RESISTANCE STRUCTURE AND SOLUTE REMOVAL PATHWAYS IN UF–DF OF SWEET WHEY

Réka Dobozi[1], Zotán Péter Jákói[2], Balázs P. Szabó[1], Szabolcs Kertész[2]

[1]Department of Food Engineering, Faculty of Engineering, University of Szeged, H-6725 Moszkvai krt. 5-7., Hungary
[2]Department of Biosystems Engineering, Faculty of Engineering, University of Szeged, H-6725 Moszkvai krt. 9., Hungary
e-mail: dobozireka@mk.u-szeged.hu

Abstract

Whey is a high-volume by-product of dairy processing, rich in valuable proteins, lactose, and minerals, yet its utilization remains limited in many regions due to challenges related to shelf life, transport, and processing infrastructure. Membrane-based separations such as ultrafiltration *(UF)* and diafiltration *(DF)* offer chemical-free, low-energy routes for valorizing whey streams, but their efficiency depends not only on the nominal molecular weight cut-off *(MWCO)* of the membranes, but also on fouling dynamics and concentration polarization phenomena. In this study, sweet whey was subjected to *UF* combined with up to four constant-volume *DF* steps using polyethersulfone *(PES)* membranes with *MWCO*s of 10, 30, and 50 kDa. Retention of chemical oxygen demand *(COD)* and lactose was determined, and the evolution of total hydraulic resistance *(R_T)* and its components – membrane resistance *(R_M)*, reversible resistance *(R_{REV})*, and irreversible resistance (R_{IRR}) – was evaluated. Results showed that *COD* retention closely followed lactose concentration changes, with strong correlations ($r \approx 0.99$), confirming that small, permeable solutes dominated *COD* trends. UF exhibited clear *MWCO*-dependent retention (10 kDa > 30 kDa > 50 kDa), whereas during *DF* the sharpest decline occurred in the first diafiltration cycle *(DF1)*, due to dilution-induced disruption of the concentration polarization layer and reduction of R_{REV}. Beyond *DF2*, resistance stabilized and the separation performance of the 30 and 50 kDa membranes converged, indicating that hydrodynamic control outweighed nominal *MWCO* differences. For the 10 kDa membrane, irreversible fouling became more prominent in later *DF* steps, increasing R_T. Overall, the first *DF* cycle resulted in the greatest removal of dissolved components with low molecular weight, while subsequent cycles contributed to a diminishing extent to the removal of these fractions, but further increased the purity of the protein fraction remaining in the retentate. These findings suggest that optimal industrial strategies should apply a limited number of *DF* steps and carefully consider fouling mechanisms to balance efficiency, product quality, and resource use.

Introduction

The dairy industry represents one of the largest and technologically most diverse sectors of the global food chain. During processing, it generates substantial by-product streams, particularly whey, with an annual production of approximately 180–190 million tons. Although whey contains considerable amounts of high biological value proteins, lactose, and minerals, it remains underutilized in many regions due to its short shelf life, geographically and seasonally fluctuating generation profile, and the lack of local valorization capacities. This underutilization results in both environmental burdens and economic losses [1]. With the growing emphasis on circular economy principles and sustainable food supply models, there is an increasing demand for technologies that selectively exploit whey as a feedstock for producing high value-added components, while simultaneously reducing energy and water consumption as well as the overall carbon footprint [2].

Membrane separation technologies – most notably ultrafiltration *(UF)* and its combination with diafiltration *(DF)* – , which generally avoid the use of chemicals and impose only mild thermal stress provide an industrially validated solution to this challenge. *UF* retains protein fractions, thereby enabling the production of whey protein concentrates *(WPC)* and isolates *(WPI)*, whereas *DF* enhances the purity and stability of the retentate by removing small molecular weight permeating components such as lactose and minerals [3, 4, 5]. The "washing" effect of multiple *DF* cycles also modifies hydrodynamic conditions: dilution lowers ionic strength and viscosity, disrupts the concentration polarization *(CP)* layer formed during *UF*, and can thereby reduce reversible resistance while increasing flux [6]. This highlights that the efficiency of *UF/DF* separation is not determined solely by the nominal molecular weight cut-off *(MWCO)* of the membrane: permeate flux and separation selectivity are equally influenced by the dynamics of surface film formation and fouling, expressed as reversible resistance *(R_{REV})* and irreversible resistance *(R_{IRR})* [7].

Although the recovery of whey proteins via *UF/DF* and the conceptual and practical role of *DF* are widely addressed in the literature [3, 4, 8], only limited scientific studies are available that comprehensively evaluate both compositional parameter retention and the temporal evolution of total hydraulic resistance *(R_T)* and its components – namely membrane resistance *(R_M)*, and the aforementioned reversible resistance *(R_{REV})*, and irreversible resistance *(R_{IRR})* – over multiple *DF* cycles using membranes of different *MWCO* values. Joint analysis of membrane selectivity and resistance distribution is crucial for understanding how the outcome of separation is shaped by the interplay of membrane cut-off, fouling, and concentration polarization.

In this study, sweet whey was subjected to ultrafiltration combined with multiple diafiltration cycles using membranes with different molecular weight cut-offs. The process was monitored in terms of chemical oxygen demand *(COD)* and lactose retention, total hydraulic resistance *(R_T)*, and the relative contributions of membrane resistance *(R_M)*, reversible resistance *(R_{REV})*, and irreversible resistance *(R_{IRR})*. The aim was to quantitatively demonstrate that as *DF* progresses, the outcome of separation is increasingly determined by the rearrangement of the resistance distribution and the extent of low molecular weight washing-out, while the influence of the nominal *MWCO* gradually becomes secondary.

Experimental

For the laboratory-scale membrane separation experiments, an ultrafiltration cell (Millipore, *Germany*) with an active membrane surface area of 40 cm^2 was used. The membranes were based on polyethersulfone *(PES)* and had nominal molecular weight cut-off *(MWCO)* values of 10, 30, and 50 kDa. Before using, the membranes were preconditioned by soaking in distilled water for 1 hour. Experiments were carried out at room temperature (22 ± 1 °C), under a transmembrane pressure *(TMP)* of 2.5 bar and a stirring speed of 300 rpm. The initial feed consisted of 150 mL of sweet whey. During the ultrafiltration phase, the system was operated until a volume reduction ratio *(VRR)* of 3 was reached. This was followed by constant-volume diafiltration *(DF)*, performed in up to four consecutive steps *(DF1–DF4)*. At the beginning of each *DF* step, the retentate volume was restored to its original value (150 mL) by the addition of distilled water (approximately 100 mL). Sampling was performed at the end of each experiment from both the permeate and retentate fractions.

The organic matter content of the filtration fractions was determined as chemical oxygen demand *(COD)* using standard dichromate test cuvettes (Hanna Instruments, *Hungary*) followed by a spectrophotometric analysis. Lactose concentration was analyzed with a milk analyzer (Bentley Instruments, Inc., *USA*) operating with near-infrared *(NIR)* sensors. Based on

the compositional parameters of the permeate and retentate samples, retention values *(R%)* were calculated.

The extent of membrane fouling and the underlying mechanisms were evaluated using the resistance-in-series model. According to this model, the total hydraulic resistance consists of three components: membrane resistance *(R_M)*, reversible resistance *(R_{REV})*, which is associated with the concentration polarization layer and loosely bound deposits removable by hydraulic rinsing, and irreversible resistance *(R_{IRR})*, which persists even after rinsing.

Results and discussion

The results of the *UF–DF* series were evaluated based on chemical oxygen demand *(COD)* and lactose retention (Figure 1), as well as the evolution of total hydraulic resistance and its components (Figure 2). The changes observed in *COD* retention during *UF–DF* primarily reflected the behavior of the small molecular weight fraction (permeable to the membrane), particularly lactose, which is present in the highest concentration. This is because protein retention remained consistently high (85–88%) for all three tested *MWCO* membranes. This interpretation is supported by the fact that, for each membrane, a strong positive Pearson correlation was observed between *COD* and lactose retention (10 kDa: r ≈ 0.997; 30 kDa: r ≈ 0.992; 50 kDa: r ≈ 0.996). These findings confirm that the decrease in *COD* was primarily caused by the change in concentration of dissolved components washed out during diafiltration.

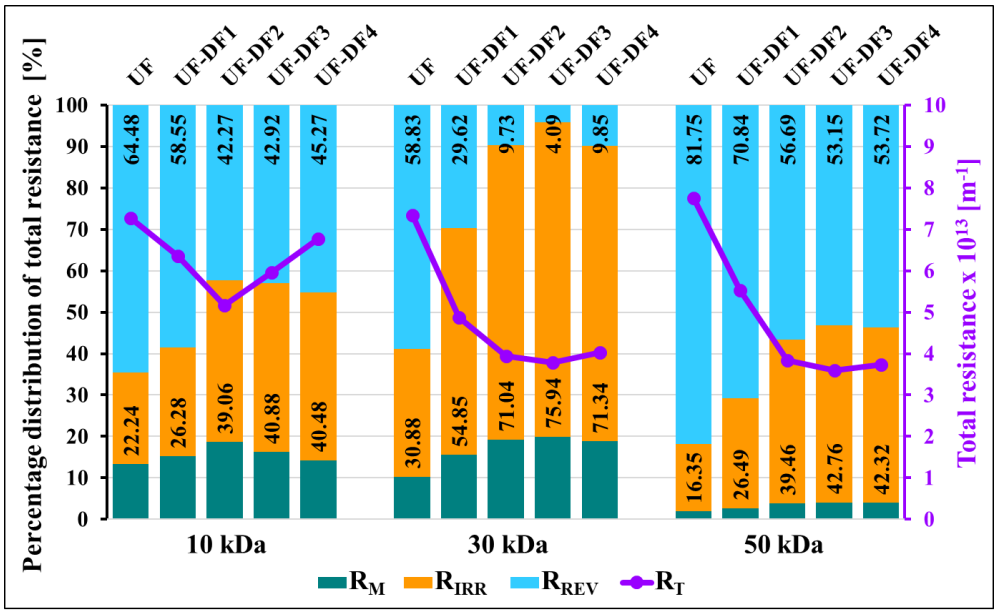

Figure 1. Distribution of resistances within the total resistance

During the *UF* phase, retention showed a clear *MWCO*-dependent pattern: *COD* retention for the 10, 30, and 50 kDa membranes was 66.2%, 59.2%, and 56.2%, respectively, while lactose retention was 44.3%, 37.6%, and 35.8% (Figure 1). In other words, membranes with smaller nominal cut-offs resulted in higher retention of organic matter and lactose. The monotonic decrease in retention with increasing *MWCO* is in agreement with previously documented trends in whey-based systems [3, 9].

Following *UF*, the absolute value of total resistance was high for all membranes tested, with the distribution of resistance components indicating dominance of the reversible fraction (R_{REV} ≈ 64.5/58.8/81.8%). This suggests that during *UF* a substantial concentration polarization *(CP)* layer formed on the membrane surface, restricting the free transport of small molecules and thus contributing to the high *COD* and lactose retention.

After the first diafiltration step *(DF1)*, *COD* retention dropped to ~53.4/42.2/42.1% for the 10/30/50 kDa membranes, while lactose retention decreased to ~17.7/14.7/13.9%. This sharp change can be attributed to dilution induced by the water added during *DF1*, which reduced retentate concentration, ionic strength, and viscosity. Consequently, the concentration polarization layer that had developed during *UF* was likely loosened or partially collapsed [8]. As a result, total resistance – and especially its reversible fraction – decreased significantly, enabling enhanced migration of low molecular weight solutes to the permeate side [4, 5].

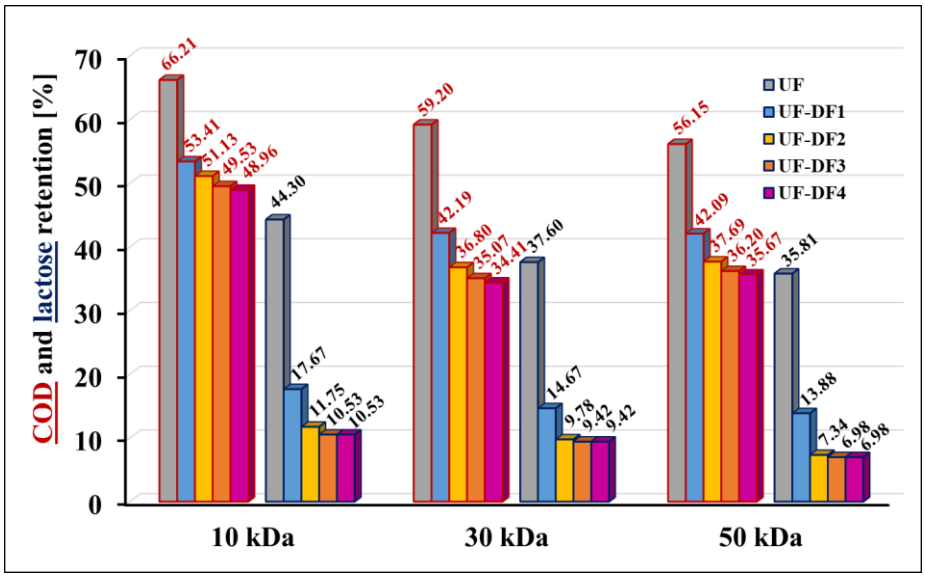

Figure 2. Evolution of *COD* and lactose retention across the different *MWCO* membranes

As diafiltration progressed *(DF2–DF4)*, the further decreases in *COD* and lactose retention became more moderate. In parallel, the evolution of total resistance also stabilized: for the 30 and 50 kDa membranes, no significant changes were observed after *DF2*, and during this stage the retention trends and the values of R_T showed convergence. This indicates that as the process advanced, separation mechanisms were primarily governed by hydrodynamic factors and the transport of permeable components, while the influence of nominal *MWCO* differences diminished [4, 9].

In contrast, for the 10 kDa membrane it was evident that, alongside the relaxation and collapse of the *CP* layer, a more persistent (irreversible) protein/peptide deposit gradually developed, which in later *DF* stages led to renewed increases in R_T. This observation is consistent with literature reports indicating that for membranes with tighter pore structures, fouling can play a more pronounced role as diafiltration progresses [6].

Taken together, these results demonstrate that separation performance and the purity of the retained protein fractions during *DF* were shaped by two main effects: (i) the solvent-driven, diavolume-proportional depletion of low molecular weight fractions from the retentate, and (ii) the hydrodynamic disintegration of the concentration polarization layer responsible for reversible resistance. The combined action of these two processes explains the sharp decrease in *COD* and lactose retention observed during *DF1*, the more moderate changes in both resistance and retention during subsequent *DF* stages, and the emergence of separation patterns for the 30 and 50 kDa membranes that became independent of nominal *MWCO*.

Conclusions

The *UF–DF* experiments confirmed that *COD* and lactose retention are primarily determined by the removal of low molecular weight components and the hydrodynamic disintegration of

the *CP* layer. During the *UF* phase, a clear *MWCO*-dependent pattern was observed; however, as *DF* progressed, the separation behavior of the 30 and 50 kDa membranes became converged, indicating the dominance of hydrodynamic control. In contrast, for the 10 kDa membrane, the irreversible component of fouling became more prominent during the later *DF* stages. The *DF1* step enabled the most substantial depletion of low molecular weight impurities (e.g., lactose, ions), while subsequent *DF* cycles produced diminishing incremental effects but nevertheless contributed to the purification of the retained protein fractions.

Our results suggest that for industrial applications it is advisable to apply a limited number of *DF* cycles, with careful selection of membrane type and cut-off value, while considering hydrodynamic factors and fouling mechanisms. These findings contribute to the optimization of whey-based membrane processes and may provide a basis for future studies on flux decline modeling and the development of cleaning strategies.

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