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Assessment of Operating Parameters, Membrane *Fouling* and Juice Quality during Acerola Ultrafiltration

Paula G. Milani*[a], Aniele M. Prato[b], Antonio R. G. Monteiro[c], Mariane F. Maioral[a], Livia B. Marchi[a], Sílvio C. da Costa[d]

[a]Graduate Program in Food Science - State University of Maringá (UEM); Av. Colombo 5790; CEP 87020-900; Maringá – Paraná – Brazil
[b]State University of Maringá (UEM); Av. Colombo 5790; CEP 87020-900; Maringá – Paraná – Brazil
[c]Food Engineering Department – State University of Maringá (UEM); Av. Colombo 5790; CEP 87020-900; Maringá – Paraná – Brazil
[d]Biochemistry Department - State University of Maringá (UEM); Av. Colombo 5790; CEP 87020-900; Maringá – Paraná – Brazil
paulinhauem@uem.br

Clarification is an important step in the fruit juices processing, because it has as result a noble product that assists to the consumer's new lifestyle. The objective of this work was to evaluate the best condition for the acerola pulp clarification through the processing with membranes, as well as the juice quality, being used a ultrafiltration module - Labscale TFF System of Millipore. The acerola pulp was centrifuged using a centrifuge FANEN, baby model 206 II - R, rotation of 50 rpm for 10 minutes, resulting in a normalized juice, due to limitations of the ultrafiltration equipment. Polissulfone membranes with cut-off 300, 100 and 5 kDa, with transmembrane pressures among 5 and 20 psi, and room temperature. The centrifugation did not cause significant variations in parameters such as soluble solids, total carbohydrates, reducing sugar, glucuronic acid, protein and vitamin C. However, it removes 100% cellulose and 60% suspension turbidity, which results in substantially improved color and clarity in comparison with the original juice, and did not affect the taste of the acerola juice. The ultrafiltration processes efficiency was evaluated using as parameters the permeated flux, the *fouling* and the rejection coefficient (R) of the compounds responsible to juice's turbidity and nutritional value. The process of clarification by ultrafiltration was efficient in the removal of substances causing turbidity, which results in a particle free clear juice or pulp suspension. This can be proved, therefore, that in the best condition, the highest coefficient of rejection of reducing sugars (22.5%), the third highest rate of rejection of glucuronic acid (12.5%) and the sixth largest coefficient was observed rejection for total sugar (19.9%), this are some of the main substances responsible for turbidity in juices. The clarification in the best condition also resulted in a juice with excellent nutritional quality, as it showed the lowest coefficient of protein rejection (4.8%), the second coefficient lower rejection vitamin C (8.4%) and showed no rejection to total phenolic compounds.The best ultrafiltration condition, obtained using membrane of 300 kDa at 15 psi of transmembrane pressure, resulted in the biggest permeate flux, with the lesser *fouling* and excellent nutritional quality of the permeate.

1. Introduction

Consumers in Brazil have purchased billions of liters of juices, integral juices, previously diluted and sweetened, because of this expanding market, the industries of fruit processing have been trying to innovate, introducing natural fruit-based products such as concentrated juices, isotonic drinks, among others, aiming at maximizing value addition. In addition, the possibility of industrial use along with the potentially great source of Vitamin C that the acerola juice represents have been attracting the interest of fruit growers from several regions of Brazil (Gomes et al., 2005).
Membrane processes are consolidated systems in various sectors of production for their capacity to operate at room temperature under low energetic consumption. Particularly, ultrafiltration and microfiltration processes

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are valid approaches for the clarification of beer (Cimini et al., 2013), milk whey (Baldasso et al., 2011) and fruit juices (Cassano et al., 2007), resulting in a clarified juice through microbiological stabilization that preserves great part of the original aroma (Vaillant et al., 2005). Ultrafiltration replaces the conventional filtration processes eliminating the use of filtration agents and associated problems through a continuous, simple process (Baldasso et al., 2011). In addition, ultrafiltration membranes retain large species such as microorganisms, lipids, proteins and colloids preventing precipitate formation, while small solutes such as vitamins, salts and sugars flow with the water through the membrane (Cassano et al., 2003).
Although acerola presents high nutritional value, a great part of its nutritional compounds is lost during the conventional industrial process of clarification; thermal damage and chemical oxidation degrade more sensitive components weakening the final product quality (Cassano et al., 2003). Furthermore, the forms of acerola juice precipitated 4-6 h after extraction impacting quality; such precipitation can be reduced through juice clarification. In this context, the objective was to study the operational conditions involved in acerola clarification, as well as to assess efficiency of the process and the nutritional quality of the clarified juice.

2. Material and Methods

2.1 Acerola pulp - Centrifugation and Ultrafiltration

We purchased the acerola (*Malpighia emarginata*) at a local supermarket in Maringá, Paraná State, Brazil and stored in the dark at –18°C. The centrifugation of the acerola pulp using as FANEN centrifuge, model Baby II 206 - R, - 50 rpm rotation of for 10 minutes. The ultrafiltration process was conducted on a labscale TFF system using tangential filtration principles, with the Pellicon^{TM} XL device. The system consists of a 500 mL acrylic reservoir with feed and retentate pressure gauges, retentate valve, and system base with integral magnetic stirred and diaphragm pump. The Pellicon^{TM} XL device is composed of polyethersulfone membranes of molecular weight cut-off 5000, 100 000 and 300 000 Daltons (Da), with filtration area 50 cm^2. The unit was operated in batch of 500 ml. Permeate stream was collected while the concentrate stream returned back to the feed tank so that the juice of the tank became more and more concentrated. The transmembrane pressure was controlled.

2.2 Physicochemical analyses

The following physicochemical analyses were performed in the feed, retentate and permeate streams: pH, turbidity, pulp content, soluble solids (°Brix) (Adolfo Lutz, 1985), total carbohydrate (Dubois et al., 1956), reductor sugar (DNS-Berkeley modified by Zanin and Moraes, 1987), vitamin C (Polesello and Rizzolo, 1990), glucuronic acid (Kitnner and Van Buren, 1982), total phenolic (Meda et al., 2005) and protein (Lowry et al., 1951).

2.4 Rejection coefficient (R) and Fouling

We assessed the parameters based on the rejection or reduction coefficient (R), presented by equation (1), supplying the quantitative measure of the membrane capacity to hold, for example, molecules responsible for turbidity, under certain operational conditions. This coefficient is established in percentual terms, where Cp and C_0 are the concentrations in permeate and feed streams, respectively.

$$R = \left(1 - \frac{C_p}{C_0}\right) * 100 \quad (1)$$

2.5 *Fouling*

The fouling in the membrane can be expressed as the reduction percentage of the hydraulic permeability (Baldasso et al., 2011). The water flux before and after each run were measured and the resulting fouling was calculated according to the equation (2) - J_{clean} and J_{fouled} were are the water flow before and after each run.

$$Fouling \quad (\%) = \frac{\left(J_{clean} - J_{fouled}\right)}{J_{clean}} * 100 \quad (2)$$

3. Results and Discussion

3.1. Influences of the centrifugation under the acerola pulp

The acerola pulp samples were previously centrifuged to remove all the suspended solids in juice, in order to facilitate the permeated flow. The parameters evaluated for the acerola pulp before and after centrifugation are illustrated in the Table 1.

Table 1: *Characteristics of acerola pulp before and after centrifugation*

Parameters	Integral pulp (IT)	Centrifuged (CE)
Pulp (%)	19	0
Turbidity (FAU)	308	123
Soluble solids (°Brix)	5.6	6.0
Total Carbohydrate*	1381.1	1315.3
Reductors Sugar*	2760.3	2705.2
Glucuronic Acid*	48.6	47.1
Protein *	260.2	248.9
Vitamin C*	806	761

*mg/100g

The centrifugation caused no significant variation for the parameters of soluble solids, total carbohydrate, reductors sugar, glucuronic acid, protein and vitamin C. However, it removed 100% of suspension pulp and 60% of turbidity, resulting in substantial improvement of color and clarity compared with the original juice, and did not affect the acerola juice taste. The use of this pulp in the ultrafiltration process presented very satisfactory results. As far as the subsequent clarification by ultrafiltration is concerned a good pre-treatment should result in a juice with low viscosity, such that the probability of formation of gel-type layer on the membrane surface is minimized and the maximum permeate flow is expected.

3.2. Influences of the transmembrane pressure under the permeate flux

The efficiency of the ultrafiltration processes was assessed using the parameters of permeated flow, fouling and rejection coefficient (R) of the compounds responsible for the juice turbidity. The chosen operating temperature was 25 °C was since some organoleptics and nutritional properties of the fresh juice, such as vitamins and proteins, are stable when the juice is held at temperature under 30 °C (Cassano et al., 2007).

In general, the permeate flow with pure water increased linearly to the increase of the transmembrane pressure, a not frequent behaviour with the acerola pulp. In micro/ultrafiltration, the increase of the transmembrane pressure caused an increase of the fouling in the membrane; unlike Darcy's Law prediction, the increase in the permeate flow was not proportional to the applied transmembrane pressure. The permeated flow was assessed varying the transmembrane pressure and the molecular membranes cut-off. These results are presented in Figure Figures 1 (A, B e C).

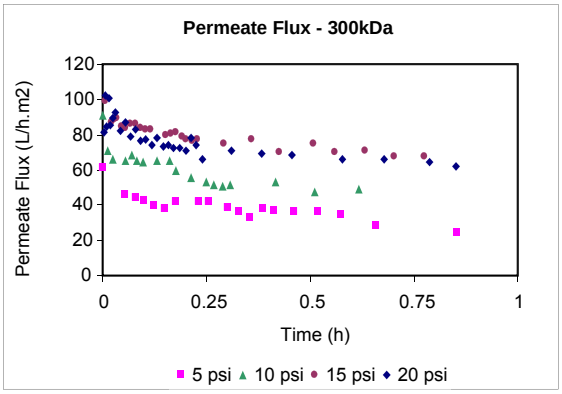
The rapid decline of the flow is attributed to the deposition and growth of a polarized layer formed by left-over pectin, cellulose, hemicellulose, etc., high molecular weight compounds increasing the Fouling resent in the juice. The growth of such polarized layer is restricted by the external turbulence caused by the stirring, finally, the flow decline is retained in a steady state flow. The permeate flux during ultrafiltration process decreases rapidly in the membranes of 300, 100 and 5 kDa, at the initial stage and gradually thereafter to reach a landing, called stabilized flow.

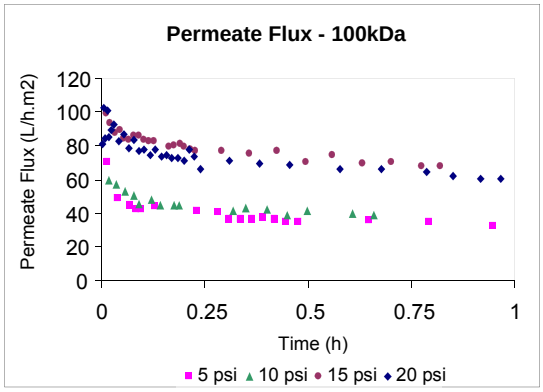
The increase from 5 to 15 psi in the transmembrane pressure for membrane of 300 kDa caused an increase in the permeate flow; however, the permeate flow with increase from 15 to 20 psi in the transmembrane pressure had a lower decrease. According to Tarleton and Wakeman (1993), this behaviour can be attributed the presence of a small percentage of fine particles that reduce significantly the permeate flow when the pore size is larger compared with the particle size. We also found that the increase in the transmembrane pressure forces the fine particles to block the membrane pore, increasing the fouling (Table 2). In the case of the acerola juice, it is formed due to the presence of pectins, that have great potential to form gels; at the initial ultrafiltration process, a layer gel is formed on the membrane, being subsequently compressed at high pressures resulting in low values of permeate flow. For membrane 100 kDa, the increase in the transmembrane pressure caused lower increase in the permeate flow. The permeate flow in 100 kDa membrane was lower 300 kDa, as expected. For 5 kDa membrane of, the permeate flow increased from 5 to 10 psi in the transmembrane pressure, but with practically no variation in the transmembrane pressure from 10 to 15 psi. The increase from 15 to 20 psi in the transmembrane pressure indicated an increase in the permeate flow. The permeate flow in 5kDa membrane was lower than 100 kDa and 300 kDa, as expected.

The permeate flow obtained for 15 psi transmembrane pressure using 300 kDa membrane (70.12 Kg/h.m^2), was higher than the most satisfactory permeate flow obtained by Barros, (2002). An increase from 10 to 20 L/h.m^2 as the temperature increased from 20 to 30°C, similar results were observed by Cassano et al., (2007).

3.3 Membrane *Fouling*

Membrane fouling can be expressed as the reduction percentage of the hydraulic permeability (eq. 2). The membrane fouling ranges from 50 to 80%, depending on the membrane molecular cut-off and on the applied transmembrane pressure, as illustrated in table 2. Membranes with smaller molecular cut-offs had higher fouling, as expected; however, the fouling did not indicate a proportional relation with the transmembrane pressure increase.





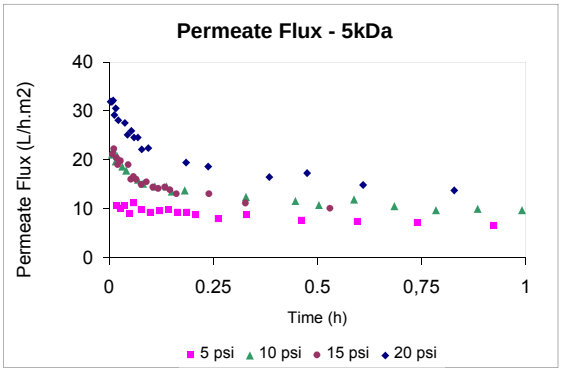


Figure 1 A, B, C: Permeate flux profile during UF of centrifuged acerola juice – molecular membrane cut-off 300 (A), 100 (B) e 5 (C) kDa.

Table 2: Fouling (%)

Transmembrane pressure (psi)	300 kDa	100kDa	5kDa
5	63.18	69.91	79.76
10	72.07	69.95	67.10
15	50.91	64.63	73.79
20	54.84	68.66	75.17

3.4 Rejection coefficient in the operational conditions

The ultrafiltration process efficiency and the permeate qualities were assessed based on the rejection or reduction coefficient (R), supporting the quantitative measure of the membrane capacity to hold, for example, molecules responsible for turbidity, under certain operational conditions. The ultrafiltration caused no significant variation to pH. The centrifugation supernatant pointed turbidity of roughly 780 FAU (Formazin Attenuation Units). The ultrafiltration process was efficient at removing the compounds responsible for turbidity. Under all of the ultrafiltration conditions, the permeate turbidity was under 2 FAU, which was lower than the values reported by Barros (2002), who used polysulfone hollow fiber membrane with molecular weight cut-off 100 kDa at 40°C and 0.8 bar (11.6 psi).

The suspended solid was completely removed through the ultrafiltration process resulting in clarified juice with negligible turbidity. Similar results were obtained by Cassano et al., (2007). The permeate of all the assessed ultrafiltration conditions established an average rejection coefficient of soluble solids (°Brix) of roughly 15 %. This value was smaller than the value reported by Barros, (2002). However, this average rejection coefficient for soluble solids was higher than the value reported by Gomes et al., (2005), 8.58 % for ultrafiltrated acerola pulp using 0.01 μm ceramic membrane. The mean coefficients for total carbohydrate, reducing sugar and glucuronic acid (pectin) were calculated and illustrated in Figure 2.

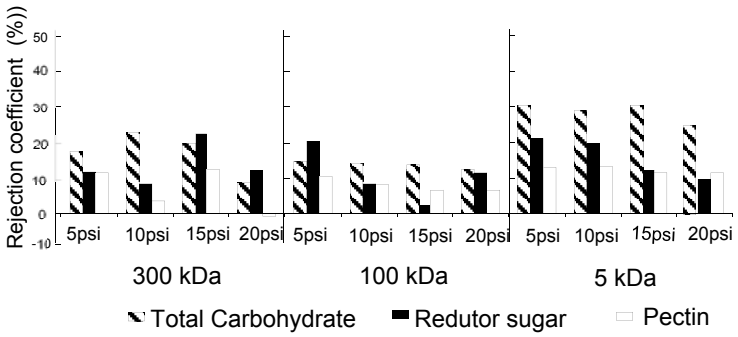


Figure 2: The rejection coefficient for the total carbohydrate, reductor sugar and pectin for the membranes molecular cut-off 300 kDa, 100 kDa and 5 kDa at transmembrane pressure of 5, 10, 15 and 20 psi.

The mean coefficient for total carbohydrate was 30 %, 15 % and 15 % to membrane of molecular weight cut-off 5 kDa, 100 kDa and 300 kDa, respectively. The membrane with the lowest molecular weight cut-off presented the highest mean rejection coefficient for total carbohydrate, as expected, except 300 kDa membrane. Matta et al., (2004), in aforementioned study observed the reduction of approximately 25 % in the amount of total carbohydrate in acerola. The rejection coefficient for reducing sugar in 300 kDa membrane remained roughly 10 % for all of the assessed transmembrane pressure, except 15 psi; for 100 kDa and 5 kDa membranes , we observed a decrease in the rejection coefficient with the increase in the transmembrane pressure, except 100 kDa at 20 psi. This indicates that the increase in the transmembrane pressure favors the passage of the compounds through the membrane.

The rejection coefficient for glucuronic acid (pectin) did not present a regular behavior for 300 kDa membrane of; however, 100 kDa membrane had a rejection coefficient decreasing with the increase in the transmembrane pressure; 5 kDa membrane remained practically constant. Gomes et al., (2005) reported a 79.20 % rejection coefficient for pectin. The clarified juice quality was assessed in terms of the rejection coefficient for vitamin C, total phenolics and proteins, illustrated in Figure 3.

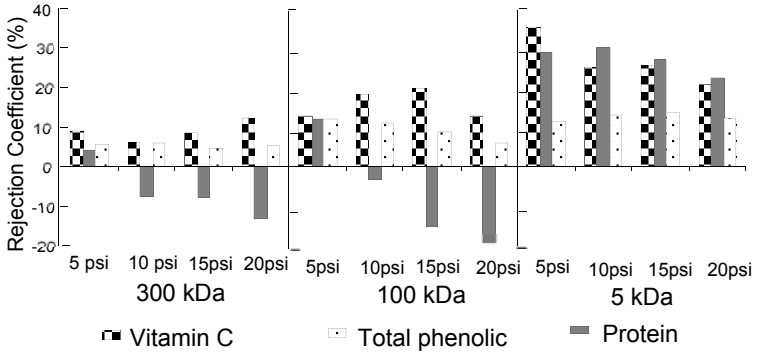


Figure 3: The rejection coefficient for the vitamin C, total phenolic and protein for the membranes molecular cut-off 300 kDa, 100 kDa and 5 kDa at transmembrane pressure of 5, 10, 15 and 20 psi.

The highest rejection coefficient for vitamin C was observed in 5 kDa membrane, decreasing as the transmembrane pressure increased. In 100 kDa and 300 kDa membranes, the transmembrane pressure did not have significant influence on the rejection coefficient for vitamin C. The positive rejection coefficient for vitamin C cannot be attributed to the membrane rejection since vitamin C presents molar mass of 176 Da, therefore, it could not be restrained in the membranes. Moreover, it could be easily oxidated if exposed to light, oxygen and freezing. Gomes et al., (2005) reported a 15.34 %rejection coefficient for vitamin C; however, Matta et al., 2004, related a concentration of 9.7 % vitamin C in the clarified juice to fresh acerola.

The rejection coefficient for total phenolic was negative for 300 kDa membrane and 100 kDa at transmembrane pressures of 10, 15 and 20 psi, decreasing as the pressure increased. This indicates that the increase in the transmembrane pressure favors the pasage of the phenolic compounds through the membrane, evincing the effect of the polarized concentration. For membrane 5 kDa, we also observed a decrease in the rejection coefficient for total phenolic with the increase in the transmembrane pressure;, however, the value was positive.Vaillant et al., (2005) related a 19 % reduction of polyphenol componds and 7 % of vitamin C in the clarified melon juice in ceramic multichannel membrane of 0.2 µm to a 35 °C maceration for one hour with enzymatic solution Rapidase. The rejection coefficient for protein didn't show significant

variation in the membranes of 300 kDa and 5 kDa remaining itself in 5 % and 10 % respectively. However, in the membrane of 100 kDa, the rejection coefficient for protein decreases with the increase of transmembrane pressure. Matta et al., (2004) reported a 30.83% reduction of protein in the clarified juice compared with fresh acerola.

According to the obtained results, the most satisfactory ultrafiltration condition used 300 kDa membrane at 15 psi transmembrane pressure. Under this condition, we observed the highest permeate flow (70.12 kg/h.m^2), and the lowest fouling (50.91%). The most satisfactory condition indicated the highest rejection coefficient for reducing sugar (22.5%), the third highest rejection coefficient for glucuronic acid (12.5%), and the sixth highest rejection coefficient for total sugar (19.9%) - these substances are the major responsible for turbidity in juices. Under the most satisfactory condition, the clarification also resulted in a juice with excellent nutritional quality, therefore with the lowest rejection coefficient to protein (4.8%), the second lowest rejection coefficient to vitamin C (8.4%), and no rejection to total phenolics.

4. Conclusion

The most satisfactory ultrafiltration condition was obtained using 300 kDa membrane at 15 psi transmembrane pressure. The clarification was efficient and the suspended solids were completely removed; the final juice presented an excellent nutritional quality. Further studies should be done to improve the clarification process and increase the marketing of products produced from fruits such as acerola.

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