Obtaining carbohydrate biopolymers (prebiotics) from brown algae

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Abstract. The article discusses the issues of obtaining prebiotic food additives - an actual area of research in modern food technology. The test results determined the safety of the brown algae Ascophyllum nodosum and Fucus vesiculosus growing on the littoral of the Barents Sea. Fucus algae contain significant the amount of alginic acid in terms of absolutely dry weight (a.d.w.) which proves the possibility of using them as raw materials for the production of sodium alginate. It was shown in the work that it is preferable to use Fucus vesiculosus for this purpose, since the content of alginic acid in it and the yield of finished products are higher. Studies of frozen algae in storage revealed a significant loss of water even after a month of storage of raw materials, while during storage of dried algae, the qualitative composition of the product remains constant. The properties of sodium alginate samples obtained from different types of fucus algae were studied. It was found that sodium alginates in appearance represent a free-flowing substance in the form of small thin plates, from light to dark brown in color, without taste and odor. Fucus sodium alginate can be used as a prebiotic, since it is a highly viscous biopolymer and belongs to natural dietary fiber.

1. Introduction
A person’s living conditions under the influence of a number of negative environmental factors contribute to the development of metabolic disorders, problems with the gastrointestinal tract (GIT) and the development of dysbiosis. Probiotics and prebiotics are important means of preventing dysbiosis. They can be part of functional foods, but the most effective are complexes of probiotics and prebiotics – synbiotics [1].

Probiotics (probiotic microorganisms) - live non-pathogenic, non-toxigenic microorganisms that enter the human intestine with food, have a beneficial effect on the human body and normalize the composition and biological activity of the digestive tract microflora (microorganisms of the genus Bifidobacterium, Lactobacillus, Propionibacterium, and also used in their association genus Lactococcus, species Streptococcus thermophilus). Products and dietary supplements containing microorganisms are also call.

In the global algae fishery, brown algae occupy first place in the total amount of raw material harvested. A unique feature of brown algae is its ability to synthesize and accumulate a complex of polyuronic acids, known as «alginic acids» [3].

Fucus algae are a valuable raw material for the production of polysaccharides (alginites, fucoidan, laminaran), which can be used as prebiotics in food products: they sorb and excrete not only radionuclides and heavy metals, but also toxins of organic origin, alginates can stimulate processes regeneration, enhance tissue epithelization.
One of the salts of alginic acid, which has found widespread use, is sodium alginate. This substance is a sodium salt of alginic acids, highly soluble in water. Brown algae are used as a source of alginates in order to obtain crude biogels from them [4].

Alginates are biocompatible, biodegradable and relatively inexpensive to manufacture, well soluble in water and have high water retention capacity, easily form hydrogels [1]. Due to all this, alginates are widely used as thickeners, gelling agents and stabilizers in medicine and pharmaceuticals, as well as in the textile industry [5].

In recent years, publications have appeared with new studies of brown algae biogels. They show effectiveness in the treatment of various gastroenterological diseases and as a remedy for dysbiosis [6, 7]. Alginites, which form the basis of the biogel, are soluble dietary fiber [5, 8, 9], have immunostimulating properties [6, 9], are powerful enterosorbents that can bind and excrete metabolic by-products, salts of heavy metals and radionuclides [11, 12]. A new trend is the use of sodium alginate in the production of dairy products with bifidobacteria. It has been proven that alginates and their oligosaccharides have prebiotic properties: they stimulate the active growth of bifidobacteria both in vitro and in vivo [11]. The product of brown algae processing, a biogel containing sodium alginate, also has the same in vivo effect [13]. Its effect on the adhesive properties of bifidobacteria has been proven. At the same time, there are no data in the literature on methods for the utilization of alginates by bifidobacteria, as well as information on their ability to break down high molecular weight alginates.

As prebiotics, polysaccharides that are in fucus algae can also be used: fucoidan - a polysaccharide consisting of fructose blocks, it enhances the processes of phagocytosis (the destruction of bacteria and foreign particles).

mannitol - six-atom alcohol - aldit, it is used as a sugar substitute for patients with diabetes.

laminaran is a biopolymer, the main chain of which is built from glucopyranose residues connected by glycosidic bonds.

Currently, there is insufficient data on the polysaccharides that make up brown algae with prebiotic properties: the ability to selectively improve the growth and activity of certain intestinal protective microflora populations. In this regard, further research in the field of isolation of the listed polysaccharides from fucus algae, the study of their prebiotic properties, as well as the creation of food products using these compounds is an actual scientific direction.

The aim of the work is to study the Barents Sea fucus algae Ascophyllum nodosum and Fucus vesiculosus as a potential raw material for the production of sodium alginate, which is contained in food products as a prebiotic and analysis of the effect of the method of conservation of algae (freezing and drying) on the quality of the resulting product.

2. Material and Methods

2.1. Research Materials

Fucus algae Ascophyllum nodosum and Fucus vesiculosus, growing on the littoral of the seas of the Arctic Ocean, were used as raw materials. Algae were collected in the Terberskaya Bay of the Barents Sea in September 2019 by MSTU employees. Fucus were sorted by species composition. In the collected material, algae of the species Fucus vesiculosus prevailed (70%) (Fig. 1 - b), the rest - algae of the Ascophyllum nodosum family (Fig. 1 - a).
2.1.1. Research Method. One of the research objectives is to study changes in the quality of algae (chemical, microbiological indicators and physical properties) during long-term storage to establish the shelf life and storage of raw materials, which is a prerequisite for the development of regulatory documentation.

Two methods of conservation of algae were used in the work: freezing and drying.

For this purpose, part of the raw algae (method 1) was frozen in a freezer (Ariada) to a temperature of minus 25 °С and put into storage at a temperature of minus 18 °С.

Algae were dried in two ways: in air at a temperature of plus 20 °С for a day (method 2) and by forced drying in a universal drying unit (UDU - development of MSTU) at a temperature of plus 25 °С for 8 hours (method 3). The algae dried in two ways were stored, packed in kraft bags, and stored at room temperature.

Sodium alginate was obtained according to the principle technology developed at the previous stages of research [10], shown in Fig. 2.

![Diagram](image)

**Figure 2.** Complex technological scheme of processing fucus algae for food purposes

During the experiments, physicochemical and microbiological research methods were used. Physico-chemical and organoleptic properties, such as mass fraction of moisture, mass fraction of alginic acid, mass fraction of iodine, mineral impurities insoluble in water, were determined in accordance with GOST 26185-84 "Marine algae, marine grasses and products of their processing. Methods of analysis. Algae were examined for compliance with the requirements of the EAEU TR
"Technical regulation of the Eurasian Economic Union" On the safety of fish and fish products for such microbiological indicators as: mesophilic aerobic and facultative anaerobic microorganisms (MAFAM) according to GOST 10444.15-94 and GOST R 31747-2012, yeast and molds - in accordance with GOST 10444.12-88. In addition, salmonella was determined according to GOST R 52814-2007.

3. Results and Discussion
In order to determine the possibility of using Fucus in food production, microbiological and physicochemical studies of algae were carried out (Table 1).

The quality of dry fucus in terms of microbiological indicators meets the requirements for raw materials used for food production. It is established that the positioned in table. According to safety indicators, the dry algae F. Vesiculosus and A. nodosum contain a small amount of toxic elements that does not exceed the standard values even for raw algae.

Work is also underway on the selection of the preservation method and the shelf life of brown algae Ascophyllum nodosum and Fucus vesiculosus. To this end, studies were carried out on the chemical composition of fresh raw materials (raw algae), as well as frozen algae stored for 1 month. The results are presented in table 2.

Table 1. Quality indicators of Fucus algae (raw) species of Fucus vesiculosus and Ascophyllum nodosum

| Shelf life, months | 0 | 1 |
|-------------------|---|---|
| Type of Fucus Characteristic | Vez. | Ask. | Vez. | Ask. |
| Water % | 74.0 | 72.9 | 62.8 | 69.1 |
| % a.d.w. | 0 | 0 | 0 | 0 |
| Ash % | 1.20 | 1.19 | 1.20 | 1.19 |
| % a.d.w | 4.60 | 4.40 | 4.60 | 4.40 |
| Algini c acid % | 3.87 | 3.66 | 2.69 | 3.23 |
| % a.d.w | 14.9 | 13.5 | 20.1 | 14.3 |
| Iodine % | 0.11 | 0.14 | 0.10 | 0.12 |
| % a.d.w | 0.44 | 0.53 | 0.40 | 0.51 |
| MAFAM, CFU per 1 g | Less 5.0×10¹ | Less 5.0×10¹ | Less 5.0×10¹ | Less 5.0×10¹ |
| Fungus, CFU per 1 g | Less 10 | Less 10 | Less 10 | Less 10 |
| Ferments, CFU per 1 g | Less 10 | Less 10 | Less 10 | Less 10 |

The content of alginic acid in Fucus vesiculosus is slightly higher than in Ascophyllum nodosum and, in terms of absolutely dry weight, is 14.9% and 13.5%, respectively. During storage of frozen algae, significant water losses are observed, with Fucus vesiculosus losing 16%, Ascophyllum nodosum - 6% water. The results of the analysis of the moisture content of algae dried by natural and forced drying methods were identical (5%) during 3 months of storage, but forced drying, in our opinion, is more economically preferable.

Table 2 presents the results of studies of the quality of alginates obtained by the developed [10] technology from two types of fucus.
Table 2. Quality indicators of sodium alginate from raw algae and product yield

| Indicators                  | Characteristic | Characteristic | Characteristic |
|-----------------------------|----------------|----------------|----------------|
|                             | *Fucus vesiculosus* | *Ascophyllum nodosum* |                |
| Appearance                  | Thin plates     | Thin plates     |                |
| Colour                      | Light brown     | Light brown     |                |
| Taste                       | Without taste   | Without taste   |                |
| Smell                       | Without smell   | Without smell   |                |
| Mass fraction of water,%    | 6.8             | 7.0             |                |
| Mass fraction of ash,%      | 18              | 16              |                |
| Mass fraction of alginic acids,% to dry substances | 92 | 90 |
| Mass fraction of substances insoluble in water, not more than, % | 0.3 | 0.3 |

Studies have shown that the characteristics of samples of sodium alginate obtained from different types of fucus algae differ only in terms of color.

During the manufacture of sodium alginate, it was found that the yield of the product from *Fucus vesiculosus* is significantly higher (1.5 times) than from *Ascophyllum nodosum*. It was established that the main losses were at the stage of formation of the galleta (allocation of alginic acids). In this regard, it is this stage of the technological scheme that requires careful testing to establish optimal conditions affecting the formation of the gel.

Work on technology optimization is ongoing.

4. Conclusions
As a result of the research:
- it has been shown that the use of sodium alginate as a prebiotic is an actual scientific line of research in the field of isolation of polysaccharides from fucus algae;
- the safety and the possibility of using fucus algae for the production of alginates used in food products were established;
- studies on the choice of preservation method and shelf life of brown algae *Ascophyllum nodosum* and *Fucus vesiculosus*, used as raw materials for the production of sodium alginate, established the possibility of preserving Fucus algae by freezing and drying, but it is preferable to use forced drying;
- the quality indicators of the obtained sodium alginate from the algae *Ascophyllum nodosum* and *Fucus vesiculosus*, which is a highly viscous biopolymer that can be used as a prebiotic (as dietary fiber) in food products, are investigated.

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