Metal-binding ability of sodium alginate relative to Fe$^{3+}$ and Cu$^{2+}$ ions

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Abstract. The article substantiates and experimentally confirms the possibility of a non-starch polysaccharide – sodium alginate to form complex compounds with iron (III) and copper (II) ions. Alginates are used in medical practice as an enterosorbent for severe poisoning with metal ions due to their ability to form complexes with heavy metals, insoluble in water.

1. Introduction
Sodium alginate is a compound that is used in many sectors of the national economy, most often in the food industry and in the medical industry. In modern medicine, there are several main areas of use of alginic acid and its compounds:
   1) as excipients in the production of certain dosage forms;
   2) as an impregnating material in the manufacture of gauze napkins or surgical sponges for bleeding of various origin and localization;
   3) as components in some dietary supplements.

In the food industry, for example, this compound is used as a thickener, has its own designation in the International Digital Codification System for Food Additives – E – 401. In medicine, sodium alginate is used in dental practice as a component for the manufacture of jaw prints [1].

By their nature, alginates are high molecular weight compounds of natural origin. Brown algae are usually sources of alginates: kelp (L. Digitata, L. Saccharina), as well as fucus (F. vesiculosus, F. distichus, F. serratus, A. Nodosum) [2, 3, 4]. Table 1 shows the content of alginic acid and its compounds in some algae [5, 6, 7].

The content of alginic acid and its compounds in all algae is approximately the same and does not exceed 35.5%, calculated on the dry matter content.

According to published data [3, 4, 8], the content of alginic compounds in algae depends on the time of year (autumn algae are richer in these compounds than spring algae) and growing conditions.

For example, kelp algae obtained in the Barents Sea are richer in alginic acid and its compounds than algae obtained, for example, in the Far East. This can be explained by the longer daylight hours, the shorter depths at which these algae grow.

Brown algae of the Fucus genus, regardless of the place of their extraction, have approximately the same chemical composition.
Table 1. Mass fraction of alginic acid and its compounds in some algae [3].

| Variety of algae     | The content of substances (in terms of dry weight, %) | min | max |
|----------------------|------------------------------------------------------|-----|-----|
| Fucus distichus      |                                                      | 21.7| 28.5|
| Fucus spiralis       |                                                      | 21.1| 24.5|
| Fucus vesiculosus    |                                                      | 22.1| 26.0|
| Laminaria digitata   |                                                      | 26.0| 35.1|
| Laminaria saccharina |                                                      | 16.0| 27.0|

In terms of structure, sodium alginate is a salt formed by alginic acid with Na\(^+\) ions. In addition to compounds with Na\(^+\) ions, alginic acid forms soluble compounds with K\(^+\) and NH\(_4\)\(^+\) ions. Salt with Ca\(^{2+}\) ions - calcium alginate is a water-insoluble compound [4, 5, 6, 9].

The structural formula of sodium alginate is shown in figure 1.

Figure 1. The structural formula of sodium alginate [2, 4].

2. Objects and methods of research

In the study, sodium alginate manufactured by Qingdao Yingfei Chemical Co., Ltd. was used as an object.

The content of the determined ions was monitored by various instrumental methods, according to the guidelines.

3. Results and discussion

To determine the possibility of the process of binding of Fe (III) Cu (II) ions by sodium alginate, curves showing the change in ion concentration over time (kinetic curves) were taken (figure 2). According to the results obtained, we can conclude that the process of binding of metal ions occurs most intensively during the first 30 minutes. Subsequently, the speed of the process decreases. In the future, in the next 5-24 hours, the speed practically does not change and the system: non-starch polysaccharide - a solution of copper (or iron) salt is in equilibrium, the speed does not change.

The mechanism of the binding of sodium metal alginate to metal ions is not yet fully understood. It is obvious that along with the course of substitution reactions, a process such as sorption of metal ions by the surface of a non-starch polysaccharide will proceed in the future. This explains the larger amounts of bound metal ions by sodium alginate, which would be expected if only ordinary reactions of substitution of sodium ions from the composition of alginate by copper or iron ions took place.

Also, according to the experimental data, the efficiency of the process of binding copper or iron ions from solutions of their salts with sodium alginate was determined. The results are presented in table 2.
A- Copper.

B- Iron.

**Figure 2.** Kinetic curves of the process of binding metal cations to sodium alginate at $T=298$ K, pH=6, $m$ sodium alginate 1.25 g/100 cm$^3$.

**Table 2.** The dependence of the efficiency of binding of copper and calcium ions by sodium alginate on the time course of the process.

| Time of the process, min. | The efficiency of the binding process, % |
|---------------------------|------------------------------------------|
|                           | Initial concentration of metal ions in solution, mg/cm$^3$ | 0.1 | 0.5 |
| 10                        | Iron                                     | 12.0 | 7.0 |
| 20                        |                                          | 19.0 | 11.0|
| 30                        |                                          | 29.0 | 14.0|
| 60                        |                                          | 37.0 | 18.0|
| 120                       |                                          | 57.0 | 22.0|
| 240                       |                                          | 65.0 | 38.0|
| 1440                      |                                          | 65.0 | 38.0|

Copper
According to the results of the experiments, it is clearly seen that sodium alginate showed high metal-binding properties, binding significant amounts of copper and iron ions.

The metal binding abilities of sodium alginate depend on the concentration of the initial solution of a metal salt: copper or iron. With an increase in the concentration of the studied ions by 5 times (from 0.1 to 0.5 mg/cm$^3$) in the model solution, the binding efficiency decreases, moreover, for iron ions by more than 40%, and for copper - by 18.5%.

4. Conclusion

Based on the results of the experiments, we can say that sodium alginate shows high metal-binding properties. Under standard experimental conditions, the binding ability of sodium alginate at an initial concentration of a metal salt solution of 0.1 mg/cm$^3$ is 70% for copper cations and 65% for iron cations.

Sodium alginate has the greatest metal-binding activity to copper ions. Perhaps this is due to the fact that the radius of the copper ion is larger than the radius of the iron ion. And if the charge of the ions is equal, the ion with a larger radius will have greater bonding ability, respectively, this is a copper ion.

The metal binding capacity of sodium alginate depends on the concentration of the initial model solution. As the concentration of copper or iron ions in the solution increases, the binding efficiency decreases.

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