The influence of chemical factors on the metal-binding capacity of non-starch polysaccharides

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Abstract. The article considers not only the possibility of non-starch polysaccharides to bind heavy metal ions, but the factors affecting this ability are determined. The ability of some non-starch polysaccharides to form complexes with heavy metal ions significantly depends on the structure, structure and external chemical factors. Considered polysaccharides are: pectin, chitosan and sodium alginate. Considered factors: temperature and pH.

1. Introduction
For this period of time, increasing attention is being paid to studying the interaction of non-starch polysaccharides with metal ions, mainly heavy, because non-starch polysaccharides, such as pectin, chitosan, sodium alginate and others, can be used, for example, for the purification of industrial and domestic wastes from residual amounts of metal ions, when determining the concentration of small amounts of metal ions in wastewater. It is also possible to use non-starch polysaccharides as enterosorbsents for poisoning the human body with ions of heavy or radioactive metals. In connection with the foregoing, a study was made of the complexation ability of some non-starch polysaccharides, such as pectin, chitosan and sodium alginate with copper ions, and the influence of factors such as the temperature of the process and the pH of the medium on the complexation process was studied.

Pectins are non-starch polysaccharides. Their molecules contain the main unit of α-D-galacturonic acid residues linked together by 1→4 bonds, and side units consisting of 2-O-substituted L-rhamnopyranose. In the polysaccharide pectin, D-galacturonic acid is in a chair type conformation. Very often in literature [1] pectin is defined as a boundedly flexible chain, because the free rotation of groups around a glycosidic bond is difficult. This is due to the fact that the OH groups at C₁ and C₄ in the pectin molecule are perpendicular to the plane of the molecule. Pectin is a linear structure. In the pectin molecule, the residues of D-galacturonic acid have a pyranose type cycle configuration (figure 1).

Chitin is a representative of the class of linear aminopolysaccharides. The chitin molecule consists of N-acetyl-2-amino-2-deoxy-D-glycopyranose units (figure 2) [2]. Chitin is a biological polymer, very widespread in nature. Chitin is present in the composition of the cell wall of any fungi. Chitin is the main and one of the most important structural components of the cell wall of the representatives of the kingdom of Fungi or Mycota. In representatives of the class Crustacea and most representatives of the class Insecta, chitin is part of the cuticle - the external hard cover. The presence of chitin in the cuticle has a protective function [3].
Alginates are the primary components of the extracellular matrix and cell walls; they form a flexible and durable fabric frame. The alginic acid content in algae is affected by the place and depth of their growth, season, stage of development. Usually it is 11 - 45% of the dry weight of the plant [5]. Alginates with a high content of polyguluronic fragments most effectively inhibit the absorption of metal cations.

2. Objects and methods of research
In the study as objects were used:
- apple pectin (manufactured by Fooding, China),
- chitosan (manufactured by Qingdao Seawin Biotech Group Co., Ltd., China),
- sodium alginate (manufactured by Shandong Topsea Seaweed Industrial Co., Ltd., China).

The study parameters were determined by spectrophotometric, potentiometric methods.
3. Results and discussion

To determine the binding parameters, a number of experiments were carried out to study the kinetics of the process of binding of copper ions by selected polysaccharides.

Based on the results of the studies, kinetic curves of the process of binding of copper ions to three polysaccharides were constructed, which are presented in figure 4.

![Figure 4](image-url)

**Figure 4.** Kinetic curves of the Cu$^{2+}$ binding process by pectin (A), chitosan (B) and sodium alginate (C) under standard conditions ($T = 298$ K, pH = 6 ± 0.5).

The probability of a change in the metal-binding ability of pectin, chitosan and sodium alginate under interaction under conditions different from standard was also studied considering changing temperature conditions and changing pH.

As a result of the experiments, it was found that the optimum pH value for the binding of copper ions by polysaccharides: pectin, chitosan and sodium alginate, at which the maximum binding is achieved, corresponds to a pH value of 6 ± 0.5 (figure 5).
Figure 5. The effect of pH on the metal binding capacity of pectin (A), chitosan (B) and sodium alginate (C) under standard conditions (T = 298 K).

The low complexing ability of sodium pectin and sodium alginate at pH values less than 6.0 can be explained by an increase in the degree of esterification of these polysaccharides, and, accordingly, a decrease in the number of free carboxyl groups that can bind to copper (II) ions. In the case of chitosan, at low pH values, the protonation of the amino groups contained in chitosan occurs, which contributes to the formation of the chitosanium macrocation. The macrocation of chitosania, as is known, does not interact with ions of divalent metals [4, 5]. The low values of the efficiency of binding of polysaccharides with copper (II) ions at pH > 6, compared with the efficiency at pH = 6.0, are explained by the formation of Cu(OH)₂. Accordingly, at this pH value, copper will be removed from the solution in the form of hydroxides, and the precipitation process in the form of copper hydroxide will prevail over the binding of copper ions to complexes [6, 7].

The effect of temperature on the formation of complexes of selected polysaccharides with copper (II) ions was also studied. As can be seen from the graphic material (Figure 6), a change in temperature also affects the metal-binding abilities of polysaccharides.
Figure 6. The dependence of metal-binding ability of the selected non-starch polysaccharides: pectin (A), chitosan (B) and sodium alginate (C) on temperature at pH = 6 ± 0.5.

The increase in the efficiency of the metal-binding ability of polysaccharides with increasing temperature can be explained by the occurrence of hydrolysis reactions. On the one hand, from literature [5, 7, 8, 9, 10] it is known that the rate and degree of hydrolysis is directly proportional to temperature. With increasing temperature, the degree of hydrolysis increases accordingly, which helps to lower the degree of esterification of polysaccharides (especially sodium pectin and sodium alginate) and increases the ability to complexation. On the other hand, with increasing temperature of the solution, the degree of dissociation of copper (II) sulfate increases, which leads to an increase in the amount of free Cu²⁺ ions in the solution. The influence of these factors increases the degree of binding of copper ions by polysaccharides and increases the efficiency of binding.

4. Conclusion
The influence of changes in the acidity of the solution and temperature on the efficiency of the complexation of copper (II) ions with the polysaccharides under consideration - pectin, chitosan and sodium alginate is manifested ambiguously and depends on the characteristics of their chemical structure. In the acidic pH range (pH=2, pH = 4), the complexing ability of the studied polysaccharides decreases due to reactions leading to a decrease in the reactivity of carboxyl groups (due to their esterification) in sodium alginate and pectin and amino groups (due to protonation) in chitosan. In a slightly alkaline pH range (pH = 7.5), the efficiency of the complexation process decreases due to the deposition of copper (II) ions by hydroxide ions. The highest efficiency of the complexation of copper
(II) ions with the polysaccharides under consideration is achieved in slightly acidic solutions at pH = 6 ± 0.5.

With an increase in temperature from 283°C to 313°C, the efficiency of the process of binding copper (II) ions to the polysaccharides under study also increases due to an increase in the reaction rate and an increase in the reactivity of functional groups.

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