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Sequential Micro- and Ultrafiltration in the Process of Production of Cottage Cheese

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Abstract—The present work is devoted to solving the tasks aimed at the study of pressure-driven membrane processes used in the manufacture of ultrafiltration cottage cheese via microfiltration followed by ultrafiltration using membranes of domestic manufacture. As a result of this study, the technological parameters of baromembrane processes (speed of solution over the membrane, operating pressure, and temperature) providing the maximum productivity and selectivity of the microbiological clearance of skim milk by microfiltration and the ultrafiltration concentration of curd have been determined. The possibility of affecting the characteristics (permeability and selectivity) of the ultrafiltration process by approaching the isoelectric point of the protein fraction due to the change in the active acidity of the curd under concentration has been considered. The applicability of the microfiltration process in cottage cheese making has been confirmed, since it leads to enhancement of the performance of ultrafiltration membranes and increases the shelf life of the resulting product.

Keywords: microfiltration, ultrafiltration, selectivity, permeability, skim milk, curd

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INTRODUCTION

Membrane technology is being increasingly implemented in the food industry in Russia, especially in the dairy sector [1]. Currently, the development of products with enhanced nutritional and biological value that fully provide the consumer's diet with complete proteins is one of the main challenges of the dairy industry [2–4]. Ultrafiltration (UF) cottage cheese, the production of which is based on pressure-driven membrane technology [5–7], belongs to such products. This technology makes it possible to preserve whey proteins in the product being obtained, as well as to increase the yield of cottage cheese approximately twofold [5] when compared to the "traditional" technology. It is known that products containing whey proteins have a short shelf life [2]; therefore, decreasing the amount of microflora in the original feedstock is an important step of milk processing which improves the safety of the end product and its shelf life. According to the literature analysis, it is reasonable to use a microfiltration (MF) process for this purpose, which can allow substantially prolonging the shelf life of dairy products, as well as to preserve valuable components of milk which are destroyed during high-temperature treatment [8, 9]. Also, based on the thesis that amino acids and, hence, proteins are amphoteric molecules by their nature because they contain both acidic and alkaline functional groups, it can be assumed that there is a correlation between the main characteristics of the UF process (selectivity and permeability) and the active acidity of the cottage cheese curd under separation.

In connection with this, it is of substantial interest to solve the task aimed at the investigation of the baromembrane processes of production of UF cottage cheese, namely, the MF microbiological clearance of skim milk and the UF concentration of curds, the applicability of the MF process, possibility for controlling the UF process by approaching the isoelectric point of the protein fraction due to the change in the active acidity of the curd under concentration, and development of recommendations on the implementation of a technology using domestic membranes.

EXPERIMENTAL

Laboratory Unit

The studies were conducted on the unit sketched in Fig. 1. MF and UF membrane devices (*1*) are intended for the separation of the test solution. An ONTs 1.5/20K–0.75/2 pump (*2*) with a FRENIC-Eco F1S frequency converter is intended for feeding the solution to a membrane cell and pressurization. Feed tank *3* of 15 dm^3 in volume is intended for the

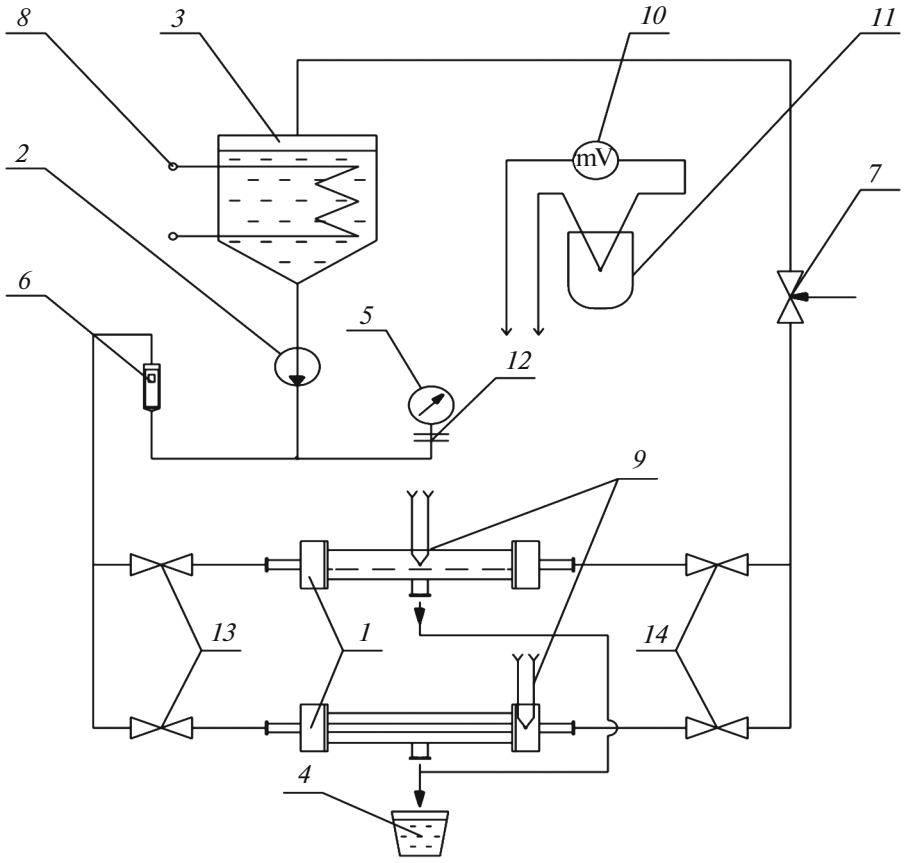

Fig. 1. Schematic of the laboratory unit for studying MF and UF processes: (*1*) membrane device, (*2*) pump, (*3*) feed tank, (*4*) permeate vessel, (*5*) pressure gauge, (*6*) flow meter, (*7*) control valve, (*8*) coil pipe, (*9*) thermocouple, (*10*) millivoltmeter, (*11*) Dewar flask, (*12*) permeator, and (*13, 14*) valves.

supply of the feed solution and its further circulation in the feed tank–pump–membrane cell loop. Permeate vessel *4* is a glass volumetric flask used for the determination of the permeate flow rate. An M0-5 manometer (*5*) with permeator *12* serves for pressure monitoring. An RS-5 flow meter (*6*) type measures the flow rate of the solution. An RU-160 control valve (*7*) is intended for pressure control. Coil pipe *8* is intended for temperature control of the test solution. Chromel–alumel thermocouple *9* is used for monitoring the temperature conditions of the MF or UF process. An F-4214 millivoltmeter (*10*) measures the electromotive force induced by the thermocouple. Dewar flask *11*, which is an airtight container made of foamed plastic and filled with ice, is designed to exclude the influence of the ambient temperature when measuring the temperature of the separation process. Valves *13* and *14* are designed to connect in series the membrane cells. All the metallic parts are made of 12Kh18N10T stainless steel.

The membrane devices capable of operating in the crossflow mode are the key elements of the laboratory unit. In the upper, plate-and-frame module (Fig. 1), a flat-sheet polymer membrane of 300 mm in diameter is installed. The membrane area is 7.0×10^{-2} m^2. In the bottom, tubular module (Fig. 1), a tubular ceramic membrane element of 800 mm in length is installed. The membrane area is 1.5×10^{-2} m^2.

Membranes

The following types of MF and UF membranes were used in the experiments: UPM-20 and UPM-50M polysufone amide flat-sheet membranes; MFAS-OS-(1-4), UAM-50P, and UAM-100P cellulose acetate membranes (Vladipor, Russia); and KMFE and KUFE series ceramic membranes based on titanium dioxide (anatase) with a supported selective layer of α-alumina (Keramikfil'tr, Russia). MF membranes are characterized by an average pore diameter from 0.4 to 1.8 μm, while UF membranes are characterized by molecular weight cut-offs of 10, 30, 50, 100, and 150 kDa.

Solutions

Skim milk corresponding to GOST (State Standard) R 53503-2009 and curds prepared from processed skim milk using the rennet technique were used as the objects of study. Milk processing consisted in its microbiological clearance by MF separation (MF pasteurization) or the thermal method (heat pasteurization). The thermal method consisted in heating the original milk to 82 ± 3°C, holding at this temperature for 20–30 s, and cooling to the experimental temperature. The readiness of the curd was determined by its acidity that should be 65–90°T (pH 4.6–4.9). Curds with various concentrations were obtained via UF concentration followed by cooling the concentrate to 4 ± 2°C.

Methods for Analysis of Solutions

Samples were taken and prepared for analysis according to GOST 9225, GOST 26809, and GOST 26929. The physicochemical parameters were determined according to standard procedures [10]: the weight fraction of moisture, according to GOST 30305.14; the weight fraction of casein, as well as total protein content, according to GOST 25179 using a refractometer and a formal titration method, with the Kjeldahl method being used as a reference; the weight fraction of fat, according to GOST 5867 by the acid Gerber method; the weight fraction of lactose, by the Lawrence method; the titratable acidity, according to GOST 3624; and general and active acidity, according to GOST 15113.5 by a potentiometric method. The quantity of mesophilic aerobic and facultative anaerobic microorganisms (QMAFAnM) was determined according to GOST R 53430-2009.

Experimental Procedure

Taking into account that the objects of the study were food media, the time of each experiment was limited to the interval of no more than 40–50 min (corresponding to the time interval of residence of a milk product in industrial continuous membrane units), which made it possible to obtain results, in the case of which the organoleptic and physicochemical parameters of samples retained their regulated values. After each set of experiments, the laboratory unit was subjected to sanitary treatment, with the membrane regeneration conditions being observed in accordance with the recommendations by the membrane manufacturers. Since the operating pressure of MF and UF processes in the experiments was no more than 0.5 MPa, no preliminary preparation of membranes associated with their compaction as a result of the action of pressure was required from our point of view.

Calculation Equations and Processing of Experimental Results

The flow velocity of the solution over the membrane was calculated according to the equation

$$u = Q/S, \quad (1)$$

where u is the velocity of flow of the solution over the membrane, m/s, Q is the flow rate of the solution in the unit (determined with the flow meter), m^3/s, and S is the cross-sectional area of the upstream channel, m^2.

The cross-section area of the upstream channel was calculated according to the equations

$$S = \pi d^2/4 \text{ (for the cylindrical device)} \quad (2)$$

and

$$S = ab \text{ (for the plate-and-frame device)}, \quad (3)$$

where d is the internal diameter of the tubular ceramic membrane element, m, and a and b are respectively the channel width and height in m.

To assess the flow regime of the solution in the pressure channel, the Reynolds number was calculated by the equation

$$\mathrm{Re} = ud_{eq}/\nu, \quad (4)$$

where d_{eq} is the equivalent diameter of the channel, m, and ν is the kinematic viscosity coefficient of the solution, m^2/s.

For a ceramic membrane, $d_{eq} = d$, while the equivalent diameter for a flat-sheet polymer membrane was calculated as

$$d_{eq} = 4S/P, \quad (5)$$

where P is the perimeter washed by the solution flow, m.

The permeability of membranes G, $dm^3/(m^2\ h)$ was calculated according to the equation

$$G = V_p/(F\tau), \quad (6)$$

where V_p is the volume of the permeate collected within 1 h, dm^3, F is the total membrane area in the module, m^2, and τ is the separation time, h.

The selectivity of membranes φ (%) was calculated according to the equation

$$\varphi = 1 - C_p/C_v, \quad (7)$$

where C_p is the concentration of the permeate and C_v is the volume concentration of the solution.

The efficiency of the microbiological clearance of skim milk E_f(%) was calculated according to the equation

$$E_f = (M_o - M_{pr})100/M_o, \quad (8)$$

where M_o is the microbiological contamination of the original milk, CFU/cm^3 and M_{pr} is the microbiological contamination of the processed milk, CFU/cm^3.

To determine each of the parameters of interest, at least three experiments were conducted. The results of

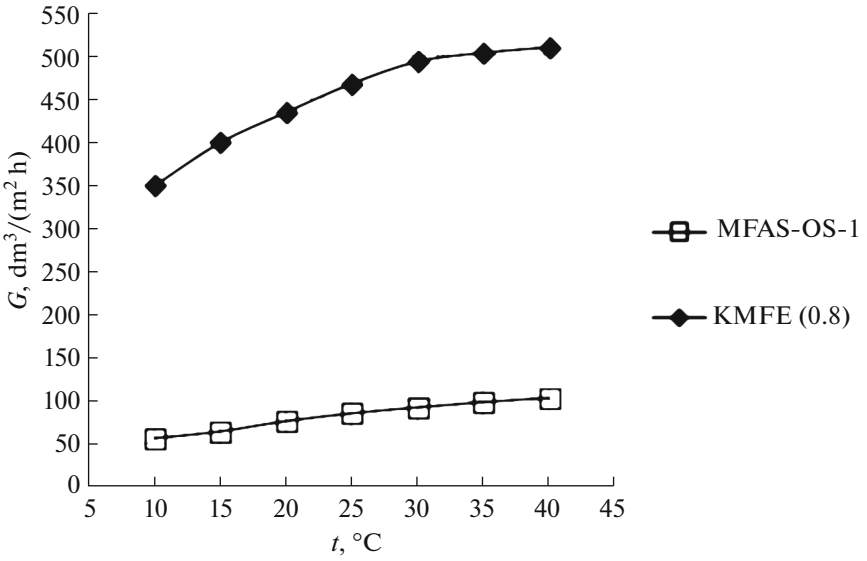

Fig. 2. Dependence of the permeability of MF membranes on the temperature (skim milk) at $u = 4.5$ m/s, $P = 0.25$ MPa, and $C = 8.5\%$ DM.

the experiments were processed by mathematical statistics methods and correlation and regression analyses at a confidence level of 95 (level of significance of 0.05).

RESULTS AND DISCUSSION

The main aim of the study was to determine the process parameters and the membrane type that would be the most adequate to tackling the problem formulated above.

MF and UF processes are usually conducted at high speeds of the feed over the membrane surface, which is determined by the low values of the diffusion coefficient of dissolved solutes with a high molecular weight (above 500) and, as a consequence, the strong influence of concentration polarization [11]. This approach was fully confirmed in the experiments with skim milk and curds. It was found that for MF membranes, it is necessary to maintain the flow velocity over the membrane surface at $u \geq 4.0$ m/s, which corresponds to Reynolds numbers of $\mathrm{Re} \geq 11400$ in the case of flow in the tubular channel and $\mathrm{Re} \geq 12000$ in the case of flow in the flat channel. For UF membranes, the speed of the curd flow over the membrane should be $u \geq 2.5$ m/s, which corresponds to Reynolds numbers of $\mathrm{Re} \geq 4450$ in the tubular channel and $\mathrm{Re} \geq 5000$ in the flat channel. Thus, further experiments were conducted at $u = 4.5$ m/s for the MF process and $u = 3.0$ m/s for the UF process.

The study of the influence of the operating pressure on the membrane characteristics showed that the, MFAS-OS-1 ($\varphi = 0.99$) and KMFE (0.8) ($\varphi = 0.998$) membranes are preferable for the MF process. For the UF process, the UPM-50M ($\varphi = 0.98$–0.99) and KUFE (0.01) ($\varphi = 0.985$–0.987) membranes are the most appropriate. Further studies were conducted only with these types of membranes. The operating pressure of the processes should be maintained within the range of 0.25–0.3 MPa for MF and 0.3–0.35 MPa, for UF.

Based on the well-known facts [11–15] that an increase in the temperature of the solution leads to an increase in the productivity of MF and UF processes, we conducted experiments on the determination of the temperature dependence of the permeability and selectivity of the membranes (Figs. 2–5). The studies were conducted within the range of temperatures of $t = 10$–40°C (MF) at which the skim milk under study does not change its physicochemical properties [16, 17] and $t = 35$–75°C (UF) at which the curd retains its rheological and physicochemical properties [6].

The experiments showed that the permeability of the membranes increases with the temperature (Figs. 2, 3), with the effect of temperature being the most significant for the ceramic membranes. Temperature elevation leads to a decrease in the viscosity of the milk and curd and, hence, an increase in the diffusion coefficient of high-molecular-weight compounds in the upstream membrane layer. This positive factor leads to a decrease in concentration polarization and, as a consequence, an increase in the permeability of the membranes. For the UF process, an increase in the temperature above 50°C leads to domination of the permeate flow rate over the mass transfer coefficient as a result of the decrease in viscosity. This factor leads to an enhancement of concentration polarization and, hence, a decline in the growth of the membrane permeability with an increase in the temperature. This decline is more noticeable in membranes with higher

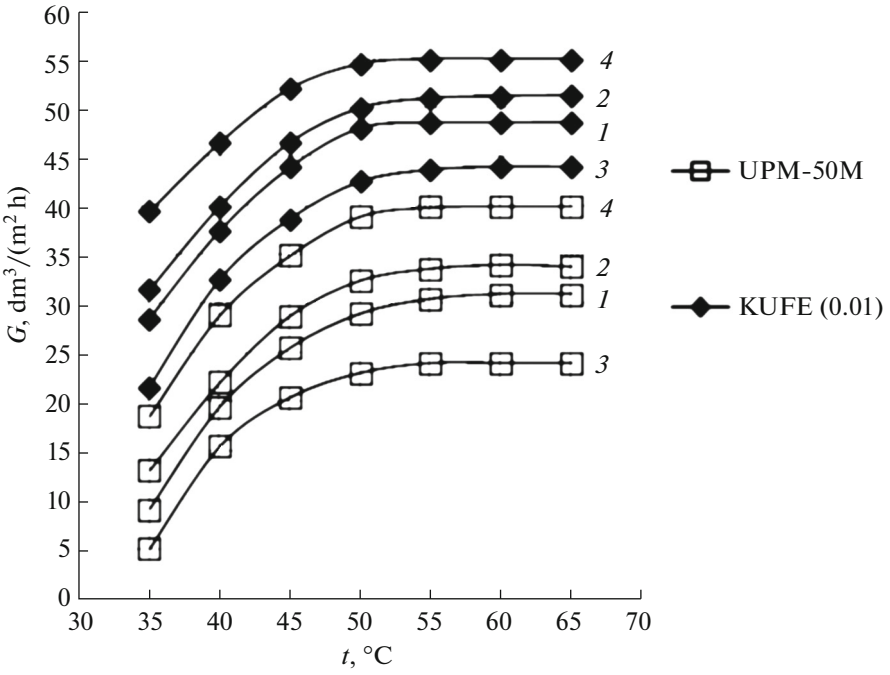

Fig. 3. Dependence of the permeability of UF membranes on the temperature (curd) at $u = 3.0$ m/s and $P = 0.35$ MPa. (*1*) $C =$ 12% DM, (*2*) $C = 10\%$ DM, (*3*) $C = 15\%$ DM, and (*4*) $C = 8.5\%$ DM.

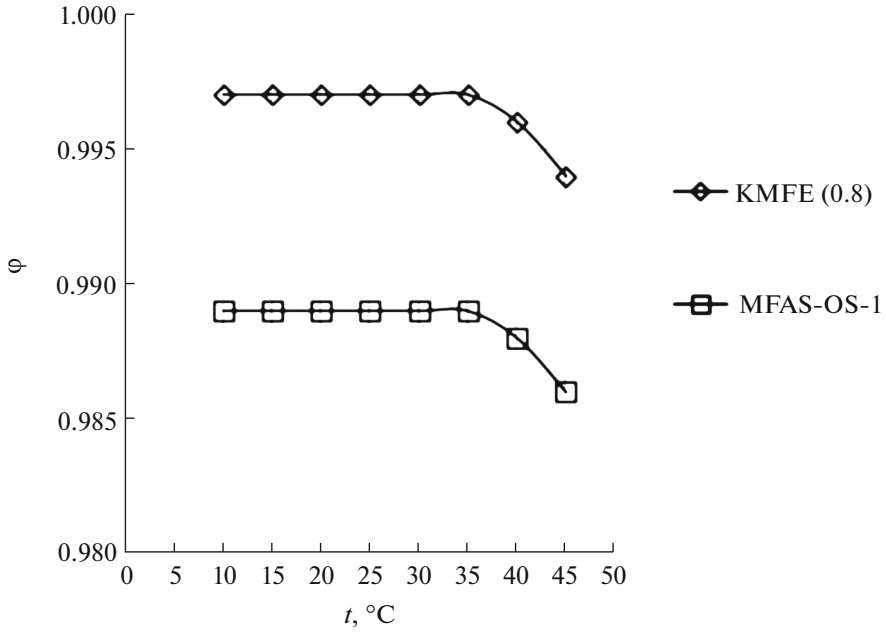

Fig. 4. Dependence of the selectivity of MF membranes on the temperature (skim milk) at $u = 4.5$ m/s, $P = 0.25$ MPa, and $C =$ 8.5% DM.

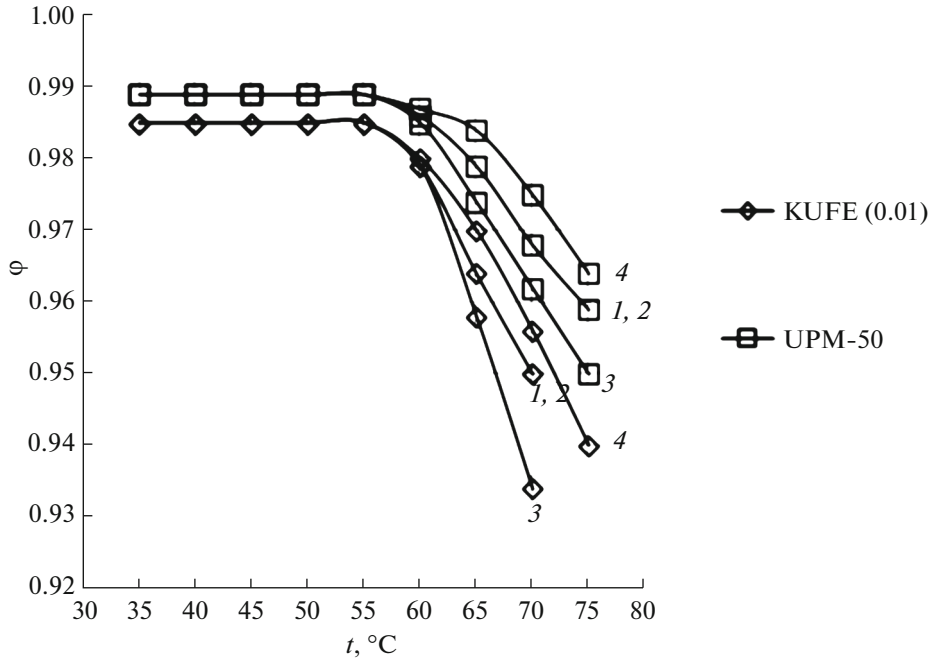

Fig. 5. Dependence of the selectivity of UF membranes on the temperature (curd) at $u = 3.0$ m/s and $P = 0.35$ MPa. (*1*) $C = 12\%$ DM, (*2*) $C = 10\%$ DM, (*3*) $C = 15\%$ DM, and (*4*) $C = 8.5\%$ DM.

permeability (ceramic membrane). The influence of concentration polarization results in that the permeability of the membranes does not increase anymore and remains almost constant with the increase in the temperature above 50–55°C.

Studying the influence of temperature on the selectivity showed that the selectivity of MF membranes decreases with an increase in the milk temperature above 35°C (Fig. 4). The decrease in the selectivity is apparently due to polymorphism of the bacteria [18]. By the action of temperature, the bacteria change their shape and the probability of their penetration into membrane pores increases.

The influence of temperature on the selectivity of UF membranes (Fig. 5) manifests itself when the curd temperature increases above 57°C. In addition, the relationship $\varphi(t)$ is substantially affected by concentration of the protein phase in the curd: the higher the concentration, the greater the decline in the membrane selectivity with the growth in temperature. In our opinion, this effect can be explained by the deformation of molecules with a high weight [18] and their penetration into membrane pores.

The dependence of the permeability of a UF membrane on the active acidity of curd is presented in Fig. 6. The experiments revealed that the UF process can be affected by approaching the main portion of the protein fraction of the feed curd to the isoelectric point. The maximum value of permeability ($G = 54$ dm^3/(m^2 h)) is observed within the pH range of 4.65–4.7, which is in a good agreement with the value of the active acidity of the isoelectric point of casein (pH 4.6–4.7). The selectivity of the UF membrane is not varied by changing the pH within the examined range and has constant values of $\varphi = 0.985$–0.987.

To confirm that it is appropriate to use the MF process in the production of UF cottage cheese, a set of experiments was performed. It was found that during the MF pasteurization of skim milk, all the valuable components are preserved in the permeate (Table 1). The amount of the permeate was 92–96%. The efficiency of the microbiological clearance of milk E_f by MF pasteurization was 99.9% versus that 90.9% by thermal pasteurization (Table 2).

The results of the study of the UF concentration of the curd prepared from MF pasteurized milk on one hand and from thermally pasteurized milk, on the other hand, are presented in Table 3. It is seen that the permeability of the UF membrane in the experiments with the curd obtained from the MF pasteurized milk is higher than that in the case of curd obtained from the thermally processed milk by about 7–10%. We believe that this effect is due to living and nonliving bacteria remaining in the thermally pasteurized milk and making a dispersed phase, which is concentrated during the curd ultrafiltration process and substantially affects the membrane flux.

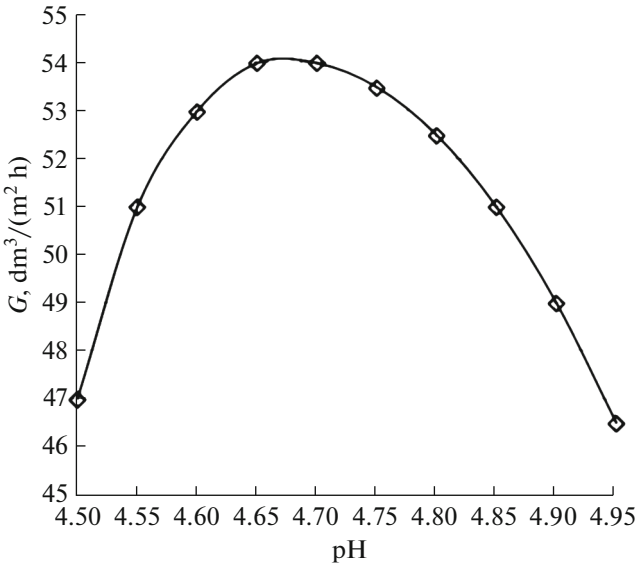

Fig. 6. Dependence of the permeability of UF membranes on the active acidity of curd at $u = 3.0$ m/s, $P = 0.35$ MPa, $t = 55$°C, and $C = 8.5\%$ DM; the KUFE (0.01) membrane.

Microbiological tests of the UF cottage cheese were also conducted in order to determine its shelf life depending on the type of the raw milk used for curd fermentation (Table 4). Samples of cottage cheese were stored under the same conditions in a refrigerator at $t = 4 \pm 2$°C. As is seen from the results of the tests, the shelf life of the UF cottage cheese obtained from the MF pasteurized milk is almost threefold longer that that of the UF cottage cheese obtained from the thermally pasteurized milk. As the criterion of acceptability of UF cottage cheese, the change in its qualitative characteristics determined by the concentration (accumulation) of mesophilic aerobic and facultative anaerobic microorganisms (QMAFAnM) in the product was considered. At QMAFAnM $\geq 5.0 \times 10^3$ CFU/cm^3, UF cottage cheese was considered as foul.

CONCLUSIONS

The studies have made it possible to determine the process parameters of pressure-driven membrane processes of the production of UF cottage cheese. For the

Table 1. Physicochemical parameters of skim milk before and after the MF process (average values)

Parameters	Skim milk	Permeate	Concentrate
Total protein, wt %	3.05	3.01	3.81
Lactose, wt %	4.65	4.65	4.65
Fat, wt %	0.05	0.01	0.8
Mineral substances, wt %	0.82	0.81	1.01
Dry matter, wt %	8.57	8.48	9.26
pH value	6.65	6.68	6.62
Acidity, °T	17.5	17.0	18.0

Table 2. Microbiological contamination of feed skim milk and skim milk after MF pasteurization and heat pasteurization (average values)

Parameters	Skim milk (M_o)	MF pasteurization		Heat pasteurization (M_{pr})
		permeate (M_{pr})	concentrate	
QMAFAnM, CFU/cm^3	2.3×10^5	1.5×10^2	4.5×10^6	2.1×10^4
Clearance efficiency (E_f), %	–	99.9	–	90.9

Table 3. The permeability of the KUFE (0.01) membrane in the curd UF process at $u = 3.0$ m/s, $P = 0.35$ MPa, and $t = 55$°C

C, % DM	G, dm^3/(m^2 h)	
	curd (MF pasteurization)	curd (heat pasteurization)
8.5	55.0	51.1
10	51.0	46.9
12	48.5	44.1
15	43.7	39.3

Table 4. Shelf life of the samples of UF cottage cheese

Shelf life, day	QMAFAnM parameter, CFU/cm^3	
	UF cottage cheese (MF pasteurization)	UF cottage cheese (heat pasteurization)
1	4.0×10^2	1.1×10^3
3	5.1×10^2	1.9×10^3
5	8.5×10^2	3.5×10^3
7	1.0×10^3	$\geq 5.0 \times 10^3$
9	1.5×10^3	–
11	2.0×10^3	–
13	2.5×10^3	–
15	3.1×10^3	–
17	3.7×10^3	–
19	4.4×10^3	–
21	$\geq 5.0 \times 10^3$	–

MF process of milk separation, a milk flow velocity of $u \geq 4.5$ m/s, an operating pressure of $P = 0.25$ MPa, a process temperature of $t = 35$°C, and a ceramic membrane with a pore diameter of 0.8 μm are preferable. For the UF process of curd concentration, a curd flow velocity of $u \geq 3.0$ m/s, an operating pressure of $P = 0.35$ MPa, a process temperature of $t = 55$°C, and active acidity of the curd of pH 4.7 ± 0.05, and a ceramic membrane with a pore diameter of 0.01 μm are more appropriate.

It has been confirmed that it is reasonable to use the MF process for making/UF cottage cheese, since it improves the productivity of UF membranes and increases the shelf life of the product.

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