DIAFILTRATION OF ULTRAFILTRATION RETENTATE OF WHEY FROM WHITE BRINED CHEESE

ДИАФИЛТРАЦИЯ НА УЛТРАФИЛТРАЦИОНЕН КОНЦЕНТРАТ НА СУРОВАТКА ОТ БЯЛО САЛАМУРЕНО СИРЕНЕ

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ABSTRACT

Whey diafiltration was carried out with a UF25-PAN polyacrylnitrilic membrane with 25 kDa molecular weight cut-off at volume reduction factors (VRF) VRF=2, VRF=4, VRF=6, VRF=8, VRF=10. The values of the principal components dry matter, protein, lactose and mineral substances in the retentates and permeate obtained were established. The relative shares of protein, lactose and mineral substances in the dry matter, the concentration factor (CF) values for dry matter, protein, lactose and mineral substances, and the protein retention factor (RF) were determined. Linear models were created for the CF of each investigated component according to the VRF, and a logarithmic model was developed for the protein RF according to the VRF. The results obtained demonstrated the efficiency of diafiltration for deep treatment aimed at a further elimination of lactose and mineral substances and subsequent utilization of the diafiltration concentrates low in lactose and mineral substances as a liquid supplement in the manufacture of extruded cereal products.

Keywords: whey; diafiltration; ultrafiltration; white brined cheese

Резюме

Проведена е диафилтрация на ултрафилтрационен суроватъчен концентрат с полиакрилнитрилна мембрана УФ25-ПАН с разделителна способност 25 кDa при коефициент на намаляване на обема VRF=2, VRF=4, VRF=6, VRF=8 и VRF=10. Установени са: стойностите на основните съставки сухо вещество, протеин, лактоза и минерални вещества в получените концентрати и филтрат; стойностите на относителния дял на общия протеин, лактозата и минералните вещества в сухото вещество; стойностите на коефициента на концентриране на сухото вещество, протеина, лактозата и минералните вещества; стойностите на коефициента на задържане на протеина; линейни модели за коефициента на концентриране на всяка една от изследваните съставки от коефициента на намаляване на обема; логаритмичен модел за коефициента на задържане на протеина в зависимост от коефициента на намаляване на обема. Получените резултати показват ефективността на диафилтрацията за дълбочинна обработка с оглед допълнителното отстраняване на лактозата и минералните вещества и възможностите за използване на получените диафилтрационни концентрати с намалено съдържание на лактоза и минерални вещества като течни добавки при производството на екструдирани продукти.

Ключови думи: Суроватка, Ултрафилтрация, Диафилтрация, Бяло саламурено сирене

Разширено резюме

Изследвана е възможността за дълбочинна обработка на ултрафилтрационен концентрат от суроватка, получена при производството на бяло саламурено сирене. Основната цел на настоящата работа е установяване съдържанието на основните млечни съставки в получените диафилтрационни концентрати и филтрати, стойностите на относителния им дял в сухото вещество, както и стойностите на коефициентите на концентриране и задържане, с оглед по-ефективното им използване като течни добавки при производството на екструдирани зърнени продукти.

Изходната суроватка е получена като вторичен продукт при производството на бяло саламурено сирене от краве мляко. Извършено е последващо отсметаняване със сепаратор-отсметанител при 40-45оС. Извършена е последваща пастьоризация при 70-72°C за 15-20 s. Пастьоризираната суроватка е подложена на ултрафилтрация при работна температура 50 □55□C до коефициент на намаляване на обема VRF=10.

Проведена е последваща диафилтрация на получения ултрафилтрационен конецнтрат при коефициенти на намаляване на обема VRF=2, VRF=4, VRF=6, VRF=8 и VRF=10.

Експериментите по мембранната филтрация са проведени на лабораторна уредба със сменяем плосък мембранен модул, комплектован с полиакрилнитрилна ултрафилтрационна мембрана от вида УФ25-ПАН с разделителна способност 25 кDa.

При извършването на всички опити са взимани проби: от получения ултрафилтрационен концентрат при VRF=10, от разредения ултрафилтрационен концентрат преди диафилтрация, а при диагилтрационно концентриране до VRF=2, VRF=4, VRF=6, VRF=8 и VRF=10 от концентрата и филтрата. Всички проби са анализирани по показателите: сухо вещество, общ протеин, лактоза и минерални вещества.

Установени са: стойностите на основните съставки сухо вещество, протеин, лактоза и минерални вещества в получените концентрати и филтрат; стойностите на относителния дял на общия протеин, лактозата и минералните вещества в сухото вещество; стойностите на коефициента на концентриране на сухото вещество, протеина, лактозата и минералните вещества; стойностите на коефициента на задържане на протеина. Получени са линейни модели за коефициента на концентриране на всяка една от изследваните съставки от коефициента на намаляване на обема, както и логаритмичен модел за коефициента на задържане на протеина в зависимост от коефициента на намаляване на обема.

Получените резултати показват ефективността на диафилтрацията за дълбочинна обработка с оглед допълнителното отстраняване на лактозата и минералните вещества и възможностите за използване на получените диафилтрационни концентрати с намалено съдържание на лактоза и минерални вещества като течни добавки при производството на зърнени екструдирани продукти.

INTRODUCTION

White brined cheese is a semi-hard cheese made mainly in the Balkan countries. It is the most widely produced cheese in Bulgaria with specific technological and flavour characteristics due to its technology [4,9]. In recent years there has been a permanent increase in the quantity of white brined cheese and whey released during its production. It contains approximately 50 % of the dry matter and a significant part of the whey proteins in milk. This has prompted the need to search for solutions related to the utilization of the valuable whey components and to environmental efficiency regarding wastewater purity. A number of investigations [3,5,6,12,22] on the use of membrane methods in the dairy industry have aimed to show the possibilities of solving the above-mentioned problems. Ultrafiltration can be successfully applied to the production of whey protein concentrates [18,31,32].

Whey proteins are used in many branches of food industry because of their nutritive, biological and functional characteristics [8,10,13,19]. Therefore the possibilities of using them to enrich various products, such as baby foods, health foods and drinks, meat, bread products and extruded products, have been explored by various authors [14,23,25,28,29,30]. A number of investigations have aimed to determine the principal components of various whey types and the subsequent characteristics and content of the whey protein concentrates obtained [7,16,19,25,27]. Their rational use is impeded by the high levels of mineral substances and lactose which are sensitive to chemical reactions leading to changes in the organoleptic characteristics of the product [1,15,21,24].

The aim of the present work was to investigate the possibility for deep treatment of the ultrafiltration retentate of whey obtained during white brined cheese manufacture, and to establish the content of the main milk components in the resultant diafiltration retentates and permeate, the values of their relative shares in the dry matter, and the concentration and RF values with a view to their more effective application as liquid supplements in the manufacture of extruded cereal products.

MATERIALS AND METHODS

The initial whey was obtained as a by-product in the production of white brined cheese from cow's milk. The whey was afterwards separated with a separator, then pasteurized at 70-72°C for 15-20 s and subjected to ultrafiltration at an operating temperature of 50÷55°C to VRF=10.

Diafiltration of the ultrafiltration retentate obtained was carried out at the following volume reduction factors: VRF=2, VRF=4, VRF=6, VRF=8 and VRF=10. The VRF was calculated using the formula:

$$VRF = \frac{V_O}{V_R} \quad (1)$$

where V_O and V_R are the volumes of the diluted ultrafiltration retentate prior to diafiltration, and the diafiltration retentate respectively.

The membrane filtration experiments were carried out on laboratory equipment with a replaceable plate and frame membrane module fitted with a UF25-PAN polyacrylnitrilic ultrafiltration membrane with 25 kDa molecular weight cut-off shown in Fig.1. This equipment was supplied with a replaceable plate and frame membrane module with membrane surface area of 1250 cm^2, a three-plunger high pressure pump (max 15 MPa) with capacity of 330 dm^3/h, a pipeline system with two manometers (0-15 MPa) for measuring the inlet and outlet pressure, and a special working pressure regulating valve.

In all experiments, samples of the ultrafiltration retentate obtained at VRF=10, of the diluted ultrafiltration retentate prior to diafiltration and of the retentate and permeate under diafiltration concentration from VRF=2 to VRF=10 were taken. They were analyzed according to the following indices: dry matter (ISO 6731: 1989); protein (ISO 8968-1: 2001); lactose (ISO 5765-1: 2002); mineral substances (ISO 936-1998). The presented values were obtained on the basis of three repetitions of the experiments.

In accordance with the results obtained, the CFs for dry matter, protein, lactose and mineral substance were calculated using the formula:

$$CF = \frac{C_R}{C_o}, \quad (2)$$

where C_R and C_O are the component concentrations in the diafiltration retentate and the diluted ultrafiltration retentate prior to diafiltration respectively. On the basis of the results obtained, the protein RF was calculated using the formula:

$$R = \left(1 - \frac{C_P}{C_R}\right)100 \quad (3)$$

where C_P and C_R are the protein concentrations in the diafiltration permeate and retentate respectively.

RESULTS AND DISCUSSION

The principal components of the ultrafiltration retentate obtained at VRF=10, of the diluted ultrafiltration retentate prior to diafiltration and of the retentates and permeate obtained by diafiltration at different VRFs are presented in Fig.2 to Fig.5. Fig.2 shows a continuous protein increase from 0.45% through 0.76%, 1.38%, 1.39%, 1.99%, to 3.00% in the diluted ultrafiltration retentate and the diafiltration retentates at VRF=2, 4, 6, 8, 10 respectively. The protein content in the initial ultrafiltration retentate at VRF=10 (3.23 %) was close to those in the new diafiltration retentate at VRF=10 (3.00 %). The incorporation of these liquid diafiltration retentates in extruded cereal products would lead to an increase in their biological and nutritive value because of the higher amino-acid content [11]. The results in fig. 3 and 4 show a significant decrease in lactose and mineral substances in the new diafiltration retentate at VRF=10 compared to the initial ultrafiltration retentate at VRF=10: 0.3 % and 8.35 % for lactose, 0.2 % and 0.88 % for mineral substances respectively. Similar results for lactose and mineral substance reduction by diafiltration were obtained in [8,17]. The incorporation of these liquid diafiltration retentates, which are low in lactose and mineral substances, in extruded cereal products would lead to a longer shelf-life and improved flavour of the extruded products. According to [21], the lower lactose and mineral substance content helped to avoid the unfavorable reactions and off-flavours during drying and storage of dried whey protein concentrates.

The data shown in Figure 6 (the average values of the three experiments were used) provide useful information on the change in the principal components' relative share as a percentage of dry matter at each degree of concentration investigated. It can be seen that the diafiltration of the ultrafiltration retentate at a VRF factor from 2 to 10 led to an increase in the relative share of protein from 22.84 % to 78.94 %. Relative share of lactose and mineral substances in the dry matter decreased, from 65.48 % to 7.89 % and from 17.26 % to 5.26 % respectively, which demonstrates the diafiltration efficiency in increasing the protein content on the one hand, and reducing the lactose and mineral substance content significantly on the other hand. These data are in agreement with [32] and [19], which show that ultrafiltrafiltration/diafiltration can result in a protein increase >75%. Along with the study of the composition of the diafiltration retentates obtained, Fig. 7 shows the dry matter, protein, lactose and mineral substance CFs which are qualitative indicators of the process efficiency. The results demonstrate that at VRF=2 to VRF=10, the dry matter CF increased 1.1 to, 1.92 times respectively. Under the same operating conditions the protein CFs were from 1.69 to 6.67 respectively, the lactose CFs were from 0.71 to 0.23, and the mineral substance CFs were from 0.94 to 0.59. The results showed that protein was concentrated as many times as the VRF value. It can also be seen that the lactose and mineral substance CFs decreased significantly when the VRF increased from 2 to 10, which demonstrates the diafiltration efficiency for lactose and mineral substance separation. The comparative results for the ultrafiltration and diafiltration retentates at VRF=10 showed higher values of protein CFs and significantly lower values of lactose and mineral substance CFs of the diafiltration retentates obtained compared to the ultrafiltration retentates at the same concentration degree. This is indicative of the possibility of applying diafiltration treatment to obtain retentates with low lactose and mineral substance content. The results related to the qualitative characteristic (selectivity) of the membrane used (Fig. 8) showed that the rise in the VRF from 2 to 10 was accompanied by an increase in the protein RF from 62.2 (VRF=2) to 93.2 (VRF=10). These results confirmed the suitability of the choice of a membrane with satisfactory selectivity. There are similar investigations [2] concerning protein retention for skim whey. They show that protein retention increases with the increase in VRF and pressure. After statistical processing, linear models for the CFs of each investigated component according to the volume reduction factor, and a logarithmic model for the protein RF according to the VRF were developed (Table 1).

CONCLUSION

Whey diafiltration was carried out with a UF25-PAN polyacrylnitrilic membrane with 25 kDa molecular weight cut-off at VRF =2 to VRF=10. The values of the principal components dry matter, protein, lactose and mineral substances in the retentates and permeate obtained were established. The relative shares of protein, lactose and mineral substances in the dry matter, the CF values for dry matter, protein, lactose and mineral substances, and the protein retention factor were determined. Linear models were created for the CF of each investigated component according to the VRF, and a logarithmic model was developed for the protein retention factor according to the VRF. The results obtained demonstrated the efficiency of diafiltration for deep treatment aimed at a further elimination of lactose and mineral substances and subsequent utilization of the diafiltration concentrates low in lactose and mineral substances as a liquid supplement in the manufacture of extruded cereal products.

REFERENCES

[1]. Almécija M., Carmen I.R., Guadix A., Guadix E.M., Effect of pH on the fractionation of whey proteins with a ceramic ultrafiltration membrane, J. Memb. Sci. (2007) 288, 28-35.

[2]. Atra, R., Vatai, G., Bekassy-Molnar, EE., Balint, A., Investigation of ultra- and nanofiltration for utilization of whey protein and lactose, J. Food Eng. (2005) 67, 325-332.

[3]. Bhattacharjee, S., Datta, S., Studies on the fractionation of β-lactoglobulin from casein whey using ultrafiltration and ion-exchange membrane chromatography, J. Membr. Sci. (2006) 275, 141-150.

[4]. Bichourova, E., Baltadjieva, M., Kuzmanov, B., Study of the microflore during the process of ripening of white brined cheese without cholesterol, J. Envir. Prot. Ecol. (2007) 8, 264-269.

[5]. Brans, G., Schroen, C.G.P.H., Van der Sman, R.G.M., Boom, R.M., Membrane fractionation of milk: state of the art and challenges, J. Membr. Sci. (2004) 243, 263-272.

[6]. Daufin, G., Escudier, H., Carrere, S., Berot, L., Fillaudeau, M., Decloux, M., Recent and emerging applications of membrane processes in the food and dairy industry, Trans IChemE (2001) 79, 89-102.

[7]. De Wit, J.N., Adamse, M., Evaluation of functional properties of whey protein concentrates and whey protein isolates. 2. Effects of processing history and composition, Neth. Milk Dairy J. (1986) 40, 41-56.

[8]. Diaz, O., Pereira, C., Cobos, A., Functional properties of ovine whey protein concentrates produces by membrane technology after clarification of cheese manufacture by-products, Food Hydrocolloids. (2004) 18, 601-610.

[9]. Erdem, Y.K., Effect of ultrafiltration, fat reduction and salting on textural properties of white brined cheese, J. Food Eng. (2005) 71, 366-372.

[10]. Firebaugh, J.D., Daubert, C.R., Emulsifying and foaming properties of a derivatized whey protein ingredient, Int. J. Food Prop. (2005) 8, 243-253.

[11]. Fox, P.F., Guinee, T.P., Cogan, T.M., McSweeny, P.L.H., Chemistry of milk constituents. In: Fox, P.F., Guinee, T. P., Cogan, T.M., McSweeny, P.L.H. (Eds.) Fundamentals of cheese science, Aspen Publisher Inc., Maryland, US, 2000, pp. 98-137.

[12]. Greiter, M., Novalin, S., Wendland, M., Kulbe, K.D., Johann, F.J., Desalination of whey by electrodialysis and ion exchange resins: analysis of both processes with regard to sustainability by calculating their cumulative energy demand, J. Membr. Sci. (2002) 210, 91-102.

[13]. Herceg, Z., Lelas, V., Kresic, G., Influence of tribomechanical micronization on the physical and functional properties of whey proteins, Int. J. Dairy Technol. (2005) 58, 225-232.

[14]. Indrani, D., Prabhasankar, P., Rajiv, J., Venkateswara Rao, G., Influence of whey protein concentrates on the rheological charcetristics of dough, microstructure and quality of unleavened flat bread (parotta), Food Res. Int. (2007) 40, 1254-1260.

[15]. Jayaprakasha, H.M., Patel, R.S., Renner, E., Characterisation of flux and composition during ultrafiltration and diafiltration of cheddar cheese whey: Recent advances in membrane-based separation science and technology, Indian J. Chem. Technol. (1996) 3, 140-144.

[16]. Kim, S. H., Morr, C. V., Seo, A., Surak, J.G., Effect of whey pretreatment on composition and functional properties of whey protein concentrate, J. Food Sci. (1989) 54, 25-29.

[17]. Marcelo, P., Rizvi, S., Physicochemical properties of liquid virgin whey protein isolate, Int. Dairy J. (2008) 18, 236-246.

[18]. Maubois, J.L., New applications of membrane technology in the dairy industry, Austr. J. Dairy Technol. (1991) 46, 91-95.

[19]. Morr, C.V., Foegeding, E.A., Composition and functionality of commercial whey and milk protein concentrates and isolates: a status report, Food Technol. (1990) 44, 100-112.

[20]. Morr, C.V., Whey utilization. In: Zadow, J.G. (Ed.). Whey and Lactose Processing. Elsevier Science Publishers, London , 1992, pp. 133-155.

[21]. Morr, C.V., Ha, W., Off-flavors of whey protein concentrates: A review, Int. Dairy J. (1991) 1, 1-11.

[22]. Muller, A., Daufin, G., Chaufer, B., Ultrafiltration modes of operation for the separation of α-lactalbumin from acid casein whey, J. Membr. Sci. (1999) 163, 9-21.

[23]. Onwulata, C.I., Konstance, R.P., Viscous properties of taro flour extruded with whey proteins to simulate weaning foods, J. Food Proc. Pres. (2002) 26, 179-194.

[24]. Pereira, C.D., Diaz, O., Cobos, A., Valorization of by-products from ovine cheese manufacture: clarification by thermocalcic precipitation/microfiltration before ultrafiltration, Int. Dairy J. (2002) 12, 773-783.

[25]. Pintado, M.E., Lopes da Silva, J.A., Malcata, X., Comparative characterization of whey protein concentrates from ovine, caprine and bovine breeds, LWT (1999) 32, 231–237.

[26]. Pouliot, Y., Membrane processes in dairy technology – From a simple idea to worldwide panacea, Int. Dairy J. (2008) 18, 735-740.

[27]. Regester, G.O., Smithers, G.W., Mangino, M.E., Pearce, J.R., Seasonal changes in the physical and functional properties of whey protein concentrates, J. Dairy Sci. (1992) 75, 2928-2936.

[28]. Siso, G., The biotechnological utilization of cheese whey: a review, Biores. Technol. (1990) 57, 1-11.

[29]. Walsh, M.K., Nam, S.H., Pettee, B.C., Carpenter, C.E., Characterization of textured whey protein produced at varying protein concentrations, J. Food Proc. Pres. (2008) 32, 503-516.

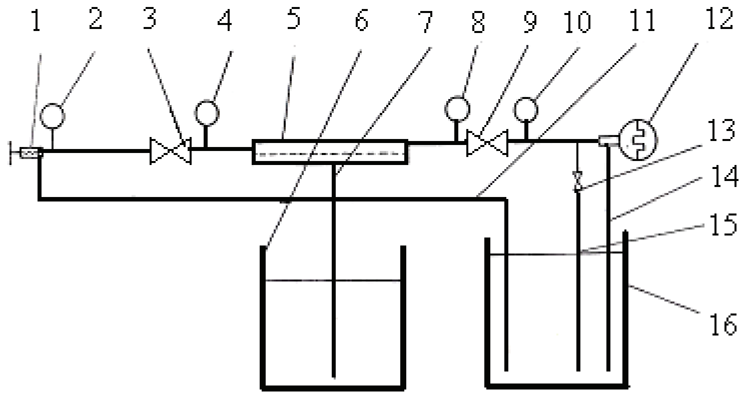
[30]. Zadow, J.G., Whey and whey powders: Production and uses. Encyclopedia of Food Sciences and Nutrition, 2003, p.p. 6147-6152.

[31]. Zall, R.R., Sources and composition of whey and permeate. In: Zadow, J.G. (Ed.) Whey and lactose processing. Elsevier Science Publishers, London, 1992, pp. 1-72.

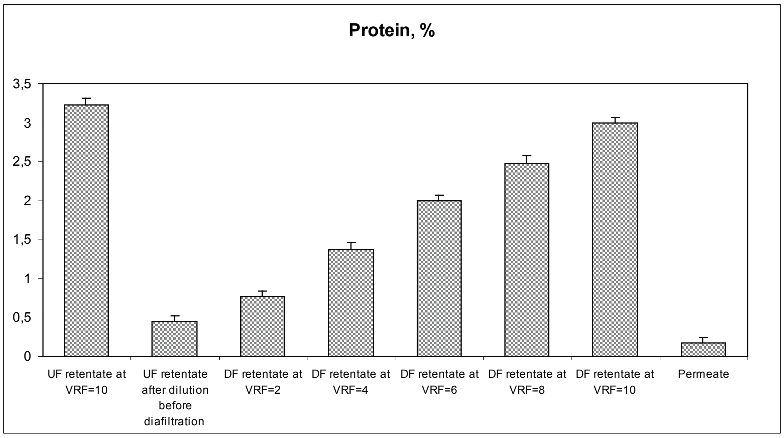
[32]. Zydney, A., Protein separations using membrane filtration: new opportunities for whey fractionation, Int. Dairy J. (1998) 8, 243-250

Таблица 1. Регресионни модели за коефициента на концентриране на сухото вещество, протеина, лактозата, минералните вещества и коефициента на задържане на протеина в зависимост от коефициента на намаляване на обема
Table 1. Regression models for dry matter, protein, lactose, mineral substance CF and protein RF according to the VRF

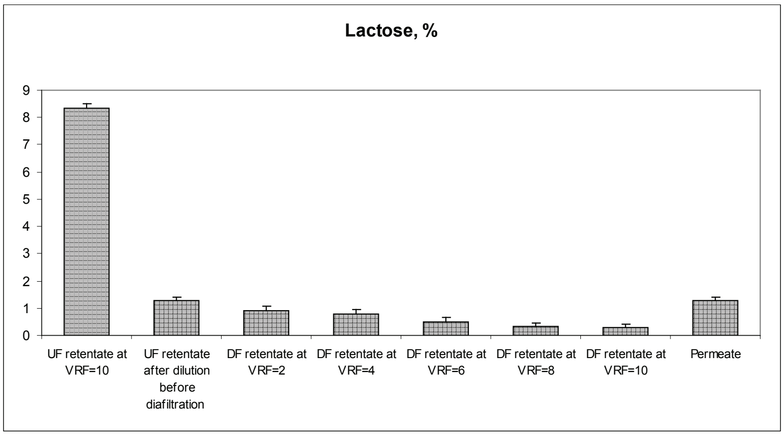
Concentration factor (CF)	Linear model	R^2
Dry matter	CF=0.1033.VRF+0.8949	1
Protein	CF=0.62.VRF+0.5511	0.98
Lactose	CF= -0.0441.VRF+1.0529	0.96
Mineral substances	CF= -0.0651.VRF+0.8341	0.94
Retention factor (RF)	Logarithmic model	
Protein	RF=19.941.ln(VRF)+49.512	0.98



фиг.1. Схема на лабораторна уредба със сменяем плосък мембранен модул
1 – вентил; 2 – манометър (0-5 MPa); 3 – вентил; 4 – манометър (0-0.6 MPa); 5 – сменяем плосък мембранен модул; 6 – резервоар; 7 – тръбопровод; 8 – манометър (0-0.8 MPa); 9 – вентил; 10 – манометър (0-15 MPa); 11 – тръбопровод; 12 – помпа; 13 – вентил; 14 – тръбопровод; 15 – тръбопровод; 16-резервоар
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

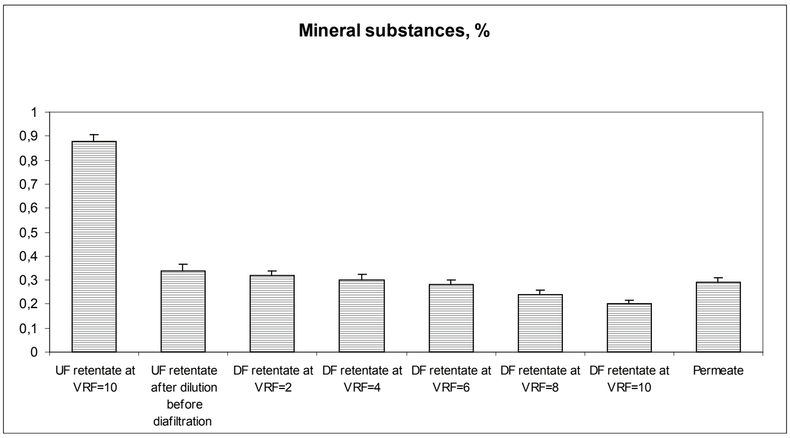


фиг.2. Съдържание на протеини в ултрафилтрационен суроватъчен концентрат при VRF=10, в разреден ултрафилтрационен концентрат преди диафилтрация и в диафилтрационни концентрати и филтрат при VRF =2 до 10
fig. 2. Protein content of ultrafiltration whey retentate at VRF=10, of diluted ultrafiltration retentate prior to diafiltration and of diafiltrtaion retentates and permeate at VRF=2 to 10



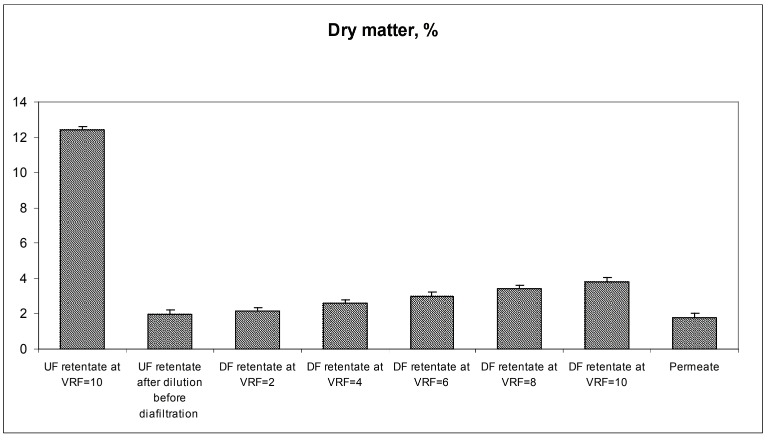
фиг.3. Съдържание на лактоза в ултрафилтрационен суроватъчен концентрат при VRF=10, в разреден ултрафилтрационен концентрат преди диафилтрация и в диафилтрационни концентрати и филтрат при VRF =2 до10

fig. 3. Lactose content of ultrafiltration whey retentate at VRF=10, of diluted ultrafiltration retentate prior to diafiltration, and of diafiltrtaion retentates and permeate at VRF=2 to 10

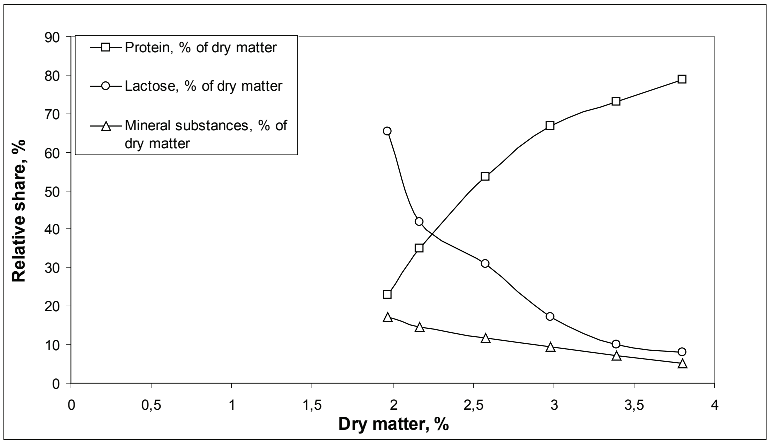


фиг.4. Съдържание на минерални вещества в ултрафилтрационен суроватъчен концентрат при VRF =5, в разреден ултрафилтрационен концентрат преди диафилтрация и в диафилтрационни концентрати и филтрат при VRF =2 до 10

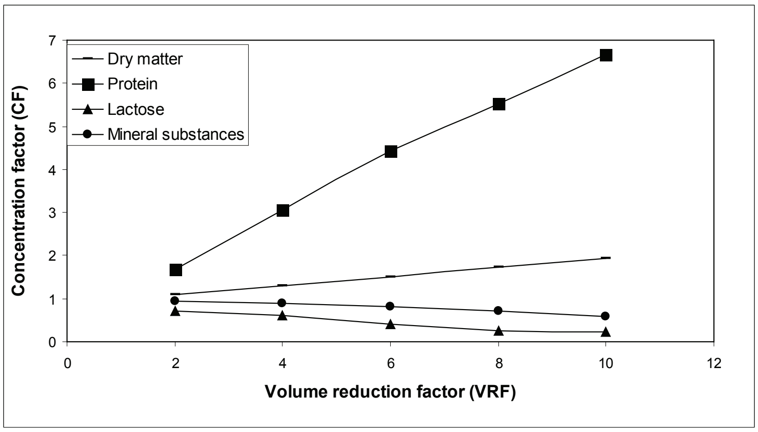
fig. 4. Mineral substance content of ultrafiltration whey retentate at VRF=10, of diluted ultrafiltration retentate prior to diafiltration, and of diafiltrtaion retentates and permeate at VRF=2 to 10



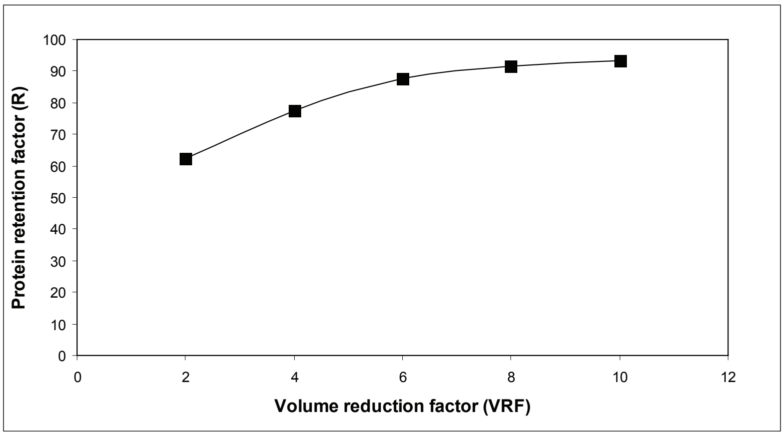
фиг.5. Съдържание на сухо вещество в ултрафилтрационен суроватъчен концентрат при Kv=5, в разреден ултрафилтрационен концентрат преди диафилтрация и в диафилтрационни концентрати и филтрат при VRF=2 до 10
fig. 5. Dry matter content of ultrafiltration whey retentate at VRF=10, of diluted ultrafiltration retentate prior to diafiltration, and of diafiltrtaion retentates and permeate at VRF=2 to 10



фиг. 6. Относителен дял на основните съставки на ултрафилтрационен концентрат след разреждане преди диафилтрация и концентрати, получени чрез диафилтрация при VRF=2 до 10
fig. 6. Relative share of the principal components of ultrafiltration retentate after dilution prior to diafiltration, and of retentates obtained by diafiltration at VRF=2 to 10



фиг.7. Стойности на коефициента на концентриране (CF) при VRF=2 до 10
fig. 7. Values of the concentration factor (CF) at VRF=2 to 10



фиг.8. Стойности на коефициента на задържане на протеина (R) при VRF=2 до 10
fig. 8. Values of the protein retention factor (R) at VRF=2 to 10