The Study of Dynamic Milk Ultrafiltration Performance Influenced by Membrane Molecular Weight Cut off

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ABSTRACT: *The effect of membrane molecular weight cut off (MWCO) at three levels (10, 20 & 50 kD) on dynamic behavior of permeate flux (J_P), hydraulic resistances (total hydraulic resistance, R_T; reversible fouling resistance, R_{rf}; irreversible fouling resistance, R_{if} and membrane hydraulic resistance, R_m) and milk solutes rejection (protein, R_P; fat, R_F; lactose, R_L; minerals, R_M and total solids, R_{TS}) are studied for the ultrafiltration of milk. Experiments are carried out using the pilot plant UF membrane system equipped with a spiral wound module and a polysulfone amide membrane. A three-stage strategy based on a resistance-in-series model (boundary layer-adsorption) was used to determine the different hydraulic resistances. The results showed that the J_P decreases greatly with increasing the process time, but the J_P values obtained for 20 kD were considerably higher than 10 kD & 50 kD during the whole process. R_T increased during operation at all levels of MWCO, but the hydraulic resistance values for 50 kD were significantly greater than 10 & 20 kD. Results for milk solutes rejection showed that the R_P and R_F are almost constant with process time at the corresponding MWCO, whereas the R_L, R_M and R_{TS} significantly increased.*

KEY WORDS: *Membrane, Milk processing, MWCO, Fouling, Flux and rejection.*

INTRODUCTION

Ultrafiltration applications has been expanded in the dairy industry since 1970's into various areas, including milk components standardization & fractionation, milk concentration in manufacturing fresh cheese varieties and whey processing [1]. Membrane processing of dairy fluids can reduce the operational costs incurred from power and steam consumptions; improve plant processing capacity and efficiency, and increase quality/yield of product. Efficiency and economical feasibility of a membrane process depends on permeate flux, fouling limit and solutes rejection. Membrane properties (type & pores size), system configuration (tubular, plate, hollow fiber & spiral wound), process hydrodynamic conditions (transmembrane pressure, crossflow velocity &

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temperature) and physico-chemical characteristics of feed (pH, composition & concentration) are most important factors which determine the flux pattern, fouling behavior and solutes concentration in the retentate and permeate streams [2]. The practical application of ultrafiltration processes is often limited by concentration polarization (CP) and progressive fouling of the membrane. Fouling of milk ultrafiltration is still a complex phenomena, with the deposition of solutes occurring both on the membrane surface and within the membrane pores, which leads to reduced permeate flux and decreased membrane selectivity during operation. Membrane fouling (both reversible and irreversible) had to be regularly eliminated in order to restore UF performance. Such operations can last 2-3 hours per 6-8 hours of production time and are performed daily in industry. Furthermore, fouling reduce the working life of membrane and increases cleaning costs [3].

However, much valuable information is available regarding the effect of hydrodynamic conditions of process [2, 4-14] and physico-chemical properties of milk [6, 9, 12, 15-17] on ultrafiltration performance (mainly flux behavior as filtration rate index), but the published references about the effect of membrane characteristics is very limited. The results have showed that the permeate flux can be improved by increasing the transmembrane pressure or cross-flow velocity and decreasing the milk solutes concentration during ultrafiltration of skimmed milk. These observations demonstrate that ultrafiltration performance is controlled by hydrodynamic and physico-chemical factors. To the knowledge of the authors no other work has been done on the effect of membrane's molecular weight cut off (MWCO) on milk ultrafiltration performance, with the exception of *Kapasimalis* and *Zall* work that has compared the permeation rate of pasteurized milk ultrafiltration using a large pore membrane (50 kD) and a small pore (10 kD) membrane [10]. Meanwhile previous studies on performance of milk ultrafiltration have generally focused on prediction of permeate flux under steady state condition [5, 6, 8, 10-14], while it is very important to know the time-dependent profile of ultrafiltration performance for designing a new process or analyzing the present process. This study aimed to determine the influence of MWCO on the dynamic behavior of permeate flux, hydraulic resistances and milk solutes rejection characteristics

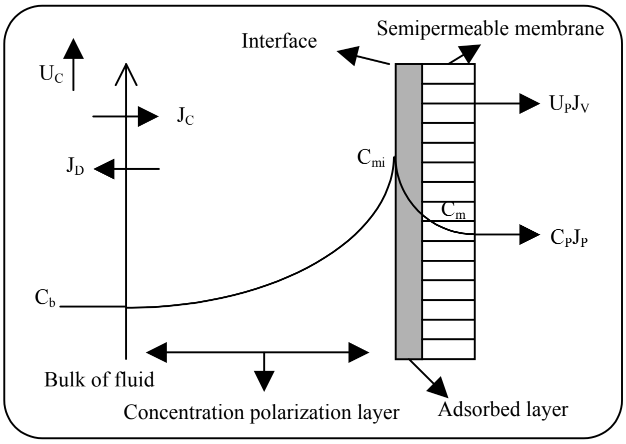

Fig. 1: Schematic presentation of hydraulic resistances based on adsorption-boundary layer model.

during ultrafiltration of skim milk and to consider the way the membrane MWCO interact with the hydro-dynamic and solution conditions, in affecting the relative resistances due to concentration polarization and adsorp-tion. Furthermore, this research facilitates identifying the role of MWCO on the mechanisms of flux decline and fouling development that control the overall performance of milk ultrafiltration process.

RESISTANCE-IN-SERIES MODEL

Many models based on *Darcy's* law have been proposed to describe the effects of concentration polarization and membrane fouling on flux decline, but the resistance-in-series (or boundary layer-adsorption) model is only model which separately accounts for the effects of the polarized and adsorbed layers for both dependent and independent pressure regions [3, 15, 18]. Based on this model, three hydraulic resistances of membrane intrinsic resistance, concentration polarization resistance (boundary layer) and fouling resistance (adsorbed layer) affect the permeate flux within the membrane (Fig.1). The resistance-in-series model was used in this study to determine these resistances separately based on a three-stage experimental strategy. The transport of pure water through a membrane is by viscous flow. The membrane hydraulic resistance can be described by *Darcy's* Law:

$$R_m = \frac{TMP}{\mu_w \times J_w} \tag{1}$$

Where μ_w is pure water viscosity, J_w is pure water flux through a clean membrane and TMP is the transmembrane pressure, which can be calculated for a crossflow ultrafiltration by the following equation:

$$TMP = \frac{P_i + P_o}{2} - P_p \quad (2)$$

Where P_i and P_o are inlet and outlet pressures, respectively and P_p is filtrate (or permeate) pressure. The total hydraulic resistance (R_T) to permeate flux was calculated by applying the resistance-in-series model (or boundary layer-adsorption model) as follow:

$$R_T = \frac{TMP}{\mu_p \times J_p} \quad (3)$$

Where μ_p is the permeate viscosity and J_p is the permeate flux. In fact, the total hydraulic resistance is sum of membrane hydraulic resistance and overall fouling resistance. Therefore:

$$R_T = R_f + R_m \quad (4)$$

$$R_f = \frac{TMP}{\mu_p \times J_P} - R_m \quad (5)$$

The overall fouling resistance (R_f) can be represented as the sum of the two components on the basis of the resistance-in-resistance model: resistance due to reversible fouling (R_{rf}) and resistance due to irreversible fouling (R_{if}). The fouling resistances were determined as:

$$R_{if} = \frac{TMP}{\mu_{wf} \times J_{wf}} - R_m \quad (6)$$

$$R_{rf} = R_f - R_{if} \quad (7)$$

Where μ_{wf} and J_{wf} are viscosity and flux of distilled water through a fouled membrane respectively.

The above equations show that different factors such as transmembrane pressure, permeate viscosity and fouling resistances affect the permeate flux reduction relative to distilled water flux. The relative flux (J_r) is obtained by the following equation [18]:

$$J_r = \frac{J_P}{J_w} = \frac{1}{1 + R'} \quad (8)$$

Where R' is the normalized resistance parameter and is equal to:

$$R' = \frac{R_{if} + R_{rf}}{R_m} \quad (9)$$

The total relative flux reduction (J_{rt}) can be expressed as:

$$J_{rt} = 1 - J_r = \frac{R'}{1 + R''} \quad (10)$$

If there is no concentration polarization and adsorption resistances then J_{rt}=0 and no flux reduction relative to pure water is observed. As $J_{rt} \rightarrow 1$, the flux reduction is very large and fouling has been strongly developed.

MATERIALS AND METHODS

Membrane system and operation procedure

Ultrafiltration of milk samples was carried out using the pilot plant UF-MF membrane system (Biocon company, Moscow, Russian). It consists of a feed tank (15 l), centrifugal pump, flow meter, spiral wound module, two pressure gauges, tubular heat exchanger, temperature sensor and two control valves (Fig. 2). The membrane was composed of polysulfone amide with external diameter 0.052 m, membrane length 0.47 m providing membrane area 0.33 m^2. The two pressure gauges measured the pressure at the inlet (P_i) and outlet (P_o) of the module. These gauges were positioned as close to the inlet and outlet of the membrane as physically possible. Temperature probe was attached to the feed tank and used for monitoring temperature during each run. The temperature of feed was continuously controlled by heat exchanger. An electronic balance and a container were used to record weight of permeate every 60 second for its flux calculation.

Skim milk powder used throughout experiments was reconstituted in warm distilled water (about 50 ^oC). Twelve kilograms of reconstituted skim milk was prepared for each run. The same batch of dried milk was used in all experiments to ensure that changes in measured parameters did not result from variation in milk composition. The effect of varying membrane MWCO (10, 20 & 50 kD) on flux, total hydraulic resistance and solutes observed rejection (Protein, fat, lactose, minerals and total solids) were studied. Experiments were carried out in batch mode, at constant feed concentration (total solids, 8.5 % ± 0.45; fat content, 0.095 % & pH, 6.59), temperature (40 ^oC), transmembrane pressure (101.33 kPa) and flow rate (15 l/min).

For each set of processing conditions, the feed tank was first recycled with warm distilled water at processing temperature to evaluate the water flux and calculate the

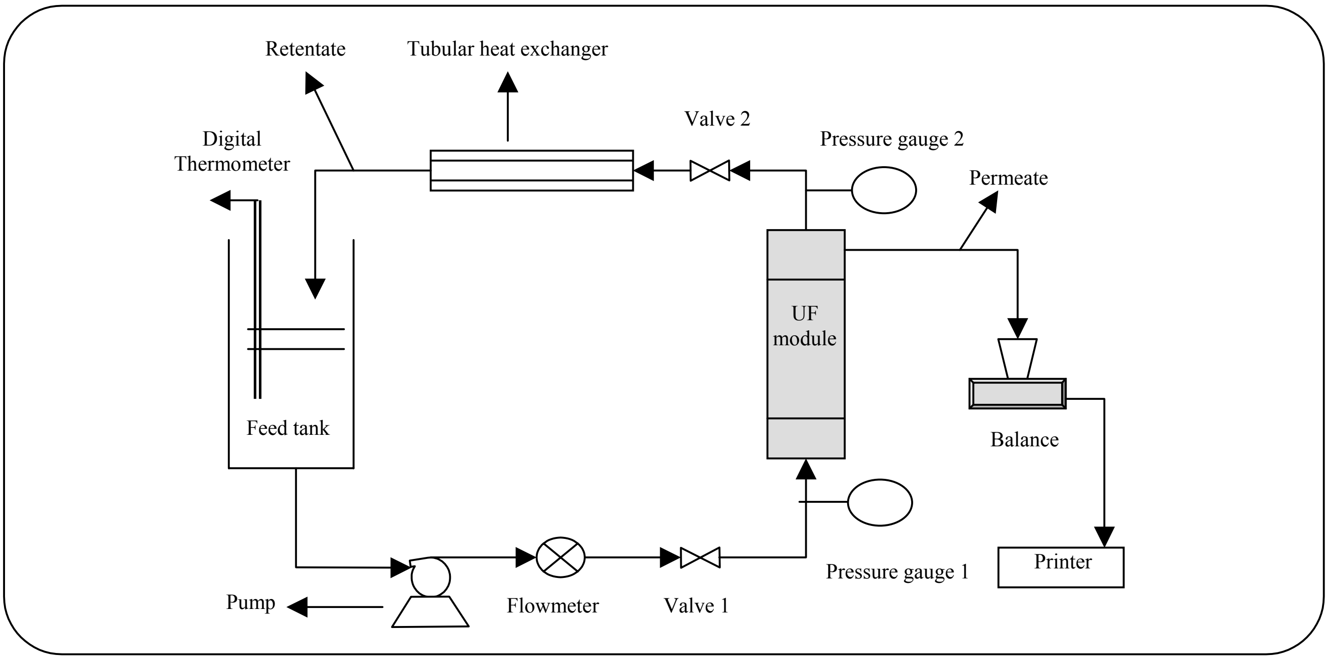

Fig. 2: Schematic diagram of the ultrafiltration unit used in this study.

R_m based on Eq. (1) and then it was recycled with milk sample at given temperature. The chosen TMP was set by two control valves. The permeate flux was measured and recorded every 60 second and the R_T was then obtained according to Eq. (3). After each run, the membrane unit was firstly flushed with distilled water for determining the water flux of fouled membrane and calculating R_{if} by Eq. (6). Then the R_{rf} was obtained using Eq. (7). Finally, the membrane system was cleaned according to the recommendation of the manufacturer and the water flux of the cleaned membrane was measured at the end of cleaning process. The cleaning procedure controlled by water flux measurement at the beginning and end of each run and also by inherent membrane resistance calculation, the difference between the two measured data must not be more than 3-5 %, otherwise fouling was not completely removed and the flushing cycle was repeated until the flux returned.

Analytical methods

Protein, lactose, fat, minerals and total solids contents of skim milk, permeate and retentate samples were measured using a Lactostar instrument (Funke Gerber Ltd., Germany) after 3, 15 and 30 minute operation in each run [2].

Viscosity and density of permeate samples were measured using an Ostwald U-tube capillary viscometer and a 25 ml picnometer, respectively at given temperature (40 ^oC) after each run [19].

pH of skim milk, permeate, retentate and flashing solutions (distillate water and NaOH solution) samples were measured using pH meter (3010, Jenway Ltd., U.K.) at 25 ^oC during the process [19]. All measurements were carried out at least in duplicate.

The observed rejection ($R_{obs.}$) for each milk component (protein, fat, lactose, minerals and total solids) was calculated according to the following equation [3]:

$$R_{obs} = 1 - \frac{C_p}{C_r} \quad (11)$$

Where C_P and C_r are the concentration of each solute in the permeate and the retentate, respectively.

RESULTS AND DISCUSSION

Permeate flux

The influence of MWCO on dynamic behavior of the permeate flux (J_P) is shown in Fig. 3. It can be seen that the fluxes decrease slightly with time during initial 5 min processing, but these tend to nearly stabilize with the progress of the run, i.e. after about 10 min. This figure also demonstrates that both initial flux and flux decline rate at 20 kD are greatly higher than 10 and 50 kD. Fig. 4

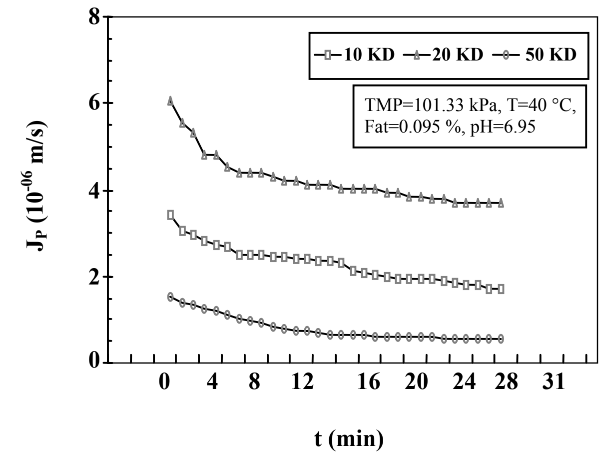

Fig. 3: Dynamic behavior of permeate flux (J_P) as a function of MWCO during ultrafiltration of skim milk.

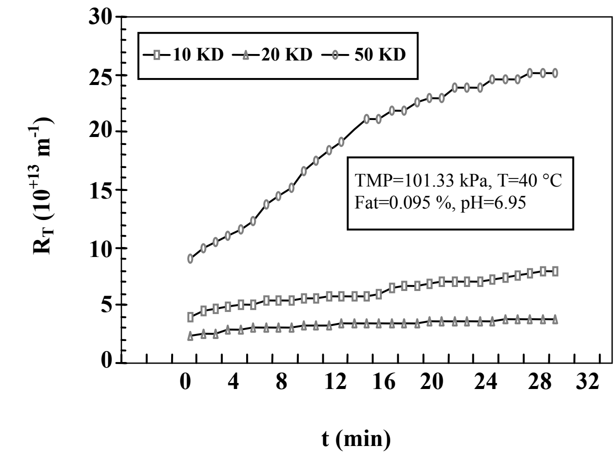

Fig. 5: Dynamic behavior of total hydraulic resistance (R_T) as a function of MWCO during ultrafiltration of skim milk.

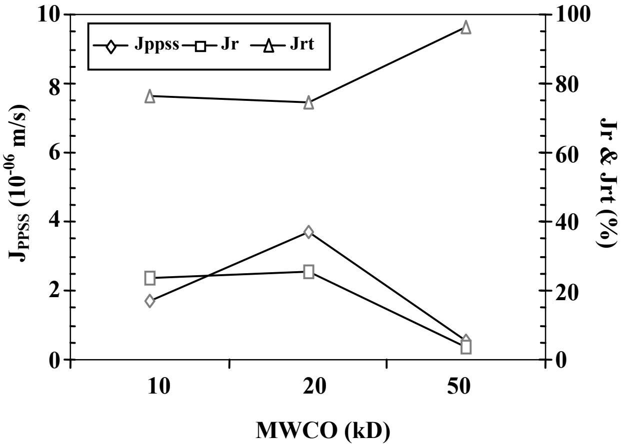

Fig. 4: The effect of MWCO on pseudo steady state flux (J_{ppss}), relative flux (J_r) and total relative flux decline (J_{rt}) during ultrafiltration of skim milk.

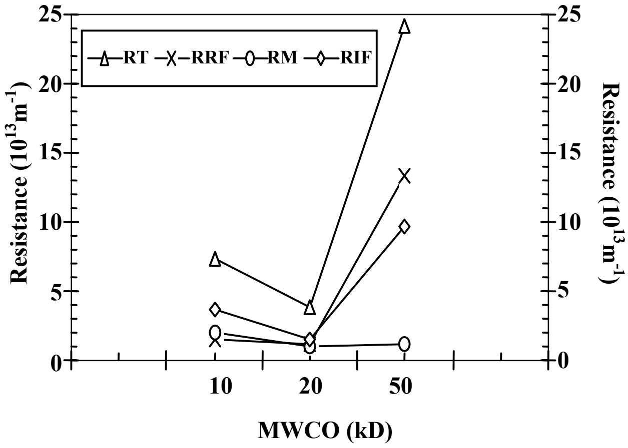

Fig. 6: The effect of MWCO on total hydraulic resistance (R_T), reversible fouling resistance (R_{rf}), irreversible fouling resistance (R_{if}) and membrane hydraulic resistance (R_m) during ultrafiltration of skim milk.

shows the effect of varying MWCO on pseudo-steady-state flux (J_{PPSS} or the value of J_P at the end of each run), relative flux (J_r) and total relative flux reduction (J_{rt}). Increasing MWCO between 10-20 kD led to a considerable increase in J_{PPSS}, whereas it decreased significantly with increasing MWCO between 20-50 kD. This figure also demonstrates that the J_r and the J_{rt} were constant at 10-20 kD range, but have changed greatly at 20-50 kD range. These results suggest that not only the milk ultrafiltration performance depend on the membrane pore size, but also the fouling is strongly severe for 50 kD membrane. This study also supports previous research work. *Kapasimalis* and *Zall* showed that the J_P for a membrane with MWCO 50 kD is lower than 10 kD [10].

Hydraulic resistances

The time dependence of the total hydraulic resistance (R_T) for three membranes is compared in Fig. 5. It can be found that the 10 kD and 20 kD membranes experienced similar extents of the R_T which were considerably smaller than that for the 50 kD membrane. As shown in Fig. 5, the R_T's value has followed the order of 20 kD<10 kD<50 kD, which confirm the results obtained for the J_P's value (Fig. 3). Fig. 6 shows the effect of varying MWCO on hydraulic resistances (R_T, R_{if}, R_{rf} & R_m). In summary, it can be concluded that:

a) The R_{if} value for 10 kD membrane was higher than the R_{rf} value, thus the J_P was mainly controlled by adsorption or irreversible fouling resistance.

b) The R_{rf} value for 50 kD membrane was higher than the R_{if} value, thus the J_P was mainly controlled by concentration polarization or reversible fouling resistance.

c) The R_{if} value for 20 kD membrane was almost identical to the R_{rf} value, therefore both reversible and irreversible fouling resistances had the same role in J_P controlling.

d) The R_m value for all membranes was almost constant and it had smallest effect on flux reduction.

e) All fouling resistances (R_T, R_{if} & R_{rf}) follow the order of 50 kD>10 kD>20 kD, therefore it seems that the 20 kD membrane is more suitable for milk ultrafiltration process.

Solutes rejection

The objectives were to specify the role of each milk solutes on the mechanisms of flux decline and fouling development as a function of membrane pores size. Fig. 7 shows the dynamic responses of the milk components rejection (R_P, R_F, R_L, R_M and R_{TS}) for different membrane MWCO's. It can be found that the R_P and R_F for each level of MWCO are almost constant with time, but the R_L, R_M and R_{TS} have increased significantly with time at the corresponding MWCO. These results clearly show the flux decline and increasing of total hydraulic resistance with time (Figs. 3 and 5) is due to increase in the rejection of these components. The total protein in milk can be divided into the caseins (80 %) and whey proteins (20 %). The physical properties of the milk components has been given in table 1 [20]. It can be seen that molecular mass of major milk protein fractions between 14-25 kD, therefore more than 90 % the milk proteins is retained by 10 kD and 20 kD membranes (Fig. 7; a & b), but the proteins retention by 50 kD membrane is less than 85 % (Fig. 7c). These results suggest that part of milk proteins (probably whey proteins) can pass through pores of 50 kD membrane. It seems that for 10 kD membrane similar to 20 kD membrane, initial flux decline could be due to sudden rejection of proteins and rapid formation of a thin film of milk proteins especially caseins near to the membrane surface (concentration polarization phenomena or reversible fouling), whereas subsequent gradual flux decline during the process is due to further adsorption of smaller soluble compounds (lactose and salts) and

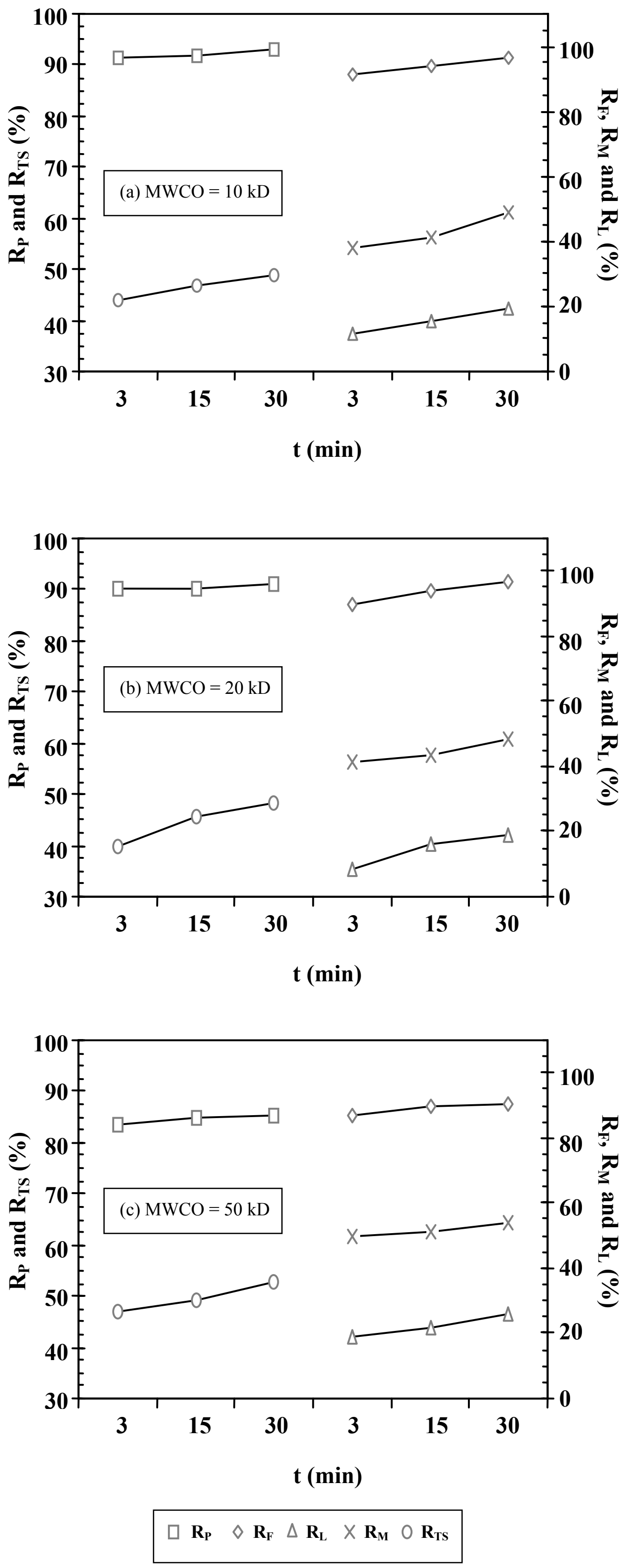

Fig. 7: Dynamic behavior of solutes rejection (protein, R_P; Fat, R_F; Lactose, R_L; Mineral, R_M and Total Solids, R_{TS}) as a function of MWCO during ultrafiltration of skim milk.

whey proteins within micellar layer and membrane pores (Figs. 3, 5 & 7).

The solutes rejection at the end of each run (30 min) as a function of MWCO is presented in Fig. 8. It can be found that the rejection of all components has not mainly changed for 10-20 kD range, however in all cases the solutes rejection for 10 kD membrane has obtained higher than 20 kD membrane. Meanwhile this figure shows that R_P and R_F have been decreased for 20-50 kD range, whereas in contrast R_L, R_M and R_{TS} have been increased under these conditions. These results suggest that for 50 kD membrane, some of macromolecules (proteins and fats) can enter into the pores and block them, thus the rejection of these components has been decreased. As a result, the possibility of smaller solutes (lactose and salts) for passing through the membrane pores has also decreased, thus it is seen that R_L, R_M and R_{TS} have increased for 50 kD membrane (Fig. 8).

CONCLUSIONS

In this research work, the effect of different membrane MWCO's on dynamic milk ultrafiltration performance has been investigated. According to the results obtained, the ultrafiltration performance was quite different for three membranes and MWCO played an important role in flux pattern, fouling behavior and retention characteristics. In 20 kD membrane, both the flux values, and flux drops with time were higher than 10 kD and 50 kD membranes, whereas the total hydraulic resistance and fouling resistances were higher and very progressive in 50 kD membrane during whole process. Increasing MWCO between 10-20 kD had not effect on relative flux and total relative flux, but these decreased greatly with an increase in MWCO from 20 kD to 50 kD. The results also suggest that increasing of fouling during milk ultrafiltration by 10 kD membrane was mainly due to the irreversible fouling, but for 50 kD, it was mainly governed by the reversible fouling. The rejections of lactose, minerals and total solids increased significantly with time at each MWCO; however, the rejections of protein and fat increased very slightly with time at the corresponding MWCO. Moreover, increasing MWCO between 10-20 kD had little influence on the retentions of milk components, but increasing MWCO up to 50 kD led to a substantial effect on the retention of each solutes.

Table 1: Physical characteristics of milk components.

Component	Mass fraction (%)	Molecular mass (Da)	Diameter (nm)
Caseins	2.28-3.50		25-130
- α_{s1} casein	1.2-1.5	22066-23722	
- α_{s2} casein	0.3-0.4	25148-25388	
- β casein	0.9-1.1	23938-24089	
- κ casein	0.2-0.4	19005-19037	
Whey proteins	0.46-0.87		
- β lactoglobulin	0.33	18205-18363	4
- α lactalbumin	0.07	14147-14175	3
Lactose	3.80-5.30	342	0.8
Salts	0.53-0.78		
- Chloride ion	0.10	35	0.4
- Calcium ion	0.12	40	0.4
Fat	0.1-4.61	-	2000-10000
Water	85.50-92.01	18	0.3

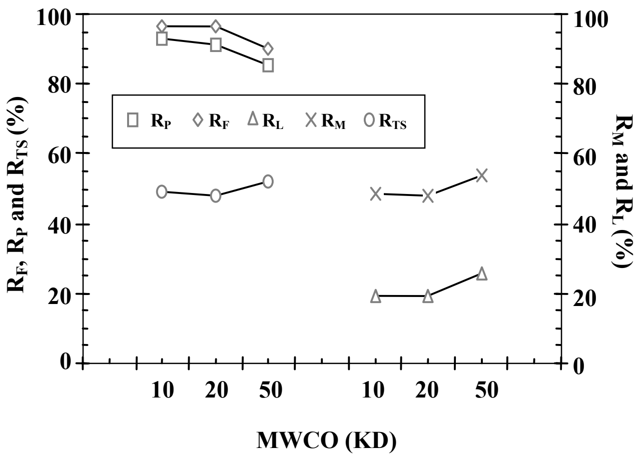

Fig. 8: The effect of MWCO on solutes rejection (protein, R_P; Fat, R_F; Lactose, R_L; Mineral, R_M and Total Solids, R_{TS}) during ultrafiltration of skim milk.

Nomenclature

J	Flux (m s^{-1})
MWCO	Molecular weight cut-off (u (Da))
P	Pressure (kPa)
R	Resistance (m^{-1}), rejection

t	Processing time (s or min)
TMP	Transmembrane pressure (kPa)

Greek symbols

μ	Viscosity (Pa.s)

Subscripts

f	Fouling
F	Fat
i	Inlet
if	Irreversible fouling
L	Lactose
m	Membrane
M	Minerals
o	Outlet
obs	Observed
P	Permeate, protein
r	Retentate, relative flux
rf	Reversible fouling
rt	Total relative flux
T	Total
TS	Total solids
w	Water
wf	Water through fouled membrane

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