Conference Paper

Development of Basic Technology for Obtaining Sodium Alginate from Brown Algae

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Abstract

The possibility of making sodium alginate from a by-product (fucus semi-finished product), obtained by producing an extract from brown algae of the Fucus family -- fucus bubbly (*F.vesiculosus*), has been studied. It has been found that up to 80% of the alginic acids contained in the feedstock remain in the fucus semi-finished product, which can also be isolated and used. The principal technology of sodium alginate from the fucus semi-finished product is developed, consisting of the following main stages: preparation of raw materials, reduction, pretreatment, extraction of alginates, isolation of alginic acid, production of sodium alginate, drying. As a result of optimization of the technological scheme, it was possible to increase the yield and improve the quality of the product: the yield of sodium alginate was 4.5% (which is 20% higher than the original), the content of alginic acids increased by 7% and was 92% in terms of dry matter, kinematic the viscosity increased almost twofold - its value reached a value of 500 cSt. Investigations carried out by the Fourier method of IR spectroscopy on the Shimadzu IR Tracer-100 (Japan) showed that the sodium alginate obtained from the fucus semi-finished by optimized technology is not inferior in quality to sodium alginate produced from laminaria (Sigma Aldrich (USA).) Sodium alginate, made from the fucus semi-finished product, can be used as one of the components of gelling fillings for the production of canned fish in jellies. A technological scheme for processing algae is proposed.

Keywords: brown algae, fucus, technology, sodium alginate, extract, semi-finished product, alginic acid kits, IR spectroscopy, fillings, canned jelly

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1. Introduction

In the global algal industry, brown algae occupy the first place in the total amount of raw material produced. This group of plants makes up the bulk of the phyto-benthos of the World Ocean, being a unique raw material for obtaining valuable food, technical and medical products. Algae have a cumulative ability to accumulate a diverse complex of microelements, in particular iodine, in quantities far exceeding their content in the environment [1-3].

A unique feature of brown algae is the ability to synthesize and accumulate a complex of polyuronic acids, known as "alginic acid", which in the form of alginates - calcium, magnesium, sodium salts - is contained in macro-fits belonging to the genus Macrocystis, Laminaria, Fucus [3-5].

Alginic acid is a polymer of uronic (guluronic and mannuric acids, connected by 1--4 glucosidic bonds) of various degrees of polymerization (DoP), as a result of which its molecular weight and rheological properties vary considerably [2, 14, 17].

Alginic acid and its salts are capable of 200--300-fold absorption of water, forming gels, which are characterized by high acid-resistance. In the food industry, they are used as [2,15-18] emulsifiers, stabilizers, gelling and water-retaining components. In algal tissues, alginic acids are in the form of potassium, sodium, or calcium salts that make up cell walls localized in the intercellular spaces of the mucus channels. Brown algae are used as a source of alginates for the purpose of obtaining from them unpurified biogels, which is an alternative and allows to solve many problems associated with the complex use of raw materials and providing the population with alginate-containing products [5-8].

One of the salts of alginic acid, which has found the widest use, is sodium alginate. This substance is a sodium salt of alginic acid, soluble in water. Sodium alginate is a polysaccharide made up of units of D-mannuronic acid, connected by β-- (1,4) - glucosidic bonds. Chemical formula: $[C_6H_8O_6]$ n. The structural formula of sodium alginate can be represented as follows in Figure 1:

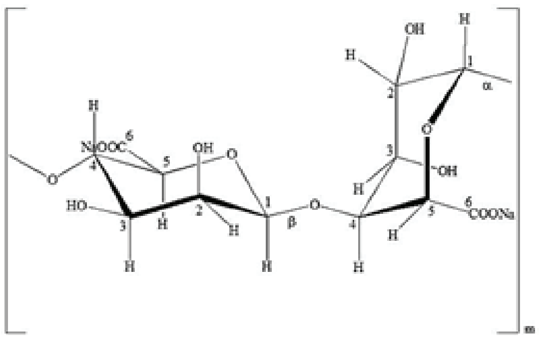

Figure 1: Structural formula of sodium a bcnbcbncnbfcnfnfcblginate.

The molecular weight of sodium alginate ranges from 50.000 to 200.000 and depends on the degree of polymerization, which can reach 750.

Sodium alginate is produced for food and technical purposes. Samples differ from each other in purity and magnitude of the main indicators.

Sodium alginate is highly soluble in water. Food sodium alginate (in accordance with the requirements of the regulatory document TU 15-544-83 "Food sodium alginate. Technical conditions") is a dry powder or small thin plates, its color varies depending on the raw material from cream (from laminar algae) to brown (from fucus). The moisture content in the product should not exceed 16%; mass fraction of ash (in terms of dry substance) - not higher than 26%; the amount of substances not soluble in boiling water is not higher than 0.3%; alginic acid content - not less than 70% (calculated on the dry matter); the kinematic viscosity of 1% sodium alginate solution (calculated on the dry matter) at a temperature of 20 °C should not be lower than 30 cSt [9-11].

Alginates are biocompatible, biodegradable and relatively inexpensive to manufacture, they dissolve well in water and have a high water retention capacity, easily form hydrogels [4, 12]. Due to all this, alginates have found wide application as thickeners, gelling agents and stabilizers in medicine and pharmaceuticals, as well as in the textile industry. But the use of alginates is especially widespread in the field of food production, in particular - sauces, pastes, gelling fillings, cream soups, ice cream, etc. [5, 13].

The MSTU researchers have developed a technology for extracting natural biogel from fucus algae. Fukus extract is used in the formulation of sauces and fillings in the manufacture of culinary fish products and canned jelly. A by-product in the preparation of fukus extract is a semi-finished product of fucus (boiled fucus), which is also used in canned food, salads and cooking.

Using the Anton Paar Physica MC302 rheometer, comparative rheological studies of the fucus extract [3] obtained from *F.vesiculosus* algae and sodium alginate from brown algae from Sigma Aldrich (USA) were carried out. The results of the analysis - flow curves - are presented in Figure 2.

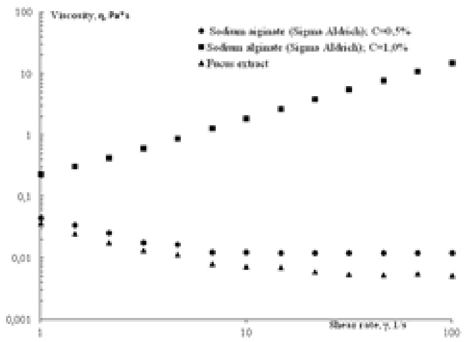

Figure 2: Flow curves of sodium alginate samples from brown algae (Sigma Aldrich) and fucus extract obtained from algae *F.vesiculosus*.

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As a result of research, it was found that extracts contain up to 0.5% sodium alginate, depending on the type of algae. Consequently, most of the alginic substances remain in the waste after receiving fucus extracts (cooked fucus semi-finished product).

2. Methods and Equipment

Fucus obtained in the process of processing F.vesiculosus alga, harvested and dried under natural conditions in August -- September 2013--2014, was used as a raw material for the production of alginates. in the bay Dalnezeletsk of Barents Sea.

The semi-finished product of the fucus was obtained in the process of making a fucus extract as follows: the fucus was washed and reconstituted in water and the fucus in water was treated with water (the ratio of fucus: water = 1:2) at a temperature of (95 ± 5)°C for 1 hour. The liquid part (fucus extract) was separated by filtration, the dense part (boiled fucus semi-finished product) was used to obtain sodium alginate.

Physico-chemical and organoleptic properties, such as mass fractions of moisture, alginic acid, mineral impurities, insoluble in water, were determined according to GOST 26185-84 ``Seaweed, sea grasses and their products. Methods of analysis. Kinematic viscosity was measured on a glass capillary viscometer by measuring the expiration time of a 1% sodium alginate solution.

Comparative rheological studies of sodium alginate samples obtained from the fucus semi-finished product and from the kelp from Sigma Aldrich (USA) were performed on an Anton Paar Physica MCR302 rheometer (USA) using a conical-lamellar working unit (the cone diameter was 50 mm and the angle between the conical surface and the plate were 1 deg). The measurements were carried out under the following deformation mode: periodic oscillations at a constant temperature (24°C) with varying amplitude. The relative error in measuring the apparent viscosity and the components of the dynamic modulus did not exceed 10%, the temperature change was within ± 0.1°C. The reproducibility of the rheological measurements was automatically monitored by parallel testing of two samples of the same contents. The IR spectra of the studied samples were recorded using a Nicolet 700 IR Fourier spectrometer (Thermo Scientific, Madison WI, USA) in the average IR range of 400--4 400 cm^{-1}.

Samples for studies were prepared according to the following method: hydrogels were kept at 12°C for 12 hours. Then they were frozen at 6°C, thawed in the dark and centrifuged. The precipitate formed was dried in an oven at 50°C for 5 hours and, finally, at 25°C for 20 hours. The obtained dry films were ground in a ball mill to the state of a high dispersion powder, mixed with KBr, pressed into a tablet, and measurements were taken.

3. Results

To achieve this goal, it was necessary to substantiate the expediency of using the fucus semi-finished product as a raw material for the production of alginate - to clarify the quantitative content of algin substances in the products of fucus processing using chemical analysis methods.

The dynamics of the distribution of alginic acids in the process of making fucus extract from F. vesiculosus alga was studied: the content of alginic substances in dry and reconstituted fucus, in fucus extract and in boiled fucus (a by-product of the extract production) was determined. The research results are presented in Table 1.

As a result of research, it has been established that up to 80% of alginic acids contained in the raw materials, which can also be isolated and used, remain in the cooked semi-finished product of the fucus. The data obtained confirmed the results of preliminary studies conducted by rheological methods, as well as the assumption that the fukus semi-finished product can be used as a source of alginates.

At the next stage, studies were carried out to study the possibility of obtaining sodium alginate from a by-product of the production of fukus extract. A principal technology was developed, consisting of the following main stages: pretreatment of the semi-finished product with calcium chloride, extraction of alginates, isolation of alginic acid, production of sodium alginate, drying (Figure 3).

Table 1: Alginic acid content in products of fucus processing in the process of making fucus extract, %.

Product name	Mass fraction,%		Data on the material balance of the products of the processing of fucus		
	of dry substances,%	alginic acid,% to dry substances	mass of product, g	mass of dry substances, g	weight of alginic acid, g
fucus dry	92.9	20.1	1000	929	187
fucus reconstituted	20.3	22.5	3750	760	171
fucus extract	0.95	18.8	6000	57	11
prepared semi-finished product of fucus (by-product)	13.1	22.4	5000	670	150

The sodium salt of alginate was obtained by adding to the resulting solution the calculated amount of dry sodium bicarbonate. The resulting sodium alginate solution was air dried and its rheological characteristics were investigated. The content of alginic

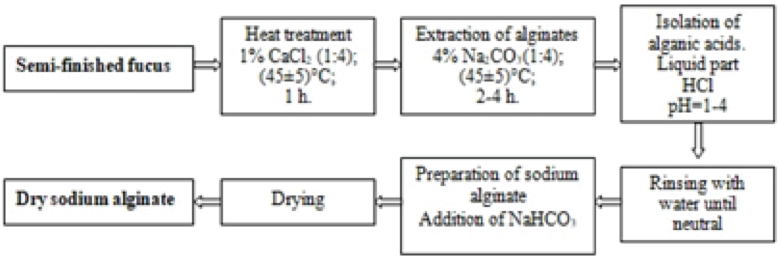

Figure 3: The basic technological scheme for obtaining sodium alginate from the fucus semi-finished product.

acids in the finished product was 83--87% in terms of dry matter, the viscosity of the alginate was rather high - 253--269 cSt, the content of insoluble substances in water was about 0.3%. The product yield was 3.7%. Thus, the resulting product complied with the requirements of the regulatory document for this type of product.

At the next stage of work, the proposed technology was optimized. The possibility of increasing the yield of the finished product and obtaining alginate with improved quality indicators was specified. For this purpose, the stage of extraction of alginates and the stage of extraction of alginic acids have been optimized.

At the extraction stage, the treatment of algae with sodium carbonate solution was varied from 2 to 4 hours. Studies have shown that with a 2-hour extraction of algae, the content of alginic acids in the finished product was on average 85%, the viscosity was 253--269 cSt at the yield of the product 3.7%. Extraction of algae for 3 x hours increased both the content of alginic acids in the product (90--92)% and the viscosity (450--500) cSt. The product yield reached 4.5%. The content of water-insoluble substances with an increase in the duration of extraction to 4-x hours led to a decrease in the quality of alginate: the content of water-insoluble substances increased to 0.89%, the viscosity decreased to 170 cSt, but the product yield increased to 4.9%. Taking into account the obtained results, the optimal extraction duration was established - 3 hours.

The second stage, which required clarification, is the stage of isolation (precipitation) of alginic acids. Isolation of alginic acids from purified cooled solution was carried out with 18% hydrochloric acid solution (6M HCl). It was established that the concentration of hydrogen ions (pH) of the medium was close to the optimum, at which the yield of alginic acids is maximized, and at which the polymer chain does not break, which guarantees high-viscosity alginate. The pH value varied from 1 to 3, since at pH = 4.0 algina was not formed.

It was found that the maximum content of alginic acid in the finished product (92%) with a maximum viscosity (500 cSt) and a rather high yield of the product was observed when hydrochloric acid was added to the concentration of hydrogen medium - pH = 3.

That is, and it was assumed that hydrolysis of polysaccharide bonds proceeds under more severe precipitation conditions (pH = 1), which leads to a decrease in the length of the chain and, consequently, to a decrease in the viscosity of the alginate.

The subsequent stages of the technological process were carried out according to the originally developed technology: the precipitated and washed with water solution of alginic acids was filtered through a nylon mesh and washed on the filter until neutral pH, obtaining a gel-like mass. The alginum was treated with dry sodium bicarbonate, as a result of which a sodium alginate solution was obtained - an odorless light brown liquid. The resulting solution was filtered and air dried. The duration of drying of sodium alginate solution was determined - 12 hours at room temperature (20 ± 2) °C. Under these conditions, the alginate dries to a residual moisture content of 7%, which corresponds to the requirements of regulatory documentation for this type of product (no more than 16%).

4. Discussion

As a result of the improvement of the technological scheme, it was possible to increase the product yield and improve the quality of sodium alginate from algae: the maximum achieved product yield was 4.5% (which is 20% higher than the initial one), the content of alginic acids in the product was 92% of the dry matter (which is 7% higher than the initial value), viscosity - 500 cSt (almost doubled).

The qualitative indicators of sodium alginate, obtained according to the refined technological scheme, are shown in Table 2.

Table 2: Quality indicators of sodium alginate.

Indicators	Characteristic
Appearance	Thin plates
Colour	Light brown
Taste	Without taste
Smell	Without smell
Mass fraction of water,%	7.0
Mass fraction of ash,%	18.0
Mass fraction of alginic acids,% to dry substances	92.0
Mass fraction of substances insoluble in water, not more than,%	0.3
Viscosity, cSt	500.0

To assess the quality of sodium alginate obtained from fucus algae, infrared spectroscopy was performed on a Shimadzu IR Tracer-100 instrument (Japan). A sample of sodium alginate from kelp produced by Sigma Aldrich (USA) with medium viscosity molecular mass Mη = 630 kDa was used as a comparison sample. The analysis showed that the spectrum of the sample obtained from the algae of the fucus, in its main features, is similar to the spectrum of sodium alginate from Sigma Aldrich. In the spectrum of sodium alginate obtained from fucus, the main absorption lines are 3438, 1616, 1415, 1302, 1095, 1029, and 815 cm^{-1} (Figure 4). Since these peaks can be attributed to the structural features of the alginate, this indicates a high content of the indicated polysaccharide in the obtained sample.

Sodium alginate, obtained from fucus algae, was used in the development of new formulations of structured food fillings based on polyelectrolyte complexes of gelatin with polysaccharides (gelling fillings) in the manufacture of canned jelly.

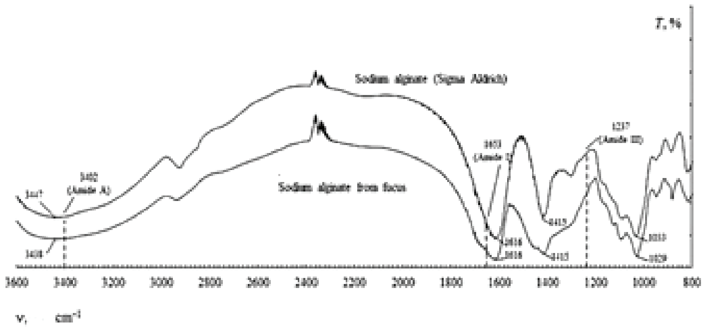

Figure 4: IR spectra of samples of sodium alginate from brown algae (Sigma Aldrich) and sodium alginate obtained from algae *F.vesiculosus*.

As a result of the research, a complex technological scheme for the processing of fucus algae, presented in Figure 5, was developed.

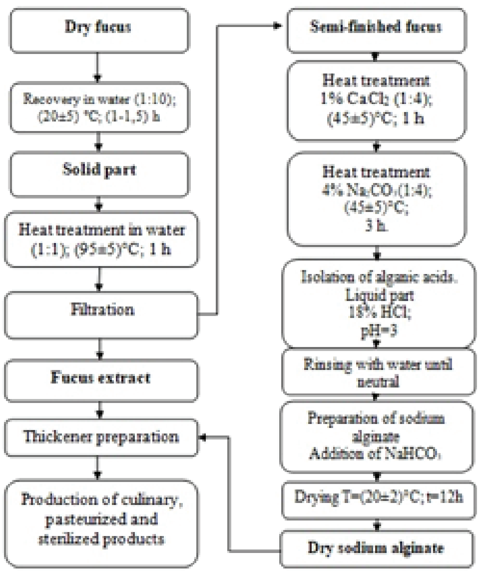

Figure 5: Complex technological scheme for processing fucus algae for food purposes.

The assortment of canned food ``Pollock with vegetables and fucus in jelly'' was exhibited at the 17th international exhibition «Sea. Resources. Technologies -- 2016», where we received a positive assessment of visitors and a diploma of a tasting product competition as part of the round table «Innovative technologies for processing aquatic biological resources of the Arctic»

5. Conclusion

As a result of the research:

-- we determined that up to 80% of the initial amount of alginic acids contained in the raw material remains in the cooked semi-fab of the fucus, which indicates the usefulness of using the by-product formed during the manufacture of fucus extract to produce sodium alginate;

-- technology has been developed to produce sodium alginate from boiled fucus semi-finished product, optimized technological process stages (extraction of alginic substances and extraction of alginic acids);

-- we found that sodium alginate, obtained from the fucus semi-finished product according to the optimized technology, is highly viscous and in quality is not inferior to sodium alginate from the kelp of the company Sigma Aldrich (USA);

-- it is shown that sodium alginate obtained from a fucus semi-finished product can be used as one of the components of gelling fills in the manufacture of canned fish in jelly;

-- we proposed a comprehensive technological scheme for processing fucus algae for food purposes.

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Conflict of Interest

The authors have no conflict of interest to declare.

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