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THEORETICAL REASONING OF THE HYDROGELS DEVELOPMENT BASED ON URONATE POLYSACHARIDES

The article reveals the role of modern scientific basis of hydrogel formation. The main mechanisms for the hydrogels formation with the participation of uronate polysaccharides on the example of the system "sodium alginate: pectin: xanthan" were analyzed. Conditions and factors for the hydrogels formation on the basis of composite systems consisting of uronate polysaccharides were considered. Modern strategies for the creation of innovative food and pharmaceutical products based on hydrogels from uronate polysaccharides were reflected..

Key words: *uronate polysaccharides, hydrogels, pectin, sodium alginate, xanthan, innovative food.*

Formulation of the problem. Uronate polysaccharides are biopolymers consisting of uronic acid, such as guluronic, mannuronic, glucuronic, galacturonic acids. Brown algae are a raw materials for the harvesting of uronate polysaccharides. Alginates are produced from these algae. Pectins are isolated from the polysaccharide base of plants. Xanthan is a microbial polysaccharide, as well as a source of glucuronic acid. Poorly nutritious parts of cattle, birds, as well as soy products and winemaking products can quickly and effectively saturate the body with hyaluronic acid.

It can be noted, resource base of uronate polysaccharides is available and diverse. This resource base is formed as a result of the animals and birds reproduction, metabolism of microorganisms and the cultivation of plants and algae. Uronate polysaccharides are used in various technologies as gel formation agents, stabilizers, thickeners, because they can bind a lot of water and form polymer hydrogels [1].

Examples of the such gels use as components of controlled-release systems of medicinal and biologically active substances were described in the literature. These gels also were used as matrix for cellular engineering, materials for implants and filling materials in surgery and dentistry, for immobilization and transportation of substances with high reactivity or those that are destroyed in an aggressive environment of the stomach with the need for their delivery as a whole in the intestine [2–7].

Polymer hydrogels, based on uronate polysaccharides are obtained by the reaction of high molecular weight polymers hydration. The resulting hydrogels are capable of cross-linking in the presence of ionic polymerization initiators, for example, calcium ions.

The absence of toxic low molecular weight substances (monomers or cross-linking agents) in the reaction system is an advantage of this approach. At the same time, the reaction proceeds under standard conditions. This greatly simplifies and reduces the cost of technology for the production of hydrogel systems based on the uronate polysaccharides and also significantly increases the possibility of their use [8-10]. Amino acids, fatty acids, vitamins, biologically active substances and even short-chain peptides, for example, glutathione, serotonin can also be cross-linking agents.

Therefore, the development of methods and approaches that allow receiving hydrogels from uronate polysaccharides on the basis of biocompatible polymers with biologically active substances in such a scheme is very important for many branches of science and technology related to human life and health.

Analysis of recent research and publications.

Hydrogels based on uronate polysaccharides (HUP) are dispersed binary systems, consisting of a three-dimensional grid and formed by cross-linked hydrophilic polymers, in which a large number of water molecules are distributed as a dispersion medium. Significant water absorption allows to HUP be an sensitive to changes in external conditions. At the same time, particles of the dispersed phase, connected together in a spatial grid, deprive the system of fluidity. Therefore, HUP exhibit mechanical properties that are similar to those of solids [3; 11; 12].

HUP properties depend on the strength and degree of the cross-links. The chemical and molecular composition of a macromolecule segment between two nodes determines the density of cross-linking, that affects the fundamental properties of hydrogels, as degree of swelling, mechanical strength and elasticity, permeability (size of mesh openings), diffusion characteristics, etc. [13].

Swelling degree of HUP depend on the chemical and spatial structures of uronate polysaccharides macromolecules, the number of hydrophilic groups, presence of ionogenic groups, cross-linking degree and external conditions (temperature, pH, ionic strength of the solution) and inversely proportional to the density of cross-links [14].

The chemical structure of the HUP determines the dynamics, and ionic strength of the solvent determines the kinetics of their swelling. Thus, HUP contains a significant number of hydrophilic groups swell faster and more in comparison with such HUP containing hydrophobic groups [2]. In connection with the above information, it was predicted, that in the case of the combination of uronate polysaccharides in a single solution it is possible to achieve the maximum swelling for a small number of dry matters. This is an important aspect for studying the processes of biologically active substances immobilization, which involve electrostatic attraction/repulsion forces, or the formation of “cross-copolymerization compounds” due to processes of ionotropic gel formation, for which the viscosity is the basis of the formation the stable elastic-plastic structures.

At present, the relationship between “composition – structure – mechanical properties” is not sufficiently studied for HUP. The absence of these results impedes their application in various fields of science and technology. For this reason, the question of studying the theoretical aspects of the HUP formation is relevant.

Formulating the goals of the article.

The main purpose of the article is to analyze the processes, which are associated with the formation of hydrogels on the basis of uronate polysaccharides for further application in various fields of science and technology, primarily related to human life and health.

Setting objectives. The ability of the HUP to absorb and retain a large number of water molecules is determined by mutual repulsions of the co-charged particles of polymer chains and the osmotic pressure due to the presence of moving counterions in the mesh gel. As a result of water penetration into the structure of the gel and the deployment of uronate polysaccharides chains, the hydrogel becomes capable of significantly increasing in volume and containing a solvent in an amount hundred of times higher than its own volume. In the formed matrix it is possible to add compounds, that have high biological activity, but unstable to the conditions of the external environment; substances regulating or providing a taste and aroma, bio objects that must pass the stomach intact, etc. Such compounds in the matrices of HUP are kept by the formation of Van der Waals bonds and released under the conditions of an “acid collapse” when the pH is transferred to an alkaline medium but higher than 7.5. The study of these processes has become the main task of the article.

Presenting of main material. It is possible to estimate the probability of formation of hydrogen bonds during the formation of HUP, taking into account the chemical structure of the main constituents of the uronate polysaccharides - uronic acids (Fig. 1). This is evidenced by the presence of strong hydrophilic groups, such as carboxyl groups of uronic acids (-COOH), hydroxyl groups (-OH), amidic (-$CONH_2$) and with a weakened hydrophilicity: aldehyde (-CHO), ketone (-CH_2OH), carbonyls (-CO), simple etheric (-$COCH_3$).

Taking into account that uronic acids with the help of glycoside bond form polysaccharide chains, we have previously studied the structures of sodium alginate and pectin dimers as the most common in food systems [16; 17]. Dimers were chosen because they are the smallest compounds with properties of macromolecules. The nature of interactions was also studied in the case of combining them [18].

Thus, the presence of a large number of hydrophilic groups indicates that the swelling of the relatively seldom carved frame of the uronate polysaccharides remains unchanged at the number of nodes for the formation of cross-links. However, the distance between them can be greatly increased by swelling of each individual link located between the cross-link units.

Taking into account that HUP have the ability to form cross-copolymers of another type, that formed by the ionotropic gelation process involving calcium

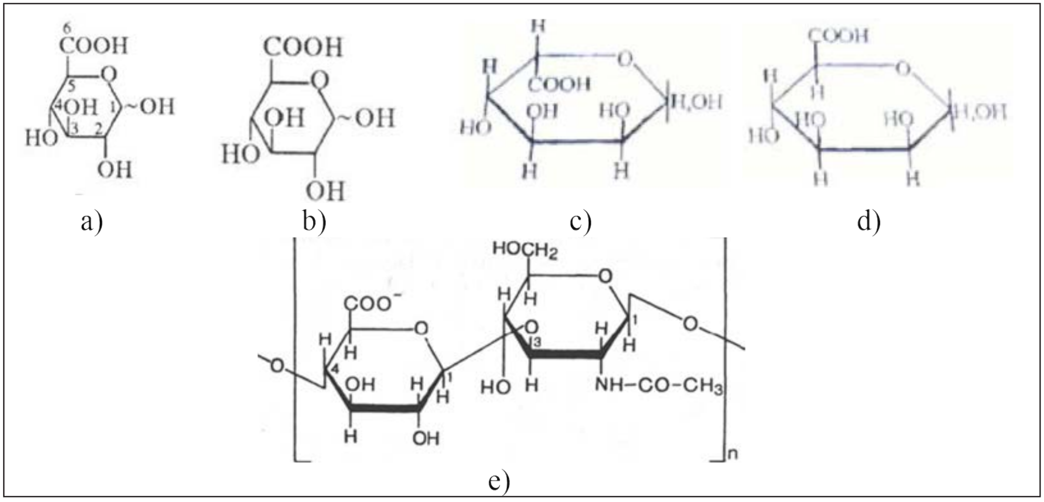

Fig. 1. The main uronic acids of the uronate polysaccharides:
a). glucuronic; b) galacturonic; c) guluronic; d) mannuronic; e) gialuronic

ions or other ions of biometals, it becomes apparent that the effect of excess water absorption can not be inherent in such structures. It should be noted that due to the interchange of ions, the size of macromolecules decreases significantly, because water molecules lose contact and diffuse to the boundary layers of hydrogel. The formation of a structured gel occurs in this case [19; 20].

Swollen structured hydrogels with external influence exhibit elastic properties, as stretching or compression. The high cross-linking density leads to higher mechanical strength, but at the same time to reduce elasticity and swelling. Significant increase in the number of cross-links, so-called "gel-points" in hydrogels on the basis of uronate polysaccharides, initiates the formation of fragile gels. As a result, the optimal cross-linking density ensures a balance between elasticity and desired durability [21]. In the case of structured HUP, the optimal number of cross-links is based on the molar ratio of four carboxylic groups to one calcium ion. However, the spatial orientation of the anionic residues should be convenient for the formation of chelating compounds with calcium.

It was established the nature of the pores formation and predicted their number on the basis of the created quantum-chemical models [16–18]. The porosity of structured and unstructured hydrogels or the size of cells is the structural property of these systems, which is determined by the distance between neighboring cross-links. Porosity is a consequence of cross-linking density, composition and concentration of uronic acid monomers. It was established, that in a stable grid the size of the cells increases with increasing of swelling.

Conclusions. Consequently, the necessary condition for the production of hydrogels on the basis of uronate polysaccharides is the presence of functional groups in the polymer that not only can react with bifunctional reagents such as water, which plays the role of solvent and cross-linking agent, but also capable to ionization, i.e. carboxyl groups uronic acids.

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ТЕОРЕТИЧНЕ ОБҐРУНТУВАННЯ ПРОЦЕСУ УТВОРЕННЯ ГИДРОГЕЛІВ НА ОСНОВІ УРОНАТНИХ ПОЛІСАХАРИДІВ

У статті розкривається роль сучасних наукових бачень процесу освіти гідрогелю. Проаналізовано основні механізми формування гідрогелів за участю уронатних полісахаридів на прикладі системи «альгінат натрію: пектин: ксантан». Розглянуто умови та фактори освіти гідрогелю на основі композиційних систем, що складаються з уронатних полісахаридів. Відображено сучасні риси стратегії створення інноваційних харчових і фармацевтичних продуктів на основі гідрогелів з уронатними полісахаридами.

Ключові слова: *уронатні полісахариди, гідрогелі, пектин, альгінат, ксантан, інноваційні харчові продукти.*

ТЕОРЕТИЧЕСКОЕ ОБОСНОВАНИЕ ПРОЦЕССА ОБРАЗОВАНИЯ ГИДРОГЕЛЕЙ НА ОСНОВЕ УРОНАТНЫХ ПОЛИСАХАРИДОВ

В статье раскрывается роль современных научных видений процесса образования гидрогелей. Проанализированы основные механизмы формирования гидрогелей с участием уронатных полисахаридов на примере системы «альгинат натрия: пектин: ксантан». Рассмотрены условия и факторы образования гидрогелей на основе композиционных систем, состоящих из уронатных полисахаридов. Отражены современные черты стратегии создания инновационных пищевых и фармацевтических продуктов на основе гидрогелей с уронатными полисахаридами.

Ключевые слова: *уронатные полисахариды, гидрогели, пектин, альгинат, ксантан, инновационные пищевые продукты.*