levels of absorption, and the gelation time, which are ensured due to additional supramolecular multipoint interactions occurring between functional groups in addition to hydrogen bonds. The obtained environmentally safe biodegradable hydrogel films with bactericidal properties based on hydroxypropyl methylcellulose and humic substances appear to be promising in terms of their operational characteristics for the preparation of transdermal delivery systems for biologically active substances.

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