Obtaining chitosan polysaccharide from various natural raw materials and studying its metal-binding ability

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Abstract. The article considers the structure and properties of chitosan obtained from natural sources of plant and animal origin. The ability of chitosan to complex formation with copper ions is studied. The isotherm of ion sorption is given, and the quantitative values of the complexation process are calculated according to the classical theory and the theory of RCC.

1. Introduction
The unique structure of chitosan determines its widespread use in various fields. The most important areas and sectors of chitosan use are food industry, medicine, biotechnology, ecology, cosmetic industry, agriculture and veterinary medicine [1]. Chitosan is a linear heteropolysaccharide. It consists of the final units of 2-amino-2-deoxy-β-D-glucopyranose residues, which are interconnected by a β- (1 → 4) -glycoside bond. Also important is the fact that some units in the composition of chitosan may consist of 2-acetamido-2-deoxy-β-D-glucopyranose residues. The general structure of this polymer is depicted by the formula shown in figure 1.

Figure 1. The structural formula of chitosan macromolecule [2].

2. Objects and methods of research
The material of the study was raw materials of various origin containing chitosan in various proportions. The generalized scheme for producing chitin, from which chitosan is subsequently obtained, is as follows: Chitin-containing raw material is ground → deproteination → washing → demineralization → washing → pigment and lipid removal → washing → chitin.

It should be noted that the source of raw materials plays a huge role in obtaining the material under study, which subsequently determines the metal-binding ability. After selecting natural raw materials, based on literary sources, the optimal methods for producing chitosan were established.
The isolation of chitosan was carried out according to generally accepted methods described by Vohidova, 2016 [5].

3. Results and discussion
To determine the metal-binding ability of the obtained product, the following studies were carried out:
1. the isolation of chitosan from the shell of shrimp and various types of mushrooms, determining the percentage yield of chitosan in terms of chitin in the feedstock.
2. The metal-binding ability of the studied samples was studied.

The data of a quantitative analysis of chitosan in terms of chitin and feedstock are given in Table 1.

| The source of chitosan | \( \Phi'_R, \text{chitosan/chitin, } \% \) | \( \Phi'_R, \text{chitosan/original raw material, } \% \) |
|-----------------------|------------------------------------------|------------------------------------------|
| Boléuts edúlis        | 72.4                                    | 2.11                                    |
| Agaricus campestris   | 71.4                                    | 1.97                                    |
| Pleurotus ostreatus   | 70.0                                    | 1.56                                    |
| Crangon crangon       | 70.1                                    | 2.01                                    |

According to the data shown in Table 1, the largest amount of chitosan was obtained by additional processing of raw materials Boléuts edúlis, which amounted to 72.4% in terms of chitin and 2.11% in terms of dry raw materials.

The metal-binding ability of the studied chitosan samples was studied using the example of binding of copper (II) ions in the range of ion concentrations from 1.50 to 12.00 mmol/dm³, at pH=6, at a temperature of 298 K.

The analysis of the studies of the binding process of copper (II) ions showed that the most intense reaction occurs only during the first 10-30 minutes. With a longer time period, the efficiency of the binding of copper ions practically does not change. As experiments showed, all the studied chitosan samples have high copper-binding properties, as they are able to connect more than 75% of copper ions at experimentally predetermined solution concentrations. In the samples of chitosan isolated from Boléuts edúlis, Agaricus campestris and Pleurotus ostreatus, the maximum efficiency that was achieved during the research was 76.5%, 76.3% and 75.3%, respectively (at \( C(\text{Cu}^{2+})=1.50 \text{ mmol/dm}^3 \)). In chitosan isolated from Crangon crangon shells, the maximum efficiency was 77.0%. With an increase in concentration to 12.0 mmol/dm³, the efficiency of chitosan obtained from Boléuts edúlis, Agaricus campestris and Pleurotus ostreatus, Crangon crangon was 56.3%; 55.2%, 55.6% and 54.8%, respectively.

Since chitosan is a good enterosorbent [3, 4], the possibility of determining the quantitative parameters of the process of binding of copper ions was also studied. For this, preliminary studies were conducted on the effect of pH on the efficiency of the process of sorption of copper ions. As a result, there was an increase in the efficiency of binding of Cu²⁺ ions with an increase in pH in the selected range (from 2.0 to 6.0). With a subsequent increase in pH values, a decrease in the binding efficiency of Cu²⁺ ions follows. A similar character of the dependence of the sorption efficiency on the pH of the medium can be associated with a change in the state of the active sites of the sorbent and the type and amount of Cu²⁺ ions in solution. The low sorption values of Cu²⁺ ions can be explained by the competition between the Cu²⁺ ions and H⁺ ions for the active binding sites in the chitosan molecule. Moreover, in an acidic medium (at appropriate pH values), it will be H⁺ that will bind and adsorb on the surface. Therefore, the surface of chitosan, as a sorbent, will have a “+” charge, which immediately leads to the repulsion of positively charged Cu²⁺ ions. In turn, this leads to a weakening of the binding efficiency of Cu²⁺ ions. With increasing pH, the number of free active binding sites on the surface of the chitosan molecule increases. A greater number of free active binding sorption centers leads to higher
capacitive sorption values. As a rule [3, 5, 6, 7], the extremum of sorption efficiency falls on that region of pH that maximally coincides with the stage of formation of Cu(OH)$_2$ in solution.

According to the data obtained, the Langmuir adsorption isotherm of Cu$^{2+}$ cations by chitosan was constructed (figure 2).

![Figure 2. Sorption isotherm of Cu$^{2+}$ ions by chitosan.](image)

In addition, it was of interest to calculate the stability constant of the complexes formed by copper (II) ions and chitosan using the classical theory of complexation and the theory of RIC.

Coordination parameters were carried out according to the methodological recommendations published in the sources [8, 9].

As a result of the studies, it was found that the polyelectrolyte nature and chemical heterogeneity of chitosan make it impossible to correctly apply the classical method for calculating the stability constant of its complex with copper (II) ion, so we chose a method for calculating stability constants through the calculation of RIC [9, 10]. Comparative data on the stability characteristics of copper (II) complexes with chitosan (lg $\beta_a$) using different methods are as follows:

- classical theory of complexation: $3.0 \pm 0.23$
- RCC method: $3.7 \pm 0.32$.

4. Conclusion

As a result of the experiments for which various sources of natural raw materials were selected, chitosan was isolated from Bolétus edúlis, Agaricus campestris, Pleurotus ostreatus and Crangon crangon with a yield of polysaccharide from the feedstock of 2.11%, 1.97%, 1.56% and 2.01%, respectively.

The high binding ability of the obtained chitosan samples with respect to copper (II) cations was determined. It was found that the interaction of chitosan binds more than 80% of copper ions in a selected concentration range under standard conditions.

The results of studies of the sorption ability of chitosan showed that the sorption process is described by the Langmuir sorption equation.

The constants of the complexation process of chitosan with copper (II) cations were calculated using the classical theory of complexation and the theory of RIC.
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