Development of metal-containing composite materials based on pectins of various natures

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Abstract

Relevance of the research. Currently, the development of pectin-based materials with various organic and inorganic fillers is attracting the active attention of scientists in various research fields. The presence of diverse functional groups in pectins allows for the production of derivatives with new physicochemical and biological properties, significantly expanding the scope of practical applications of chemically modified pectins in the food, pharmaceutical industries, medicine and cosmetology.

The structure of pectin polysaccharides is characterized by wide structural diversity. For example, citrus pectin, according to most authors, contains predominantly a homopolymer consisting of α-(1,4)-D-galacturonic acid residues; apple and beet pectins, in addition to the homopolysaccharide, are characterized by the presence of a heteropolysaccharide, the repeating unit of which also includes residues of the neutral monosaccharide L-rhamnose. Pumpkin is an unconventional source of branched pectins, the heteropolysaccharide blocks of which have side chains consisting of neutral oligomers (galactans and arabinans).

Pectins are known to be effective biosorbents, capable of detoxifying the body of radionuclides, various metabolites (including glucose and cholesterol), toxins, and other low-molecular-weight biologically active substances (BAS). In addition to these properties, this class of biopolymers exhibits antiulcer, wound-healing, immunomodulatory, antioxidant, antimicrobial, and other kinds of activities.

In recent years, researchers have focused on developing various methods for modifying pectins (alkylation, amidation, phosphorylation, sulfation, thiolation, etc.) to produce materials with tailored properties. A special place is occupied by the development of methods for the inclusion of cations of silver, nickel, cobalt, copper, iron, magnesium, zinc and other biogenic metals in their composition. This opens up the prospect of more effective practical applications of metal-containing

composite materials (metal complexes) not only in the food industry and medicine, but also in cosmetology for the production of creams, ointments, gels, patches with antifungal properties.

It has now been established that complexation not only reduces the toxicity of ligands but also enhances the biological effect through their gradual release and prolonged action. The solubility of metal complexes in water is crucial, as it enhances the bioavailability of the drugs and enables their wider practical use.

The goal of this work. Obtaining and studying metal-containing composite materials (metal complexes) based on apple, citrus and pumpkin pectins and establishing the influence of the chemical structure of biopolymers on the properties of their complexes for subsequent practical application in the food industry and cosmetology.

The research tasks.

1. To give a general characteristic of commercial pectins (apple and citrus) and pectin isolated from pumpkin.

2. To explore the effect of synthesis conditions on water-soluble complexes with Cu^{2+}, Fe^{2+}, Zn^{2+}, and Mg^{2+} cations based on pectin matrices of various chemical structures and determine the degree of cation incorporation using IR spectroscopy.

3. To study the physicochemical properties (kinematic viscosity, molecular weight, water-holding capacity, solubility) of native and modified carbohydrate biopolymers.

4. To determine the antioxidant activity of the native pectins and metal-containing composite materials based on carbohydrate linear, branched, homo- and heterobiopolymers by spectrophotometric method.

5. To study the effect of pectins with different chemical structures (apple, citrus, pumpkin) on the properties of baby food (apple juice, apple and carrot puree) in accordance with GOST requirements.

6. To study the antifungal activity of native pectins and copper complexes against *Penicillium sp.* and to evaluate the toxicity of copper complexes using

protozoa: stylonychia (*Stylonychia*), infusoria-shoe (*Paramecium caudatum*), tetrahymena pyriformis (*Tetrahymena pyriformis*).

Scientific novelty.

1. For the first time it was established the dependence of the physicochemical properties of metal-containing composite materials based on natural pectins on the chemical structure of the polysaccharide matrices.

2. The high antioxidant activity was established for all metal complexes based on pumpkin pectin, which is characterized by the most complex branched structure and a low degree of esterification (36,3%).

3. It was demonstrated the possibility of application of IR spectroscopy to assess the degree of incorporation of metal cation into the pectin matrix by the magnitude of the signal of the free carboxyl groups of the native pectins and the resulting complexes. The degree of metal cation incorporation was found to depend on their electronegativity in the following order: $Cu^{2+}>Fe^{2+}>Zn^{2+}>Mg^{2+}$.

4. It was demonstrated the ability of pumpkin pectin to inhibit the growth of *Aspergillus niger* and *Penicillium notatum* fungal cultures when added to baby food products (juice, puree).

5. The copper complex based on pumpkin pectin was shown 1,5-2 times higher antifungal activity compared to the native polysaccharide.

Theoretical and practical significance.

It was substantiated theoretically the influence of the chemical structure of the carbohydrate polymer matrix on the physicochemical and biological properties of pectins and their metal-containing composite materials. It was shown that a polysaccharide with a complex branched structure (pumpkin pectin) has a higher sorption efficiency of metal cations, which can be explained by the interaction with carboxyl and hydroxyl groups of not only acidic, but also neutral monosaccharides. The maximum antifungal activity of copper complexes based on branched pumpkin pectin compared with copper complexes based on apple pectin, which has a linear structure, is due to a higher degree of inclusion of copper cations in the branched pectin matrix.

The antioxidant activity of pumpkin pectin and all its metal complexes is due not only to the low degree of esterification but also by branched structure of the macromolecule.

Differences in the rheological properties of pectins may be related to their molecular weight, which is higher for linear heteropolysaccharides (apple pectin) compared to linear homopolysaccharides (citrus pectin) and branched pumpkin pectin.

Recommendations have been developed for the practical use of pumpkin pectin as a natural non-toxic preservative extending the shelf life of foodstuffs. Copper complexes of pumpkin pectin can be recommended for use in cosmetology as components of creams, ointments, gels, patches with antifungal properties.

The methods obtaining, as well as physicochemical and some biological properties of metal complexes based on polysaccharides of various structures, allowed us to gain new knowledge that can be used in the framework of the courses «Fundamentals of Bioorganic Chemistry», «Biochemistry» and «Chemical Basis of Biological Processes», «General Chemical Technology» for bachelor's, master's, and postgraduate students in the fields of «Chemical Technology», «Analytical Chemistry» and «Fundamental and Applied Chemistry».

The results obtained are the scientific basis for the development and implementation of valuable products in a single continuous technological cycle: pectins from various natural sources and metal complexes based on them as components for the creation of new types of food products and cosmetics.

Laboratory regulation LR 20.59.99-001-76353675-2025 has been developed for the production of a pectin complex with copper cations.

Technical specifications TS 10.89.15-002-76353675-2025 have been developed for pectin metal complexes.

Act of implementation for the production of pectin complexes with copper cations has been received at REPLANET LLC in Lipetsk.

Provisions submitted for defense:

1. Obtaining pectin polysaccharides from various plant sources (mint, celandine, wormwood, cherry leaves) for selection the optimal method of isolation pumpkin pectin. Determination of impurity components (saponins, flavonoids, phenolic acids, tannins, proteins, nucleic acids).

2. Evaluation the degree of esterification, the presence of free carboxyl groups and the complexing capacity of apple, citrus and pumpkin pectins isolated in the laboratory and purchased from retailers.

3. The results of studying the synthesis conditions of metal-containing composite materials and determining the degree of incorporation of Cu^{2+}, Fe^{2+}, Zn^{2+}, and Mg^{2+} cations into a pectin matrix of various nature by IR spectroscopy.

4. Dependence of the physicochemical properties (kinematic viscosity, molecular weight, water-holding capacity, solubility) and antioxidant activity of native and modified pectins on the chemical structure of the polysaccharide.

5. Effect of pectins with different chemical structures on the properties of baby food (juice, puree).

6. Antifungal activity of native pectins and copper complexes against *Penicillium sp.*