Ingeniería Ambiental

Revista Mexicana de Ingeniería Química

Vol. 14, No. 3 (2015) 735-744

RECOVERY OF CARBOHYDRATES FROM NIXTAMALIZATION WASTEWATERS (NEJAYOTE) BY ULTRAFILTRATION

RECUPERACIÓN DE CARBOHIDRATOS DE LAS AGUAS RESIDUALES DE LA NIXTAMALIZACIÓN (NEJAYOTE) POR ULTRAFILTRACIÓN

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Received April 8, 2015; Accepted July 14, 2015

Abstract

Nejayote extract is a polluting by-product from Nixtamalization of maize; therefore in this study was evaluated a membrane operation for the treatment and recovery of industrial usable compounds. Nejayote extract was processed by ultrafiltration (UF) membrane on laboratory scale. In experimental tests performed according to the total recycle mode, the effect of transmembrane pressure (TMP) on permeate flux has been studied. The permeate flux no showed a considerable increase for TMP values higher than 1.3 bar, which is considered as limiting TMP (TMP_{lim}) that provides the maximum permeate flux. Filtrated Nejayote extract has been produced in experimental test carried out according to the batch concentration mode working in optimal operating conditions. The extract was analyzed in terms of total soluble solids (TSS), total solids content (TSC), pH, electrical conductivity, turbidity, total polyphenols, total carbohydrates, total organic carbon (TOC) and calcium content. The UF process permitted a good level of recovery; it was corroborated with the removal of 95.3 % on turbidity, 22.0 % on TSC, 37.0 % on TSS, 14.7 % on Calcium and 29.3 % on TOC on Nejayote. From retentate was recovered considerable sugar content (rejection of 46.6 % in total carbohydrates). Finally, high fouling index in the membrane (87 %) was determined after treatment of Nejayote; however, the total of the initial water permeability was recovered by enzymatic cleaning (cleaning efficiency 100 %).

Keywords: Nejayote, wastewater, total polyphenols, total organic carbon, sugars.

Resumen

El Nejayote es un subproducto contaminante de la nixtamalización de maíz; por ello en este trabajo se evaluó una operación de membrana para su tratamiento y recuperación de componentes útiles en la industria. El Nejayote fue procesado a través de una membrana de Ultrafiltración (UF) a escala laboratorio. En las pruebas experimentales realizadas en modo recirculación, se estudio el efecto de la presión transmembranal (TMP) sobre el flux de permeado. El flux de permeado no mostró aumento considerable para valores de TMP mayores a 1.3 bar, que corresponde a la TMP limitante (TMP_{lim}) que provee el flux de permeado máximo. Se produjo Nejayote filtrado en prueba experimental acorde al modo de concentración por lotes en condiciones de operación óptimas. El extracto fue analizado en términos de sólidos solubles totales (TSS), contenido de sólidos totales (TSC), pH, conductividad eléctrica, turbidez, polifenoles totales, carbohidratos totales, carbono orgánico total (TOC) y contenido de calcio. El proceso de ultrafiltración permitió buen nivel de recuperación, al eliminar 95.3 % en turbidez, 22 % en TSC, 37 % en TSS, 14.7 % en Calcio y 29.3 % en TOC del Nejayote. Del retenido fue recuperado un contenido considerable de azúcares (rechazo del 46.6 % en carbohidratos totales). Finalmente, se determinó un alto índice de ensuciamiento (87 %) en la membrana después del tratamiento del Nejayote; sin embargo, el total de la permeabilidad inicial fue recuperada por limpieza enzimática (eficiencia de lavado del 100 %).

Palabras clave: Nejayote, agua residual, polifenoles totales, carbono orgánico total , azúcares.

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1 Introduction

The Nejayote is a by-product from the Nixtamalization process in the Maize processing industry (Valderrama-Bravo *et al*., 2012). This byproduct is considered as a dangerous wastewater to the water and environmental pollution due to its high alkalinity, physico-chemical composition (Gutiérrez-Uribe *et al*., 2010; Valderrama-Bravo *et al*., 2012) and organic matter contents (Ferreira-Rolón *et al*., 2014). Currently, the Nejayote is directly discarded in the sewage but there are few studies where have been treated to obtain raw material employed as an ingredient to improve boiler foods (Velasco-Martinez *et al*., 1997), to enrich bread (Acosta-Estrada *et al*., 2014), tortillas (Gutiérrez-Uribe *et al*., 2010) or as a culture medium for probiotics and production of bacteriocins (Ramírez-Romero *et al*., 2013).

The water pollution impact by this wastewater can be reduced recoverying components from the water stream, it has been reported the presence of bioactive compounds in the Nejayote such as carbohydrates identified as arabinoxylans (Niño-Medina *et al*., 2009; Ayala-Soto *et al*., 2014) and polyphenols (Gutiérrez-Uribe *et al*., 2010; Lopez-Martinez *et al*., 2009). Until now, there is no evidence about recovery of bioactive and chemical compounds from Nejayote. Membrane processes have been successfully employed for recovering bioactive compounds from different wastewaters of food processing industry such as artichoke wastewaters (Conidi *et al*., 2014), orange press liquor (Conidi *et al*., 2012) and olive mill wastewaters (Cassano *et al*., 2013).

In this work, membrane operation is proposed as an alternative for the treatment and recovery bioactive comprounds from Nejayote. The aim of this work was to evaluate, on laboratory scale, the effect of different parameters, such as transmembrane pressure (TMP) on permeate flux in order to identify process conditions that would ensure acceptable flux for the treatment of Nejayote. In addition, it was analyzed the behavior of physico-chemical composition of the extract during the process in terms of total soluble solids (TSS), polyphenols, total carbohydrates (as sugars), electrical conductivity, pH, turbidity, total solids content (TSC), total organic carbon (TOC) and calcium content. Membrane parameters such as water permeability, fouling index and cleaning efficiency were analyzed and discussed.

2 Materials and methods

2.1 Solutions and reactants

2.1.1. Preparing the extracts

To prepare Nejayote, Nixtamalization was carried out as follows. Total of 5 kg of corn was cooked during 38 min at 92 °C in a solution prepared with 50 g of calcium hydroxide (Nixtacal-Mexico) dissolved in 10 L of water. Then corn kernels were rested during 12 h; the Nejayote (cooking liquor) was drained by decantation. The extract was then stored at -17 °C until used.

2.2 Treatment of Nejayote by ultrafiltration membrane

2.2.1. Experimental set-up and procedures

The UF step was performed using a laboratory unit with feed tank, and peristaltic pump, a water bath in recipient, a manometer and pressure-regulating valve. The UF unit was equipped with a polysulfone hollow fiber membrane (Amersham Biosciences Corp. Model UFP-100-E-4A, USA) of 100 kDa. The specifications of the membrane are reported in Table 1. UF experiments were carried out according to the recirculation configuration at an operating temperature of 25 ±1 °C at different transmembrane pressures (0.3, 0.6, 1.0, 1.3 and 1.7 bar) in order to find the optimal pressure that provides the limiting flux for carrying out batch concentration configuration.

Table 1. Characteristics of the membrane used for the treatment of Nejayote.

Membranes	UF
Manufacturer	Amersham Biosciences
Membrane type	UFP-100-E-4A
MWCO (Da)	100,000
Membrane surface area (cm^2)	420
Membrane material	Polysulfone
Configuration	Hollow fiber
pH operating range	2-14
Temperature range (ºC)	2-50
Transmembrane pressure operating range (bar)	0.4-3

2.2.2. Batch concentration configuration

The experimental run was performed according to the batch concentration mode up to a final volume reduction factor (VRF) of 6 at TMP 1.3 bar using as feed batch of 2, 000 g. The system was operated at a temperature of 25 ±1 °C. The feed flow rate (Q_f) was fixed at 58 L h^{-1}. The VRF was defined as the ratio between the initial feed volume and the volume of resulting retentate according to equation (1) (Garcia-Castello *et al*., 2011):

$$VRF = \frac{V_F}{V_R} = 1 + \frac{V_P}{V_R} \tag{1}$$

where V_F, V_P and V_R are the volumes of feed, permeate and retentate, respectively. The permeate flux was measured gravimetrically as the change of permeate weight with time using a digital balance (A&D Model EJ-2000, Korea), the productivity of the membrane in terms of permeate flux was expressed in kg m^{-2} h^{-1}. Samples of feed, permeate and retentate taken during experimental runs were kept in the freezer (-17 °C) until analysis.

2.3 Membrane paramenters

2.3.1. Water permeability

Water permeability (Lp) was determined as the slope of the straight line obtained plotting the water flux (Jv) values against the applied transmembrane pressure (TMP). According to the Darcy's law (Strathmann *et al*., 2006):

$$L_P = \frac{Jv}{TMP} \tag{2}$$

It measured in fixed conditions of temperature (25 °C).

2.3.2. Fouling index

The fouling index (I_f), expressed as a percentage drop in water permeability, was performed by measuring the water permeability before and after treatment of Nejayote, according to equation (3):

$$\%I_f = \left(1 - \frac{Lp_1}{Lp_0}\right) \times 100 \tag{3}$$

where Lp_0 and Lp_1 are the water permeabilities measured before and after treatment of Nejayote, respectively.

2.3.3. Cleaning efficiency

After the treatment of Nejayote, UF membrane was rinsed with tap water (20 min, 25 ºC, 1.3 bar, 58 L h^{-1}) and their water permeabilities were measured again (Lp_2). After cleaning with water, the UF membrane was submitted to an enzymatic cleaning with Ultrasil 67 (Ecolab, Minnesota; USA) at 0.5 % (v/v) (60 min, 55 °C, 1.3 bar, 58 L h^{-1}). At the end of the cleaning procedure, the membrane was rinsed with tap water for 30 min at 58 L h^{-1} and water permeability was measured again (25 ºC, 58 L h^{-1}). Cleaning efficiency (C_E) was evaluated by using the flux recovery (FR, %) method (Chen *et al*., 2006) according to equation (4):

$$\%C_E = \left(\frac{Lp_3}{Lp_0}\right) \times 100 \tag{4}$$

where Lp_3 is the water permeability measured after enzymatic cleaning.

2.4 Physico-chemical parameters evaluated on Nejayote

Feed, permeate and retentate samples coming from the membrane operation were analyzed in terms of Total soluble solids (TSS), polyphenols, total carbohydrates (as sugars), electrical conductivity, pH, turbidity, total solids content (TSC) and total organic carbon (TOC).

2.4.1. Polyphenols

Total phenols were estimated colorimetrically by using the Folin-Ciocalteu method (Singleton *et al*., 1999). The method is based on the reduction of tungstate and/or molybdate in the Folin- Ciocalteau reagent by phenols in alkaline medium resulting in a blue colored product, using a spectrophotometer (Perkin Elmer Model Lambda XLS, UK) at λ_{max}= 756 nm, results were expressed as mg gallic acid L^{-1}.

2.4.2. Total carbohydrates

Total carbohydrates in terms sugars were estimated colorimetrically by using Dubois method (Dubois *et al*., 1956), using a spectrophotometer (Perkin Elmer Model Lambda XLS, UK) at λ_{max}= 490 nm; results were expressed as mg glucose mL^{-1}.

2.4.3. Total soluble solids (TSS)

Samples was centrifuged at 5,670 x g, 10 min with Thermoscientific centrifuge (Model Megafuge 40), the supernant was dried at 100 ± 2ºC, 24 h. TSS was expressed as g 100 g^{-1}

2.4.4. Electrical conductivity

Electrical conductivity was measured by 510 model pH meter (OAKTON, L.A., USA) using a special electrode to determine electrical conductivity. It was calibrated with a KCl 0.1 M solution; the electrical conductivity was expressed as μS cm^{-1}.

2.4.5. pH

pH was measured by 510 model pH meter (OAKTON, L.A., USA). It was calibrated with buffer solutions of pH 4 and 7.

2.4.6. Total solids content (TSC)

Total solids content in samples was determined according to equation (5):

$$\%TSC = 100 - \%Moisture \tag{5}$$

where the moisture was determined by method 925.09 (AOAC, 1998).

2.4.7. Turbidity

Turbidity in samples was analyzed with HI93703 model Microprocessor Turbidity-meter (Hanna instruments, Romania); it was calibrated with patron solutions 0 - 1000 NTU's.

2.4.8. Total organic carbon (TOC)

TOC was determined employing by Shimadzu equipment (Model TOC-5000) expressed as mg L^{-1} (Akechi, Abe and Fujiyama, 2008).

2.4.9. Calcium content

The calcium content in samples was analyzed by atomic absorption spectroscopy. The samples were hydrolyzed with Nitric acid at ebullition and were diluted with Nitric acid 2 %. The measurements were performed using an atomic absorption spectrometer (GBC, model SavantAA version 3.02, Australia) at 422.7 nm. Results were expressed as mg L^{-1}.

2.5 *Statistical analyses*

Results were expressed as mean ± standard deviation (SD), and one-way analysis of variance (ANOVA) were performed using SAS statistical software (V6.0, SAS Institute Noth Caroline, USA). Tukey's multiple range test was used to compare the means. Differences among the means of p <0.05 were considered significant.

2.6 *Rejection towards each component by ultrafiltration membrane*

To determine the rejection (R_i) of specific compound by the membrane was determined as equation (6) (Cissé *et al*., 2011):

$$\%R_i = \left(1 - \frac{Cp_i}{Cf_i}\right) \times 100 \tag{6}$$

where Cp_i and Cf_i are the concentration of specific compound in permeate and feed, respectively.

3 Results and discussion

3.1 *Effect of operating parameters on permeate flux*

UF experiments carried out according to the total recycle mode, were performed in order to study the effect of TMP on the permeate fluxes of Nejayote. Figure 1 shows permeate flux values at steady state versus the applied TMP. It can see that in first 40 min of the runs during the separation process, the permeate fluxes decreased up to a steady state in all TMP applied to the membrane system.

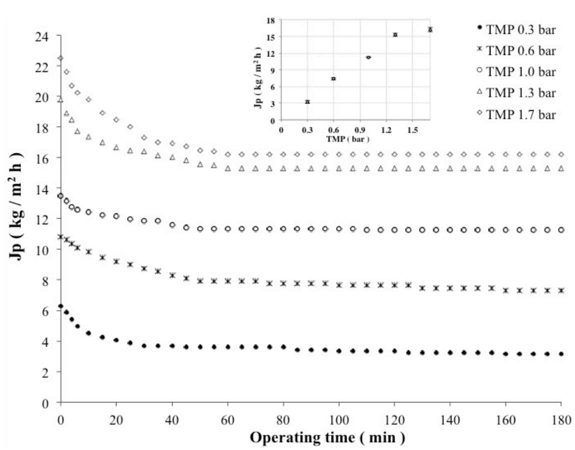


Fig. 1. Operating time of permeate flux at different

transmembrane pressures (Operating conditions: Q_f : 58 L h^{-1}, T: 25 ±1 °C).

Figure 1 represents the average of permeate fluxes of steady-states on each TMP, the figure shows that for small pressures the flux is proportional to the applied pressures, as the pressure is increased flux shows a deviation from a linear behavior and it becomes independent of pressure (Cassano *et al*., 2007). In these conditions a limiting flux is reached at a TMP value of 1.3 bar and any further pressure increase determines no significant increase of the permeate flux, in these conditions was found the optimal TMP for the separation of Nejayote by batch concentration configuration, this TMP is well known limiting TMP (TMP$_{lim}$). The existence of a limiting flux can be related to the concentration polarization phenomenon that arises as the feed solution is convected towards the membrane where the separation of suspended and soluble solids from bulk solution takes place. A concentration profile from bulk solution to membrane surface is generated by the rejected material accumulated on the membrane, the formation of a viscous and gelatinous-type layer is responsible for an additional resistance to the permeate flux in addition to that of the membrane (Cassano *et al*., 2007). Basically, Cassano *et al*. (2007) reported that the (TMP$_{lim}$) values depends on physical properties of the suspension and feed flow rate, the cross flow velocity affects the shear stress at the membrane surface and, consequently, the rate of removal of deposited particles responsible of flux decreased.

3.2 *Batch concentration configuration*

Due to an increasing of temperature produces an increase in permeate fluxes, a temperature of 25°C was chosen to perform the experimental separation according to the batch concentration mode. Figure 2 shows the time course of the permeate flux and of the volume reduction factor (VRF) referred to the treatment of the Nejayote according to the batch concentration mode in optimal operating conditions (TMP: 1.3 bar, Qf: 58 L h^{-1}, T: 25 ±1 °C). Results showed that permeate flux decreased gradually with the operating time by increasing the VRF due to concentration polarization phenomenon and gel formation. The initial permeate flux was about 22 kg m^{-2} h^{-1} decreased to about higher values of 10 kg m^{-2} h^{-1} when VRF reached 6. It means, only a 45 % reduction of the initial flux was obtained when the VRF reached the final value. Conidi *et al*. (2014) reported almost similar productivity in terms of initial

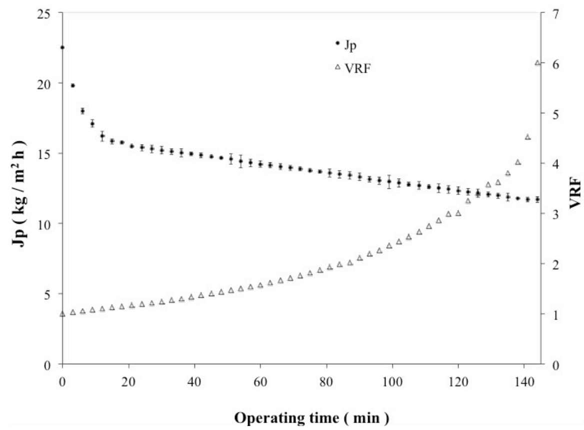


Fig. 2. Ultrafiltration (100;kDa) of Nejayote. Time course of permeate flux and VRF (Operating conditions: TMP: 1.3 bar, Q_f: 58 L h^{-1}, T: 25 ±1 °C).

permeate flux (19 kg m^{-2} h^{-1}) using UF membrane (50 kDa) in the valorization of artichoke wastewaters by integrated membrane process, the initial permeate flux decreased up to 10 kg m^{-2} h^{-1}; it means, a reduction around 47 % of the initial permeate flux.

3.3 *Membrane parameters : Fouling index and cleaning efficiency*

Before of the treatment of Nejayote, the UF membrane presented a water permeability of 65.904 L m^{-2} h^{-1} bar^{-1}. After the separation of the Nejayote, the water permeability decreased up to 8.19 L m^{-2} h^{-1} bar^{-1} (see Figure 3), which represented a fouling index of 87.57 %. The water permeability of the membrane was recovered a 25.87 % by cleaning with water (Table 2).

However, a complete recovery (100 %) of the initial water permeability (65.904 L m^{-2} h^{-1} bar^{-1}) was obtained after a cleaning procedure with enzymatic detergent.

Table 2. Water permeability, fouling index and cleaning efficiencies of UF membrane.

Parameters	100 kDa UF membrane
Lp_0 (L m^{-2} h^{-1} bar^{-1})	65.9
Lp_1 (L m^{-2} h^{-1} bar^{-1})	8.19
Lp_2 (L m^{-2} h^{-1} bar^{-1})	17.05
Lp_3 (L m^{-2} h^{-1} bar^{-1})	65.9
I_f (%)	87.57
C_E after cleaning with water (%)	25.87
C_E after enzymatic cleaning (%)	100

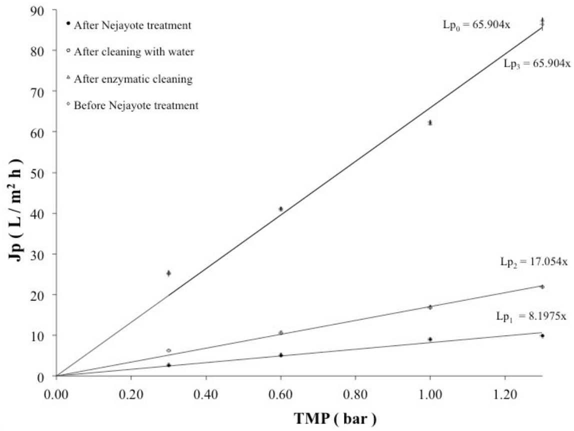


Fig. 3. Pure water permeabilities before (Lp_0) and after (Lp_1) treatment of Nejayote with UF membrane. After cleaning with water (Lp_2) and enzymatic cleaning (Lp_3) (Operating conditions: Q_f: 58 L h^{-1}, T: 25 ±1 °C).

It is important to note that a complete recovery of the initial permeability can be positive to the viability of the process because the membrane can be reused many times with this extract.

3.4 Physico-chemical characterization of Nejayote

Table 3 shows the physico-chemical composition of Nejayote that was treated by UF membrane, the extract presented TSS of 1.00 g 100 g^{-1} and TSC 1.02 g 100 g^{-1}. In addition the wastewater presented a pH values about 13.41, turbidity values about of 145 NTU, electrical conductivity of 1896 μS cm^{-1} and calcium content of 955.70 mg L^{-1}. Basically, The physico-chemical composition of Nejayote depends on several factors such as Lime quality, type of maize, grain quality, cooking time and other cooking parameters in the Nixtamalization process as were reported by Gutiérrez-Uribe *et al*. (2010) and Ruiz-Gutiérrez *et al*. (2010).

In terms of bioactive compounds, the Nejayote reported higher content compared to other types of wastewaters, the Nejayote presented high content on total polyphenols about 970 mg L^{-1}, high content compared to 516 mg L^{-1} and 211 mg L^{-1} for artichoke wastewaters (Conidi *et al*., 2014) and olive mill wastewaters (Garcia-Castello *et al*., 2010), respectively. Nejayote presented around 3.02 mg mL^{-1} on total carbohydrates in terms of glucose, higher content than reported Conidi *et al*. (2014) for artichoke wastewaters of 0.96 mg mL^{-1}. All of the above, the Nejayote can be considered as an important source for recovering high-added value components such as polyphenols and sugar components.

Finally, as well-known the Nejayote is a polluting wastewater which has an organic load in terms of TOC around 2784 mg L^{-1}, less content than other wastewater such as olive mill wastewaters of 13,436 mg L^{-1} (Cassano *et al*., 2013).

3.5 Effect on physico-chemical composition of Nejayote by ultrafiltration membrane

The extract was submitted to processing with UF (100 kDa) membrane and Table 4 shows the physico-chemical evolution in permeate samples during the treatment at each VRF values. Results show a continually decreasing on TSS content obtaining a final permeate with values about of 0.80 g 100 g^{-1} (representing a rejection by the membrane about 19.9 %, see Figure 4) while in final retentate presented 2.1 g 100 g^{-1} (Table 3). Same behavior was found on TSC values where a decreasing from 1.02 up to 0.80 g 100 g^{-1} was obtained in permeate and a final retentate of 2.09 g 100 g^{-1}, the rejected total solids was of 22.05 %. Statistical significant differences were determined on physicochemical properties of the extract by the UF process at each VRF.

On the other hand, Safavi and Nakayama (2000) demonstrated high electrical conductivity of the calcium hydroxide in aqueous solution and it is directly related to the concentration. The initial electrical conductivity was about 1896 μS cm^{-1} and the final permeate presented 1558 μS cm^{-1} (Table 4) where membrane process influenced in a decreasing of 17.82 %, on the contrary, a considerable increasing was determined in final retentate sample (3758 μS cm^{-1}, Table 3).

Table 3. Physico-chemical composition of Nejayote before and after treatment with UF (100 kDa) membrane.

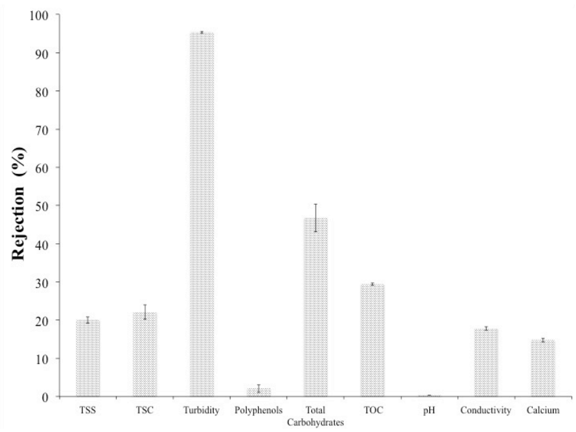
Sample	Mass amount (kg)	TSS (g 100g^{-1})	TSC (g 100g^{-1})	Turbidity (NTU)	pH	Conductivity (μS cm^{-1})	Total carbohydrates (mg mL^{-1})	Polyphenols (mg L^{-1})	TOC (mg L^{-1})	Calcium (mg L^{-1})
Feed	2.00	1.00±0.01^b	1.02±0.06^b	145.6±1.2^b	13.41±0.0^a	1896.6±0.5^b	3.02±0.05^b	970.3±16.0^a	2784.6±1.0^b	955.7±3.0^b
Permeate	1.66	0.8±0.09^c	0.80±0.02^c	6.7±0.3^c	13.37±0.0^a	1558.6±1.1^c	1.61±0.08^c	950.0±14.4^c	1966.4±0.2^c	814.8±5.2^c
Retentate	0.34	2.1±0.05^a	2.09±0.00^a	1379.0±24.2^a	13.44±0.0^a	3758.3±2.0^a	7.72±0.03^a	958.3±12.1^b	6172.0±2.3^a	1490.1±1.3^a

Data represents the means ± standard deviation with triplicate for each test. Different superscript letters in the column indicate statistical significance (p <0.05) according to the Tukey least significant different test.

Table 4. Behavior of physico-chemical composition on permeate samples from Nejayote treated by UF membrane.

VRF (Samples)	TSS (g $100g^{-1}$)	TSC (g $100g^{-1}$)	Turbidity (NTU)	pH	Conductivity (μS cm^{-1})	Total carbohydrates (mg mL^{-1})	Polyphenols (mg gallic acid L^{-1})	TOC (mg L^{-1})
1	1.00±0.01^a	1.02±0.06 ^{a}	145.6±1.2^a	13.41±0.0^a	1896.6±0.5^a	3.02±0.05^a	970.3±16.0^a	2784.6±1.0^a
2	0.9±0.00 ^{b}	0.92±0.00^b	20.5±0.4^b	13.39±0.0^b	1580.3±2.0^b	2.85±0.06^b	962.9±19.5^b	2044.7±0.2^b
3	0.85±0.05^c	0.91±0.05^c	18.9±0.4^c	13.39±0.0^b	1576.0±1.7^c	2.59±0.04^c	957.4±13.7^c	2039.1±0.6^c
4	0.83±0.00^d	0.90±0.00^d	13.6±0.4^d	13.39±0.0^b	1561.0±3.2^d	2.18±0.07^d	955.5±13.4^d	2037.2±0.4^d
5	0.80±0.05^e	0.84±0.08^e	9.7±0.7^e	13.38±0.0^c	1558.6±0.5^e	2.08±0.07^e	951.8±16.2 ^{e}	2025.6±0.4^e
6	0.80±0.09^e	0.80±0.02^f	6.7±0.3^f	13.37±0.0^d	1558.6±1.1^e	1.61±0.08^f	950.0±14.4^f	1966.4±0.2^f

Data represents the means ± standard deviation with triplicate for each test. Different superscript letters in the column indicate statistical significance (p <0.05) according to the Tukey least significant different test.



Fig, 4. Rejection of 100 kDa UF membrane towards each component at VRF 6.

Last results can be supported by a decreasing of 14.74 % on calcium content by the membrane, the permeate samples presented content about 814.80 mg L^{-1} (from feed content 955.70 mg L^{-1}) while retentate samples showed an increasing around 1490.10 mg L^{-1} (Table 3). However, there were no significant changes on pH values, the final permeate obtained 13.37 (rejection about 0.30 %) while retentate presented values about 13.44; Table 3, it can be attributed because 100 kDa membrane is no capable to retain hydroxyl ions in solution.

The main changes were found in the turbidity of the extract, the initial turbidity was decreased rapidly during the membrane process. The permeate samples start to present low turbidity values from VRF of 2, The obtained permeate resulted a clear fraction (see Figure 5) with turbidity values around 6.79 NTU and the final retentate presented a significant increasing (1379 NTU), the rejection of the membrane on turbidity was higher than 90 %. In addition, the turbidity rejected by the membrane can be related to the content of total carbohydrates in the extract, the rejection on carbohydrates of the membrane was about 46.68 %, it means, the final permeate presented content of 1.61 mg mL^{-1} (from 3.02 mg mL^{-1} in feed, Table 3) and it was determined a high concentration of carbohydrates in retentate, 7.72 mg mL^{-1} which represent a fraction rich in sugar compounds with high added value due to Ayala-Soto *et al*. (2014) determined that main sugars presented in Nejayote are arabinoxylans which are produced from the hydrolysis of the maize fiber in the nixtamalization process. Table 4 shows the evolution of the carbohydrates content in the permeate samples and a clear decreasing in these components was confirmed using a 100 kDa membrane.

Concerning to the total polyphenols content, the membrane did not present a significant rejection (2.07 %) of these components. A similar concentration was determined in the permeate and retentate samples (content about of 950 mg L^{-1}), however, it was amazing to conserve polyphenols in the permeate obtained because the final permeate just presented total polyphenols and 0.80g 100 g^{-1} of TSC related to soluble calcium as reported by Pflugfelder *et al*. (1988). Low rejection on polyphenols using UF membrane was reported by Conidi *et al*. (2014), rejection between 1.2- 8.6 % on polyphenols was determined in the treatment of artichoke wastewaters.

The initial TOC values in the feed were decreased from 2784.60 to 1966 mg L^{-1} in the permeate samples, Table 4 shows a continually decreasing was observed in permeate samples during the evolution of membrane process. The final rejection of the membrane was 29.38 %, it means, an increasing on organic load in retentate up to 6172 mg L^{-1} that could be associated to the total carbohydrates obtained in the concentrated fractions while the organic charge in the clear permeate can be associated to the total polyphenols content due to the soluble calcium is no considered as organic component. Cassano *et al*., (2013) demonstrated that UF technology can reject large quantities of TOC, from 33.7 to 72.1 % in the fractionation of olive mill wastewaters.

3.6 Mass balance of the UF process

Finally, the mass balance of the UF process for TSC, TSS, carbohydrates, TOC, Calcium and polyphenols is determined. This balance is referred to an UF run which starting from 2 kg of Nejayote, 1.66 kg of permeate and 0.340 kg of retentate were obtained (Table 3). It means, 83% of the initial aqueous phase (permeate) was recovered by the separation process and just in 17 % of the aqueous phase was concentrated the main compounds. The total rejection in terms of total mass for TSC, TSS and Calcium content were about 34.9 %, 33.6 % and 29.02 %, respectively. In case of total polyphenols, the UF process presented a total mass rejection about 18.5 %. For carbohydrates the higher rejection on these compounds was confirmed, the total mass rejection on carbohydrates was 55.6 %, it means, the major components present in the retentate are carbohydrates. Finally, the final mass rejection on TOC was about 41.3 % that supports the contribution for avoiding the environmental pollution by the effluent using the membrane process, at the same time, chemical compounds could be recovered.

Conclusions

The selection of the best TMP for UF treatment of Nejayote was performed on the basis of the experimental results. The separation of the extract was carried out up to VRF of 6 by batch concentration mode at TMP 1.3 bar. The physicochemical properties evaluated on Nejayote showed statistically different changes at each VRF during process evolution. The filtration of Nejayote by ultrafiltration permitted to separate the extract in two valuable fractions. First, carbohydrates from the wastewater were recovered in a concentrated retentate. On the other hand, a clear permeate was obtained with high content in polyphenols which can be extracted with other membrane techniques. After treatment of Nejayote, the UF membrane presented high fouling index but the initial water permeability was recovered by enzymatic procedures.

Finally, the treatment of Nejayote by membrane technologies show strong evidence for recovering bioactive compounds from this stream, resulting a real via to reduce the biochemical oxygen demand that contribute to avoid the water and environmental pollution.

Acknowledgements

The authors acknowledge CONACyT (Grant 439602/267705) and IPN (SIP 20150178) for financial support. To ITM-CNR, Italy and Dr. Alfredo Cassano, for the research stay in their laboratories.

Nomenclature

VRF	volume reduction factor
TMP_{lim}	transmembrane pressure limiting, bar
TMP	transmembrane pressure, bar
UF	ultrafiltration
Lp	water permeability, L m^{-2} h^{-1} bar^{-1}
Jv	water flux, L m^{-2} h^{-1}
If	fouling index, %
Lp_0	water permeability before treatment of Nejayote, L m^{-2} h^{-1} bar^{-1}
Lp_1	water permeability after treatment of Nejayote, L m^{-2} h^{-1} bar^{-1}
Lp_2	water permeability after cleaning with water, L m^{-2} h^{-1} bar^{-1}
Lp_3	water permeability after enzymatic cleaning, L m^{-2} h^{-1} bar^{-1}
C_E	cleaning efficiency; %
TSS	total soluble solids, g 100 g^{-1}
TOC	total organic carbon, mg L^{-1}
TSC	total solids content, g 100 g^{-1}
Q_f	feed flow rate, L h^{-1}
F_R	flux recovery, %
R_i	rejection towards specific compound (i)
Cp_i	concentration of compound (i) in permeate sample
Cf_i	concentration of compound (i) in feed sample

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