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Semi-empirical model for the evaluation of protein retention during tangential filtration of whey using ceramic membrane elements

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***Abstract*—This paper considers some results of using tangential filtration by ceramic membrane elements for the treatment of whey. Five samples of filtrate which was obtained by four different ceramic membranes were used for experiment. These membranes have pore size 400, 200, 100, 65 and 50 nm. A semi-empirical model for the evaluation of protein retention during tangential filtration of whey using ceramic membrane elements is discussed in more detail below. The optimal membrane pore size for specified applications has been determined on the base of the proposed model. Results of the work could be used in the calculation of filtration equipment to improve the efficiency of dairy production and neutralize their waste water.**

Keywords*— *tangential filtration, ceramic membrane, whey, membrane retention, semi-empirical model.

I. Introduction

Milk processing is one of the important areas of the agricultural industry. According to the International Dairy Federation (IDF), more than 100 kg of milk per person is consumed annually in the world. About 21% of this volume is accounted for by the production of cheese and curd [1]. A large amount of whey is used in the production of cheese and cottage cheese. Production of one ton of cottage cheese is accompanied by the release of 6 to 10 tons of whey. Many enterprises consider cottage cheese whey as a waste product and dump it into sewers or natural waterways.

Curd whey contains up to 4.7% lactose, up to 1% protein, up to 0.8% fat and up to 0.6% minerals [2]. The level of whey acidity is 50–85 °T. Whey belongs to the 4th class of hazards, therefore its discharge into natural water sources or sewage is prohibited. Whey contains about 50% dry matter from the original milk, which indicates productivity losses when whey is disposed into the sewer system [3].

The main objective of whey processing is the extraction of nutrients from it, specifically whey proteins. Whey proteins can be dried [4] to obtain the finished product or used in the production of dairy products in the enterprise.

One of the best technologies for treating whey and extracting whey proteins is tangential filtration using ceramic membranes [5, 6]. During the process of tangential filtration, the filtered flow moves parallel to the membrane surface, ensuring that it is kept clean. The filtrate is discharged through the side wall of the surface. The applied ceramic materials provide high resistance to pH and temperatures, which allow them to be used without restrictions in the dairy industry [7,8].

For this work, the dependence of the retention for proteins is researched by tangential filtration using ceramic membrane elements.

II. Experimental part

A. Materials and equipment of experiment

The experiment was performed to obtain raw data on the treatment of whey using tangential filtration by ceramic membranes with different pore sizes. Curd whey was the experimental material, which was obtained from an industrial production site at Nadezhda Dairy, Sverdlovsk Region, Russia. The raw material for the experiment was received directly from the culture tank.

An open-loop laboratory ultrafiltration unit was used to filter the whey and separate the residual protein and fat. The Installation diagram is shown in Figure 1.

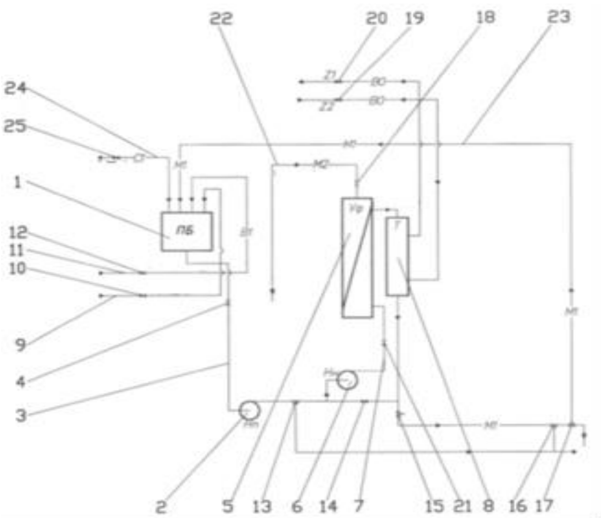

Fig. 1. . Scheme of laboratory ultrafiltration unit

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The installation includes: 1 – supply tank; 2 – feed pump; 3 – suction pipe; 5 – ultrafiltration unit; 6 – pressure pump; 7 – supply pipe; 8 – heat exchanger; 9 – pipeline supply of the initial solution; 11 – clean water supply pipeline for flushing the installation; 13 – a three-way valve for switching the solution supply to the pipeline of the pressure pump or to the drain; 14 – backflow preventer; 15 – adjusting valve; 16, 17 – three-way valves designed to switch the supply of concentrate to the supply tank or to the drain; 18, 19, 20 – valves designed to regulate the flow of coolant in the heat exchanger; 22 – permeate withdrawal line; 23 – solution circulation pipe; 24 – pipeline supply of the washing solution; 4, 10, 12, 21, 25 – shut-off valves. Flow designations: M1 – retentate; M2 – permeate; B0 – coolant; B1 – pure water.

The unit is equipped with two pumps: a feed pump Hn and a pressure pump Hn. The feed pump transfers the filtered fluid from the supply tank to the system. The pressure pump provides pressure that regulates the flow of the baromembrane separation. The feed pump has a flow rate of up to 35 m^3/h and a head up to 20 m, and a pressure pump has a flow rate of up to 40 m^3/h and a head up to 35 m.

One-channel ceramic membranes on the base of Al_2O_3 with different pore diameter were used for the experiment. The pore diameters (*D*) were 400, 200, 100, 65 and 50 nm. A microphoto of the membrane element structure is presented in Figure 2. These membrane elements were produced by “Keramicfilter” company (Moscow, Russia).

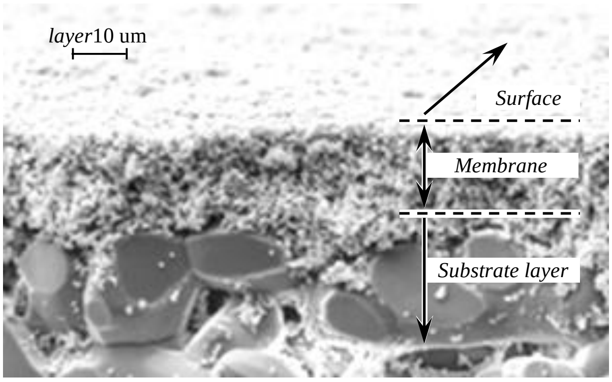

Fig. 2. Microphoto of membrane element section (made by using electronic microscope JEOL-5600)

B. The methodology of the experiment and results

During the experiment, the whey from the culture tank was supplied to the tank. The coolant from ice water system was fed to the heat-exchange unit to maintain the temperature of the whey. A sample is taken from the filtrate drain line (22, see Figure 1). During the experiment, the working pressure was 1 atm. The filtrate was collected in laboratory tubes and sent to the laboratory for analysis. When conducting laboratory tests, the following were used: scales “LA 230S №17109636” brand “Satorius”. Accuracy class 1; Butyrometer for skimmed milk 0–0.5 mark “Himpribor”.

There were two main parameters to this research – mass fraction of protein and mass fraction of fat in the samples. During the experiment, four experimental samples were obtained for pore sizes (*D*) 400, 200, 100, 65 and 50 nm. Results of experiment are presented in Table I.

According to experimental data, all ultrafiltration membranes extracted fat to the level of the threshold sensitivity of laboratory equipment. Only filtering of whey proteins is considered below. A graphical representation of the data on the concentration of protein in the initial whey and filtrate is shown in Figure 3.

TABLE I. PARAMETERS OF THE OBTAINED SAMPLES

Parameters	Whey*	Filtrate after membrane element with different pore size (nm)				
		400	***200***	***100***	***65****	***50***
Protein, %	0,75 ± 0,05	0,61 ± 0,05	0,57 ± 0,05	0,47 ± 0,05	0,22 ± 0,05	0,19 ± 0,05
Fat, %	0,25 ± 0,03	0,02	< 0,02 (not found)	< 0,02 (not found)	< 0,02 (not found)	< 0,02 (not found)

a. *Note*: The parameters of whey for experiment with membrane with pore size 65 nm, were as follows: (0,65 ± 0,05) % protein; (0,16± 0,03) % fat.

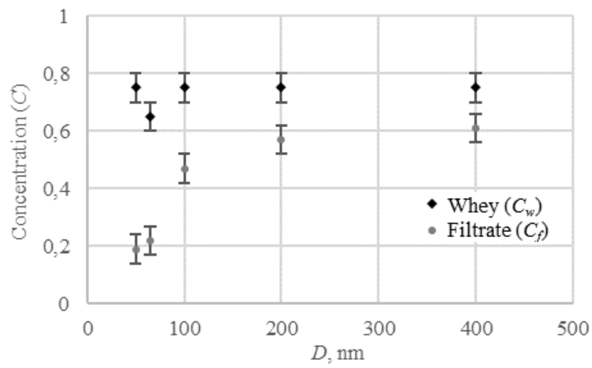

Fig. 3. Concentration of protein in the initial whey and concentration of protein in the filtrate

The semi-empirical model proposed below is the result of the analysis of experimental data.

III. Semi-empirical model

A. Model base and criterion

The indicator *Q* (retention) was used to assess the quality of protein filtration:

$$Q = C_c / C_w = 1 - C_f / C_w \, , \tag{1}$$

The C_w is the mass fraction of protein in the initial whey; C_c is the mass fraction of protein in the concentrate; C_f is the mass fraction of protein in the filtrate. The error of *Q* was also determined by analyzing the experimental data [9].

$$\Delta Q = Q \, (\Delta C_f / C_f + \Delta C_w / C_w) \, , \tag{2}$$

The ΔC_w and the ΔC_f are errors in determining the mass fraction of protein in the initial whey and mass fraction of protein in the filtrate. The values of *Q* and ΔQ for different values of the pore sizes of the membranes are given in Table II.

The semi-empirical model for evaluation of retention for proteins during tangential filtration of whey by using ceramic membrane elements is based on the relationship between the retention (*Q*) of membranes and their pore size (*D*). The semi-empirical model is based on a comparison of model data and experimental data. The goal is to create a model that provides maximum similarity between experimental parameters and theory parameters derived from the model.

Criteria for determining the main parameters of the semi-empirical model must be selected. Unfortunately, the χ^2-criterion that is often used in practice (minimizing the sum of squares of the difference between experimental and calculated values) is not applicable in this case [9] due to the significantly different errors (ΔQ) of different experimental data points (see Table II).

Therefore the probabilistic estimate of the calculated value $Q(D)$ lying in the normally distributed interval of the experimental value Q_i with the standard deviation ΔQ_i at each experimental point D_i is used as a criterion for the correspondence between the calculation and the experimental results. The probability of the correspondence of the calculated value to the experiment (p_i) is determined as follows:

$$p_i = \exp\{-0.5\,[(Q(D_i) - Q_i)/\Delta Q_i\,]^2\}\ . \tag{3}$$

If the calculated values and experimental values are exactly consistent, then the value of p_i is 1. The value of p_i drops to 0 with the increasing difference between calculated and experimental values.

The multiplying p_i for each point ($\Pi_i\,[p_i]$) determines the agreement between theoretical curve and experimental data set. The higher the values of multiplication, the more consistency between theory and experimental data.

This criterion is more convenient to convert from the multiplication of many numbers to the sum of the values associated with them to applying the machine computation. It can be done using the logarithm operation: $\ln\{\Pi_i\,[p_i]\} = \Sigma_i\{\ln\,[p_i]\}$. Thus, the selection of the parameters of the semi-empirical model occurs by varying them to obtain the maximum value of the following criterion:

$$P = -\,0.5\,\Sigma_\mathrm{i}\,[(Q(D_i) - Q_i)/\Delta Q_i\,]^2 \rightarrow \max\ . \tag{4}$$

The value of P determines the similarity of calculation and experiment data.

B. *Selection of model equation*

There are typical trend lines for an analytical description of the observed experimental dependence of Q on D, for example, power (5) or exponential (6) functions:

$$Q(D) = \alpha \mathrm{D}^{-\beta}\ ; \tag{5}$$

$$Q(D) = \gamma \exp\{-\,\delta D\}\ , \tag{6}$$

α, β, γ and δ are parameters of trend functions.

These simple functions correspond to the general form of experimental dependence. The selection of the parameters of the functions was performed using the criterion (4). The values of the parameters and the values of the functions are given in Table II. The values from the Table II show that the power function is closest to the experimental dependence.

However, usage of these trends does not reflect the nature of the passage of protein from the whey through the ceramic membrane during tangential filtration. Therefore, these trends can lead to significant errors when used out of experimental range. For this reason, we propose a semi-empirical model of protein separation, which qualitatively reflects the principle of filtration and will be able to give correct values for a wider range of values of D. Exact quantitative values of the model are obtained by varying them within the criterion (4).

A qualitative model of the penetration of filtered particles through a membrane barrier can be built on a comparison of pore sizes (D) and filtered particles sizes (s). If $s > D$, then the particle is delayed by the membrane, and if vice versa, it passes. There is a variation in the sizes of pores and filterable particles in practice. It is appropriate to take this into account in the model by introducing the indicator Δs. This parameter represents the standard deviation of the normal distribution, if we consider the separation process as probabilistic and assume it does not contain any dominant factors.

Consideration of the protein molecules as particles with a given average size and a given deviation of average size can lead to significant inaccuracies. Protein molecules can greatly change their geometric configuration. At the same time, a decrease in their transverse dimensions becomes less likely in comparison with its stretching. This means that the distribution ceases to be symmetrical and becomes non-Gaussian.

Decreasing the transverse size of molecules may result in a denser packing of protein atoms or with the longitudinal stretching of the protein molecule into a chain. There are many mechanisms of increasing the cross-section of protein molecules: e.g. agglomeration (coagulation) of proteins, formation of water clusters due to loose chemical reactions; any intermolecular cross-linking(which is facilitated by the high speed of whey movement during tangential filtration) and many others. All these features could be considered by replacing the indicator Δs in the distribution equation for multiplication parameters δs with a value of D (i.e. $\Delta s = \delta s \cdot D$).

Using this approximation allows us to propose the following calculation formula for retention of proteins during tangential filtration using ceramic membrane elements:

$$Q(D) = 1 - \Phi\,(D;\, s;\, \delta s D) =$$

$$= 1 - 0{,}5\ \mathrm{erf}\,\{(D - s)\,/\,(\delta s D\, 2^{0.5})\}, \tag{7}$$

The $\Phi\,(x;\,\mu;\,\sigma)$ is the integral normal distribution with expected value μ and standard deviation σ; $\mathrm{erf}\,(x)$ is error function.

The results of the calculation performed using the expression (7) are given in Table II and in Figure 4. These results show that the best correspondence between the calculation and the experimental data was observed precisely for the proposed semi-empirical model.

TABLE II. EXPERIMENTAL AND CALCULATED VALUES OF *Q FOR FILTRATE*

Type		Filtrate after membrane element with different pore size (nm)					Notice
		50	*65*	*100*	*200*	*400*	
Experimental data (1), (2)	Q_i	**0.75**	**0.66**	**0.37**	**0.24**	**0.19**	—
	ΔQ_i	0.25	0.20	0.06	0.04	0.03	—

Power function (5), (3), (4)	Q	**0.61**	**0.52**	**0.40**	**0.26**	**0.17**	$\alpha = 6.54$ $\beta = 0.61$
	p_i	0.85	0.78	0.93	0.84	0.87	$\boldsymbol{P = -0.6}$
Exponential functions (6), (3), (4)	Q	**0.42**	**0.40**	**0.37**	**0.28**	**0.17**	$\gamma = 0.475$ $\delta = 0.003$
	p_i	0.41	0.43	1.00	0.49	0.83	$\boldsymbol{P = -1.8}$
Proposed model[b] (7), (3), (4)	Q	**0.71**	**0.57**	**0.39**	**0.24**	**0.18**	$s = 75.34$ $\delta s = 0.90$
	p_i	0.99	0.90	0.96	1.00	0.99	$\boldsymbol{P = -0.1}$

b. *Note*: More accurate parameter values for the proposed semi-empirical model for the evaluation of protein retention during tangential filtration of whey by using ceramic membrane element is: $s = 75.3422$; $\delta s = 0.8964$.

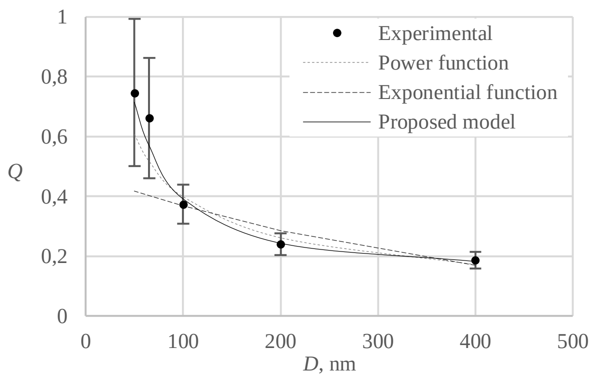

Fig. 4. Experimental data and calculated curves for different function and proposed model

C. *Implementation of the proposed model*

It is worth noting that expression (7) is very convenient for use in any modern computing software package and would be suitable for calculation using spreadsheet technology. For example, Microsoft Excel contains a built-in function (NORMDIST for English version or НОРМРАСП for Russian version). If it is necessary to refine the parameters s and Δs of expression (7), the application of criterion (4) would be required, which could also be implemented in any modern computing software package, including Excel.

The value of the parameter, determined for the function (7) indicates the effective size of the protein particles in the curd whey. It is approximately equal to 75 nm. The value of the δs parameter indicates the proportionality of the spread protein particle size and the size of the filtering pore.

Using the expression (7), we evaluated the pore sizes of the ceramic membrane required for complete ($Q > 0.99$) protein retention during the tangential filtration of whey. The resulting size was equal to $D_0 < 25$ nm. Using such membranes would allow one to isolate the necessary protein components of the whey and to direct it to the production of curd or cheese. It would also increase the efficiency and environmental friendliness of dairy production.

IV. Conclusion

The main result of this work is equation (7), which is a semi-empirical model for the evaluation of protein retention during tangential filtration of whey using ceramic membrane elements. The numerical parameters of the model are presented in Table II. The maximum pore size of the membrane was established for efficient operation of the filtration unit for whey. It is $D_0 < 25$ nm.

An additional result of this work was the identification of a criterion for the correspondence between the calculation and the experiment (4). This criterion is important for tuning equation (7) for other fluids and filters.

In general, the results of the work can be used in the calculation of filtration equipment to improve the efficiency of dairy production and neutralize their waste water.

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