ORANGE JUICE CLARIFICATION BY MICROFILTRATION: EFFECT OF OPERATIONAL VARIABLES ON MEMBRANE FOULING

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***Abstract*— Orange juice was clarified by cross-flow microfiltration by a PVDF/PMMA flat membrane synthesized in our laboratory. The effect of transmembrane pressure (Δp=0.4-1bar) and feed flow rate (v=0.77-1.25 m/s) on permeate flux at T=25ºC was studied. Permeate flux increases with increasing feed velocity, while no significant increase of permeate flux with pressure is observed (flux controlled by mass transfer). Resistances responsible for permeate flux in the steady state conditions were evaluated by applying the resistance-in-series model. Results indicate that the reversible gel layer resistance of the membrane was the dominant resistance (≈ 70% of total membrane resistance) and it was mainly caused by the adsorption and deposition of solutes on the membrane surface. The PVDF/PMMA membrane showed high performance on both permeate flux and clarified juice quality. The maximum permeate flux at steady-state condition (J = 47 L/m^{2}h) was achieved at Δp = 1 bar and v = 1.25 m/s. Total solids (TS) are completely removed from permeate juice and the content of soluble solids, acidity and pH present in the feed and in the clarified permeate are practically the same.**

***Keywords*— microfiltration, orange juice, clarification, fouling.**

I. INTRODUCTION

Fruit juices are of great interest for their nutritional and antioxidant properties due to the presence of ascorbic acid, fibers and amino acids. Unfortunately during industrial transformation some of the characteristics that determine the quality of the fresh product are modified therefore reducing the quality of the final product (i.e. thermal damage and chemical oxidation). Membrane processes have been consolidated in various sectors of production, being the separation process a non-thermal system without phase changes or aggregates of chemical agents. The introduction of this technology in the transformation of fruit juices cycle represents a technological solution to the problem of the production of juices with high quality, natural taste, and free of additives. Clarification, stabilization, depectinization and concentration of juices are typical stages where membrane processes such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) can be used (Cassano *et al*., 2003; Carrin *et al*., 2001). The MF and UF in particular represent a valid alternative to the use of traditional coagulant agents (such as gelatin, bentonite, and silica) whose effluents cause problems of environmental impact. Other advantages of these techniques compared to the conventional processes are their simple continuous production and low energy consumption. The main disadvantage in practical application of micro/ultrafiltration is the reduction of permeate flux with time caused by the adsorption of solutes on outer membrane and inner pore surface, pore blocking by solutes retention or cake layer formation on membrane surface. A rapid reduction of the permeate flow, a phenomenon known as fouling, reduces the competitiveness of the process. The fouling phenomenon is caused by various mechanisms: adsorption, pore plugging, concentration polarization, and cake formation. To analyze the phenomena of flux decline, some researchers have proposed the resistance-in-series model (Ko and Pellegrino, 1992). Jiraratananon and Chanachai (1996) studied the variation of some of the resistances as a function of temperature at the clarification of passion fruit juice. Their results showed that at low temperatures (30 and 40ºC) resistance due to polarization was the controlling one, while at a higher temperature (50ºC) the dominating resistance was that of fouling. Todisco *et al*. (2002) studied the clarification of black tea using ceramic membranes and they found out that the resistance that controls the process is solely due to concentration polarization, even at low pressure and high cross flow velocity. Vladislavjević *et al*. (2003) analyzed the variation of permeate flux and fouling resistance with time filtration and the effect of operating pressure and feed flow rate during ultrafiltration of apple juice using ceramic membrane. Fouling resistance decreased with feed flow rate at a transmembrane pressure (ΔP) below 300 kPa. Youn *et al*. (2004) investigated the clarification of apple juice recomposed using MF and UF. They found that the rate of resistance of irreversible fouling to total resistance was about 41 % for MF and about 24 % for UF. However, the resistance rate owing to reversible fouling versus total resistance was about 46 % for MF and about 71 % for UF. Rai *et al*. (2006) analyzed the effect of different pretreatment methods on permeate flux and quality during ultrafiltration of mosambi juice. This study indicated that the contribution of cake resistance was about 82 % to the total resistance and that the quality of the filtrated juice was of high clarity allowing almost complete recovery of the original juice. Ushikubo *et al.* (2006) evaluated the effect of enzyme treatment, transmembrane pressure and crossflow velocity in the permeate flux of umbu juice and in the fouling and polarized layer resistance. Crossflow velocity is the major variable responsible for increased flux, since it reduces the polarized layer. The effect of operating parameters on membrane fouling and juice quality during the clarification of blood orange juice by ultrafiltration was analyzed by Cassano *et al.* (2007). The mathematical analyses of the decline revealed that at fixed operating conditions of transmembrane pressure and temperature, the fouling mechanism evolves from a partial pore blocking to a complete pore blocking condition in dependence of the axial velocity.

Based on the resistance-in-series model, Li *et al.* (2007) investigated the effect of membrane microstructure and operational conditions on fouling behavior of ceramic membranes during microfiltration of raw soy sauce. Results showed that total resistance and concentration polarization resistance increased strongly with increasing nominal pore size while cake resistance and internal fouling resistance decreased slightly.

Nandi *et al.* (2009) studied the applicability of low cost membrane for mosambi juice microfiltration. The decline in permeate flux was analyzed using different membrane pore blocking models. Results showed that fouling resistance was about 85 % of the total resistance for centrifuged mosambi juice and about 50 % for enzyme treated centrifuged mosambi juice. Sarkar *et al.* (2009) studied the effects of electric field (both constant and pulsed mode), cross-flow velocity and transmembrane pressure on permeate flux and energy consumption during clarification of mosambi juice.

The main objective of this work was to evaluate the microfiltration performance of orange juice using hydrophilic PVDF-PMMA membranes synthesized in our laboratory. The effect of transmembrane pressure and cross flow velocity on both permeate flux and juice quality were investigated. The experimental results were analyzed in terms of resistance-in-series model.

II. EXPERIMENTAL

A. Materials

Membrane preparation and characterization: The MF membrane was prepared by inversion phase technique. Casting solution consisted of 15% PVDF (Solef from Solvay), 5% PMMA (Aldrich) and 5% PVP in dimethylformamide (DMF) (Merck). Then, the nascent membrane was immersed in bi-distillated water coagulation bath and then transferred to fresh water for 24 h.

Membrane water permeability, L_h, was calculated from Darcy's law, measuring the permeate flow of pure water as a function of transmembrane pressure. The distribution of pore radius was determined by air–liquid displacement method using a Capillary Flow Porometer CFP-1100-AEXI, from Porous Materials, Inc. A mean pore radius size value of 0.2 µm was evaluated.

Orange juice: Oranges were provided by LEIME Company (Buenos Aires, Argentina). The variety used ("Navel oranges") is exported to the European and Asian markets. Raw orange juice is produced by squeezing fresh oranges, then filtering it with a sieve of 400 mesh (Tyler normal size), and finally storing it at -8ºC. The juice is characterized by its content of soluble solids, content of total solids, titratable acidity and pH value.

B. Juice Microfiltration Procedure

The microfiltration unit used is shown in Fig. 1. All filtration experiments have been performed in a Minitan-S cell with an effective membrane area of 3.68×10^{-3} m^2 and channel hydraulic diameter is $d_h = 0.76 \times 10^{-3}$m. The feed solution was pumped continuously through the microfiltration unit from a reservoir by means of a peristaltic pump at a predetermined cross flow velocity v and transmembrane pressure ΔP.

Each test was carried out during approximately 80-90 minutes with total retentate recycling. The operating pressure between 0.4-1 bar and the cross flow velocities between (v=0.77, 1, and 1.25 m/s) were maintained constant by the pump controller and the needle valve located in the outer string. Feed flow rate was measured with the flowmeter, and permeate flux data were determined by time weighing the permeate solution with the analytical balance and processed with a computer software. The operational temperature of T=25ºC was maintained constant by using a thermostatic bath.

C. Membrane Cleanness Procedure

1st step- After each juice microfiltration experiment, the fouled membrane was rinsed with distilled water for 30 min. The feed water flow was the maximum velocity achieved by the peristaltic pump (v=1.3 m/s). This procedure allows eliminating reversible fouling resistance. When the permeate water flow reached a steady state condition, the water hydraulic permeability of the irreversible fouled membrane was determined

2nd step- After rinsing the membrane was submitted to a cleaning procedure using 2 % (w/w) enzymatic detergent solution for 30 min. Then the membrane module was rinsed with distilled water for 10 min.

3rd step- Finally the membrane was cleaned with 2 % (w/w) NaOCl solution for 30 min, followed by rinsing with water for 30 min. Water flux was measured again to check cleaning efficacy. If necessary, the cleaning procedure was repeated until the hydrodynamic permeability of the cleaned membrane was similar to that of the original membrane (95-100 %).

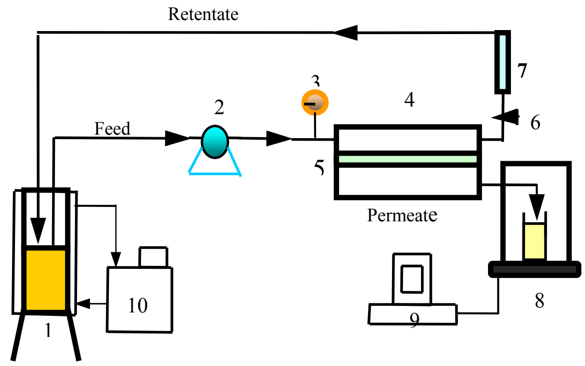

Figure 1: Schematic diagram of the microfiltration system: (1) feed-retentate reservoir, (2) feed pump, (3) pressure gauge, (4) Minitan cell, (5) membrane, (6) needle valve, (7) flowmeter, (8) analytical balance, (9) computer, (10) thermostatic bath

The entire washing steps were carried out at room temperature (≈25°C).

D. Juice Quality Analyses

Permeate and retentate juice samples taken from de microfiltration experiments were collected and stored at -8°C for quality analyses.

The total soluble solids (TSS) content was directly determined in ° Brix with an ARTAGO RX-5000 refractometer. The acidity expressed as citric acid (%) was determined with sodium hydroxide 0.1N by acid-base titration of orange juice samples. The content of total solids (TS) was determined by weighing a sample of a given amount of orange juice centrifuged for 15 minutes at 3300 rpm. After that, the liquid was removed and the solids were weighted again. pH value and juice viscosity were measured with a CHECKER pH meter and a Cannon-Fensked viscometer respectively.

III. RESULTS AND DISCUSSION

A. Permeate flux analysis

Permeate flux decline during operating time is important because it lowers filtration membrane performance. Figure 2 shows the variation of the juice permeate flux with time in the range 0.4-1 bar at a constant value of cross flow velocity v=1 m/s. Permeate flux decreases rapidly at the initial time stage and gradually thereafter. After 20 minutes of microfiltration process, a less pronounced flux decay followed by the achievement a pseudo steady-state (at t ≈ 60 min) is observed. The rapid flux decline during the first 15-20 minutes is usually attributed to irreversible pore blocking and the growth deposition of a gel layer formed by cellulose, hemicelluloses, and high molecular weight compounds (polysaccharides, protein, colloidal materials, etc.) present in the juice. These solutes deposit on the surface of a secondary dynamic membrane as the microfiltration goes on, increasing total membrane resistance. The same permeate flux behavior with the pressure at v=1.25 and v=0.77 m/s was observed.

In general, permeate flux increased with higher feed velocities, temperatures and lower pressures. The presence of solutes in the solvent leads to different permeate flux behavior with the applied pressure. Usually, three regions are present when permeate flux as a function of ΔP is represented. At low pressure the permeate flux is proportional to the applied pressure, region controlled by pressure. At a higher pressure the permeate flux approaches a limiting value independent of further increases in pressure, region controlled by mass transfer. Between these two regions there is an intermediate region in which controlling factors, pressure and mass transfer, are present. Figure 3 shows the effect of transmembrane pressure on permeate orange juice flux in steady-state conditions, J (L/m^{2}h), at different cross flow velocity. It is clear from this figure that the experimental data are mainly located between the intermediate region and the controlled mass transfer region, where the pressure increase determines no significant increase of the permeate flux. This behavior could be explained by two main opposite factors: the increase of the driving force (ΔP) leads to a higher permeate flux through the membrane pore and it simultaneously causes a major compactation of the deposited solutes layer on the membrane surface, leading to an increase of fouling resistance and a decay in permeate flux. Fouling increase due to pressure was verified through the resistance model analysis.

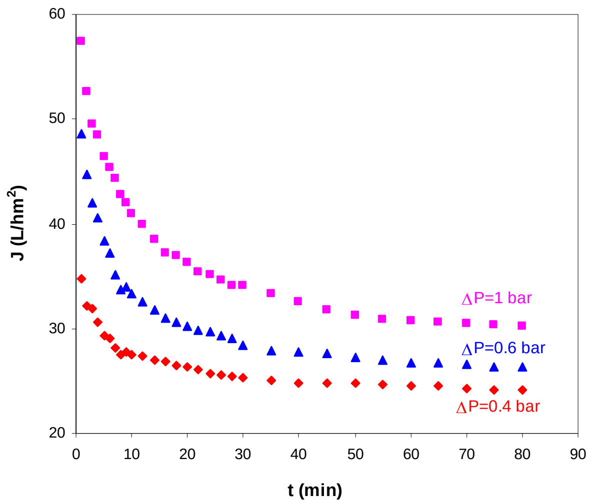

Figure 2: Variation of permeate flux with time at different ΔP (T= 25ºC, v= 1 m/s)

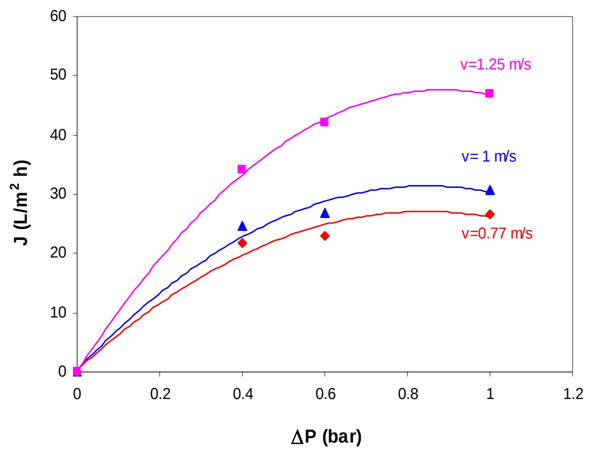

Figure 3: Effect of ΔP on steady-state permeate flux (T=25ºC)

The feed tangential velocity affects the liquid turbulence and mixing inside the channels of the module. Figure 4 shows the influence of cross flow velocity on permeate flux at T=25°C and ΔP=1bar. As expected, permeate flux increased with higher operating tangential velocities, due to the increase of the shear stress at the membrane surface and, consequently, this effect enhances the rate of removal of deposited solutes responsible of flux decay. In this case, when cross flow velocity increased from 0.77 to 1.25 m/s permeate flux increased from 26.77 to 47.19 L/m^{2}hbar.

B. Fouling Resistance Interpretation

Permeate juice flux in steady state across porous membrane can be expressed by

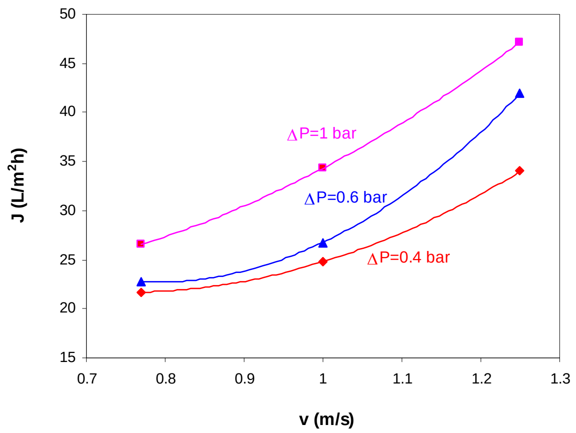

Figure 4: Effect of cross flow velocity on steady-state permeate flux (T=25ºC)

$$J=\frac{\Delta P}{\eta R_t}\Rightarrow R_t=\frac{\Delta P}{\eta J} \qquad (1)$$

where η is the permeate solution viscosity and R_t the total membrane resistance.

The R_t can be interpreted with the resistance- in-series model. In our permeate flux interpretation we considered that R_t is given by

$$R_t = R_m + R_r + R_i \qquad (2)$$

being R_m the intrinsic membrane resistance, R_r the reversible fouling resistance (i.e. cake or gel layer, adsorption, concentration polarization, etc.) and R_i the irreversible fouling resistance (i.e. adsorption, complete and partial pore blocking, internal pore blocking, etc.).

Membrane resistance (R_m) is experimentally determined by measuring the pure water flux (J_w) through the new or clean membrane as:

$$J_w=\frac{\Delta P}{\eta_w R_m}\Rightarrow R_m=\frac{\Delta P}{\eta_w J_w}=\frac{1}{\eta_w L_h} \qquad (3)$$

where η_w and L_h is the water viscosity and the hydraulic permeability respectively.

Resistance due to irreversible fouling is determined from the pure water permeate flux (J_i) of the fouled membrane after physically cleaning with pure water, as this washing procedure takes off the reversible membrane barriers:

$$J_i=\frac{\Delta P}{\eta_w (R_i+R_m)}\Rightarrow R_i=\frac{\Delta P}{\eta_w J_i}-R_m . \qquad (4)$$

Finally, the reversible resistance can be determined from Eq. (2) as

$$R_r = R_t - R_i - R_m . \qquad (5)$$

From the pure water permeate flux versus transmembrane pressure, the hydraulic permeability of the new microfiltration PVDF-PMMA membrane was calculated at 25°C, being its value L_h=1195 L/m^{2}hbar. Membrane resistance, R_m=3.01 x 10^{12} m^{-1}, was calculated from Eq. (3). After the 3rd step of the cleaning procedure the hydraulic permeabilities of clean membranes were found to be practically the same to the new membrane permeability within the experimental error of ±5%. The viscosity values of η_w = 1.00 (mPa s) and η = 1.03(mPa s) were used for R_m and R_t resistance data evaluation respectively.

The membrane resistance values as a function of the pressure at the feed velocity v=1m/s is shown in Fig. 5. Total resistances have been calculated from the stabilized permeate flux when the pseudo steady state had been reached (t ≈ 60min.). From this figure it can be observed that the total and the reversible resistance had a pronounced increase as ΔP increased, while the irreversible resistance showed a smooth increment. The same behavior was observed when the other feed velocities (v=0.77m/s and v=1.25m/s) were studied. This phenomenon is usually explained by assuming that an increase of pressure enhances the convective permeate flux of the solution towards the membrane. Consequently more solutes are deposited on the membrane surface increasing the concentration polarization and the gel layer thickness which in turn produces an important increase of R_t and R_r (Cassano *et al*., 2008).

The influence of cross flow velocity on the total, reversible and irreversible fouling resistance at ΔP = 0.4 bar is shown in Fig. 6. R_t, R_i and R_r decreased with cross flow velocity because an increase of v reduces concentration polarization and deposits of solutes on the membrane surface enhancing the mass transfer coefficient. The same resistance-velocity dependence was observed when the other transmembrane pressure (ΔP=0.6 bar and ΔP=1 bar) are analyzed.

The data of membrane total resistance and the ratio of irreversible and reversible fouling resistance to total resistance (R_i/R_t and R_r/R_t), at different ΔP and cross flow, are reported in Table 1. These resistance ratios are considered important because they are related to the major or minor difficulties of the fouled membrane to recover the original permeate flux during the filtration process (Youn *et al.*, 2004).

Table 1 shows that the main controlling resistance, over the whole range of ΔP and v investigated, was due to reversible resistance (R_r/R_t between 64-76%). The irreversible fouling resistance represent 22-36 % of the total resistances, while the intrinsic membrane resistance only varied between 2-7% of R_t. Therefore, the

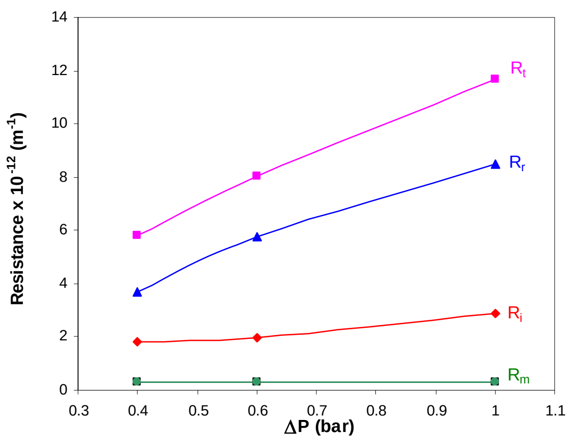

Figure 5: The effect of ΔP on membrane resistances (T=25ºC, v = 1 m/s)

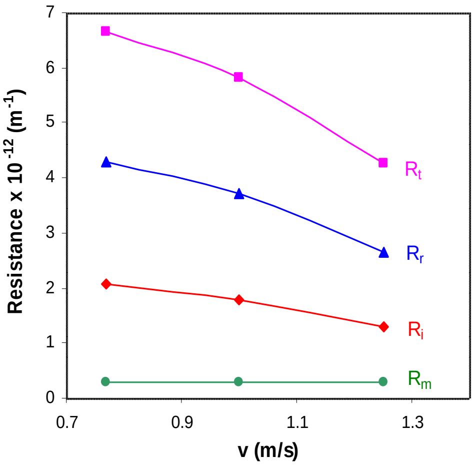

Figure 6: The effect of cross flow rate on membrane resistance (T=25ºC, ΔP=0.4 Bar).

Table 1- Membrane total resistances and resistance ratios

ΔP (bar)	R_t 10^{-12} (m^{-1})	R_m/R_t %	R_i/R_t %	R_r/R_t%
v = 0.77 (m/s)				
0.4	6.65	4.53	30.98	64.36
0.6	9.43	3.19	29.78	66.91
1.0	13.56	2.22	22.20	75.59
v=1 (m/s)				
0.4	5.81	5.10	30.98	63.80
0.6	8.06	3.74	24.56	71.71
1.0	11.69	2.57	24.36	72.79
v=1.25 (m/s)				
0.4	4.26	7.07	30.51	62.44
0.6	5.31	5.67	31.07	63.28
1.0	8.39	3.62	26.01	69.59

recovery of around a 70% of original permeate flux could be easily reached by physically cleaning the PVDF/PMMA microfiltration membrane.

C. Permeate Orange Juice Quality

The physicochemical properties of orange juice and clarified juice are shown in Table 2.

Table 2. Physicochemical properties of orange juice and clarified juice

Component	Feed	Permeate Juice ΔP = 0.4 (bar)	ΔP = 0.6 (bar)	ΔP = 1.0 (bar)
v= 0.77 (m/s)				
Total Solid (%)	3.30	0	0	0
TSS (ºBrix)	12.1	11.5	11.5	12.0
Acidity (% citric acid)	1.13	1.10	1.10	1.10
pH	3.56	3.46	3.52	3.51
v= 1.00 (m/s)				
Total Solid (%)	3.30	0	0	0
TSS (ºBrix)	12.1	11.6	11.5	12.1
Acidity (% citric acid)	1.13	1.11	1.10	1.11
pH	3.56	3.50	3.47	3.37

Table 2 (cont.)

Component	Feed	Permeate Juice ΔP = 0.4 (bar)	ΔP = 0.6 (bar)	ΔP = 1.0 (bar)
v= 1.25 (m/s)				
Total Solid (%)	3.30	0	0	0
TSS (ºBrix)	12.1	12.1	11.9	11.5
Acidity (% citric acid)	1.13	1.13	1.11	1.10
pH	3.56	3.46	3.36	3.48

The content of soluble solids, acidity and pH present in the feed and in clarified permeates are practically the same. The total solids (TS) are completely removed by clarification.

IV. CONCLUSIONS

Orange juice clarification was performed in a tangential microfiltration system, using a 0.2 µm mean pore size PVDF/PMMA membrane. The effect of transmembrane pressure and feed cross flow-rate (at T=25ºC) on the permeate flux and membrane fouling was investigated. In all the operational conditions the permeate flux decreased rapidly during the first 20 minutes and then a less pronounced flux decay was observed, followed by the achievement of a steady-state at around $t \approx 60$ min. The steady-state permeate flux increased by increasing both the transmembrane pressure and the feed cross flow. The maximum value of clarified permeate flux of 47 L/m^2h in the steady-state was achieved at ΔP = 1 bar and v = 1.25 m/s.

Membrane fouling was analysed through the resistance-in-series model. The permeate flux in the steady state conditions revealed that the reversible resistance (polarization concentration and cake layer) was the main controlling resistance (64-76% of the total membrane resistance), being the irreversible fouling resistance 22-36 % of the total resistance. The best experimental conditions to obtain the minimum membrane fouling were v=1.25m/s and ΔP=0.4 bar. It is pointed out that the fouled membrane can recover around 70% of its original permeate flux by washing it with pure water.

The clarified orange juice presented a complete removal of the total solids (100% of retention), while the other analyzed physicochemical properties (soluble solid, acidity and pH) were practically the same as those of the raw orange juice.

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