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RESEARCH OF THE SECONDARY MILK RAW MATERIALS PURIFICATION FROM PROTEIN COMPONENTS BY NATURAL POLYSACCHARIDES

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Abstract

Membrane separation processes at most modern milk processing enterprises are included in standard technologies for processing of secondary milk raw materials. However the separations process could still be improved by pre-cleaning of raw materials with plant polysaccharides using. The purpose of the work is an experimental study of the process of preliminary purification of secondary milk raw materials from protein components by natural polysaccharides before its membrane separation.

Fresh cottage cheese whey obtained under production conditions (nationwide standard (GOST R) 53438-2009) and liquid extract of Jerusalem artichoke tubers (industrial type) were used as raw materials. The key indicators of process effectiveness were identified: the ratio of serum and liquid extract, the mass fraction of solids in the working solution, its transmittance, and the thickness of the layer of precipitate formed. To determine the main parameters of the studied raw materials generally accepted methods had been used: the ratio of serum and liquid extract was experimentally determined depending on the optimal physical and chemical composition, and the mass fraction of solids in the working solution was found by refractometric method, and the thickness of the layer of precipitate formed was experimentally measured by caliper rule.

It was found that the highest degree of preliminary purification could be achieved with the following indicators: solids - 7.5 - 7.7%, (including: lactose - 4.4 - 4.5%, total nitrogen - 0.6 - 0 , 7%, milk fat - 0.06 - 0.1%, minerals - 0.6 - 0.7%, insulin - 1.2 - 1.3%, pectin - 0.5 - 0.6%, the acidity of the working solution was 18 - 20 °T, the density was 1030 - 1035 kg/m^3, the sediment layer thickness was 9 - 10 mm and the ratio of cottage cheese whey and Jerusalem artichoke liquid extract had been established at 70 : 30 volume units. Subsequent membrane separations of the membrane permeability of the cottage cheese whey purified at the previous stage could be increased by 16 - 21% in comparison with the traditional method of ultrafiltration.

The experiments proved that at the subsequent membrane separations of the cottage cheese of whey purified at the previous stage the membrane permeability could be increased by 16 - 21% in comparison with the traditional method of ultrafiltration with the same membrane's porosity. The fact of plant polysaccharides enrichment of curd whey has been established, that could be considered as a positive effect for functional foods development.

Key words: *Plant polysaccharides, Milk raw materials, Cottage cheese whey, Membrane separation.*

1. Introduction

The population food patterns in recent years has been characterized by a constant decreasing of the biologically valuable products consumption, especially the dairy products intensively become popular with the consumers. Whey is one of the raw materials reserves. In addition, the analysis of scientific literature [1, 2, 4, and 11 - 14] and independently obtained research results [8, 9] suggest that today curd whey is the most frequently produced by-product in the dairy products manufacturing. However, it should be noted that the domestic industry is not yet fully using such valuable raw materials because of its unstable physical and chemical parameters that is an obstacle for its further processing, including baromembrane methods. Whey obtained under the industrial production of grain curd is a valuable secondary dairy raw material as it contains up to 50 - 52% of milk solids and 68 - 70% of lactose [14]. But for the subsequent usage of whey in technologies like milk-containing beverages and some foods production it would be better if it could be enriched with carbohydrates and components of the mineral complex.

Principal possibility and practicability to use some polysaccharides, which are contained in the modern food's formulations, including the plant origin raw materials are currently well justified [9, 13]. The high content of certain carbohydrates, biologically active substances, as well as the cheapness and availability of production of such raw materials make it possible to use Jerusalem artichoke in the form of its liquid extracts in order to develop the new food compositions with regulated functional properties.

However, it should be noted that the low efficiency of traditional methods of pretreatment causes insufficient usage of deep processing methods, in particular through the use of baromembrane separation processes. In addition, the scientific literature provides a very limited amount of experimental and theoretical data on the results of membrane separation of liquid polydisperse systems, the main component of which is whey with a modified addition of a natural polysaccharides composition complex.

The purpose of the research work is an experimental study of the process for preliminary purification of secondary milk raw materials from protein components by natural polysaccharides before its membrane separation.

2. Materials and Methods

The experiment included cottage cheese whey (Table 1), made in Dairy Plant "Stavropolsky" as a secondary part of cottage cheese making according to the national standard (GOST) 31534-2012 [16, 17].

To determine the main parameters of the studied raw materials generally accepted methods had been used: the ratio of serum and liquid extract was experimentally determined depending on the optimal physical and chemical composition, and the mass fraction of solids in the working solution was found by refractometric method, and the thickness of the layer of precipitate formed was experimentally measured by caliper rule.

Liquid extract of Jerusalem artichoke tubers (industrial type) were used as source of natural polysaccharides. Most often, it is produced at a temperature no higher than 25 - 30 ^{0}C, [3, 13], for preserving the native properties, first of all, the main components of the raw material - the complex "inulin and pectin". Physical and chemical characteristics of liquid Jerusalem artichoke extract (Table 2) makes it possible to use it for pre-cleaning of cottage cheese whey.

The experimental confirmation of increased membrane permeability of cottage cheese whey ultrafiltration process was conducted in the KrosFlo® Research IIi TFF Tangential Flow Filtration System. Due to its peculiar design, it is possible to use cassettes with the polymer membrane elements with the total active filtration area of 0.01 m^2 for the microfiltration of liquid polydisperse systems, as well as to control the circulation speed at constant pressure and carry out the process at varied pressure and constant speed. The cassette type membrane Novaset LS with the average conventional pore size (ACSP) 20 kDa (Table 3) was used to determine the effectiveness of the process membrane separation cottage cheese whey after its pre-cleaning by plant polysaccharides. According to the main parameter (the holding threshold), these membranes can be used for

Table 1. Physicochemical characteristics of cottage cheese whey as an object for pre-cleaning

Factor	Numerical value
Dry solids weight ratio, %, minimum	6.1 - 6.3
Including:	
Lactose	4.4 - 4.6
Mineral	0.6 - 0.63
Total nitrogen	0.9 - 0.94
Fats	0.1 - 0.12
Acidity, °T	45 - 47
Density, kg/m³	1,022 - 1,024

Table 2. Physicochemical characteristics of liquid Jerusalem artichoke extract [14]

Factor	Numerical value
Dry solids weight ratio, %, minimum	12.2 - 12.3
Including:	
Inulin	9.1 - 9.2
Pectin	1.4 - 1.3
Protein	1.2 - 1.3
Mineral	0.9 - 1
Acidity, °T	7 - 8
Density, kg/m³	1,042 - 1,046

Table 3. Operational parameters of cassette type membrane Novaset LS (USA, Novasep)

General factors	Numerical value
ACSP of membranes	20 kDa
Pressure, MPa	0.1 - 0.7
Air Diffusion Rates, MPa	0.05
Temperature, °C	5 - 50
pH of the detergent medium	2 - 12
Operational life, hours	up to 4,000

ultrafiltration of any dairy raw materials. The effectiveness of cottage cheese whey ultrafiltration was evaluated by the degree of membrane permeability increasing (in comparison with the serum purified in the traditional way) while maintaining their selectivity for protein substances acceptable from the technological point of view.

The adequacy of the obtained equations was checked using Fisher criterion, the calculated value of which cannot exceed the table value, depending on the number of experiments performed and the number of factors studied. The equations coefficients were analyzed in accordance with the Student's criterion (at a significance level of 0.05 when p = 0.95).

3. Results and Discussion

3.1 Research of the cottage cheese whey process pre-cleaning by liquid extract of Jerusalem artichoke tubers

Results of experimental research had confirmed the data [6, 13], that enrichment of the cottage cheese whey by the natural polysaccharides provided the mixture dividing into two phases, and one of which the protein complex precipitated in that is formed by a liquid Jerusalem artichoke extract and whey components. Cottage cheese whey, partially purified from proteins, is characterized by a rather stable physicochemical composition and can be directed to ultrafiltration with subsequent use of its separation products in the foods making with an increased (in comparison with analogues) shelf life.

The physicochemical properties of cottage cheese whey after pre-cleaning (Table 4) showed that mixing of the whey with a liquid Jerusalem artichoke extract provided it's enriching with some components contained in plant materials.

The liquid Jerusalem artichoke extract added to cottage cheese whey (Figure 1) improved its organoleptic characteristics (Table 5). This could be explained by the influence of some organic acids (citric, malic, amber, etc.) contained in Jerusalem artichoke tubers. Mass fraction of dry substances was about 6-8%, and the ratio of the carbohydrate complex in it was up to 70% of dry substances (Table 6).

Experiments proved that at the subsequent membrane separations of the cottage cheese whey purified at the previous stage the membrane permeability could be increased by 16 - 21% in comparison with the traditional method of ultrafiltration with the same membrane's porosity

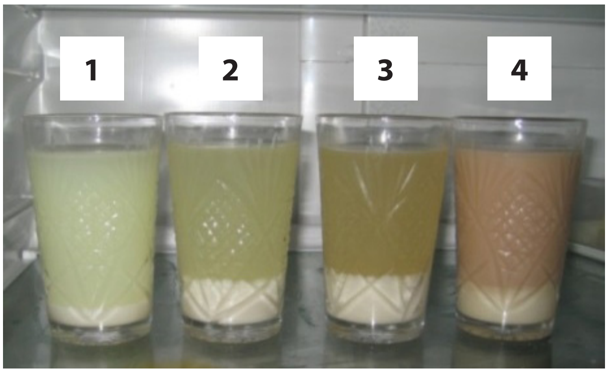

Figure 1. The samples of cottage cheese whey after pre-cleaning by liquid extract Jerusalem artichoke tubers: 1 - Sample 1- up to 10% of extract; 2 - Sample 2 - up to 20% extract; 3 - Sample 3 - up to 30% extract; 4 - Sample 4 - up to 40% extract

Table 4. The basic composition of cottage cheese whey before and after pre-cleaning (t = 12 - 14 °C, p = 0.95)

Name	Initial whey [14]	Whey after pre-cleaning
Calcium, mg%	0.098	0.14
Phosphorus, mg%	0.058	0.075
Manganese, mg%	0.040	0.059
Zinc, mg%	0.032	0.098
Cuprum, mg%	0.007	0.001
Ferrum, mg%	0.003	0.535
Vitamin C (Ascorbic acid), mg%	0.5	12.50
Vitamin B2 (Riboflavin), mg%	0.12	0.32
Vitamin E (Tocopherol), mg%	0.025	7.65

Table 5. Organoleptic characteristics of cottage cheese whey after pre-cleaning by liquid extract Jerusalem artichoke tubers

Factor	Initial whey [14]	Cottage cheese whey after pre-cleaning
Flavor and aroma	Typical to this type of raw material	Sweet and sour, pronounced flavor with a slight carrot flavor
Appearance	Yellowish green liquid without suspensions	Yellowish liquid with a brown tone, slightly opalescent

Table 6. Main components in the cottage cheese whey after pre-cleaning by liquid extract Jerusalem artichoke tubers (p = 0.95)

Factor	Sample 1	Sample 2	Sample 3	Sample 4
Dry solids weight ratio, % minimum	5.8 - 6.5	6.5 - 7.2	7.2 - 7.7	7.6 - 8.3
Including:				
Lactose	4.3 - 4.4	4.3 - 4.4	4.3 - 4.4	4.3 - 4.4
Total nitrogen	0.4 - 0.5	0.5 - 0.6	0.6 - 0.7	0.7 - 0.8
Inulin	0.6 - 0.8	0.9 - 1.1	1.2 - 1.3	1.3 - 1.4
Pectin	0.1 - 0.3	0.3 - 0.5	0.5 - 0.6	0.6 - 0.9
Mineral	0.4 - 0.5	0.5 - 0.6	0.6 - 0.7	0.7 - 0.8
The sediment layer thickness, mm	6	7.5	9	7.8
Acidity , °T	17	17	18	18
Density, kg/m³	1,024	1,027	1,030	1,033

3.2 The effect of cottage cheese whey pre-cleaning by Jerusalem artichoke liquid extract on the permeability and selectivity of membranes during ultrafiltration

Major factor influenced on the selectivity and permeability of the polymer membranes at ultrafiltration of liquid systems is a transmembrane pressure (Δp) 5, 7, 9, 10, 13, 15].

The results of experimental studies, represented in the form of graphical dependence of the form Q = f (Δp) and Ψ = f (Δp), are illustrated in Figures 2 and 3.

Experimental data shown the way of Q = f(Δp) dependence changes for the 20 kDa membrane during separation of the initial whey and cottage cheese whey after pre-cleaning by ultrafiltration is quite similar: permeability increasing is proportional to the increase in the transmembrane pressure in the pipe of the baromembrane device. However, the values $tg\varphi_i = dQ/d\Delta p$ for relevant plots were different. Since the physical meaning of tgφi is the rate of function Q = f(Δp) increment this suggests that both of the membrane permeability Q and its growth intensity increase during ultra-filtration of the cottage cheese whey after pre-cleaning. This phenomenon is derived from the fact that the liquid extract Jerusalem artichoke tubers added to the cottage cheese whey obtained from the production of the grained curd by the conventional method causes changes in the physical and chemical properties of whey due to its separation by ultrafiltration method. The plots review for the function Q = f(Δp) shown that at the same value of the other parameters of process, the significant increment of the membrane permeability had been established at the transmembrane pressure increasing within Δp = 0.12 - 0.14 MPa to Δp = 0.32 - 0.34 MPa. Then the Q value remained practically stable. Value of Δp parameter increasing over 0.38 - 0.42 MPa had insignificant impact on the membrane permeability during ultrafiltration of both liquid systems, and when the initial whey was used as an object of separation, the Q value tended to decrease.

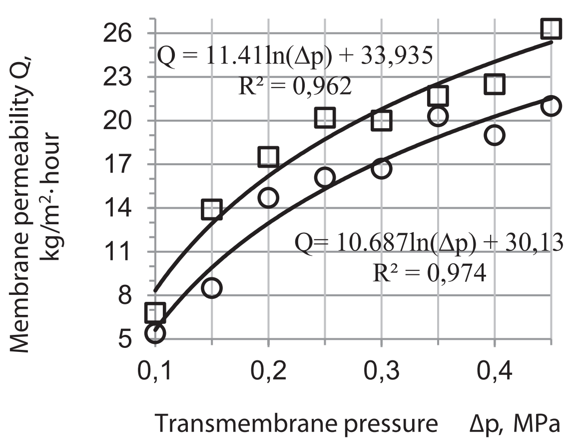

Figure 3. Correspondence of the membrane selectivity Q (□ - the cottage cheese whey after pre-cleaning by liquid extract Jerusalem artichoke tubers, ○ - the initial whey) on the transmembrane pressure Δp during the separation by ultrafiltration with ACSP 20 kDa (t = 10 - 12 °C, v = 0.1 - 0.3 m/s, Cd.s. = 8 - 8.2%)

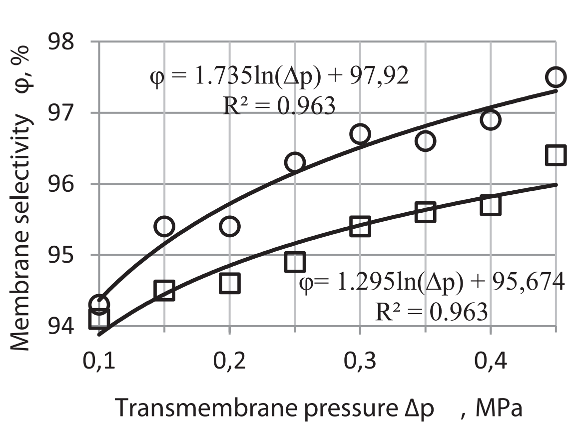

Figure 2. Correspondence of the membrane permeability Q (□ - the cottage cheese whey after pre-cleaning by liquid extract Jerusalem artichoke tubers, ○ - the initial whey) on the transmembrane pressure Δp during separation by ultrafiltration with ACSP 20 kDa (t = 10 - 12 °C, v = 0.1 - 0.3 m/s, Cd.s. = 8 - 8.2%)

From the sieve model of ultrafiltration point of view a significant membrane selectivity increasing at $\Delta p > 0.42 - 0.44$ MPa most probably relates to the start of mechanic pores obstruction with disperse phase particles and complicated by partial deformation of polymer membrane structure. In total, this causes reduction in the effective size of the flow section of pore space. This explanation would suggest that the area of the efficient transmembrane pressure value in the pipeline of the baromembrane device should be limited within $\Delta p = 0.28 - 0.38$ MPa. The validity of such conclusion is proved by the results of experimental data review to assess the dependence of the membrane selectivity φ on the value of transmembrane pressure. In general, the pattern of changes in the parameter φ for both types of whey is also identical, but, during ultrafiltration of the cottage cheese whey after pre-cleaning by liquid extract Jerusalem artichoke tubers, the rate of φ increasing is lower in comparison with the initial whey as the object of baromembrane separation. That results let us to provide the suggestion that the intensity of adsorptive intermolecular interactions "disperse phase particles - membrane" identified by physical and chemical properties of the cottage cheese whey after pre-cleaning, is lower than the same factor for the initial whey.

4. Conclusions

- Secondary milk raw materials process pre-cleaning from protein components by natural polysaccharides had been studied. The highest degree of secondary milk raw materials purification after pre-cleaning by plant polysaccharides had been established by mixing 30 ± 2 volume units of liquid extract Jerusalem artichoke and 70 ± 2 cottage cheese whey.

- Experiments proved that at the subsequent membrane separations of the cottage cheese of whey purified at the previous stage the membrane permeability could be increased by 16 - 21% in comparison with the traditional method of ultrafiltration with the same membrane's porosity.

- The fact of plant polysaccharides enrichment of cottage cheese whey has been established, that could be considered as a positive effect for functional foods development.

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