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Research Paper

Quality of Kiwifruit Juice Clarified by Modified Poly(Ether Ether Ketone) Hollow Fiber Membranes

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Keywords

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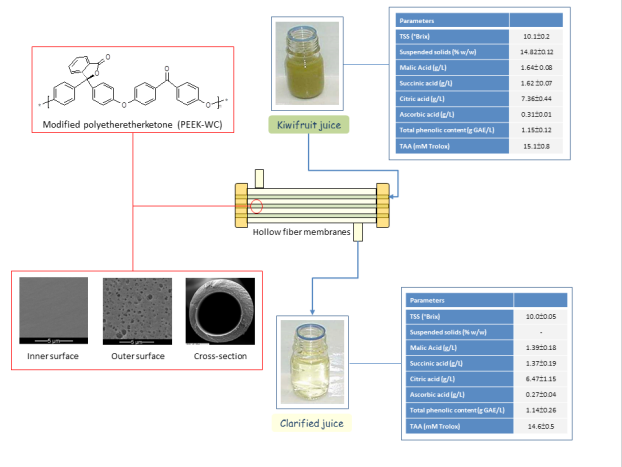
Highlights

- Modifed poly(ether ether ketone) membranes were prepared through the phase inversion process.
- Hollow fiber membranes were used to clarify depectinized kiwifruit juice.
- Suspended solids were totally removed producing a clear juice.
- Antioxidant compounds were recovered in the permeate stream.
- Chemical cleaning restored the original water permeability of hollow fiber membranes.

Graphical abstract



Abstract

Poly(ether ether ketone) with cardo group-based (PEEK-WC) membranes, in hollow fiber (HF) configuration, were prepared via the dry-wet spinning technique through the phase inversion process and used to clarify kiwifruit juice. The depectinised juice was processed according to a batch concentration configuration in selected operating conditions (transmembrane pressure, 1.6 bar; feed flowrate 70 L/h; temperature, 25±2 °C) up to a volume reduction factor (VRF) of 1.8. The quality of clarified juice was analysed in terms of total antioxidant activity (TAA), content of ascorbic, malic, succinic and citric acid, total polyphenols, suspended solids and total soluble solids (TSS). The prepared membranes allowed to remove suspended solids producing a clear juice with a content of organic acids, vitamin C and polyphenols comparable to that of the fresh juice. Accordingly, the TAA of the fresh juice was well preserved in the clarified juice.

1. Introduction

Kiwifruits contain high levels of biologically active compounds, including ascorbic acid, phenolics, anthocyanins, chlorophylls, carotenoids, tannins, flavanols and flavonoids [1]. In particular, they contain more ascorbic acid than the average amounts found in other fruits such as grapefruit, oranges, strawberries and lemons and, ten times as much as that found in apples and peaches [2]. Antioxidant properties of kiwifruit are strongly affected by the presence of bioactive compounds. Indeed, both total polyphenols and vitamin C are major contributors to the total antioxidant

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capacity in Actinidia fruit [3-5].

A series of epidemiologic studies demonstrated that kiwifruit can provide several specific benefits for maintaining health and well-being. For example, kiwi gold fruits extracts showed selective cytotoxic activity against human oral tumor cell lines and anti-HIV activity, radical generation and O_2^- scavenging activity [6]. *In vitro*, kiwifruit juice was shown to suppress the DNA damaging action of H_2O_2 even when it is diluted 10,000 times [7, 8]. In addition, consumption of kiwifruit may be beneficial in cardiovascular disease by reducing platelet aggregation and lowering blood triglycerides levels [9]. Kiwifruit polyphenols are also potentially able to give antioxidant support in diabetes and pre-diabetes [10]. On the basis of these characteristics kiwifruit offers benefits for specific health conditions and, consequently, it has a great potential for industrial exploitation [11].

The main goal of the kiwifruit processing is to obtain safe and stable products able to retain as much as possible the peculiarity of fresh fruit, as well as green colour, aroma, nutritional value and structural characteristics.

Clarification of fruit juices is needed in order to remove haze forming substances, including suspended materials, cell debrides and high molecular weight proteins which are potential source of microbial growth [12]. Conventional methods of producing clarified juice involve many steps, such as enzymatic treatment (depectinization), centrifugation, use of fining agents (gelatin, silica sol, bentonite), filtration with diatomaceous earth and sterilization for removal of microorganisms [13, 14]. These processes are inherently slow and time consuming. Additionally, the use of fining agents is characterized by different drawbacks such as the risks of dust inhalation with consequent health problems due to handling and disposal, environmental problems and significant costs.

Membrane-based processes, such as microfiltration (MF) and ultrafiltration (UF), represent a valid alternative to the use of traditional fining agents and filter aids [15]. MF and UF membranes retain large species such as microorganisms, lipids, proteins and colloids, while small solutes such as vitamins, salts and sugars flow together with water. Advantages over conventional fruit juice processing are in terms of increased juice yield; possibility of operating in a single step reducing working times; possibility of avoiding the use of gelatines, adsorbents and other filtration aids; reduction in enzyme utilisation; easy cleaning and maintenance of the equipment; reduction of waste products; elimination of needs for pasteurisation. In addition, the low temperatures used during the process preserve the fruit juice freshness, aroma and nutritional value [16, 17].

MF and UF processes can be used to separate juices into a fibrous concentrated pulp and a clarified fraction free of spoilage microorganisms. Then, the clarified fraction can undergo non-thermal membrane concentration, such as membrane or osmotic distillation, and eventually whole juice reconstitution by combination with pasteurised pulp in order to obtain a product with improved sensorial properties.

Polysulfone (PS), polyethersulfone (PES), polyacrylonitrile (PAN) and polyvinylidenefluoride (PVDF) are common polymers used to prepare MF and UF membranes. The hydrophobic nature of these polymers leads to severe membrane fouling during juice processing caused by proteins, pectins and high molecular weight solutes [18]. Therefore, the use of hydrophilic polymers or methodologies to prepare membranes with antifouling properties (i.e. blending with hydrophilic polymers, like, cellulose acetate, introduction of additives to enhance the hydrophilicity, such as polyethylene glycol) is a topic of active investigation in the field of juice clarification [19].

Poly(ether ether ketone) (PEEK) is a new generation of polymers with high thermal and mechanical stabilities, both of which are the properties required for the polymeric membranes in practical applications, including UF and pervaporation processes [20].

PEEK is intrinsically hydrophobic, contact angle of parent PEEK is 88° [21].

Poly(oxa-*p*-phenylene-3,3-phtalido-*p*-phenylene-oxa-*p*-phenilene-oxy-phenylene) is a new kind of poly (ether ether ketone), named PEEK-WC, obtained by polycondensation reaction between 4,4-dichlorobenzophenone and phenolphthalein (see Figure 1) [22, 23]. The introduction of the sterically cumbersome cardo-group in the molecular chain makes it amorphous and soluble in a large variety of solvents, both polar and non-polar allowing the preparation of membranes with different techniques. In addition, the character of this polymer is strongly influenced, resulting more hydrophilic than the parent PEEK, as witnessed by the low value of the contact angle.

In previous works the clarification of kiwifruit juice has been studied by using tubular PVDF membranes [24] and hollow fiber (HF) PEEK-WC membranes [25]. These studies were mainly addressed to the evaluation of the effect of operating and fluid-dynamic conditions (such as transmembrane pressure, feed flowrate, temperature and suspended solids concentration) on the permeate flux, in order to identify process conditions able to produce acceptable fluxes. In both studies the decline of permeate flux was analyzed according to the resistance-in-series model [26, 27].

In this study, however, PEEK-WC HF membranes were used to clarify kiwifruit juice after a preliminary depectinization step. A special attention was paid at evaluating the potential of the prepared membranes in the recovery of bioactive compounds characterising the functional and health-benefit properties of kiwifruit juice. At this purpose, permeate and retentate streams were characterized regarding total antioxidant activity (TAA), total polyphenols, Vitamin C and organic acids content, as well as suspended solids and total soluble solids. An analysis of membrane fouling and cleaning efficiency was also performed through the evaluation of the hydraulic permeability of the membrane measured before and after the treatment with juice and cleaning procedures.

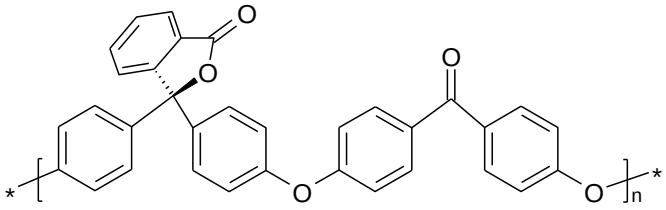

Fig. 1. Chemical structure of modified polyetheretherketone (PEEK-WC) [22].

2. Experimental

2.1. Preparation of fresh kiwifruit juice

Hayward kiwifruits, of Chilean origin, were purchased from the local open market (Cosenza, Italy). Unpeeled fruits were manually washed in water and cut in pieces. The kiwifruit pieces were milled using a multiple shaker-liquidizer (Aristarco s.r.l., Treviso, Italy) in order to facilitate and accelerate the action of pectolytic enzymes added later. After pulping, sodium sulphite (Sigma-Aldrich, Milan, Italy) was added (2-3 g kg^{-1} of pulp) in order to inhibit the enzyme polyphenol oxidase that determines a browning of the pulp. A pectinase from *Aspergillus aculeatus* (Pectinex Ultra SP-L, Novo Nordisk A/S, Novo Allè, Bagsuaerd, Denmark) (10 g kg^{-1} of pulp) was also added, as reported in the previous work [24], in order to hydrolyse both high and low esterified pectins and, partially, cellulose, hemicellulose, starch and proteins. This can decrease the viscosity to a greater extent. This also enables a faster and more extensive maceration of the fruit, thereby liberating juice and releasing flavour components and subsequently pigmentation [28]. The puree was incubated for 4 hours at room temperature (~25 °C) and then filtered with a Nylon cloth. This method gave an average juice yield of 75-80% (w/w). The juice was stored at –17 °C and defrosted to room temperature before use.

2.2. Membrane preparation

Modified PEEK-WC HF membranes were prepared according to the dry-wet spinning method [29]. In order to prepare highly porous membranes, poly(vinylpyrrolidone) (PVP K17 by BASF) was used as a pore forming additive. Membranes were prepared from solutions of PEEK-WC and PVP both at 15 wt.% in dimetylformamide (DMF) under continuous mechanical stirring at room temperature, as reported in previous works [23, 30].

The polymer solution (dope) prepared as described above, was stored in a vessel at controlled temperature, degassed and then kept under a nitrogen blanket. Afterward, it was fed to the spinneret by means of a gear pump; contemporary, also the bore fluid was fed to the spinneret following a separate path. The dope and the bore fluid flow rate were 12 g/min and 15 g/min, respectively. The spinneret was positioned over the coagulation bath at a distance of 30 cm (air gap). After the extrusion through the spinneret, the jet entered into the coagulation bath where the phase separation and the hollow fiber formation occurred. The fiber was continuously extracted by means of a couple of take-up rolls and finally collected on a rotating wheel. A schematic drawing of the spinning setup is reported in Figure 2.

Inner and outer diameter of HF membranes were 1.19 mm and 1.62 mm, respectively (membrane thickness 0.215 mm). Membrane modules were prepared by embedding four HF membranes inside a 20 cm long glass tube (effective membrane length 18 cm) with epoxy resin (Stycast, Emerson and Cuming, Belgium). The total surface membrane area of each module was 26.9 cm^2.

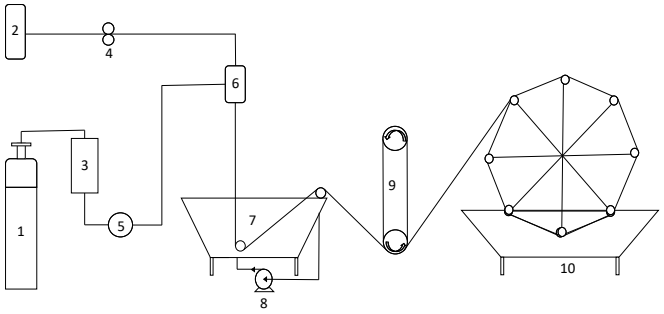

Fig. 2. Schematic drawing of the spinning setup. 1: N_2 gas cylinder, 2: bore fluid tank, 3: dope tank, 4: bore fluid pump, 5: dope pump, 6: spinneret, 7: coagulation bath, 8: circulation pump, 9: take-up rollers, 10: collection unit.

2.3. UF laboratory plant

Experiments were performed by using a laboratory bench plant (DSS LabUnit M10) supplied by Danish Separation System AS, Nakskov, Denmark.

The equipment consisted of a 5 L feed tank, a cross-flow pump (ECO type GA4-KDT-TTU), two pressure gauges (0–2.5 bar) located at the inlet (P_{in}) and outlet (P_{out}) of the membrane module, a pressure control valve, and a multitube heat exchanger fed with tap water. The temperature (T) of the feed was controlled by circulating cooling water through the heat exchanger; the axial feed flow-rate (Q_f) and the transmembrane pressure (TMP) were controlled by using a needle concentrate valve and by setting the speed of the pump.

A schematic diagram of the experimental set-up is illustrated in Figure 3.

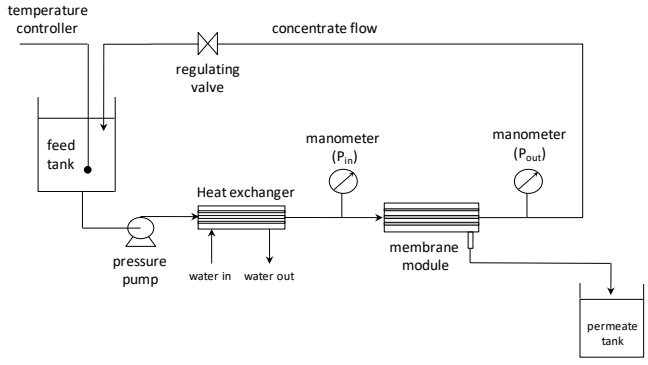

Fig. 3. Schematic diagram of the experimental set-up.

2.4. Membrane characterization

The prepared membranes were characterized by scanning electron microscopy (SEM) analysis, dextran rejection, hydrophobicity/hydrophilicity and hydraulic permeability determination based on pure water permeation through the membranes.

The membrane morphology was studied by scanning electron microscopy (SEM) observations of the cross section and of the inner and outer surfaces (Cambridge Stereoscan 360). HF samples were freeze fractured in liquid N_2 to produce a clean brittle fracture and were subsequently sputter coated with gold before SEM observation.

The dextran rejection was determined by feeding a 0.2 g/L aqueous dextran (average MW 68,800) solution (at 0.5 bar and Q_f = 40 l/h) and measuring the dextrane concentration in the permeate and feed streams after 60 min, respectively. The dextran concentration was determined by a colorimetric method, according to the procedure of Dubois et al. [31].

The hydrophobic/hydrophilic character of the investigated membranes was estimated by contact angle technique. Water contact angles were measured using the sessile drop method at ambient temperature by CAM 200 contact angle meter (KSV Instruments LTD, Helsinki, Finland), depositing the liquid on the membrane surface using an automatic microsyringe.

Water permeability of HF membranes was determined by measuring deionized water permeate flowrate for different pressures at 25 °C. TMP was adjusted by a circulating valve and corresponded to the average of measured inlet and outlet relative pressures. The permeate flux (L/m^{2}h) for each TMP was calculated as follows:

$$J_p = \frac{Q_p}{A_m} \quad (1)$$

where Q_p (L/h) is the permeate flowrate measured for a certain TMP and A_m (m^2) the membrane surface area.

The hydraulic permeability was determined by the slope of the straight line obtained plotting the water flux values at 25 °C versus the applied TMP (0-1 bar). The value obtained for a new clean membrane was indicated as L_{p0}.

2.5. Clarification of kiwifruit juice

UF experiments were performed by using the prepared membranes according to the batch concentration configuration (permeate is collected separately and retentate is recycled to the feed tank). The UF system was operated at a TMP of 1.6 bar, a feed flowrate (Q_f) of 70 L/h and a temperature (T) of 25 °C up to a volume reduction factor (VRF) of 1.8.

VRF is defined as the ratio between the initial feed volume and the volume of the resulting retentate given by:

$$VRF = \frac{V_f}{V_r} = 1 + \frac{V_p}{V_r} \quad (2)$$

where V_f , V_p and V_r are the volume of feed, permeate and retentate, respectively.

2.6. Cleaning procedures and fouling index

The hydraulic permeability of membranes was measured after the treatment with kiwifruit juice and indicated as L_{p1}. A first cleaning step was performed recirculating distilled water for 30 min through the membrane module at a TMP of 0.2 bar in order to remove the reversible polarized layer. The hydraulic permeability measured after this step was indicated as L_{p2}. In the second step the membrane module was cleaned with a NaClO solution (4000 ppm) at a temperature of 40 °C for 60 min and then rinsed with distilled water for 30 min. The hydraulic permeability measured afterwards was L_{p3}.

The fouling index of HF membranes was calculated by comparing the hydraulic permeability before and after operating using the juice, according as follow:

$$IF = \left(1 - \frac{Lp1}{Lp0} * 100\right) \quad (3)$$

where L_{p0} and L_{p1} are the hydraulic permeability before and after juice clarification.

Cleaning efficiency (CE) was evaluated by using the flux recovery method [32] according to the following equation:

$$CE = \left(\frac{L_{p3}}{L_{p0}}\right) * 100 \quad (4)$$

where L_{p3} is the water permeability measured after the chemical cleaning.

2.7. Juice analyses

Samples of fresh, clarified (collected from the permeate stream) and concentrated (retentate stream) juice coming from the UF experiments were collected and stored at -20 °C for further analyses.

TAA was determined by an improved version of the 2,2'-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) (ABTS) free radical decolourisation assay [33] in which the ABTS radical cation is generated by reaction with potassium persulphate before the addition of the antioxidant [34]. The decolourisation of the ABTS is measured as the percentage inhibition of absorbance at 734 nm. The concentration of antioxidant giving the same percentage inhibition of absorbance of the radical cation at 734 nm as 1 mM 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox) was calculated in terms of Trolox Equivalent Antioxidant Capacity (TEAC) at 5 min contact. ABTS, potassium persulphate and Trolox were obtained from Sigma-Aldrich (Milan, Italy).

Total phenol content (TPC) was determined colorimetrically by using the Folin-Ciocalteau [35]. The method is based on the reduction of tungstate and/or molybdate in the Folin-Ciocalteu reagent by phenols in alkaline medium resulting in a blue colored product (max 756 nm). Results were

expressed as g/L gallic acid equivalents (GAE).

Spectrophotometric measurements were performed by a UV-160A UV-Visible Recording spectrophotometer (Shimadzu Scientific Instruments, Inc., Japan) at 30 °C.

The quantitative determination of ascorbic, malic, citric and succinic acids was determined by high-performance liquid chromatography (HPLC) using a HPLC D-7000 System Manager (Merck Hitachi, Darmstadt, Germany) equipped with an UV detector. The following conditions were used: an Alltima C18 HP5U column, 5 m, 250x4.6 mm (Alltech Associates, Inc., Deerfield, IL) with a mobile phase of H_3PO_4 0.05 M, flux = 0.7 ml/min, T = 25°C, pressure = 85 bar, λ= 205 nm. The external standard method was applied. A calibration curve with five standard concentrations was constructed and each standard was injected three times. The samples to be detected were also injected three times.

Total soluble solids (TSS) measurements were carried out by using a hand refractometers (Atago Co., Ltd., Tokyo, Japan) with a scale range of 0-32 °Brix.

The suspended solid content (SS) was determined in relation to total juice (w/w%) by centrifuging, at 2000 rpm (number of g = 670.72) for 20 min, 45 mL of a pre-weighted sample; the weight of settled solids was determined after removing the supernatant.

The rejection (*R*, %) of the UF membrane towards specific compounds was determined as:

$$R = \left(1 - \frac{C_p}{C_f}\right) \cdot 100 \quad (5)$$

where C_p and C_f are the concentration of a specific component in the permeate and feed, respectively.

3. Results and discussion

3.1. Membrane characterization

Figure 4 shows SEM images of the prepared hollow fiber membranes. These membranes are characterized by a sponge-like structure due to the addition of polyvinylpyrrolidone (PVP) to the polymer solution which leads to the suppression of macrovoids. Large pores on the outer surface (see Figure 4-b) were obtained in conditions of water vapour supersaturated atmosphere.

The rejection of prepared membranes towards 68,000 MW dextran was of 2%, while the water permeability measured at 25 °C was of 332 L/m^{2}hbar. The contact angle was measured at 69.7±2.7° indicating a good wettability.

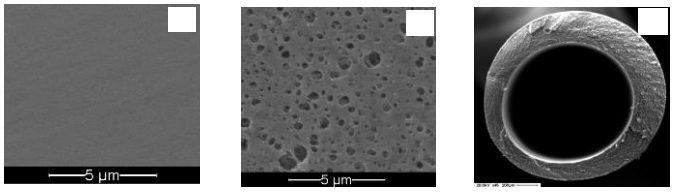

Figure 4. SEM images of (a) inner surface (b) outer surface and (c) cross-section of HF membranes.

3.2. Clarification of kiwifruit juice

Kiwifruit juice was clarified according to a batch concentration configuration under selected operating conditions (TMP = 1.6 bar, *T* = 25±2 °C, Q_f = 70 L/h).

The juice was processed at 25 °C in order to minimize potential heat-induced flavour changes. In addition, proteins are stable when the juice is held at temperatures lower than 30 °C. At higher values a haze formation is observed in few minutes [36].

The time course of permeate flux and VRF are illustrated in Figure 5. The initial permeate flux of 45 L/m^{2}h sharply decreased during the first 20 minutes of the process, followed by a gradual and continuous decrease, resulting in a final permeate flux reduction of approximately 44% compared with the initial value. The permeate flux decline during the process can be attributed to several phenomena including the decrease in the driving force due to osmotic pressure increase, resistance of the concentration polarization (boundary) layer, the formation of a gel layer and membrane fouling caused by pore clogging and adsorption [37-39]. In particular, permeate flux did not change significantly after 190 min processing indicating the formation of a gel layer where the solute concentration reaches its maximum value. At this point, the convective transport through the membrane is counterbalanced with back diffusion of solute into the bulk solution and a steady-state value of about 26 L/m^{2}h is established. This value is higher than that obtained in the clarification of depectinized kiwifruit juice with 15 kDa PVDF membranes in tubular configuration [24, 40].

Recently, ceramic MF membranes prepared from fly-ash precursor have been used for the clarification of centrifuged kiwifruit juice [41]. The prepared membranes showed sharp flux declines within the initial 10-15 min, up to reach final values between 2.81 and 20 L/m^{2}h after 60 min. Flux declines were of the order of 72-94% in relation to the initial permeate flux value. Results revealed that fouling models, including intermediate pore blocking and cake filtration, were mainly involved in flux decline mechanisms.

The permeate flux-time behaviour was in agreement with results obtained by Maktoufa et al. [42] in the treatment of depectinized lemon juice with a UF ceramic membrane having a MWCO of 15 kDa. Similar results were reported by Echavarría et al. [17] during the clarification of peach, pear, apple and mandarin juices through tubular polysulphone membranes of 8 kDa.

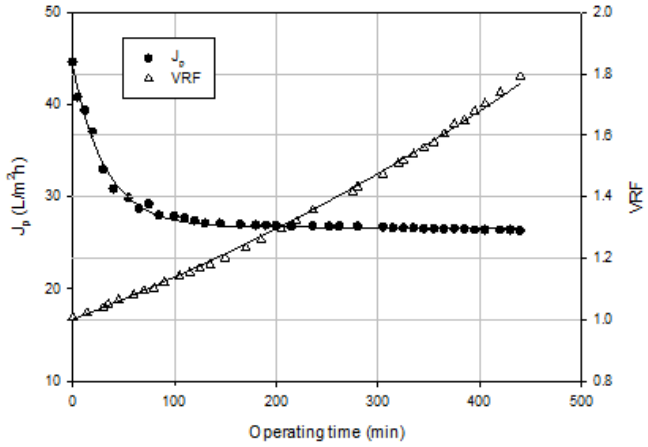

Fig. 5. Clarification of kiwifruit juice by PEEK-WC HF membranes. Time course of permeate fluxes and VRF (operating conditions: TMP, 1.6 bar; Q_b, 70 L/h; T, 25±2 °C).

In Figure 6, the hydraulic membrane permeability after each cleaning cycle is reported. The initial hydraulic permeability (L_{p0}) of about 332 L/m^{2}hbar was reduced to 71.37 L/m^{2}hbar after the treatment with kiwifruit juice. The fouling index was of ~78%. A first cleaning with distilled water allowed to recover only 26% of the initial hydraulic permeability (85 L/m^{2}hbar); a complete restore of the initial hydraulic permeability was then reached through a chemical cleaning with NaClO.

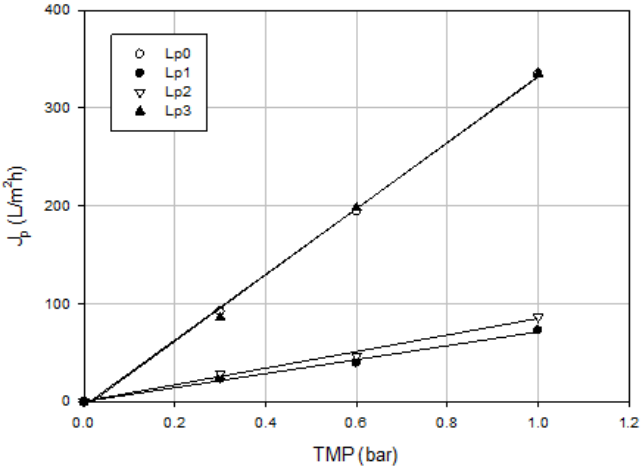

Fig. 6. Hydraulic permeability of PEEK-WC HF membranes before and after washing cycles (L_{p0}, initial hydraulic permeability, L_{p1} hydraulic permeability after kiwifruit juice treatment, L_{p2} hydraulic permeability after cleaning with water; L_{p3} hydraulic permeability after chemical cleaning).

A poor recovery of the hydraulic permeability after cleaning with water was also observed in the clarification of kiwifruit juice with tubular PVDF membranes [24]. In this case, membrane water permeability dropped by 32% after juice ultrafiltration. A good restore of the hydraulic permeability of the membrane (about 96% of the initial one) was observed after a cleaning treatment performed by using alkaline and acid detergents. The flux decline during ultrafiltration experiment was ascribed to fouling layers formed by a combination of suspended particles and adsorbed macromolecular impurities.

Similarly to previous studies [25], the obtained results confirm a greater contribution of the irreversible fouling to the total resistance in comparison to the reversible one. Assuming that the total resistance of the membrane is constant during processing, the other resistances are time-dependent functions affecting the permeate flux change over time. Irreversible fouling phenomena generally occur at the beginning of the process leading to a steady-state permeate flux after a certain time [43].

3.3. Physicochemical properties of fresh kiwifruit juice and clarified juice

It is well known that kiwifruit possess antioxidant properties, which are influenced by their biologically active substances. A high correlation between the content of total polyphenols and vitamin C on the one hand and antioxidant activity on the other was found [3]. The health-promoting properties of different varieties of hardy kiwi (*Actinidia (A.) arguta*, *Actinidia deliciosa* and *Actinidia eriantha*) have been recently assessed by Leontowicz et al. [44]. At this purpose, the preservation of the antioxidant status of processed kiwifruit products is a topic of great interest for marketing and consumption.

The physicochemical composition of depectinized kiwifruit juice before the UF treatment is reported in Table 1. Results related to the TSS (total soluble solids) content and total polyphenols are in agreement with data reported by Dawes and Keene [45]. The content of ascorbic acid (0.34 g/L) and TAA (15.3 mM Trolox) were higher than the amount determined in kiwifruit smoothie-type beverages [46].

Among the investigated organic acids the most represented is citric acid (7.5 g/L) followed by succinic acid (1.8 g/L) and malic acid (1.68 g/L). Similar results were reported by Chou et al. [47] in the characterization of Taiwanese kiwifruit (*Actinidia setosa*) aqueous extracts.

The influence of the clarification treatment with the PEEK-WC HF membranes on kiwifruit juice composition can be also evaluated from data reported in Table 1. HF membranes were able to retain suspended solids ensuring a very clear solution, which is desirable since suspended colloids can cause technological problems (precipitation) in the beverage industry, while the TSS content remained unchanged due to their permeation through the membrane.

Table 1
Physicochemical properties of kiwifruit juice treated by PEEK-WC HF membranes.

Parameters	Feed	Permeate	Retentate
TSS (°Brix)	10.1±0.2	10.0±0.05	10.8±0.6
Suspended solids (% w/w)	14.82±0.12	-	16.81±0.25
Malic Acid (g/L)	1.64± 0.08	1.39±0.18	1.82±0.23
Succinic acid (g/L)	1.62 ±0.07	1.37±0.19	1.60±0.14
Citric acid (g/L)	7.36±0.44	6.47±1.15	7.1±0.46
Ascorbic acid (g/L)	0.31±0.01	0.27±0.04	0.32±0.03
Total phenolic content (g GAE/L)	1.15±0.12	1.14±0.26	1.14±0.33
TAA (mM Trolox)	15.1±0.8	14.6±0.5	14.1±0.1

The content of vitamin C was not particularly affected by the UF process: the rejection of HF membranes towards this component was of 13%. The clarified fraction was also enriched in organic acids (succinic, malic and citric) due to the low rejection measured (in the range 12-15%). The content of organic acids was also well preserved in the pomegranate juice clarified with UF membranes [48].

Phenolic compounds were also well preserved in the permeate fraction due to the low rejection of the HF membranes towards these components (0.4%). A similar trend was also observed for the antioxidant activity according to the ABTS test: HF membranes showed a low rejection towards TAA (of about 3.8%) and consequently a permeate fraction with a radical scavenging activity comparable with that of the fresh juice, was obtained. The rejection values of HF membranes towards polyphenols and TAA decreased by increasing the operating time in the range 5.6-2% and 1.6-0.5%, respectively (see Figure 7). These rejection values were lower than those reported for the clarification of fruit juices with membranes having similar characteristics. Indeed, PEEK-WC HF membranes used in the clarification of pomegranate juice before a concentration step by osmotic distillation, showed a rejection towards TAA and polyphenols of 17.8% and 16.5%, respectively [49]. A rejection of 20% towards polyphenols was measured by Qin et al. [41] in kiwifruit juice treated with inorganic membranes having hydraulic permeabilities in the range 458-6136 L/m^{2}hbar.

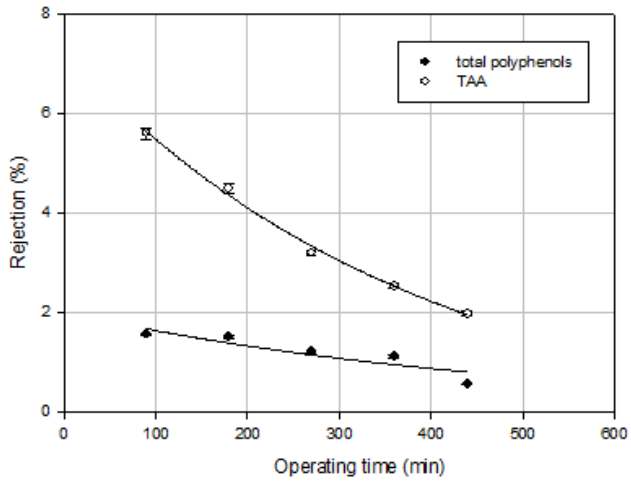

Fig. 7. Rejection of total polyphenols and TAA as a function of the operating time during the treatment of kiwifruit juice with HF membranes.

Figure 8 shows the effect of VRF on the recovery of malic, ascorbic and succinic acid in the UF permeate. The recovery of citric acid as a function of VRF is also illustrated in Figure 9.

The recovery of bioactive compounds in the clarified juice, with respect to the initial feed, is clearly affected by the VRF of the process: an increase of the collected permeate determines an increase of these compounds in the clarified juice. The lower recovery of ascorbic acid in the permeate stream could be attributed to an oxidation of this compound caused by continual recycling of the juice around the UF plant.

In Table 2 the mass balance of the UF process for the different bioactive compounds, is reported. This balance is referred to an experimental run in which, starting from 1.2 L of depectinized kiwifruit juice, 0.5 L of permeate and 0.7 L of retentate, were obtained.

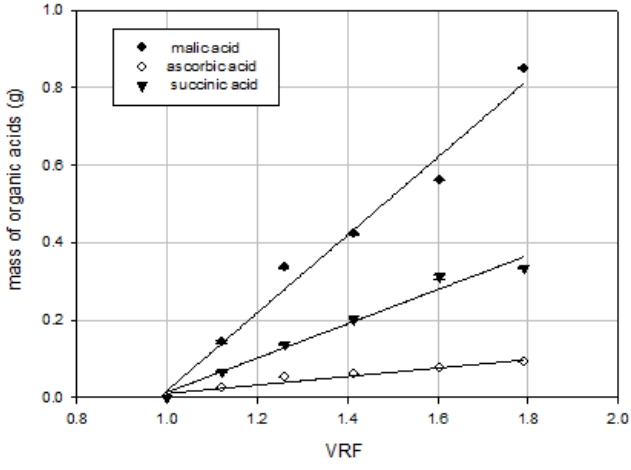

Fig. 8. Effect of VRF on the recovery of malic, ascorbic and succinic acids in the clarified juice.

Total polyphenols, ascorbic and malic acid were completely recovered in the permeate stream in agreement with the recovery factor of the process. A loss of about 7% was observed for succinic and citric acids that was probably due to an interaction with the membrane and consequent adsorption of solute on the membrane surface or inside the pore.

4. Conclusions

Depectinized kiwifruit juice was clarified by PEEK-WC membranes in hollow fiber configuration in selected operating conditions. The prepared membranes exhibited a steady-state permeate flux of about 26 L/m^{2}h and a good restore of the initial hydraulic permeability after chemical cleaning.

The UF treatment allowed to remove totally the suspended solids of the fresh juice. On the other hand, bioactive compounds, including ascorbic, succinic, malic and citric acids as well as polyphenols were well preserved in the clarified juice. Accordingly, the total antioxidant activity of the ultrafiltered juice (14.6 mM Trolox) was comparable to that of the fresh depectinised juice (15.1 mM Trolox). The recovery of organic acids in the clarified juice increased linearly with the volume reduction factor as expected on the basis of the low retention of HF membranes towards these compounds.

Based on the obtained results, the current study confirms the good potential applicability of PEEK-WC HF membranes for the production of a clear kiwifruit juice with improved organoleptic and nutritional quality in comparison with conventional clarification procedures.

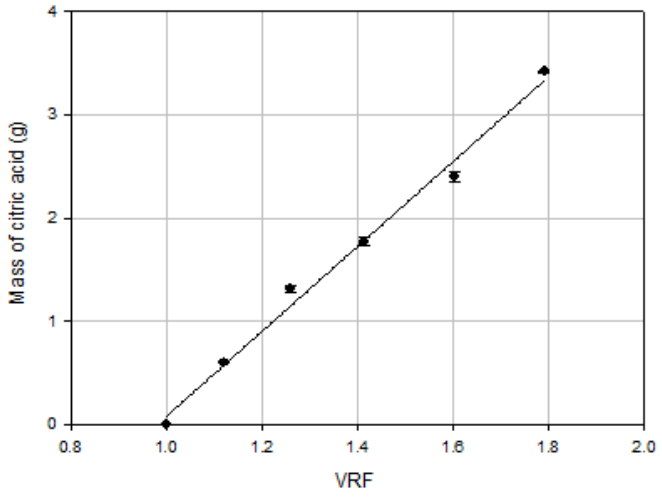

Fig. 9. Effect of VRF on the recovery of citric acid in the clarified juice.

Table 2
Mass balance of the UF process.

	Feed	Permeate		Retentate		Balance
Volume	1.200 L	0.5 L	41.67%	0.7 L	58.33%	100.0%
Malic acid	1.97 g	0.695 g	35.27%	1.274 g	65.98 %	99.9%
Ascorbic acid	0.372 g	0.135 g	36.29%	0.224 g	60.21%	99.5%
Citric Acid	8.83 g	3.23 g	36.63%	4.97 g	56.28%	92.9%
Succinic acid	1.94 g	0.685 g	35.30%	1.12 g	57.73%	93.0%
Total polyphenols	1.38 g	0.57 g	41.18%	0.8 g	58.23%	99.4%

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