Bulgarian Journal of Agricultural Science, 23 (No 2) 2017, 325–329
Agricultural Academy

INVESTIGATION OF PROCESS CHARACTERISTICS DURING DIAFILTRATION OF ULTRAFILTRATION WHEY RETENTATE FROM KASHKAVAL PRODUCTION

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Abstract

Dushkova, M., S. Kozludzhova, K. Dinkov, M. Miteva-Petrova, S. Petrov and N. Menkov, 2017. Investigation of process characteristics during diafiltration of ultrafiltration whey retentate from kashkaval production. *Bulg. J. Agric. Sci.***,** 23 (2): 325–329

Diafiltration of ultrafiltration retentate from whey was carried out with a UF10-PAN polyacrylnitrile membrane with 10 kDa molecular weight cut-off at different operating conditions (working pressure, volume reduction ratio and temperature). The multifactorial model created and the response surfaces for the effect of the three investigated factors show that the highest value of the flux is obtained at high level of working pressure and temperature and low level of volume reduction ratio. The selectivity and concentration factors of dry matter and protein increase when the volume reduction ratio increases, while the concentration factor of mineral substances decreases.

Key words: diafiltration, ultrafiltration, flux, selectivity, whey, kashkaval
List of abbreviations: UF10-PAN – ultrafiltration polyacrylonitrile membrane with 10 kDa molecular weight cut-off; DMSO – dimethyl sulfoxide; VRR – volume reduction ratio; UF – ultrafiltration; DF – diafiltration

Introduction

Whey is a liquid by-product from the dairy industry produced during the manufacture of cheese and caseins. Whey proteins have a high nutritional value, due to the high content of essential amino-acids, especially sulfur-containing ones. Besides the nutritional properties, the whey proteins have functional properties which impart beneficial physical properties when used ingredients in food, mainly due to its high solubility, water absorption, gelatinization and emulsifying capacities (Hinikova et al., 2012).

Membrane processes are used for purification, separation and concentration of various food and pharmaceutical products (Wickramasinghe et al., 2010; Le at al., 2014). Baromembrane processes – microfiltration, ultrafiltration, nanofiltration and reverse osmosis are the most widely used processes in food technology (Marella et al., 2013). Membrane technology, especially ultrafiltration (UF), has been used in the dairy industry to produce whey-protein concentrates, because this technology allows the selective concentration of the proteins in relation to the other components (Baldasso et al., 2011).

Ultrafiltration (UF) is a pressure-driven process using a semi-permeable membrane to separate macromolecules or colloids from liquids and it is based on a simple sieving mechanism (De Bruijn et al., 2005; Van Reis et al., 2007).

Diafiltration (DF) is a double ultrafiltration which is used for the production of whey-protein concentrate (WPC). Diafiltration is used for protein purification to eliminate problems association with high concentrations in the retained product, generating high purification, while retaining good performance process. Also, it should be

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pointed out that the addition of small DF volumes several times is more effective than a big volume at one time only (Kumar et al., 2013).

The aim of this study was to investigate the flux depending on the working pressure, volume reduction ratio and temperature, as also the selectivity depending on the volume reduction ratio during diafiltration of ultrafiltration retentate from whey issue to the Kashkaval production with UF10-PAN polyacrylonitrile membrane.

Materials and Methods

Materials

The experimental investigations were carried out with skim whey from the hard cheese Kashkaval.

Ultrafiltration membrane

Diafiltration of ultrafiltration retentate was carried out with polyacrylonitrile membrane UF10-PAN with 10 kDa molecular weight cut-off. The membrane was prepared by dry-wet phase-inversion method of polymer solutions prepared with a solvent of dimethyl sulfoxide (DMSO) and the membrane is temperature-treated in an aqueous medium for 10 min at 60°C.

Experimental system

The diafiltration of ultrafiltration retentate was carried out on laboratory equipment with a replaceable plate and frame membrane module fitted with a UF10-PAN polyacrylnitrile ultrafiltration membrane with 10 kDa molecular weight cut-off shown in Figure 1. This equipment was fitted with a plate and frame membrane module with membrane surface area of 1 250 cm^2; a three plunger high-pressure pump (max 15 MPa) with a capacity of 330 $dm^3.h^{-1}$; a pipeline system with two manometers (0 MPa to 15 MPa) for measuring the inlet and outlet pressure; and a special working pressure regulating valve.

Diafiltration was carried out under the following operating conditions: transmembrane pressure 0.2 MPa and 0.5 MPa, temperature 20°C and 50°C and volume reduction ratio 2, 6 and 10. All experiments were carried out at feed flow rate of 330 $dm^3.h^{-1}$. After experimental measurements of permeate volume (V, cm^3) for the time defined (τ, s) under different working conditions, the flux (J, $dm^3.m^{-2}.h^{-1}$ was calculated using the following formula:

$$J = 3{,}6.V/F.\tau \qquad (1),$$

where F = 0.125 m^2 is the membrane surface area in the module.

Determination of quality characteristics of UF10-PAN membrane

In all experiments, samples of the ultrafiltration retentate obtained at VRR=10, of the diluted ultrafiltration retentate prior to diafiltration and of the retentates and permeate during diafiltration concentration from VRR = 2 to VRR = 10 were taken. They are analyzed according to the following indices: dry matter (ISO 6731:2010); total protein (EN ISO 8968-1:2014); mineral substances (BSG 6154:1974). The presented values were obtained on the basis of three replications of the experiments.

➢ ***Concentration factor*** – the following formula was used:

$$CF = C_R/C_O \qquad (2),$$

where C_R, % and C_O, % are the dry matter, total protein content and mineral substances in diafiltration retentate and diluted ultrafiltration retentate prior to diafiltration respectively.

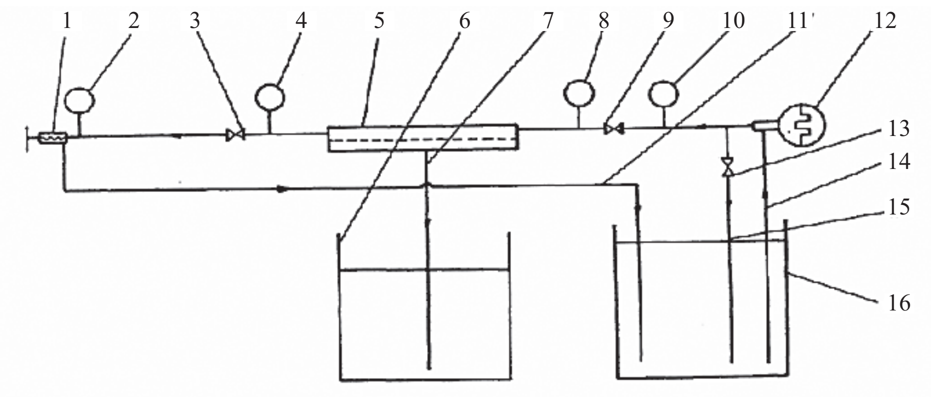

Fig. 1. Scheme of laboratory equipment with a replaceable plate and frame membrane module
1 – valve; 2 – manometer (0–5 MPa); 3 – valve; 4 – manometer (0–0.6 MPa); 5 – replaceable plate and frame membrane module; 6 – tank; 7 – pipeline; 8 – manometer (0–0.8 MPa); 9 – valve; 10 – manometer (0–15 MPa); 11 – pipeline; 12 – pump; 13 -valve; 14 – pipeline; 15 – pipeline; 16 – tank

➢ ***Selectivity (retention factor):*** it was determined according to the following formula:

$$R = (1 - C_P/C_R).100 \quad (3),$$

where C_P, % and C_R, % are the dry matter and total protein content in diafiltration permeate and retentate respectively.

Statistical analysis

Full multifactorial experimental design ($N = 2^3$) is used to show the influence of pressure (p, MPa), volume reduction ratio (VRR) and temperature (T, ºC) on the flux during diafiltration of ultrafiltration retentate from whey issue to the Kashkaval production. The experimental design with natural and coded values of the factors is presented in Table 1. Experiments at each point of the design were carried out with three replications.

Table 1
Experimental design with natural and coded values

№	Natural values			Coded values		
	p, MPa	VRR	T, ºC	X_1	X_2	X_3
1	0.2	10	20	-1	1	-1
2	0.5	2	50	1	-1	1
3	0.2	2	50	-1	-1	1
4	0.2	2	20	-1	-1	-1
5	0.5	10	50	1	1	1
6	0.5	2	20	1	-1	-1
7	0.5	10	20	1	1	-1
8	0.2	10	50	-1	1	1

Regression model for the dependent parameters (pressure, volume reduction ratio and temperature) was obtained using StatGraph v2.0 statistical software (trial version).

Results and Discussion

Table 2 shows the averages and standard deviations of the flux depending on the three investigated factors. The results vary between 11.94 $dm^3.m^{-2}.h^{-1}$ at p = 0.2 MPa, VRR = 10, T = 20ºC and 38.65 $dm^3.m^{-2}.h^{-1}$ at p = 0.5 MPa, VRR = 2 and T = 50ºC.

The follow adequate model at confidence interval 95% with significant coefficients was obtained:

$$J = 22.6725 + 5.69.X_1 - 5.525.X_2 + 1.6875.X_3 - 1.6775.X_1.X_2 + 0.105.X_1.X_3 - 0.84.X_2.X_3 - 0.4525.X_1.X_2.X_3 \quad (4)$$

$$R = 0.99;\ F = 2,3 < F_T = 3,6$$

The standardized diagram of Pareto for the significance of the investigated factors is presented in Figure 2. It shows that the three factors, as well as the interactions between them are significant. The regression model obtained and standardized diagram of Pareto show that the factors pressure and temperature have a positive effect, but the volume reduction ratio – negative. The results for the effect of the three investigated factors show that the pressure and the volume reduction ratio influence equally on the flux and the temperature has the least effect. This is confirmed by the obtained equation coefficients respectively – 5.69 for pressure, 5.525 for volume reduction ratio and 1.6875 for temperature and by Figure 3 showing the single effect of each of the investigated factors on the flux.

The response surface of the flux depending on the working pressure (X_1) and volume reduction ratio (X_2) is presented in

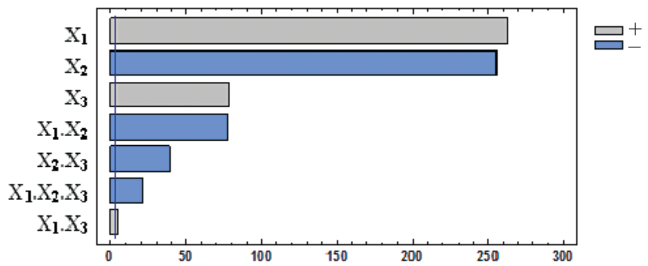

Fig. 2. Diagram of Pareto for the significance of the invetsigated factors

Table 2
The experimental design with natural and coded values for the flux depending on the invetsigated factors

№	Natural values			Coded values			Flux J, $dm^3.m^{-2}.h^{-1}$			
	p, MPa	VRR	T, ºC	X_1	X_2	X_3	J_1	J_2	J_3	J
1	0.2	10	20	-1.0	1.0	-1.0	11.44	11.94	12.44	11.94±0.50
2	0.5	2	50	1.0	-1.0	1.0	38.1	38.7	39.25	38.65±0.60
3	0.2	2	50	-1.0	-1.0	1.0	22.4	22.8	23.2	22.8±0.40
4	0.2	2	20	-1.0	-1.0	-1.0	18.2	18.9	19.56	18.86±0.70
5	0.5	10	50	1.0	1.0	1.0	21.1	21.7	22.26	21.66±0.60
6	0.5	2	20	1.0	-1.0	-1.0	32	32.5	32.98	32.48±0.50
7	0.5	10	20	1.0	1.0	-1.0	20.3	20.7	21.06	20.66±0.40
8	0.2	10	50	-1.0	1.0	1.0	13.7	14.3	14.93	14.33±0.60

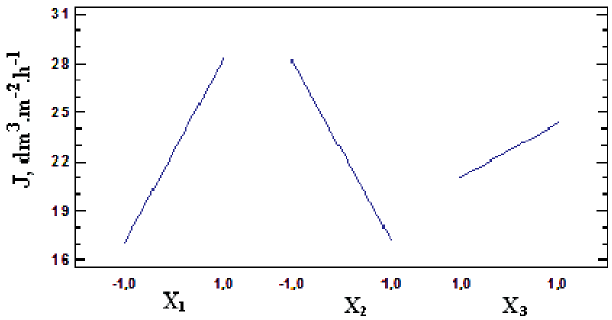

Fig. 3. Single effect of the investigated factors on the flux

Figure 4. It shows that the highest value of the flux is obtained at high level of the working pressure and low level of the volume reduction ratio. The lowest value of the flux is obtained at low level of working pressure and high level of volume reduction ratio. It can be seen that the effect of working pressure is more pronounced at low level of volume reduction ratio in comparison with the high level of the same factor. The figure shows that the effect of volume reduction ratio is more significant at high level of working pressure in comparison with low level of the same factor. The increase in working pressure leads to an increase in the flux because it is the driving force of the membrane process. On the other hand, the increased concentration polarization due to the increase in volume reduction ratio and the concentration respectively, embarrass the process (Macedo et al., 2011).

The response surface of the flux depending on the volume reduction ratio (X_2) and temperature (X_3) is presented in Figure 5. It shows that the highest value of the flux is obtained at low level of the volume reduction ratio and high level of temperature. The lowest value of the flux is obtained at high level of volume reduction ratio and low level of temperature. The increase in temperature leads to a decrease in the viscosity of the product which has a positive effect on the flux (Konrad et al., 2012).

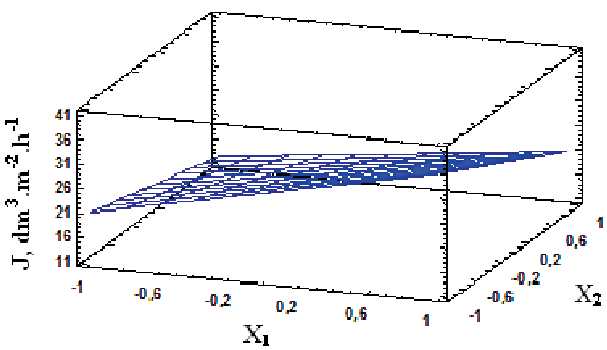

Fig. 4. Response surface of the flux depending on the working pressure (X_1) and the volume reduction ratio (X_2) at $X_3 = 0$

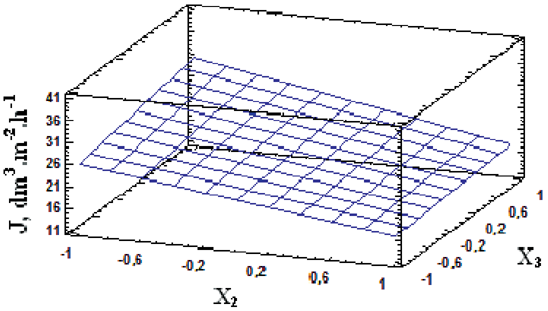

Fig. 5. Response surface of the flux depending on the volume reduction ratio (X_2) and the temperature (X_3) at $X_1 = 0$

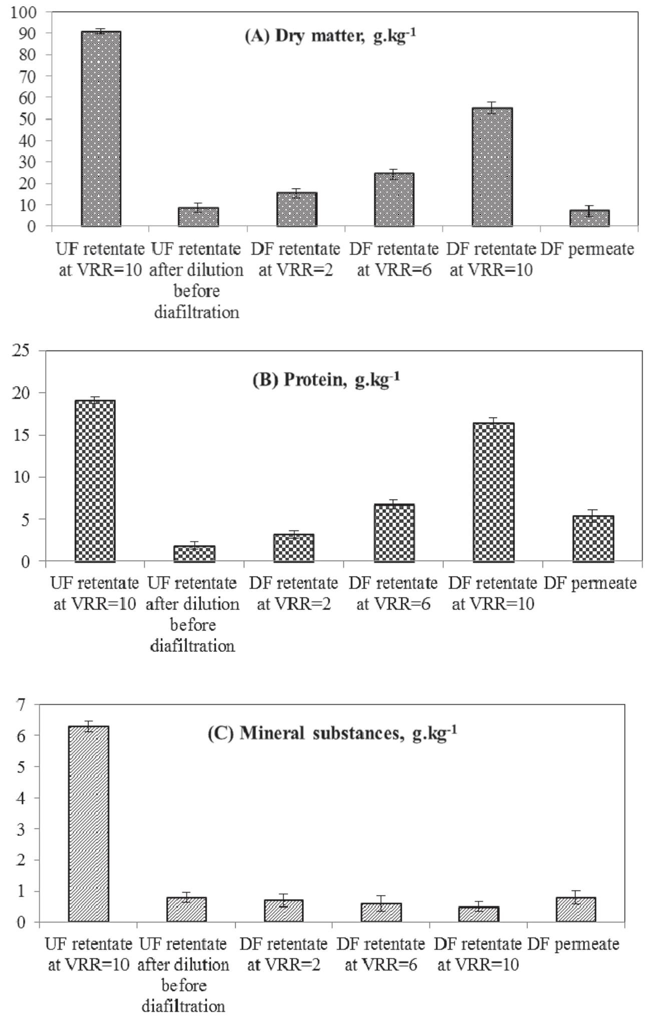

Fig 6. Dry matter (A), protein (B) and mineral substances (C) of ultrafiltration whey retentate at VRR = 10, of diluted ultrafiltration retentate prior to diafiltration and of diafiltration retentates and permeate at VRR = 2-10

The dry matter, protein and mineral substances contents are presented in Figure 6. The results show that the dry matter and protein contents increase during diafiltration at volume reduction ratio from 2 to 10, while the mineral substances content decreases.

The values of the concentration factor of dry matter, proteins and mineral substances depending on the volume reduction ratio are presented in Figure 7. It can be seen that the increase in volume reduction ratio leads to an increase in concentration factors of dry matter and proteins, and a decrease in concentration factor of mineral substances. This is indicative of the possibility for applying diafiltration treatment to obtain retentates with high protein and low mineral substances content.

The results related to the qualitative characteristic (selectivity) of the membrane, presented in Figure 8, show an increase in selectivity for dry matter from 539 g.kg^{-1} (VRR = 2) to 872 g.kg^{-1} (VRR = 10) and from 704 g.kg^{-1} to 888 g.kg^{-1} for proteins. These results confirmed the suitability of the choice of a membrane with a satisfactory selectivity. Atra et al. (2005) established that the protein retention increases with the increase in volume reduction ratio during ultrafiltration and nanofiltration of whey.

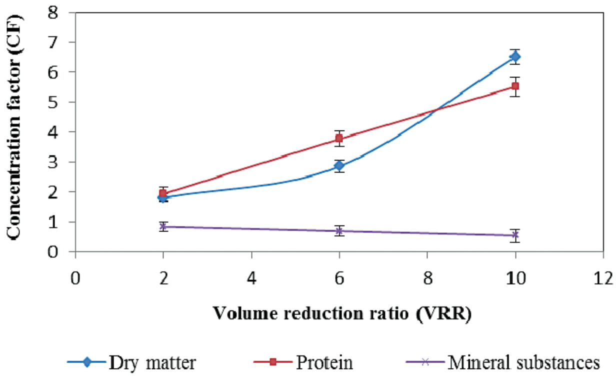

Fig. 7. Values of the concentration factor (CF) depending on the volume reduction ratio

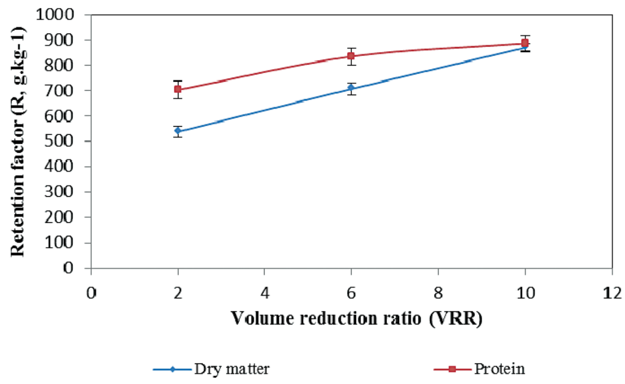

Fig. 8. Values of retention factor (R, g.kg^{-1}) depending on the volume reduction ratio

Conclusion

The multifactorial model created and the response surfaces for the effect of the working pressure, volume reduction ratio and temperature show that the highest value of the flux is obtained at high level of working pressure and temperature and low level of volume reduction ratio. The selectivity and concentration factors of dry matter and protein increase when the volume reduction ratio increases, while the concentration factor of mineral substances decreases.

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Received March, 2, 2017; accepted for printing March, 10, 2017