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Rationalisation of productive cycles in the agro-food industries by innovative processes

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Fruit and vegetable juices are beverages of high nutritional value since they are enriched with minerals, vitamins and other beneficial components for human health that are generally indicated as antioxidants. Unfortunately during the industrial transformation, a large part of the characteristics determining the quality of the fresh product undergoes a remarkable modification: the thermal damage and the chemical oxidation degrade more sensitive components reducing the quality of the final product.

Fruit juices present on the market

- **simple squeezing** and then submitted to a mild pasteurisation
- **NFC**, not from concentrate juice freezed just after squeezing
- **RFC**, juices reconstituted from concentrate

The production of concentrated fruit juices is of interest at industrial level since they can be used as ingredients in many products such ice creams, fruit syrups, jellies and fruit juices beverages. Furthermore, fruit juices concentrates, because of their low water activity, have a higher stability than single-strength juices.

In addition, package, storage and shipping costs are remarkably reduced.

When the concentration is carried out by **EVAPORATION**, most of the aroma compounds contained in the raw juice are lost and the aroma profile undergoes an irreversible change with a consequent remarkable qualitative decline. Besides, the heat required to perform the evaporation results in some “cooked” notes recognised as off-flavors.

Commercial freeze concentration systems, in which water is removed as ice and not as vapor (**CRYOCONCENTRATION**), permit to preserve the volatiles during the water removal process but, they are not able to substitute far the evaporative concentration of products with large diffusion (i.e. citrus juices) since they require a remarkable energy consumption. Besides the achievable concentration (about 40 °Brix) is lower than the values obtained by evaporation (60-65 °Brix).

MEMBRANE PROCESSES are today consolidated systems in various productive sectors, since the separation process is athermal and involves no phase change or chemical agents. The introduction of these technologies in the industrial transformation cycle of the fruit juices represents one of the technological answers to the problem of the production of juices with high quality, natural fresh taste and additive-free.

Ultrafiltration membranes retain large species such as micro-organisms, lipids, proteins and colloids while small solutes as for example vitamins, salts, sugars, flow through the membrane together with water. Therefore the possibility of microbial contamination in the permeate stream is minimised avoiding any thermal treatment and, consequently, loss of volatile aroma substances.

Clarified juice coming from the ultrafiltration process can be commercialised or submitted to a concentration process in order to obtain a product suitable for the preparation of juices and beverages.

The **Reverse Osmosis** process permits to separate principally water from the juice but it is limited by high osmotic pressures; it is used as a preconcentration technique which permits concentration values of about 30 °Brix corresponding to osmotic pressures of about 50 bar. Aroma compounds and other important chemical constituents such as anthocyanins, vitamins, sugars, acids, calcium, potassium, magnesium and phosphorus are rejected in the process.

The limitation of high osmotic pressures can be reversed by continuing juice concentration by **Membrane Distillation** or **Osmotic Distillation**.

INTEGRATED MEMBRANE OPERATIONS

The introduction of membrane operation units is studied as a fundamental step towards the rationalisation of traditional industrial processes in terms of energy consumption, of product recovery and improvement of quality in agro-food productions.

The combination among each other of different membrane operations such as enzyme membrane reactors, microfiltration, ultrafiltration, nanofiltration, reverse osmosis and osmotic distillation, is studied in order to identify their synergistic effects on the optimisation of processes for the production of fruit juices.

The possibility to realise integrated membrane systems in which all the steps of the productive cycle are based on molecular membrane separations can be considered a valid approach for a sustainable industrial growth within the ***PROCESS INTENSIFICATION*** strategy. The aim of this strategy is to introduce in the productive cycles new technologies characterised by low encumbrance volume, advanced levels of automation capacity, modularity, remote control, reduced energy consumption, etc..

New products from fruit and vegetables with high nutritional value (PNR- Tema 2)

Duration: 36 months

Project Coordinator: PARMALAT

Aim of the project is the development of new technologies for the production of liquid foods from fruit and vegetable as alternative to the traditional processes of the agro-food industry. An integrated membrane process for the clarification and concentration of carrot and citrus fruit juices is developed for the production of juices with high nutritional value and high organoleptic quality.

Funding Board ⇒ **MIUR**

Collaborations ⇒ Istituto Mario Negri Sud; Parmalat - Centro Ricerche; San Giorgio Flavors S.r.l.; Emmegi Agroindustriale; Stazione Sperimentale Industria Conserve Alimentari; Tecnoalimenti S.C.p.A.; Università di Parma

- Blood orange juice, mostly Tarocco variety, were from Sicily (1999 Production): the concentration of the raw juice was about 12.0-12.6 °Brix with a pH of 3.5. Traditionally concentrated orange juice was produced by a multiple effect TASTE (thermally accelerated short time evaporator) evaporator at a final concentration of 56.3 °Brix by Parmalat SpA.

- Lemon juice was from Sicily (1999 Production): the concentration was about 7.1 °Brix with a pH of 2.8.

- Carrot juice was produced by chemical and physical treatment and it was supplied in freezed packages at pH 4.48 and with a concentration of 6 °Brix.

Ultrafiltration process

UF is most commonly used to separate a solution that has a mixture of some desirable components and some that are not desirable. Typical rejected species include sugars, bio-molecules, polymers and colloidal particles.

The driving force for transport across the membrane is a pressure differential (UF operates at 2-10 bar).
UF processes perform feed clarification, concentration of rejected solutes and fractionation of solutes.

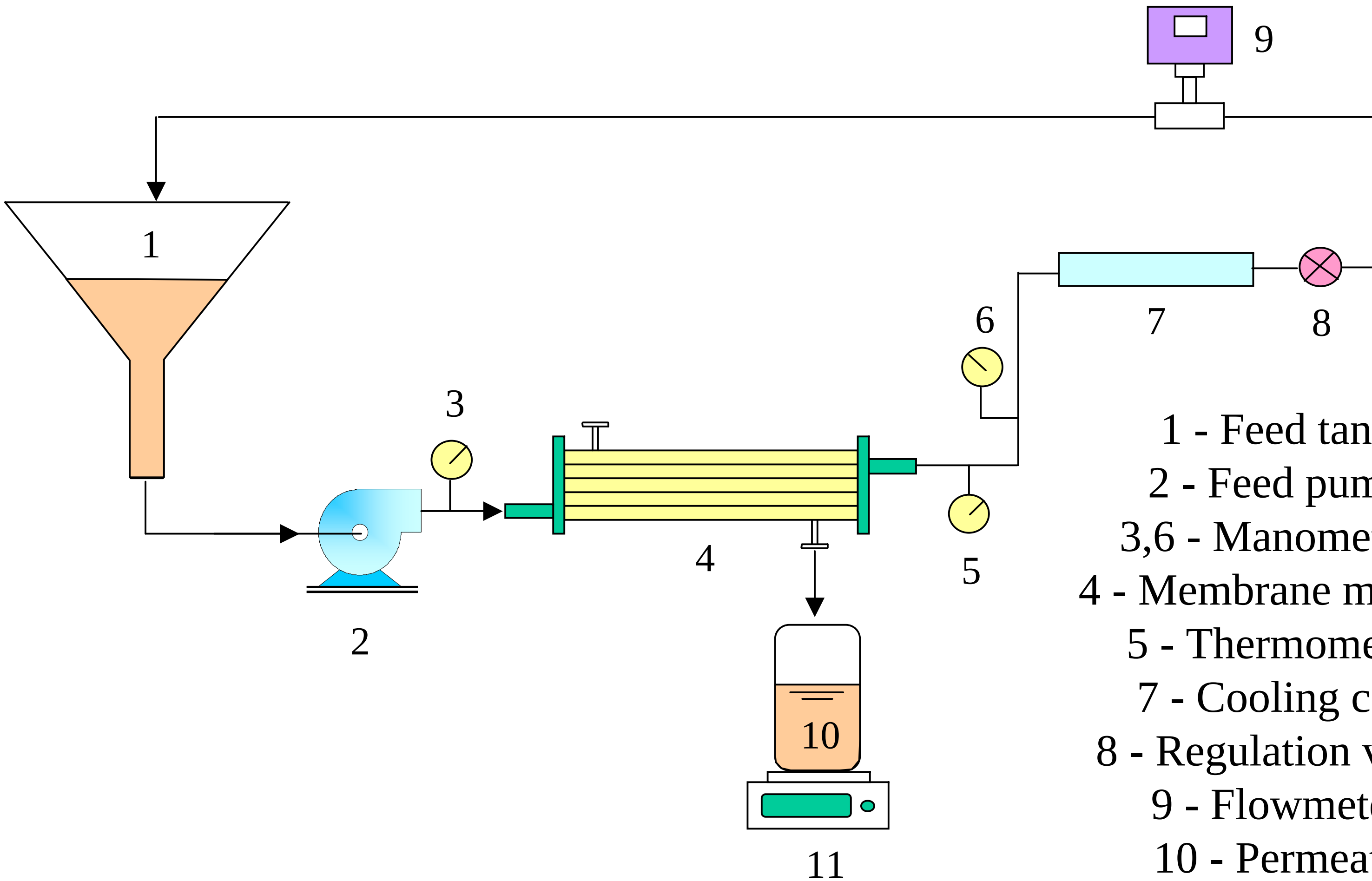
UF membranes are capable of retaining species in the range of 300-500,000 dalton of molecular weight, with pore sizes ranging from 10-1000 Angstrom (10^3-0.1 μm). These are mostly described by their nominal molecular weight cut-off (1000-100,000 MWCO), which means, the smallest molecular weight species for which the membranes have more than 90% rejection.

Clarification of citrus and carrot juice by ultrafiltration

Juices were submitted, without any preliminary treatment, to a clarification process by UF using a laboratory pilot plant supplied by Verind SpA (Rodano, Milan, Italy). The plant, with a 25 l feed tank, was equipped with a Koch tubular membrane module

Type	Koch Series-Cor™ HFM 251
Configuration	Tubular
Membrane polymer	PVDF
NMWCO	15 kDa
Membrane surface area	0.23 m^2
Average pores diameter	59 Å
pH operating range	2-11
Temperature operating range	0-55 °C
Pressure operating range	0.8-5.5 bar

Ultrafiltration pilot plant

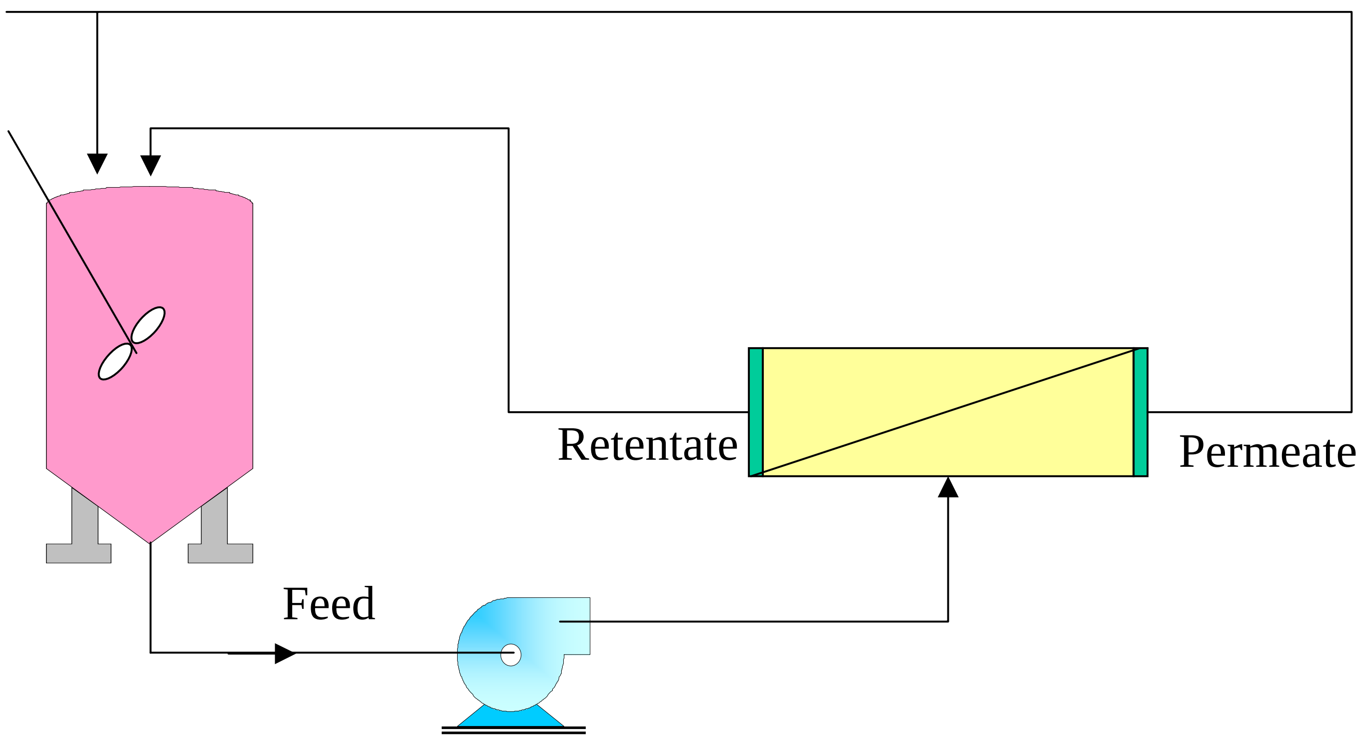


1 - Feed tank
2 - Feed pump
3,6 - Manometers
4 - Membrane module
5 - Thermometer
7 - Cooling coil
8 - Regulation valve
9 - Flowmeter
10 - Permeate
11 - Digital balance

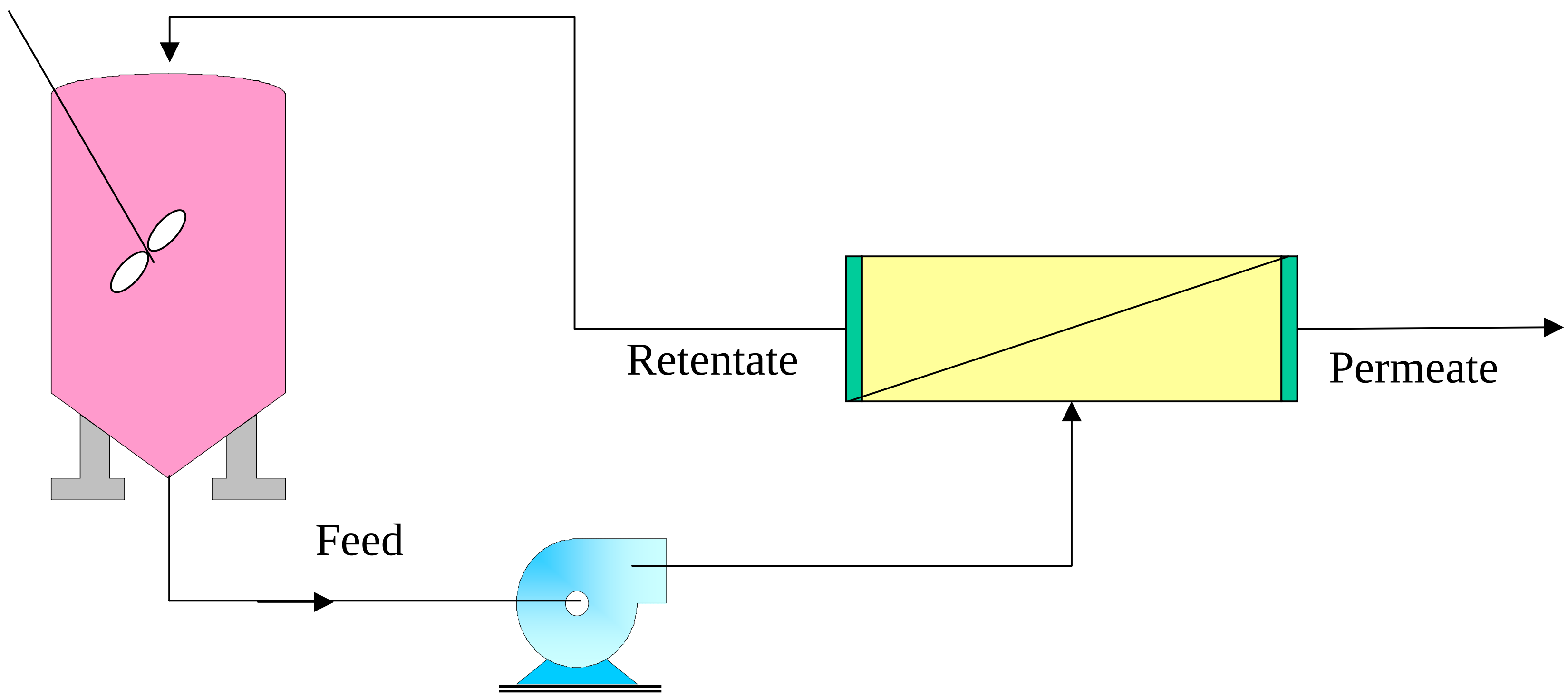
UF laboratory pilot plant

Experiments were carried out according to the ***total recycle mode*** (recycling both permeate and retentate stream in the feed tank) and to the ***batch concentration mode*** (collecting separately the permeate stream).

The total recycle mode was used in order to measure the permeate flux in different operating conditions and to identify the optimal operating conditions for the clarification process.



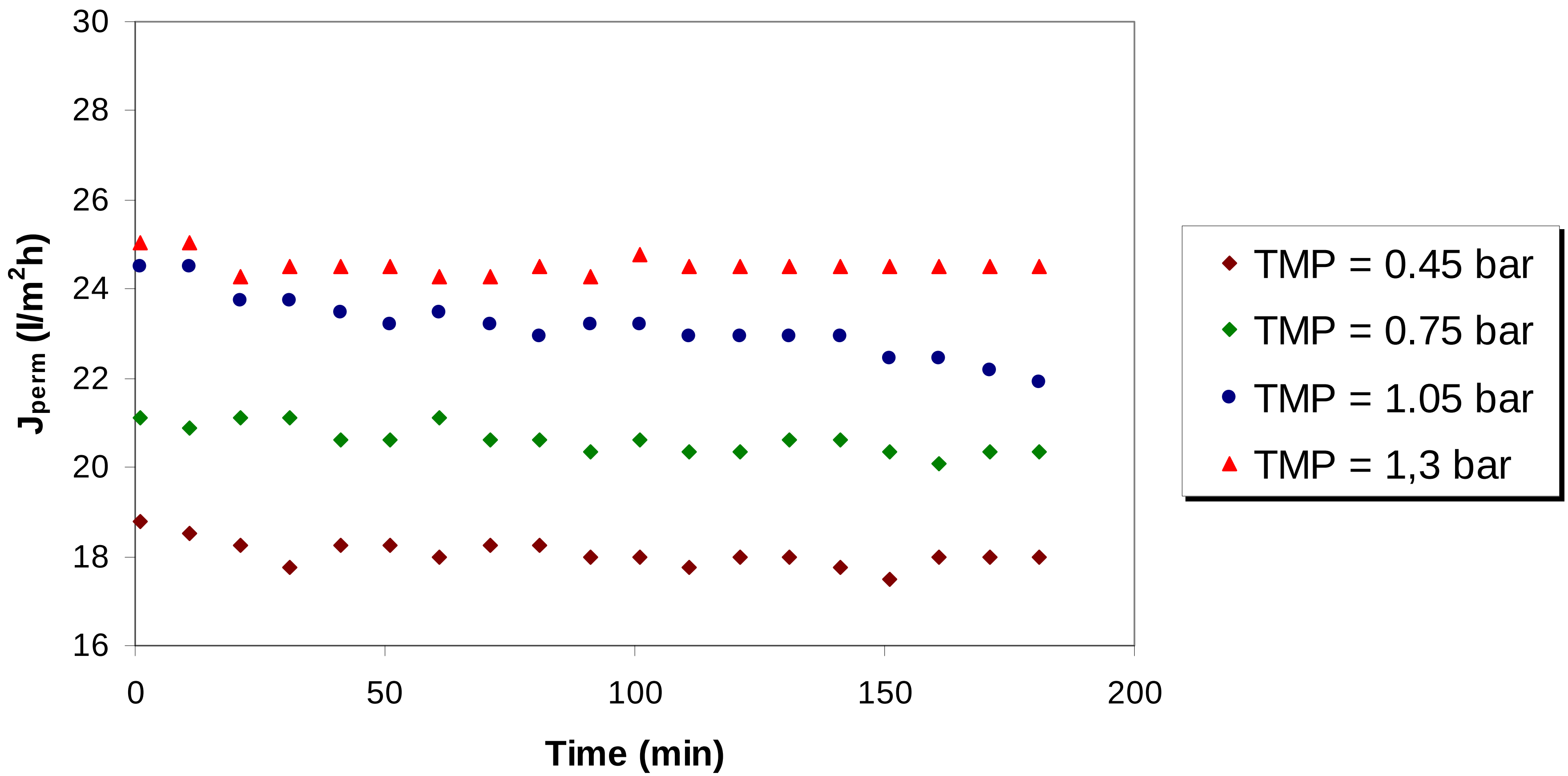
Scheme of the *total recycle* configuration



Scheme of the *batch concentration* configuration

Effect of the TMP on permeate flux

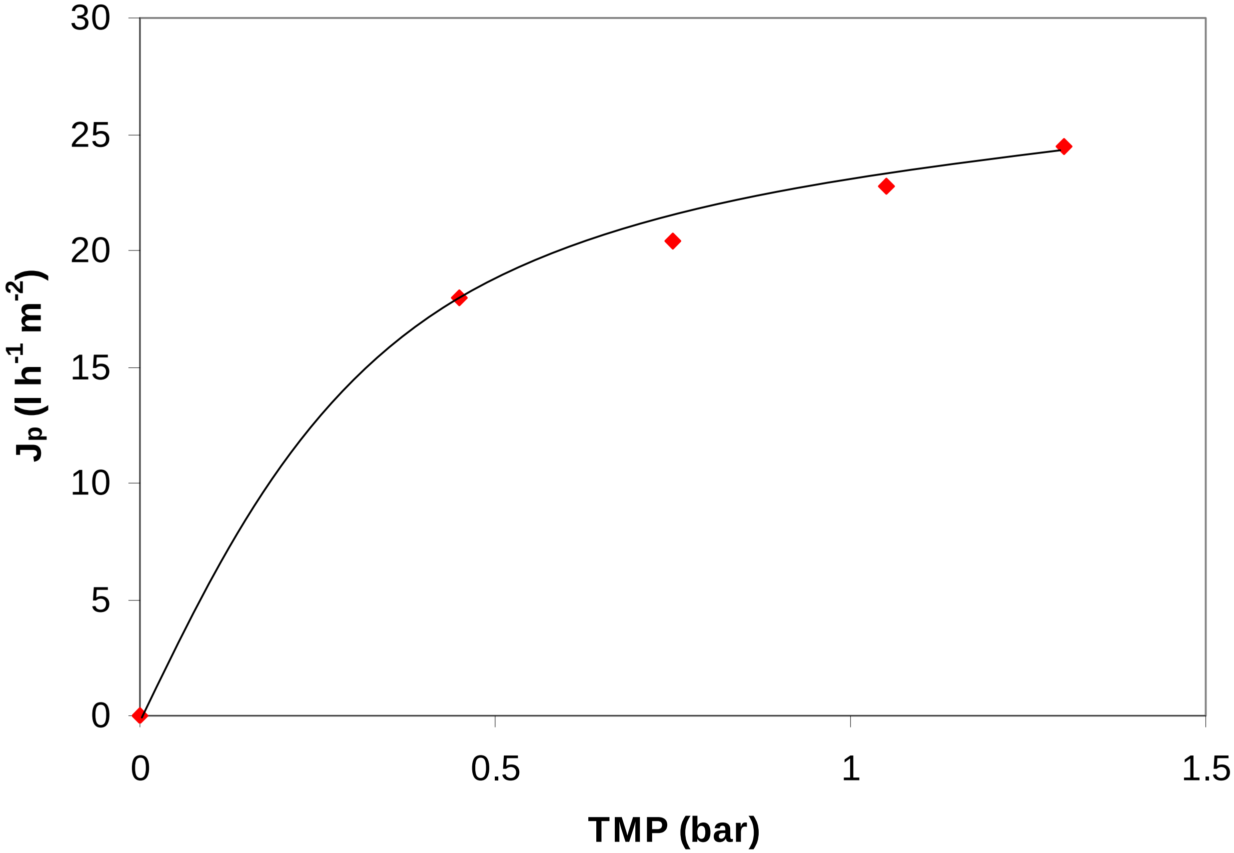
Permeate flux increases with ***pressure*** up to a limiting value (TMP_{lim}) which depends on the physical properties of the suspension and feed flow rate. Any increase in pressure is a source of inefficiency, because the energy input increases for no increase in production rate. Besides beyond TMP_{lim} membrane fouling becomes increasingly important and the flux decline is accelerated.



Ultrafiltration of carrot juice

Time course of permeate flux at different operating TMPs

Operating conditions: T = 23.5 °C; Qf = 800 l/h

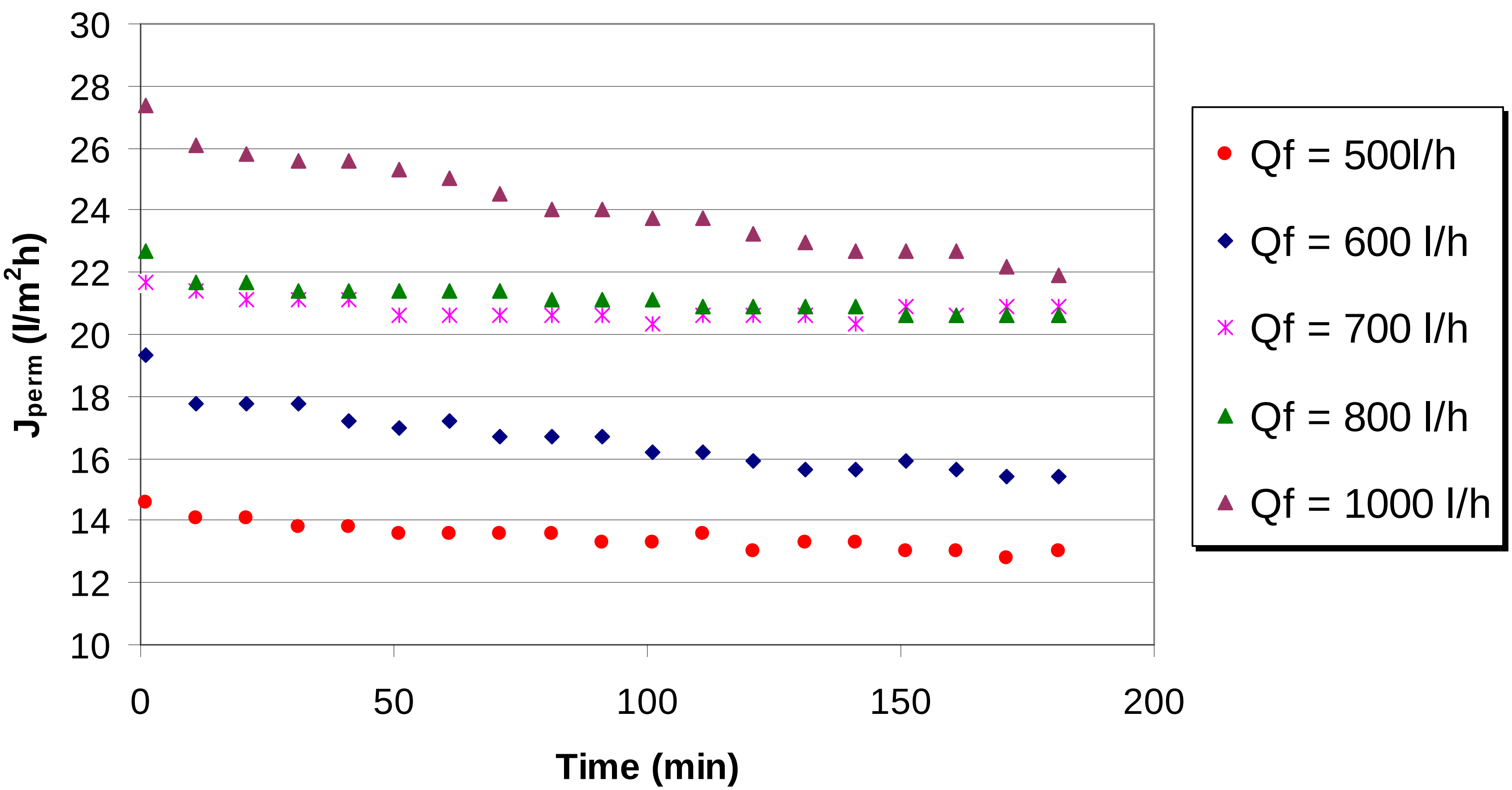


UF of carrot juice. Effect of the transmembrane pressure on the permeate flux

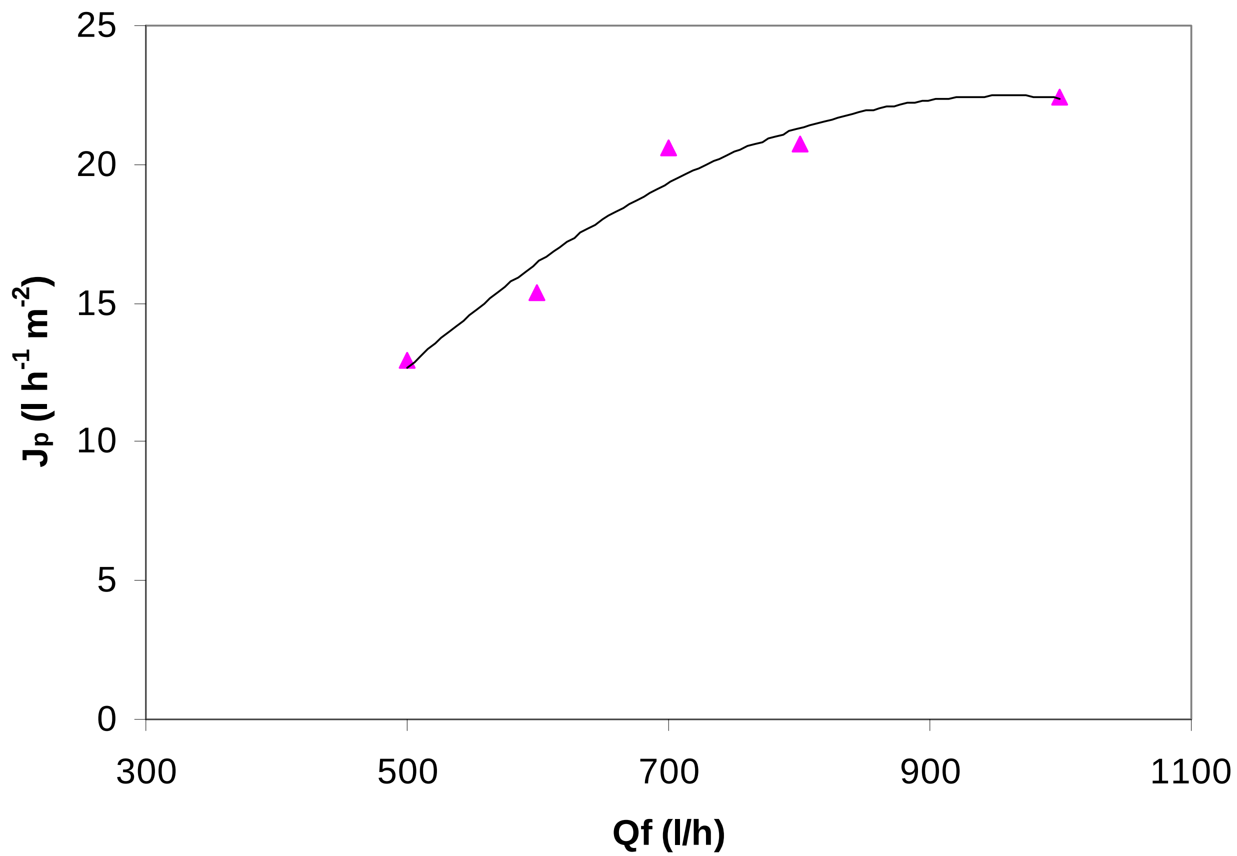
(Operating conditions: T = 23.5 °C; Qf = 800 l/h)

Effect of the feed flow rate on permeate flux

The ***feed flow rate*** is another important parameter for the performance of the ultrafiltration process. The cross-flow velocity affects the shear stress at the membrane surface and, consequently, the rate of removal of deposited particles responsible of flux decay.



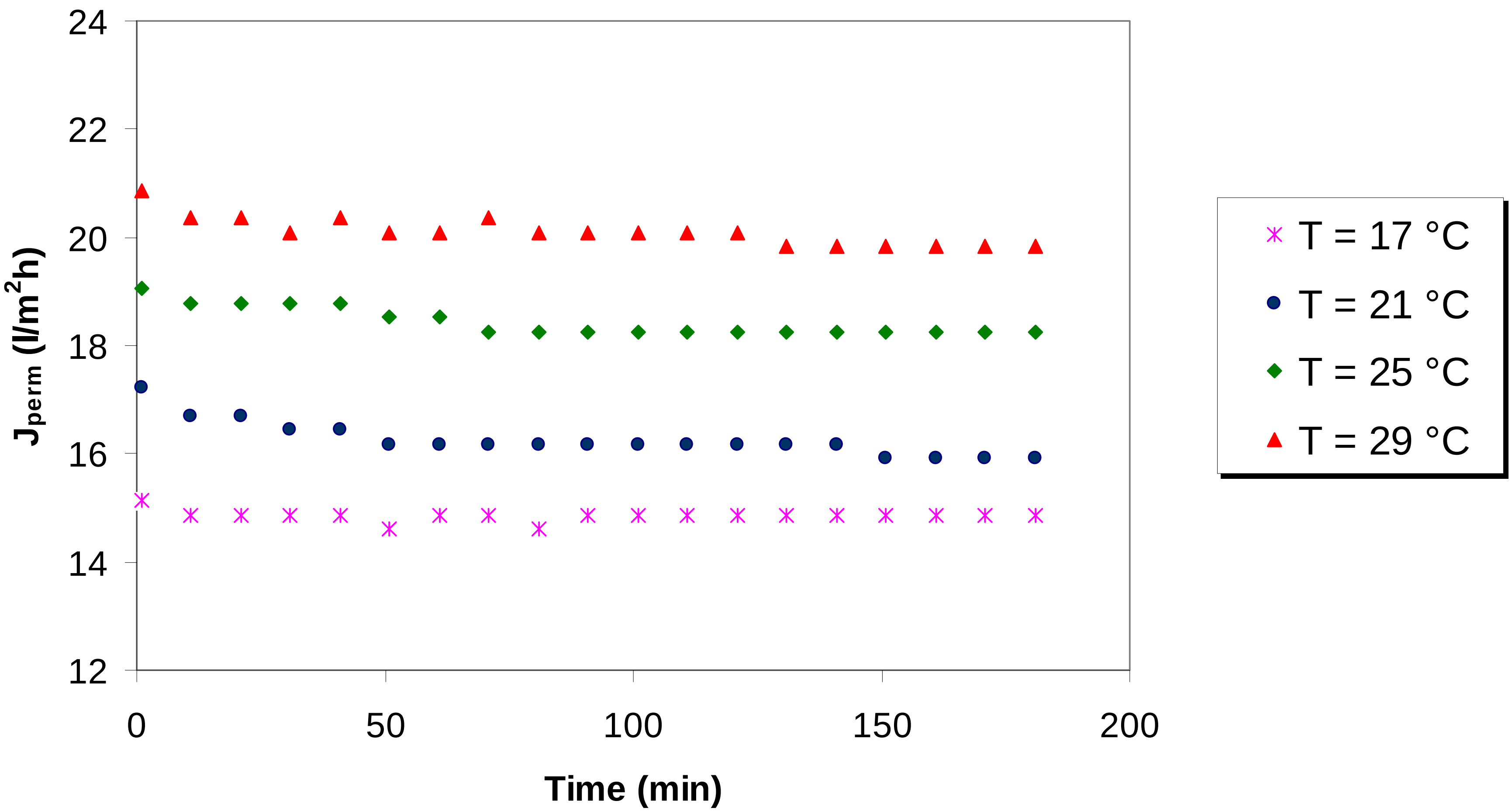
Ultrafiltration of carrot juice
Time course of permeate flux at different axial flow rates
Operating conditions: T = 23.5 °C; TMP = 0.85 bar



UF of carrot juice. Effect of the axial flow rate on the permeate flux
(Operating conditions: T = 23.5 °C; TMP = 0.85 bar)

Effect of the temperature on permeate flux

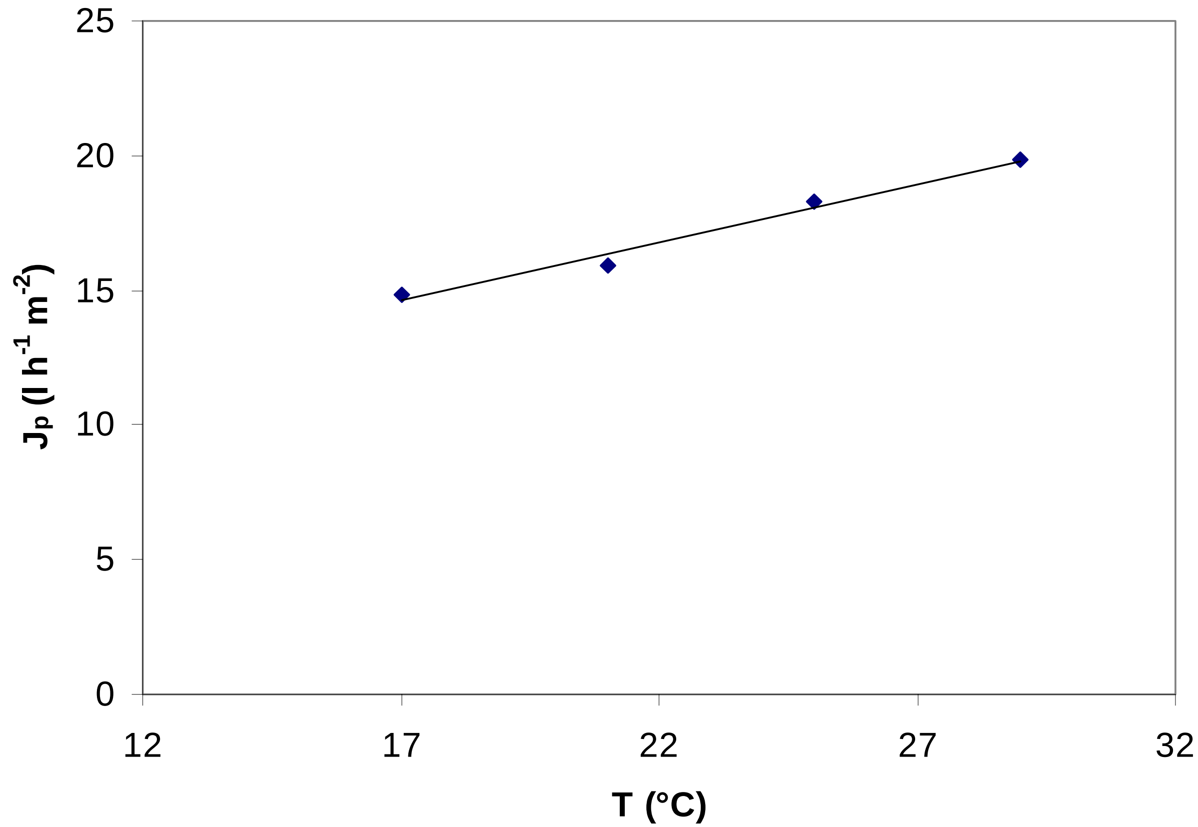
When the ***operating temperature*** is raised the feed viscosity is reduced and diffusion coefficients of macromolecules increase. The effect of these two factors is to enhance mass transfer and so increase the permeation rate



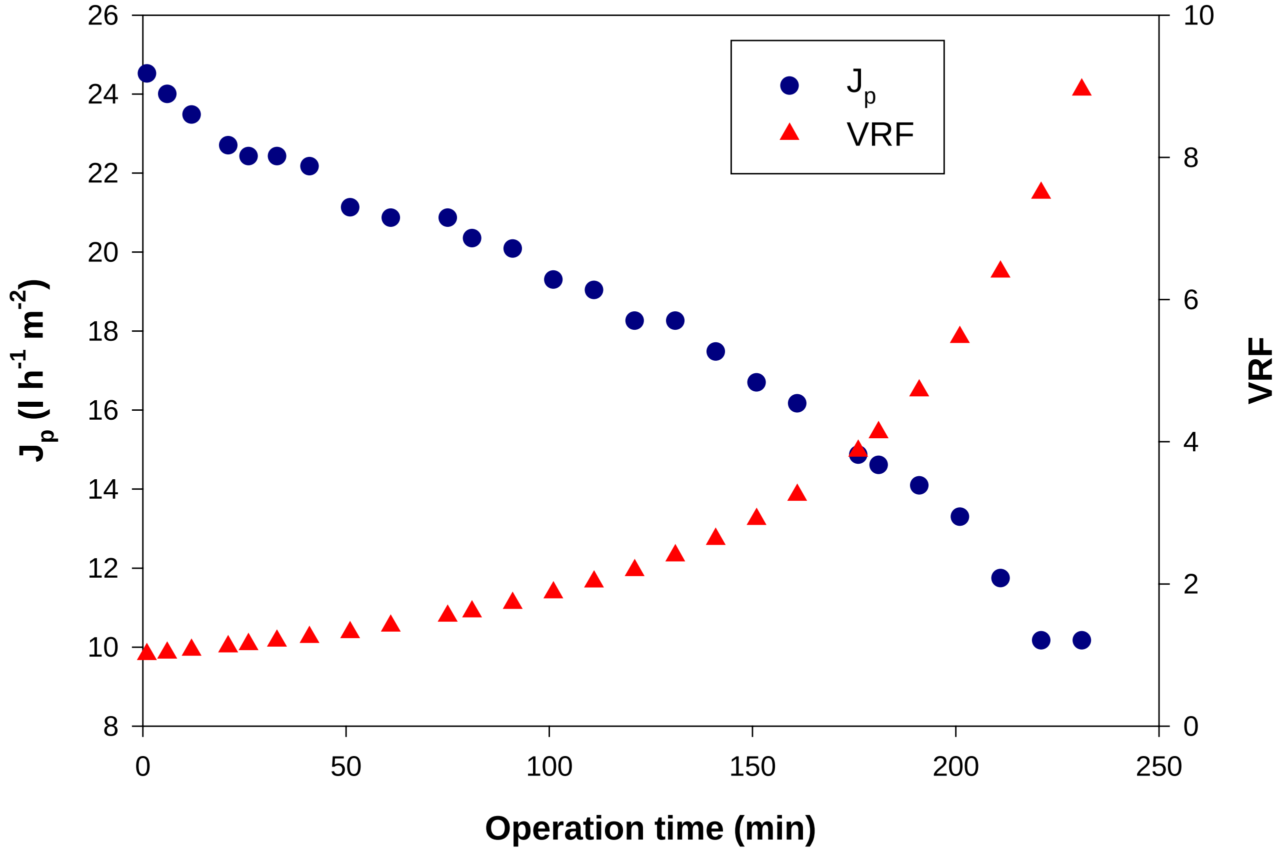
Ultrafiltration of carrot juice

Time course of permeate flux at different temperatures

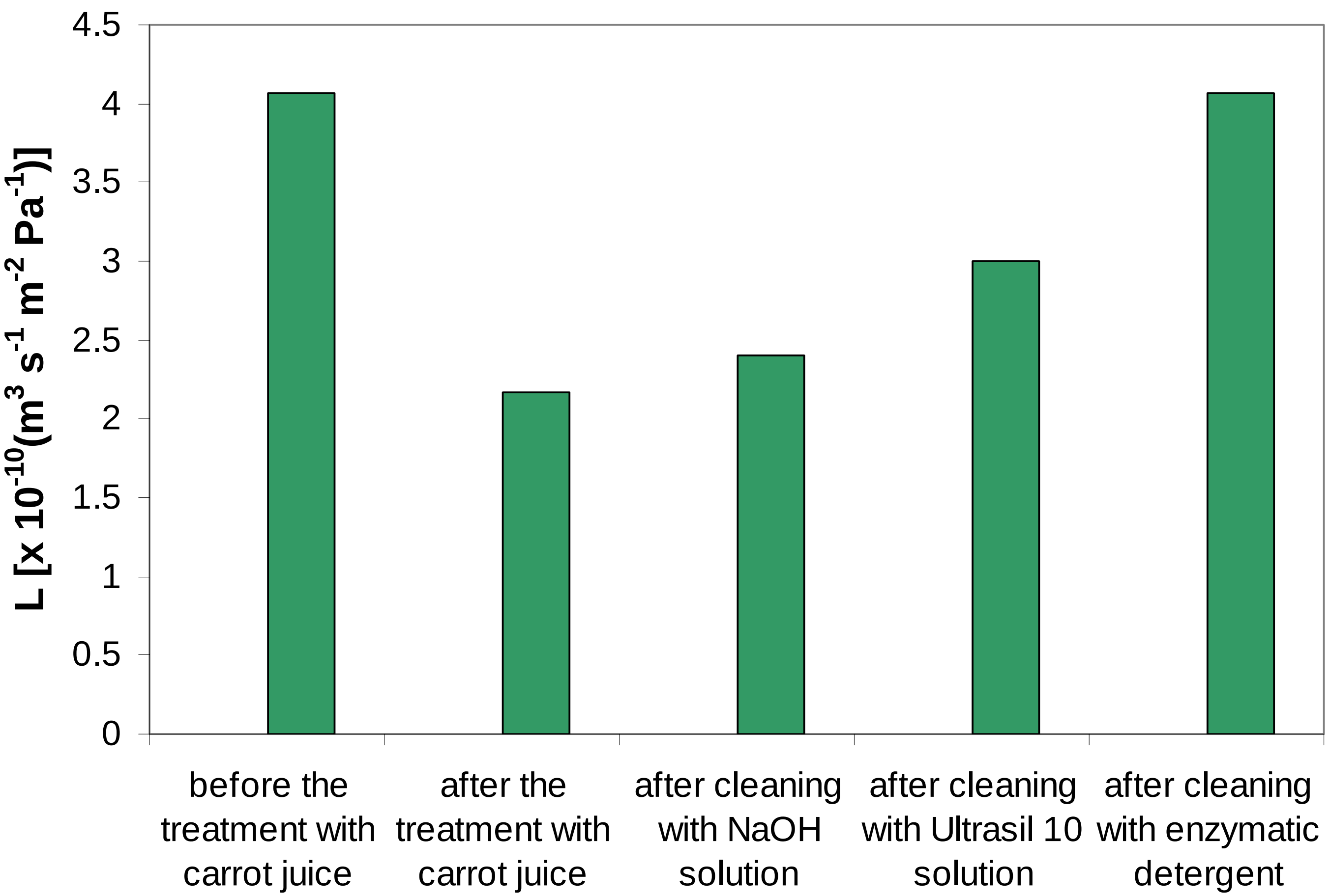
Operating conditions: TMP = 0.85 bar; Qf = 800 l/h



UF of carrot juice. Effect of the temperature on the permeate flux
(Operating conditions: Qf = 800 l/h; TMP = 0.85 bar)



UF of carrot juice. Time course of permeate flux and VRF
(Operating conditions: T = 23.5 °C; Qf = 800 l/h; TMP = 1.03 bar)



Regeneration of water permeability in UF membrane module
(Operating conditions: $T = 25$ °C; $v_f = 0.09$ m s^{-1})

Advantages of the UF treatment

⇒ reduction of clarification times

⇒ removal of suspended solids and turbidity

⇒ simplification of the clarification processes

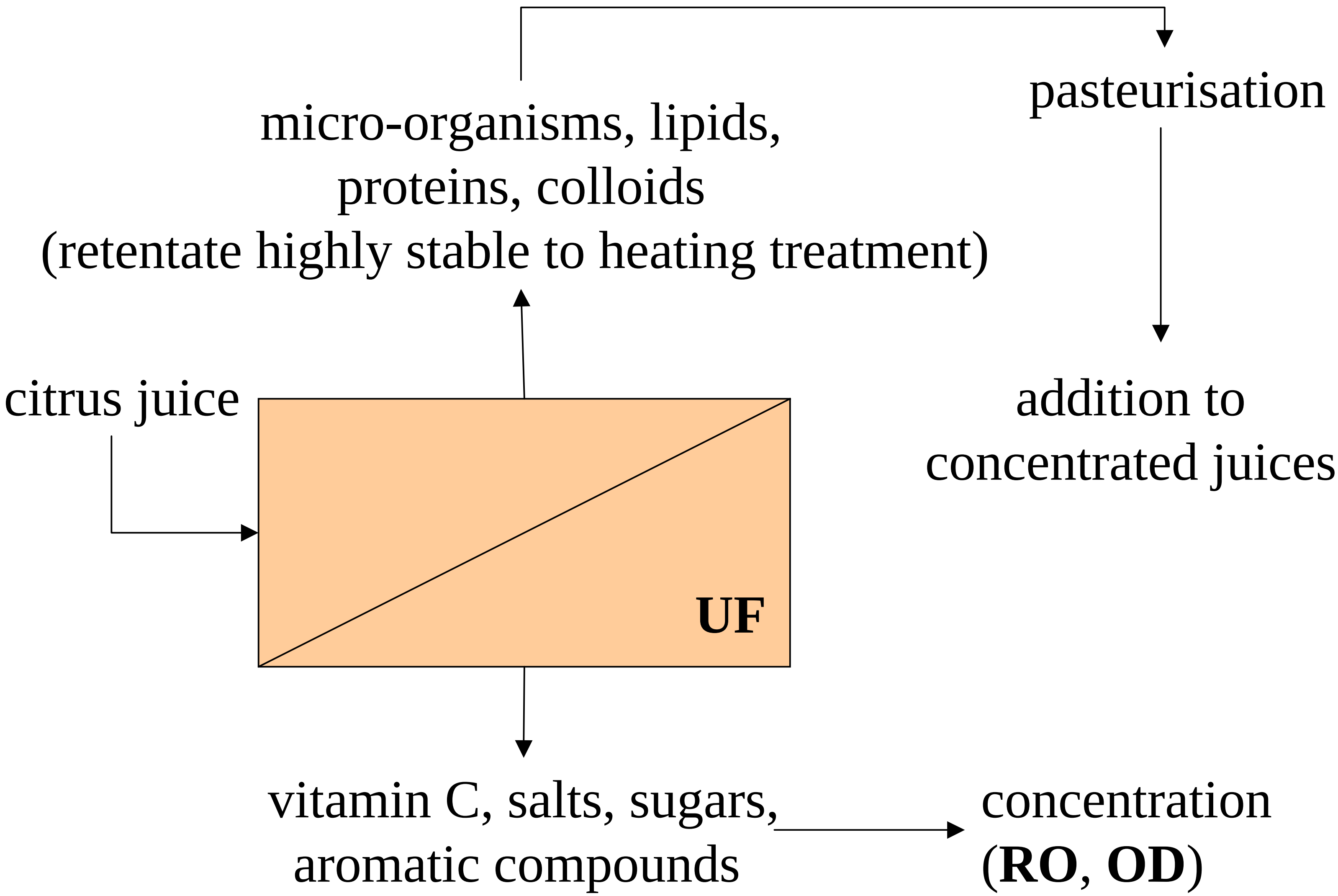
⇒ increasing of clarified juice volumes

⇒ possibility to operate at room temperature preserving the juice's freshness, aroma and nutritional value

⇒ possibility to avoid gelatines, adsorbents and

other filtration coadiuvant

⇒ improvement of the productive process


pasteurisation
micro-organisms, lipids, proteins, colloids (retentate highly stable to heating treatment)
addition to concentrated juices
citrus juice
UF
vitamin C, salts, sugars, aromatic compounds
concentration (RO, OD)

Osmotic distillation process

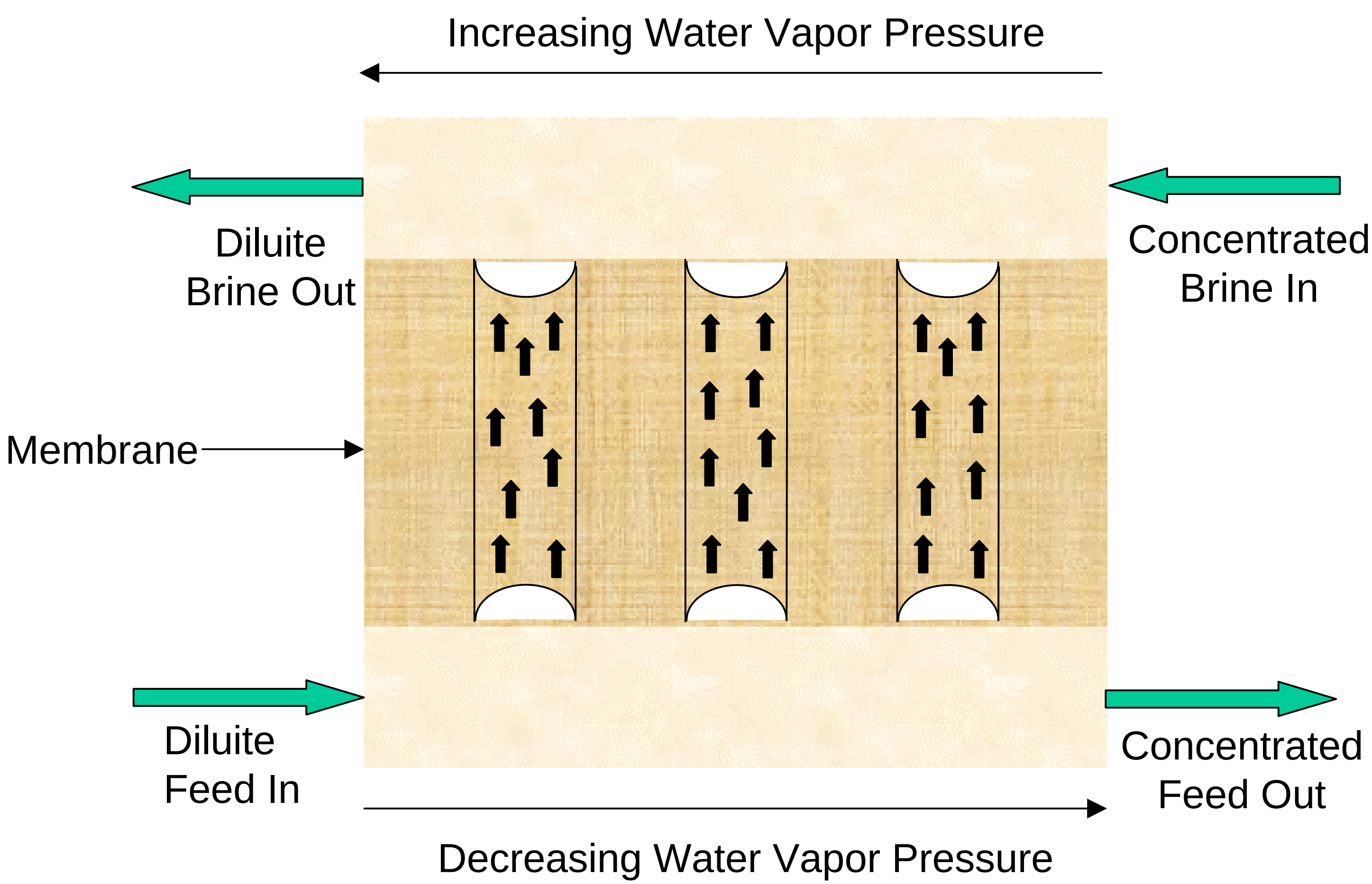
OD is a new membrane process also called "isothermal MD" that can be used to remove selectively water from aqueous solutions under atmospheric pressure and at room temperature, avoiding thermal degradation

It involves the use of a microporous hydrophobic membrane to separate two circulating aqueous solutions at different solute concentrations: a dilute solution and an hypertonic salt solution. The difference in solute concentrations, and consequently in water activity of both solutions, generates, at the vapour-liquid interface, a vapour pressure difference causing a vapour transfer from the dilute solution towards the stripping solution.

The water transport through the membrane can be summarised in three steps:

- evaporation of water at the dilute vapour-liquid interface
- diffusional or convective vapour transport through the membrane pore
- condensation of water vapor at the membrane/brine interface.

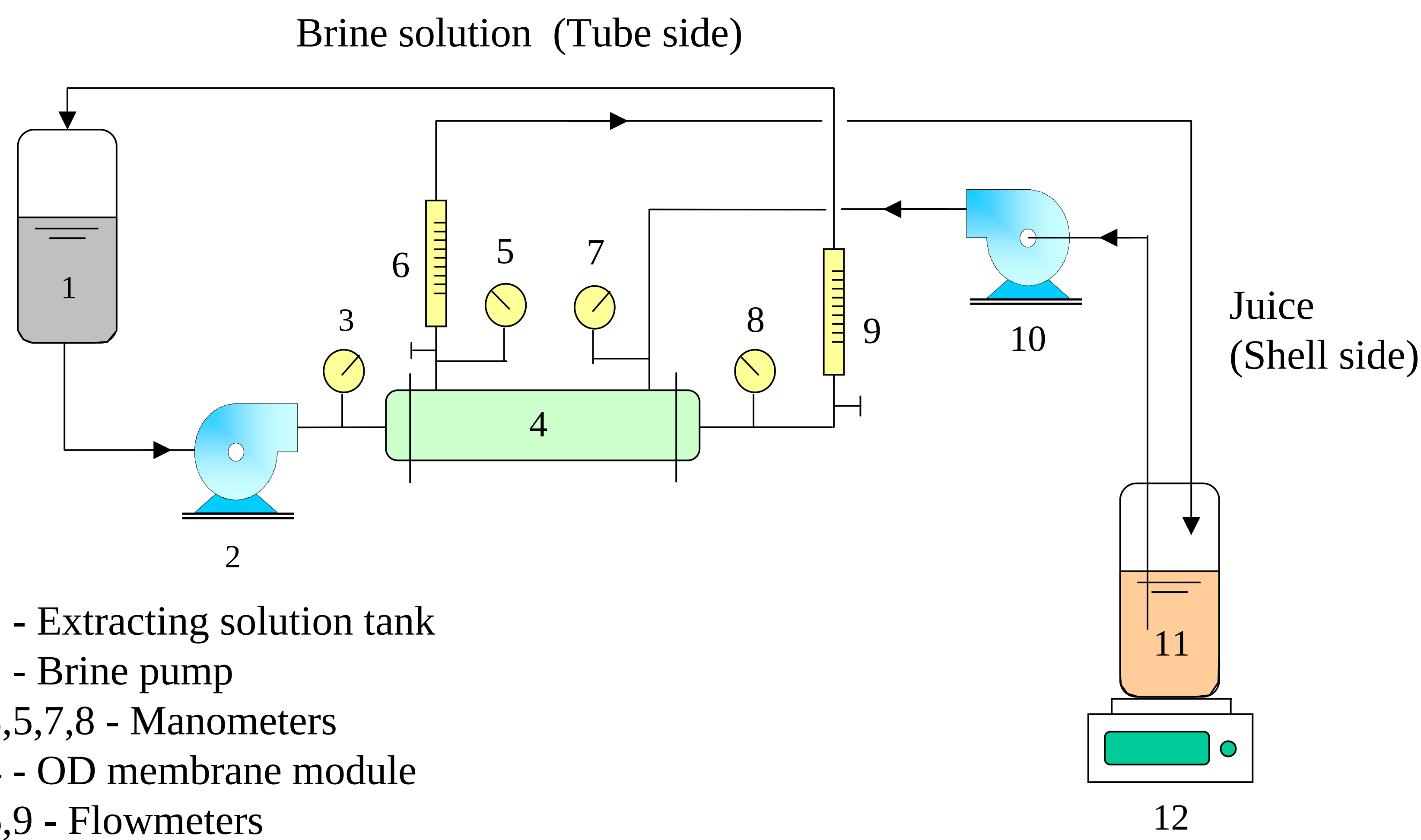
During the OD process the stripping solution is diluted due to the water transfer from the feed stream. It can be reconcentrated by evaporation and in this sense it can be recycled and reused in the process.



Mechanism of osmotic distillation through a microporous hydrophobic membrane (Hogan et al., 1998

The clarified juice was submitted to OD experiments using a laboratory plant equipped with a Hoechst-Celanese Liqui-Cel membrane contactor. The juice was recirculated in the shell side of the membrane module; Calcium Chloride Dihydrate, recirculated in the tube side of the module, was used as stripping solution. It was chosen because it is not toxic, and it is ready available at low cost.

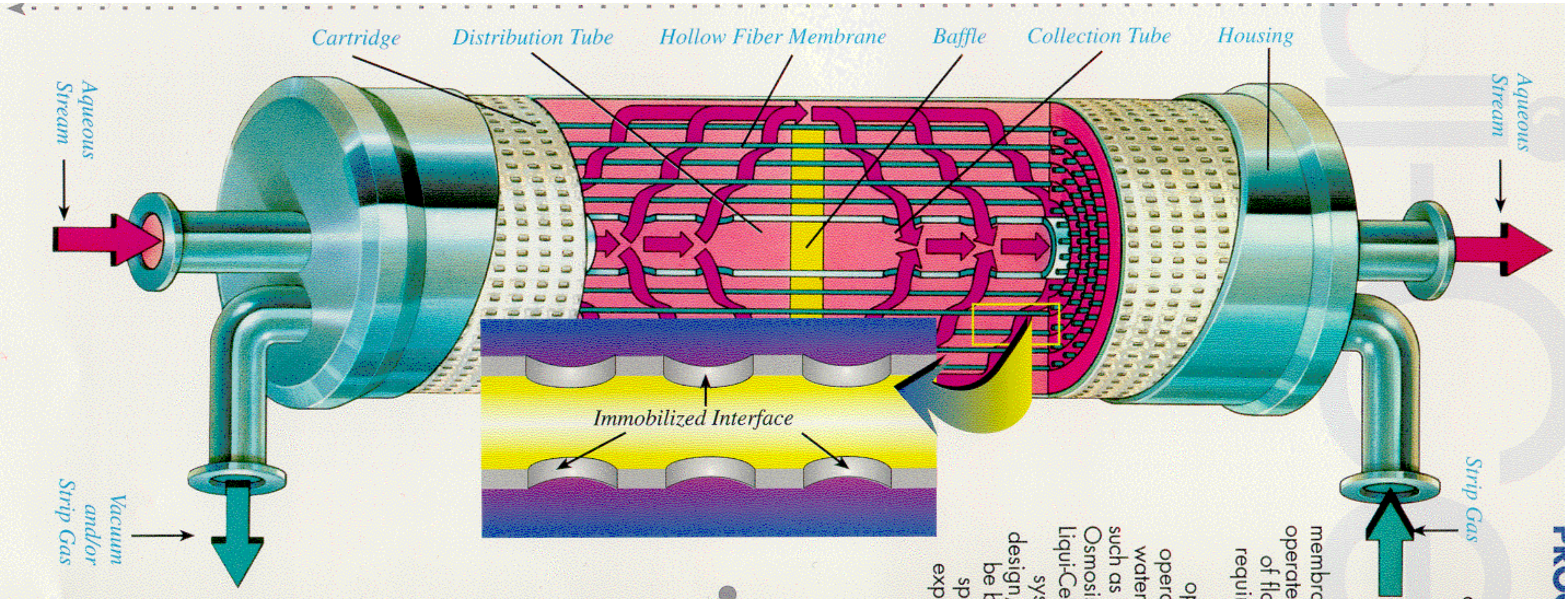
Fiber Characteristics	Celgard® Microporous
Fiber type	Polypropylene Hollow fiber
Cartridge Operating Limits	
Maximum Transmembrane Differential Pressure	4.2 kg/cm^2 (60 psi)
Maximum Operating Temperature Range	40 °C (104 °F)
Cartridge Characteristics	
Cartridge Dimensions (DxL)	8x28 cm (2.5x8 in)
Effective Surface Area	1.4 m^2 (15.2 ft^2)
Effective Area/Volume	29.3 cm^2/cm^3
Fiber Potting Material	Polyethylene

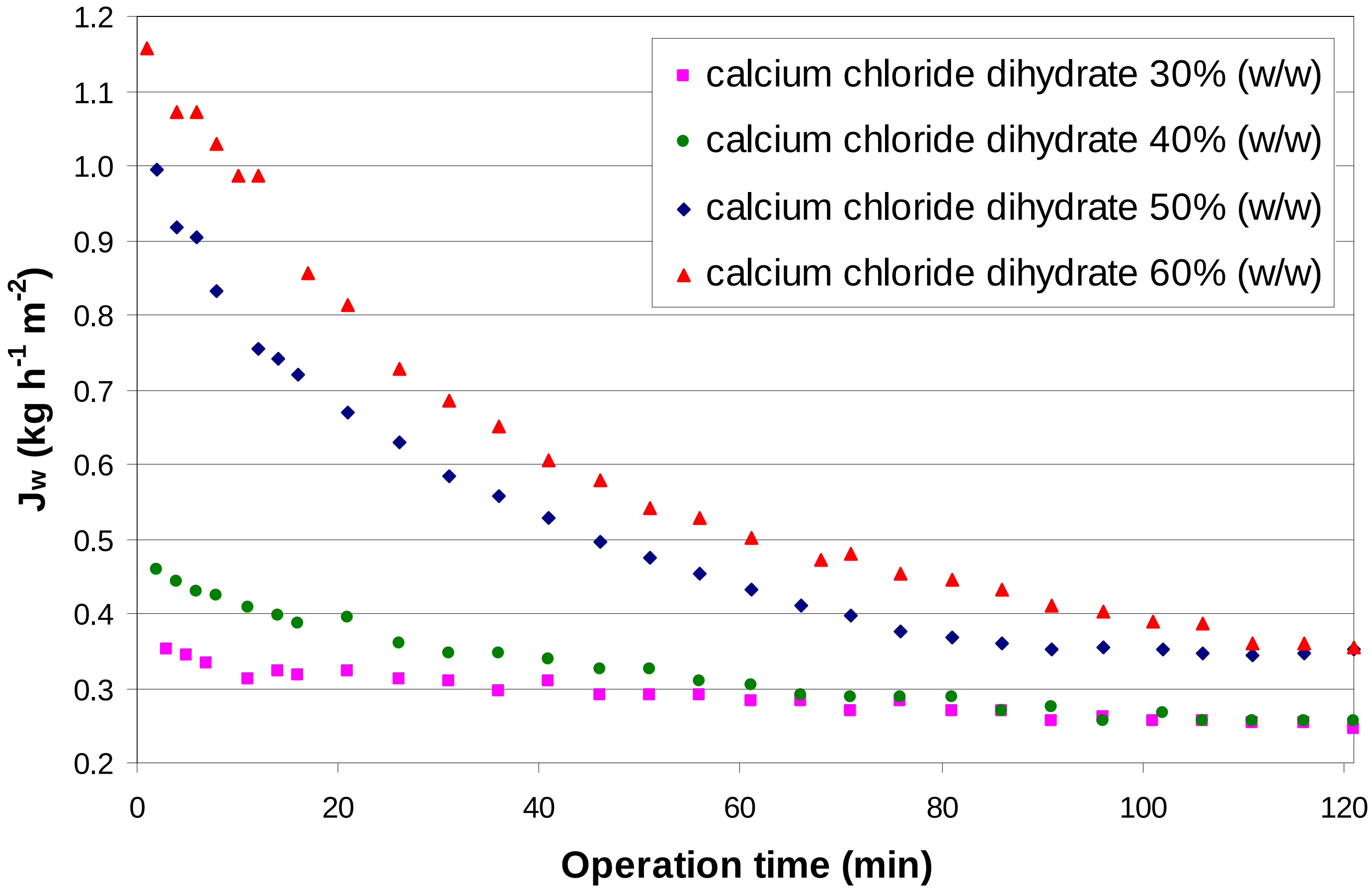


1 - Extracting solution tank
2 - Brine pump
3,5,7,8 - Manometers
4 - OD membrane module
6,9 - Flowmeters
10 - Feed pump
11 - Feed tank
12 - Digital balance

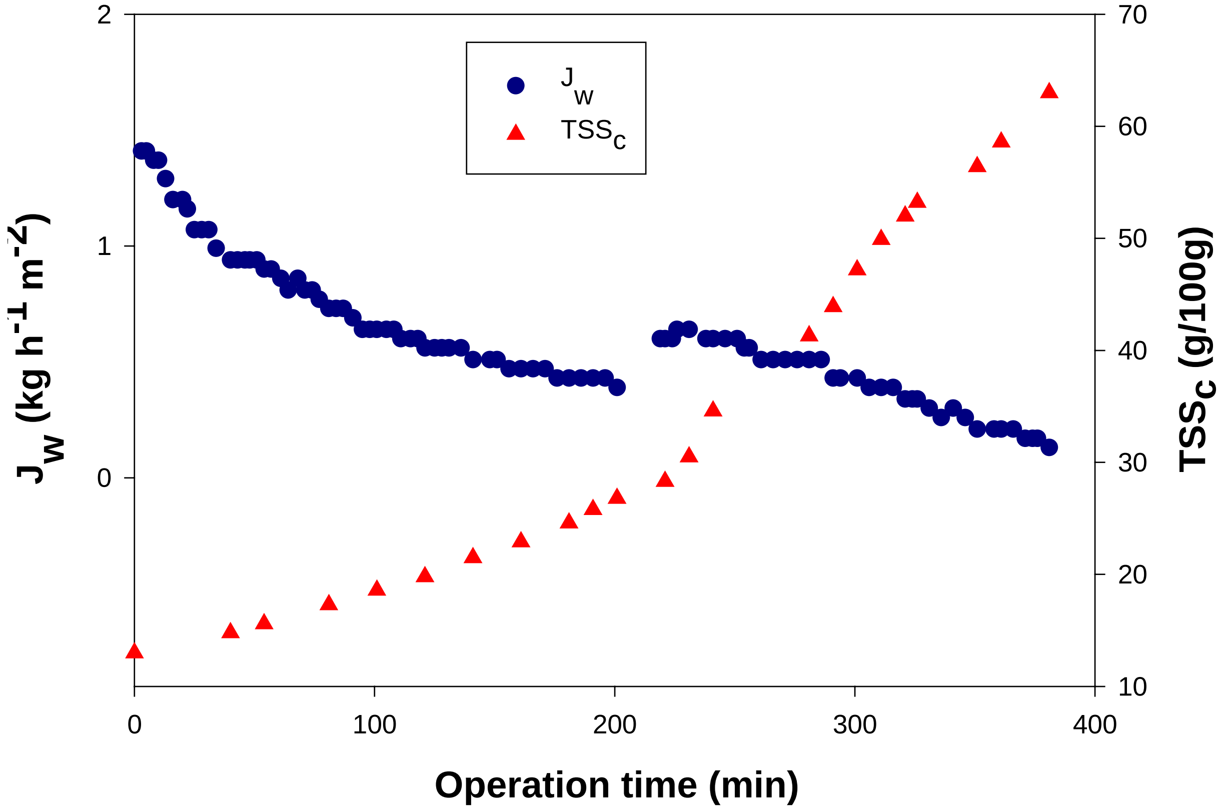
Osmotic distillation laboratory plant

2.5”x8” LiquiCel module - Hoechst Celanese

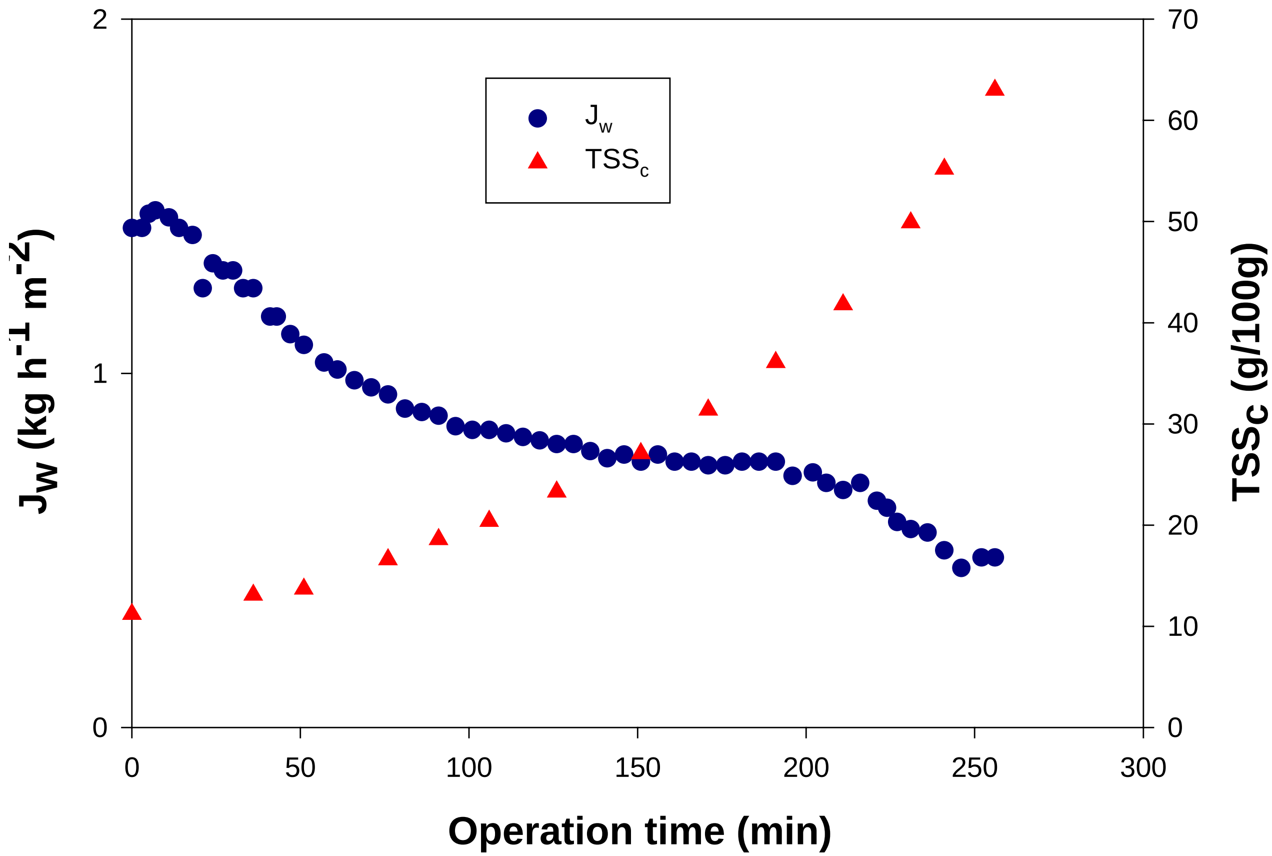




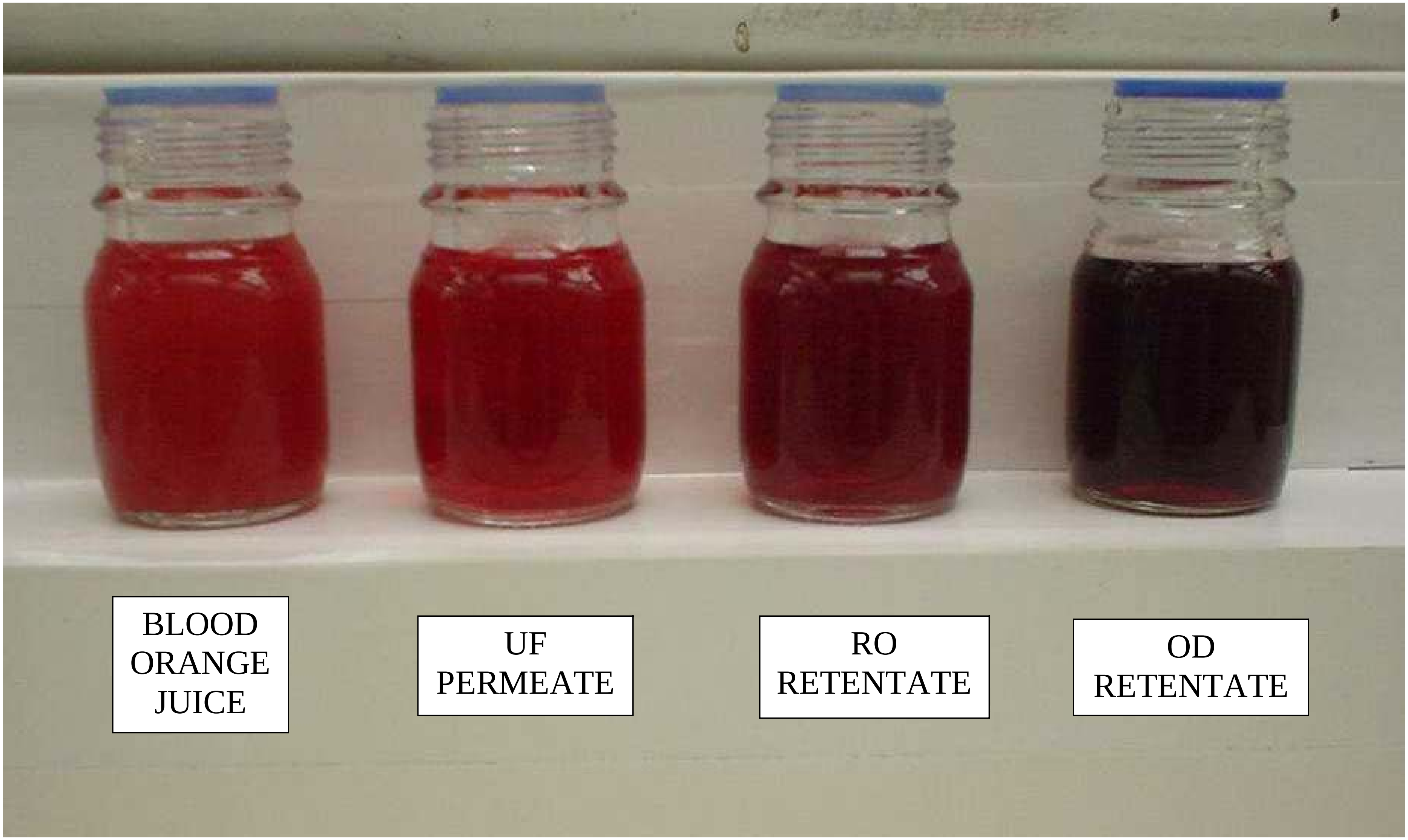
Characterisation of OD membrane module with water
(Operating conditions: T = 25 °C; Q_f = 29.8 l h^{-1}; Q_b = 37.8 l h^{-1})



OD of carrot juice coming from a sequence UF-RO
Time course of evaporation flux and TSS concentration
(Operating conditions: T = 26 °C; Q_f = 28 l h^{-1}; Q_b = 69 l h^{-1}; TMP = 0.13 bar)

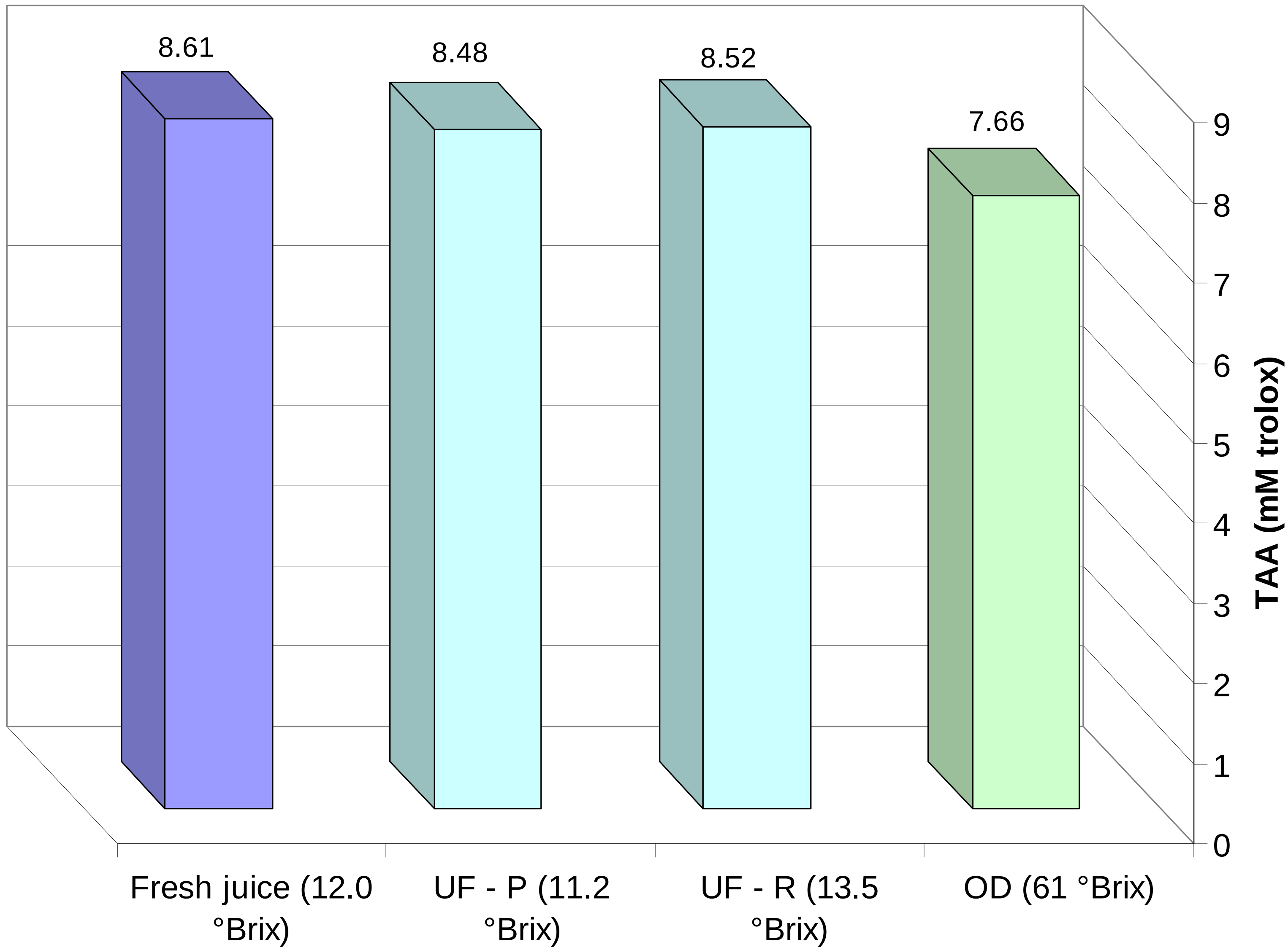


OD of blood orange juice coming from a UF treatment
Time course of evaporation flux and TSS concentration
(Operating conditions: T = 26 °C; Q_f = 28 l h^{-1}; Q_b = 69 l h^{-1}; TMP = 0.13 bar)


BLOOD ORANGE JUICE
UF PERMEATE
RO RETENTATE
OD RETENTATE

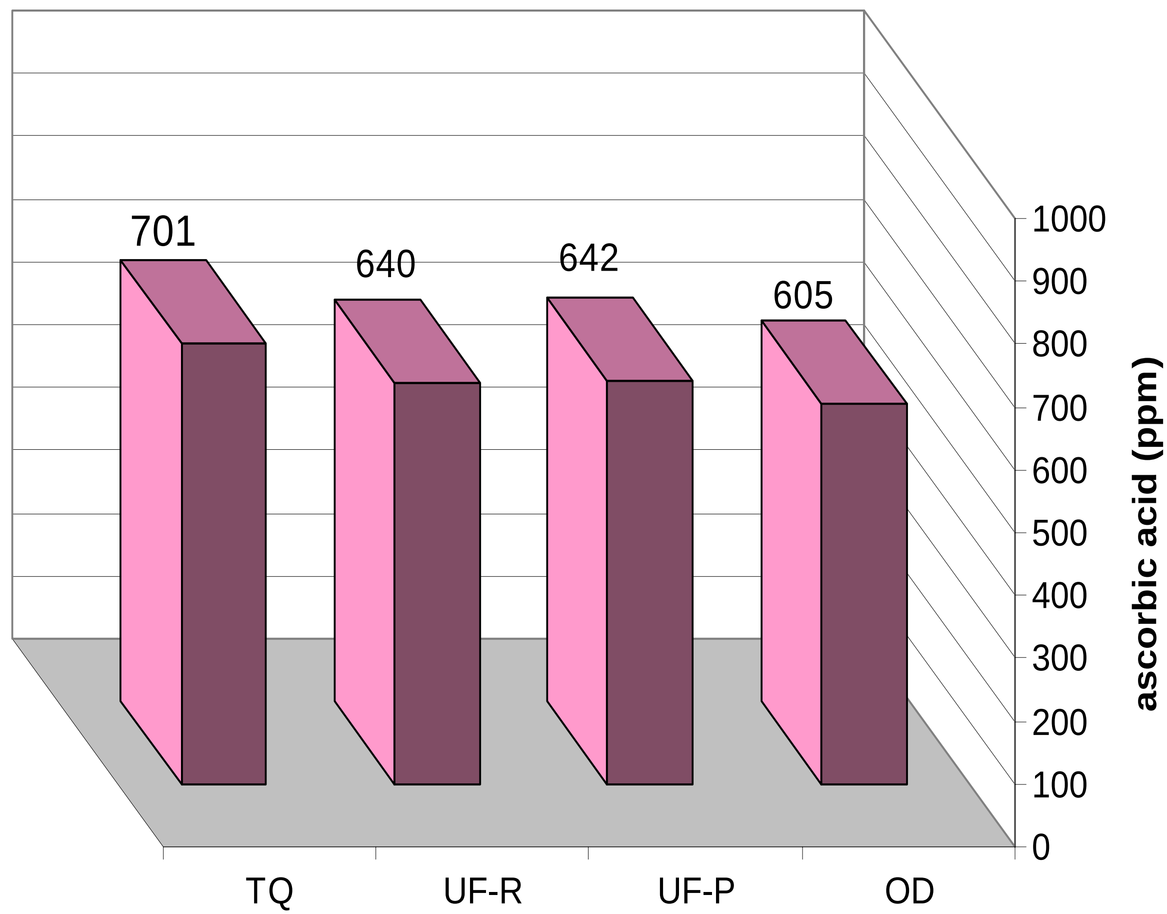
TAA measurements

In the traditional concentrated juice (TC, 56.3 °Brix) a decrease of the antioxidant activity (20-25%) was measured (6.85 ± 0.20 mM trolox), in comparison with the fresh juice (8.61 ± 0.07 mM trolox). During the ultrafiltration process TAA was maintained both for the permeate and for the retentate (UFP 8.48 mM trolox; UFR, 8.52 mM trolox). The subsequent concentration treatment by osmotic distillation did not induce other significant changes to TAA, independently from the final concentration obtained: the highly concentrated sample at 61 °Brix still showed a high value of TAA (7.66 mM trolox).

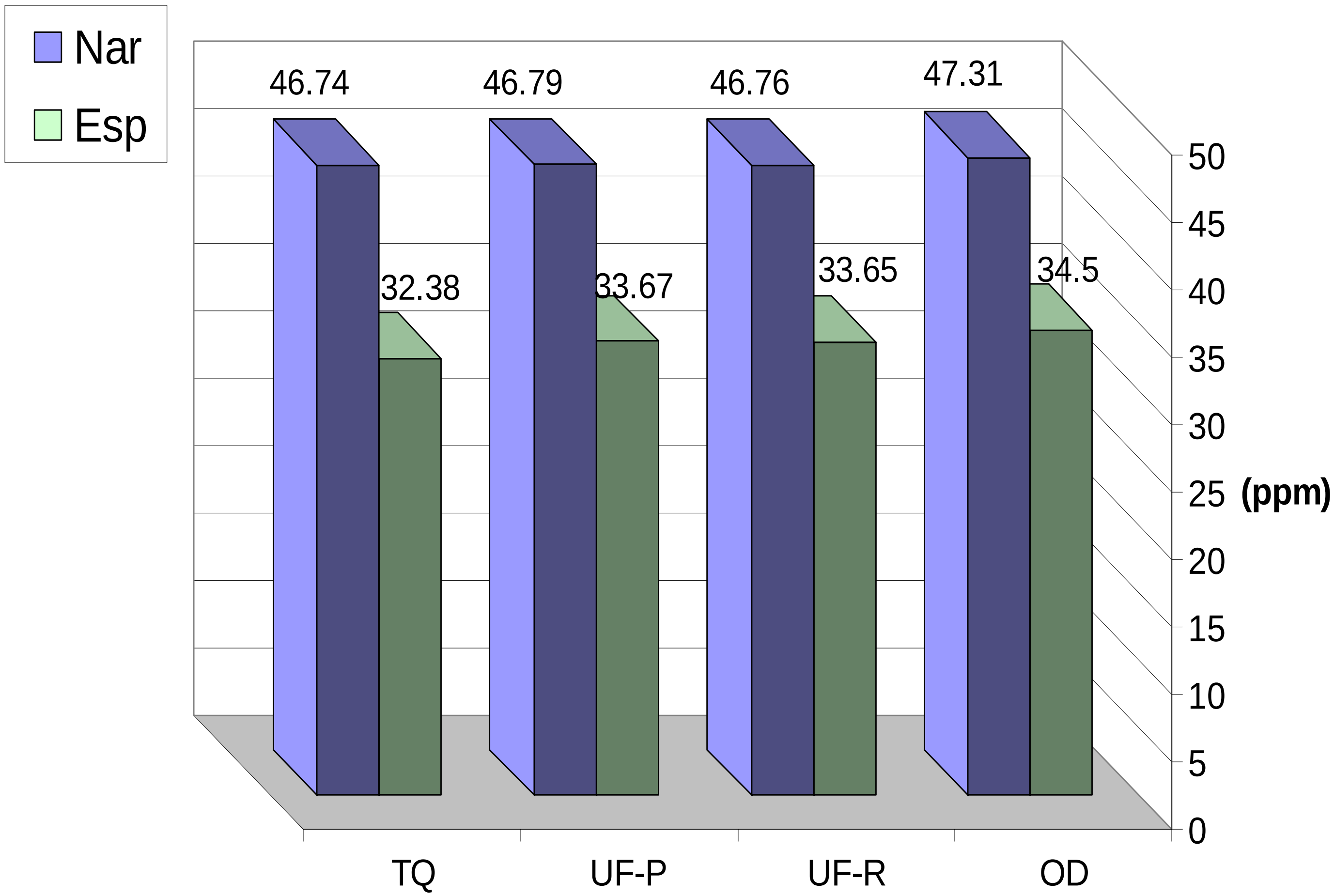


TAA variation in samples coming from a UF-OD sequence

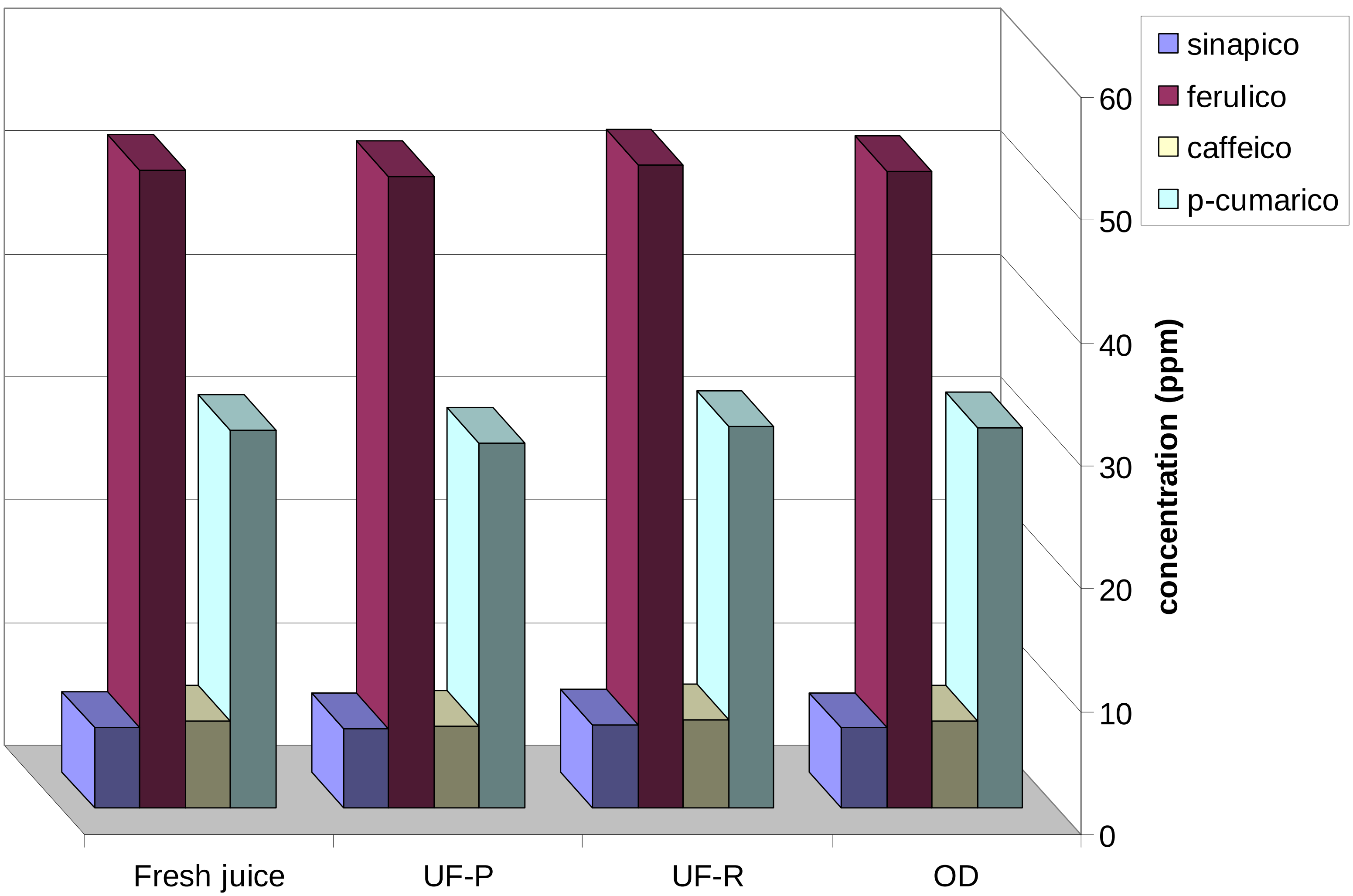
Ascorbic acid measurements in samples of blood orange juice treated by membrane processes



Flavonoids in samples of blood orange juice treated by membrane processes



Hydroxycinnamic acids in samples of blood orange juice treated by membrane processes



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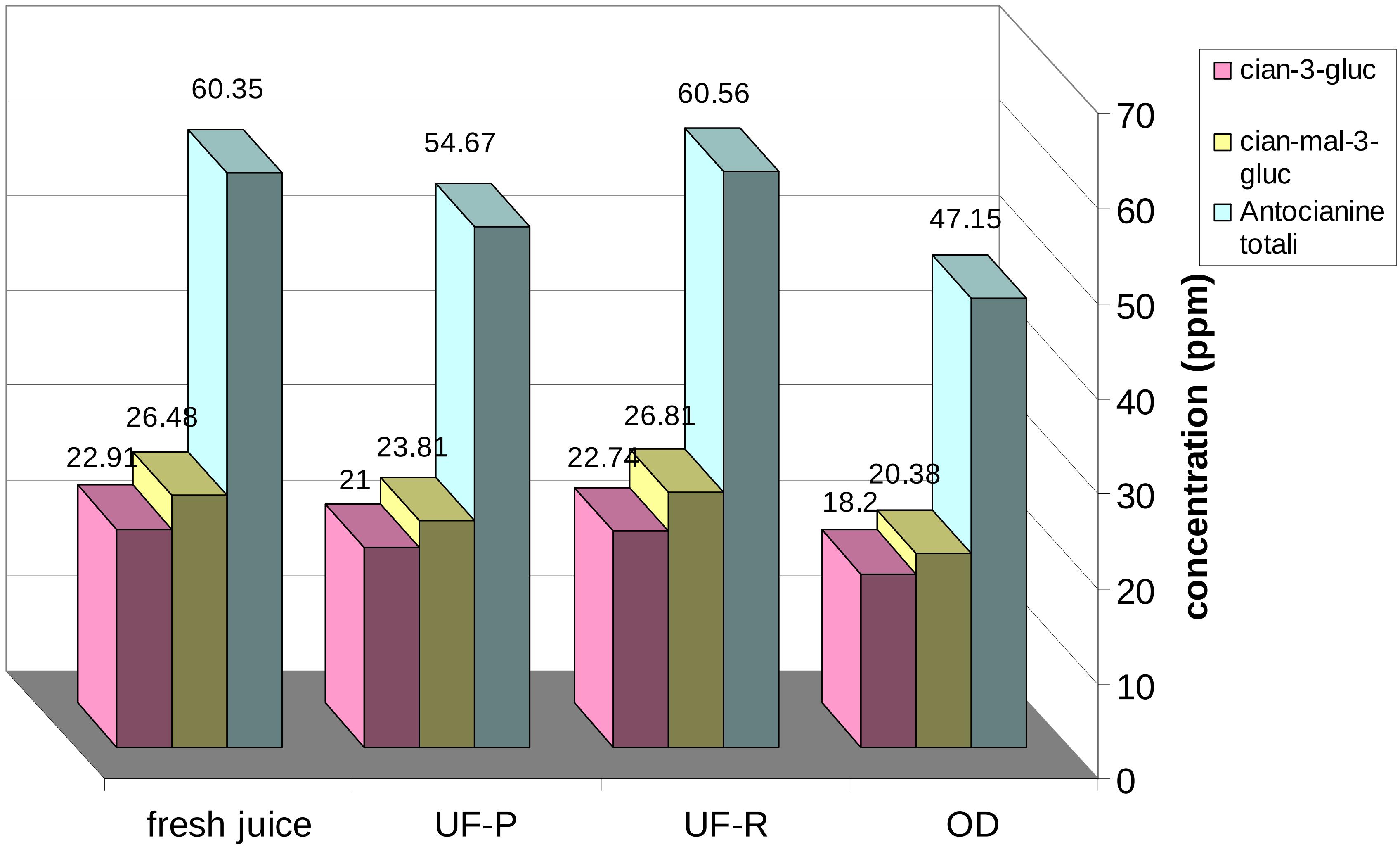
Anthocyanins in samples of blood orange juice treated by membrane processes



UF and OD permit to preserve the TAA of the juice also in highly concentrated samples (61 °Brix). Slight reductions were observed for the ascorbic acid and anthocyanins whereas the other components remained practically unchanged (hydroxycinnamic acids and flavonoids). On the contrary, a very high degradation of these components was observed in the thermal concentrated juice.

The juice concentrated with the proposed membrane technology retain its bright red colour and large part of its pleasant aroma, which is on the contrary completely lost during thermal concentration.

Thus, this product is more similar to a fresh orange juice, being aroma, colour and natural antioxidants better preserved during concentration.

Integrated membrane processes for clarification and concentration of kiwifruit juice

Research activities concerning the clarification and concentration of kiwifruit juice are in progress. **Ultrafiltration** *is studied for the clarification of the raw kiwifruit juice. Studies on the identification of suitable membranes, the optimal operating conditions and feed pretreatment are in progress.*

The UF permeate is concentrated by **osmotic distillation***. In this process the optimal operating conditions and the effect of these parameters on the evaporation fluxes are under studying.*

A **pervaporation** *step for the recovery of aroma compounds from UF or OD streams is under studying. An integrated membrane process for the production of concentrated kiwifruit juice with high nutritional value will be developed.*

Collaborations ⇒ Citrus Research Institute, Chinese Academy of Agricultural Sciences, Beibei, Chongqing, China

KIWIFRUIT PROPERTIES

- Kiwifruit originates from an indigenous plant of southern China (*Actinidia Chinensis*)
- Italy is the world's largest kiwi producer with a production of about 300,000 tons/year (33% of the world-wide production) and a cultivation area of 19,000 hectares distributed mainly in 4 regions (Latium, Emilia-Romagna, Piedmont and Apulia)
- Kiwifruit is the most nutrient dense of all fruits with an index of 16 (daily value/100 grams)
- It has impressive antioxidant capacity, containing a wealth of phytonutrients (carotenoids, lutein, phenolics, flavonoids and clorophyll
- Content in sodium and fat is very low (kiwifruit contain no cholesterol)

Kiwifruit offers benefits for specific health conditions

⇒ ***CANCER*** (antimutagenic component helping to prevent genetic mutations)

⇒ ***DEPRESSION*** (inositol as a precursor of an intracellular second messenger system, can
be beneficial in the treatment of depression)

⇒ ***DIABETES*** (inositol may play a positive role in regulating diabetes)

⇒ ***EYE HEALTH / MACULAR DEGENERATION*** (kiwifruit is rich in phytochemicals, xanthophylls and lutein that have an important role in the prevention of macular degeneration)

⇒ ***HYPERTENSION*** (the sodium-to-potassium ratio is extremely favorable in kiwifruit)

⇒ ***IMMUNITY*** (kiwifruit is considered an immune booster due to its high level of vitamin C)

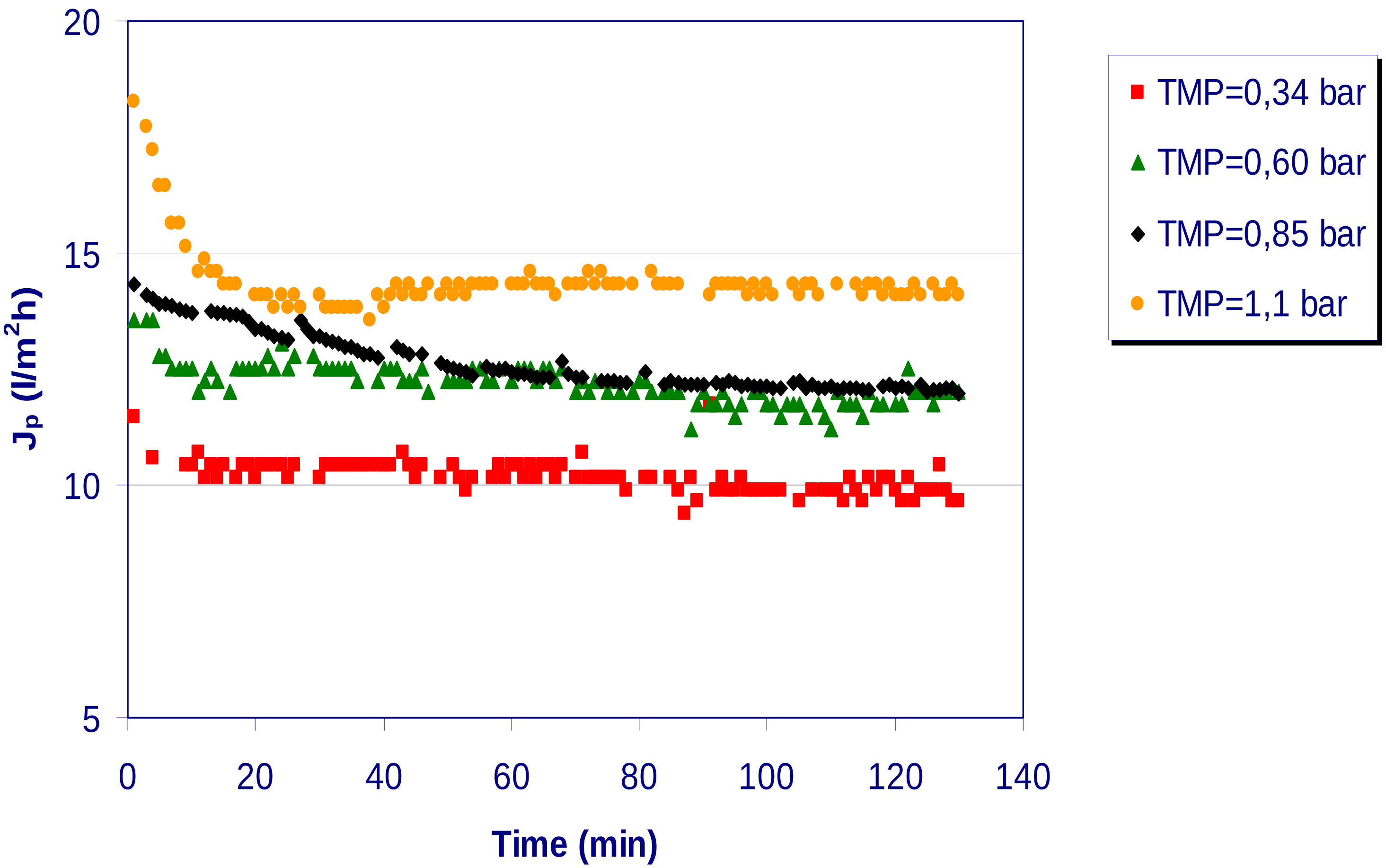
⇒ ***PHYSICAL FITNESS*** (kiwifruit contains a wide range of minerals essential for replenishing)

⇒ ***STRESS REDUCTION*** (high level of serotonin)

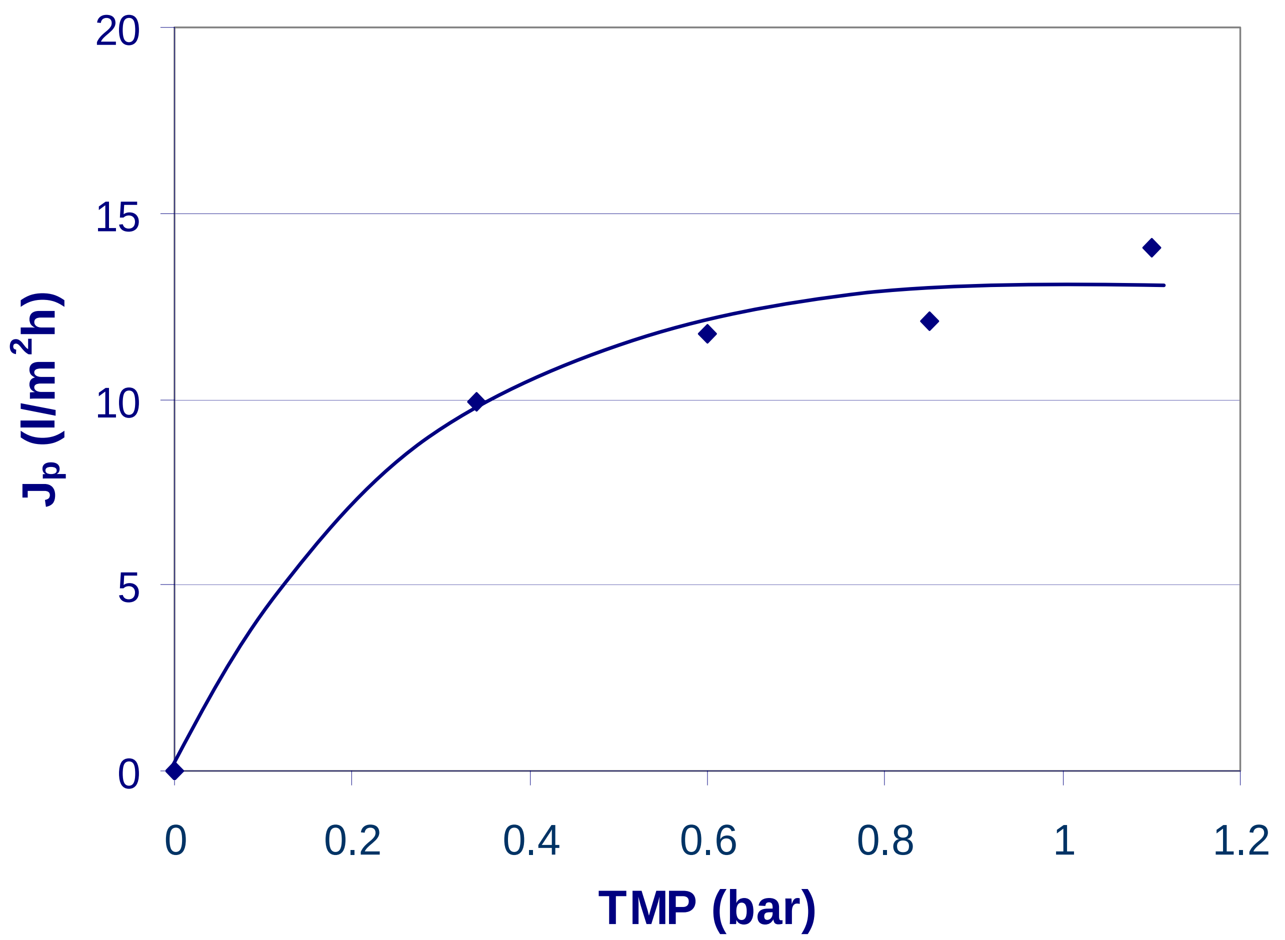
⇒ ***WEIGHT CONTROL*** (kiwifruit contains the best balance of nutrients per calorie)

- For all the above mentioned characteristics and other important properties (resistance during preservation, sensory characteristics, etc.) *kiwifruits have a great potential for industrial exploitation*

- The production of concentrated fruit juices is of interest at industrial level since it reduces the storage volumes (reducing transport and storage costs) and facilitates preservation

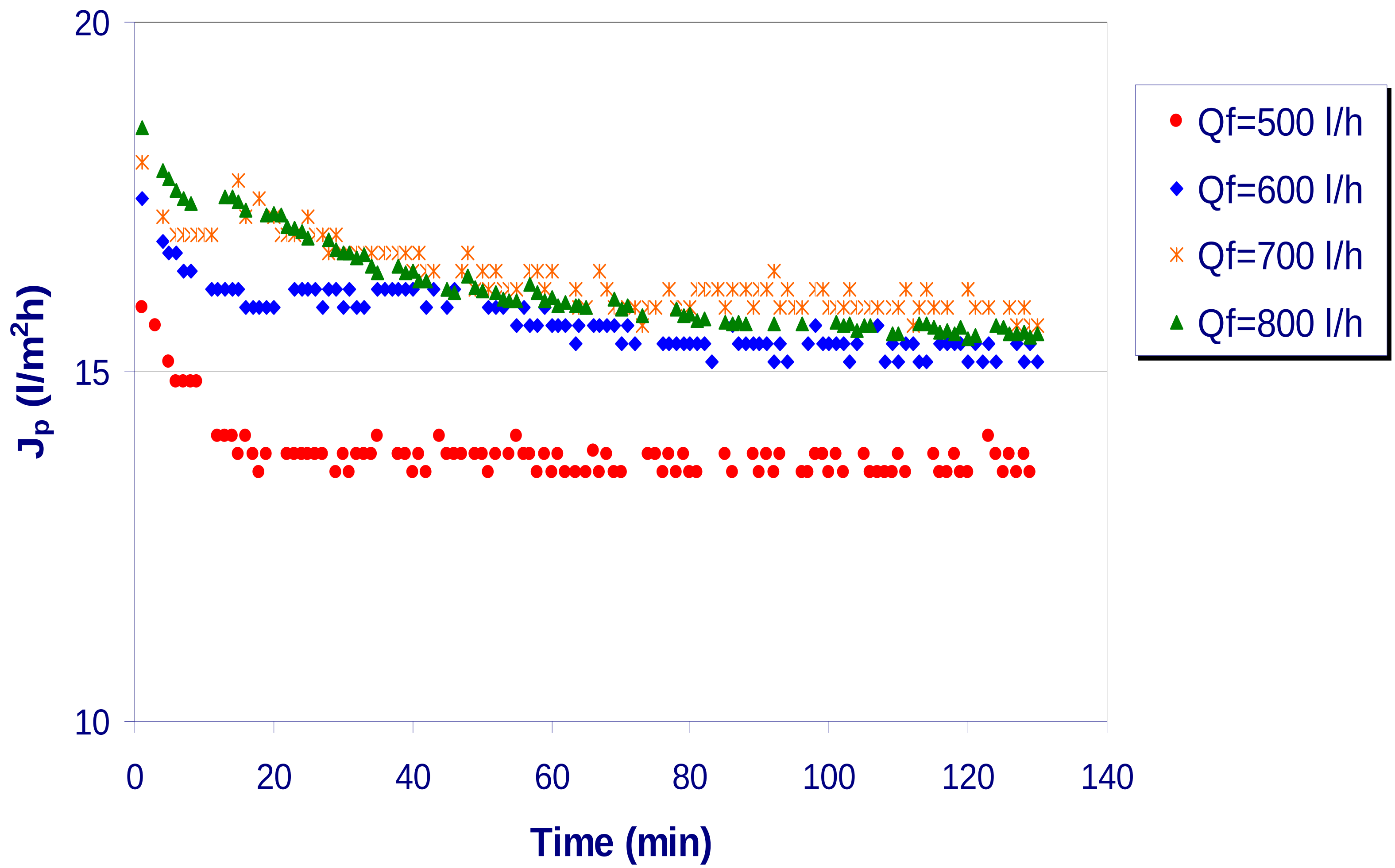


UF of kiwifruit juice. Time course of permeate flux at different TMP
(T = 25 °C; Qf = 800 l/h)



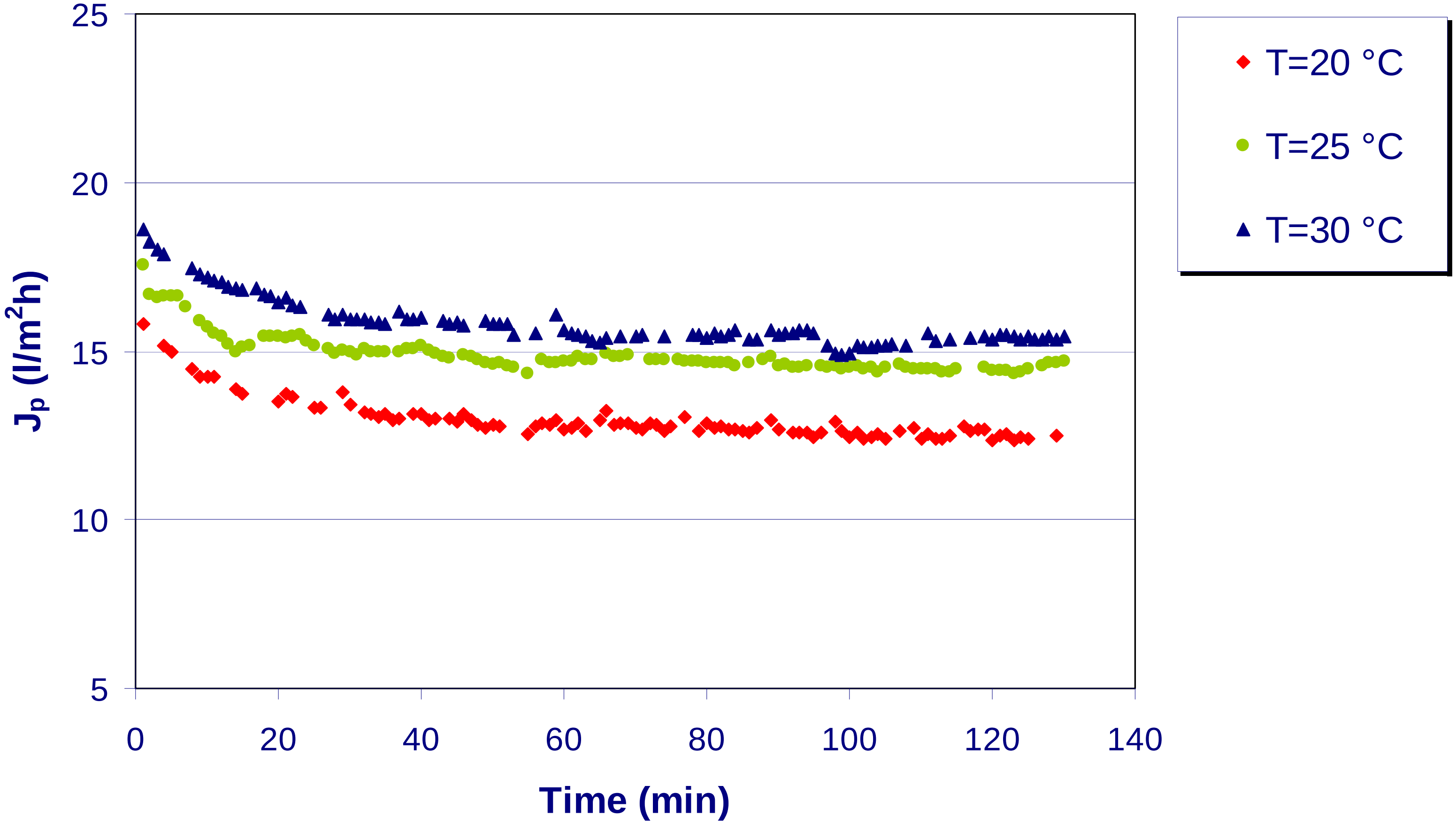
UF of kiwifruit juice. Permeate flux vs. TMP

(T = 25 °C; Qf = 500 l/h)

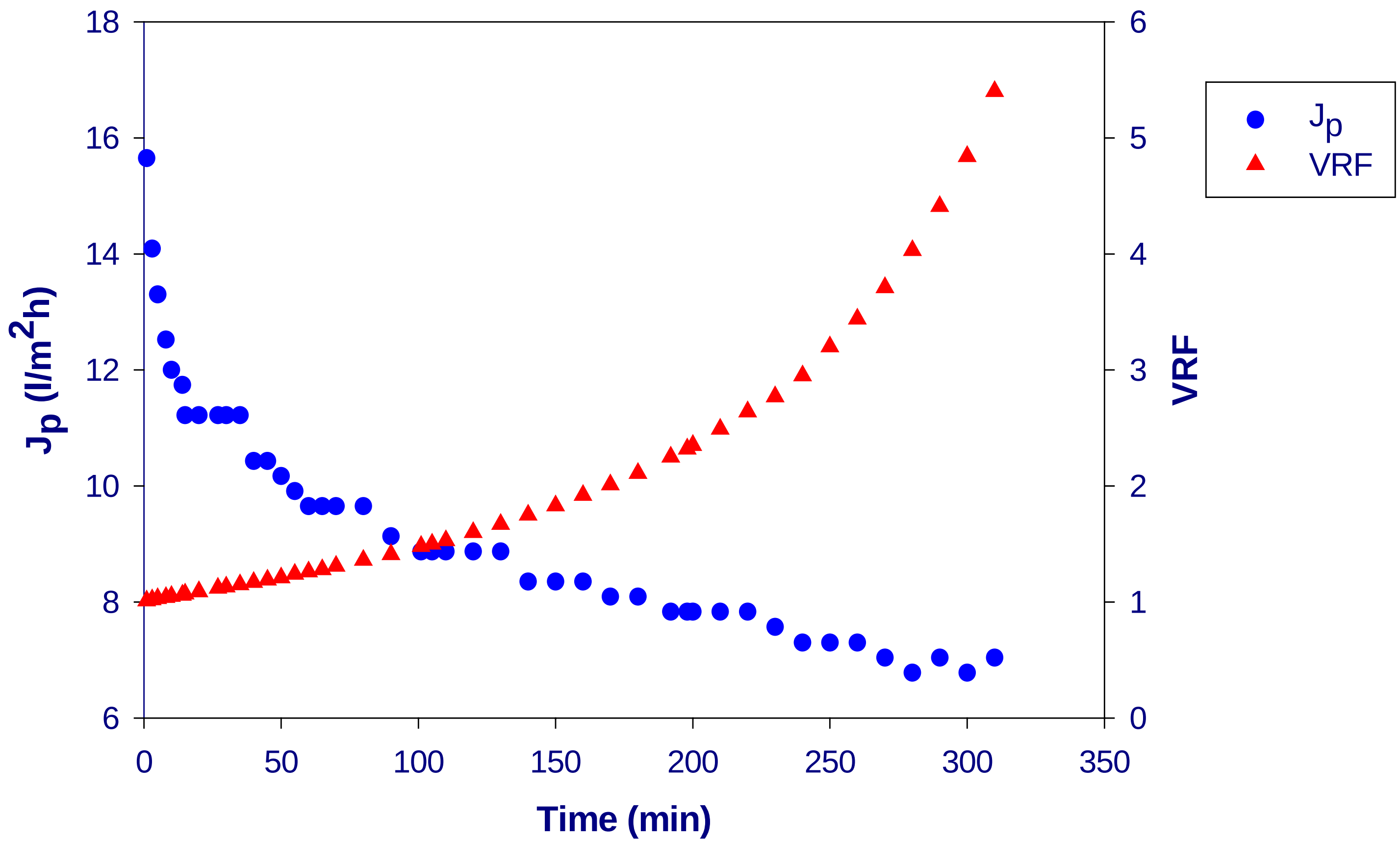


Time course of permeate flux at different axial feed flow rates

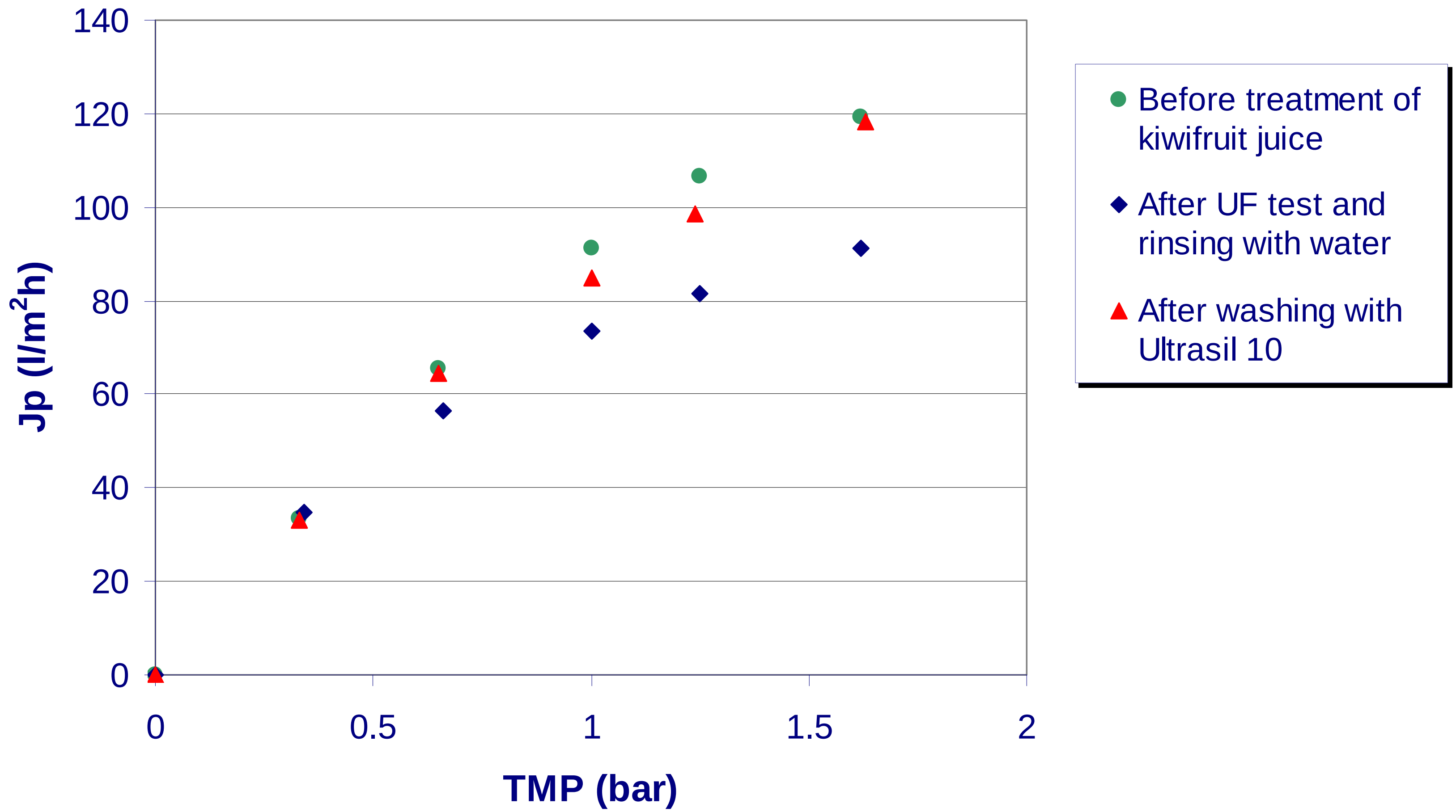
(TMP = 0.85 bar; T = 25 °C)



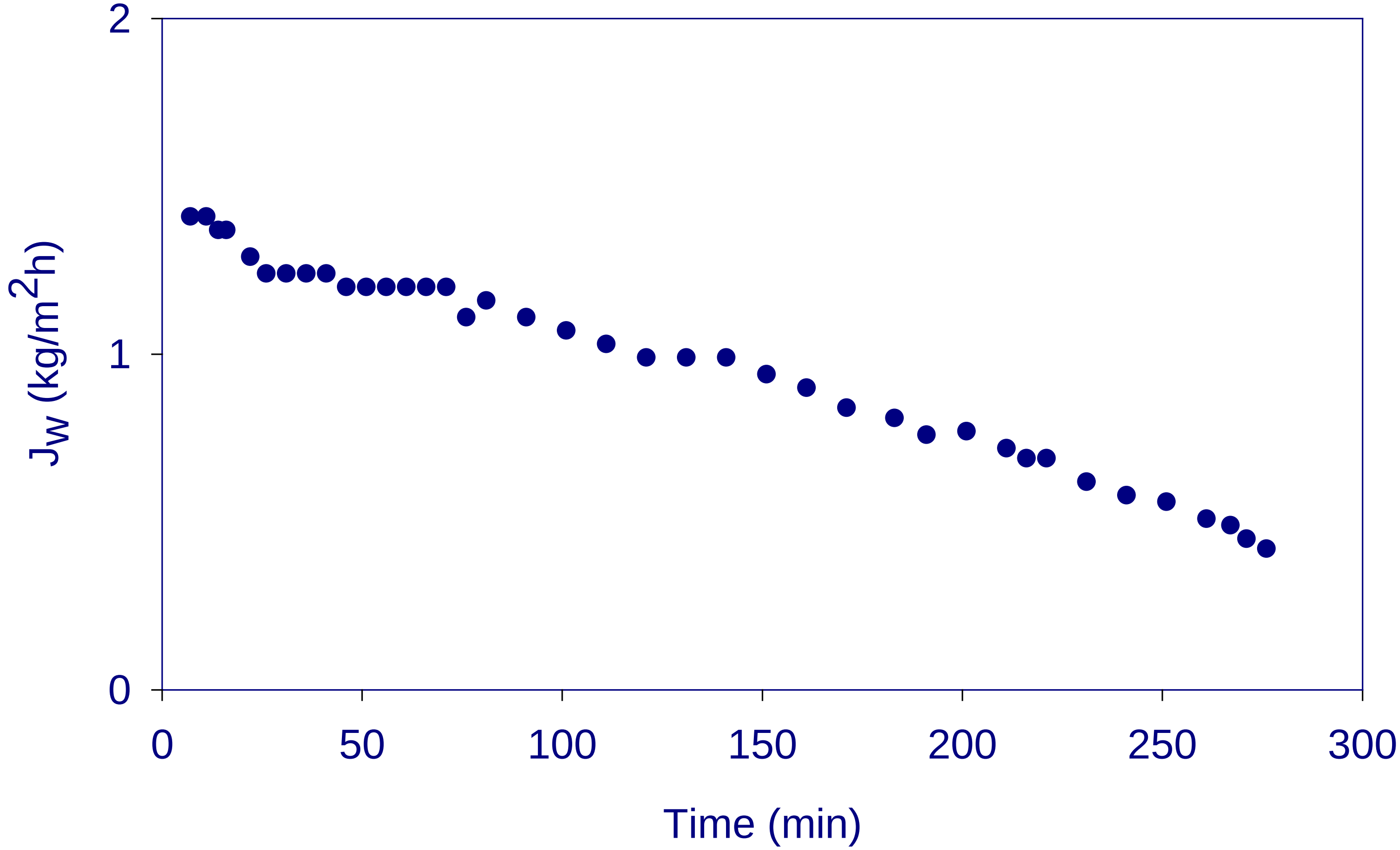
UF of kiwifruit juice. Time course of permeate flux at different temperatures
(TMP = 0.85 bar; Qf = 800 l/h)



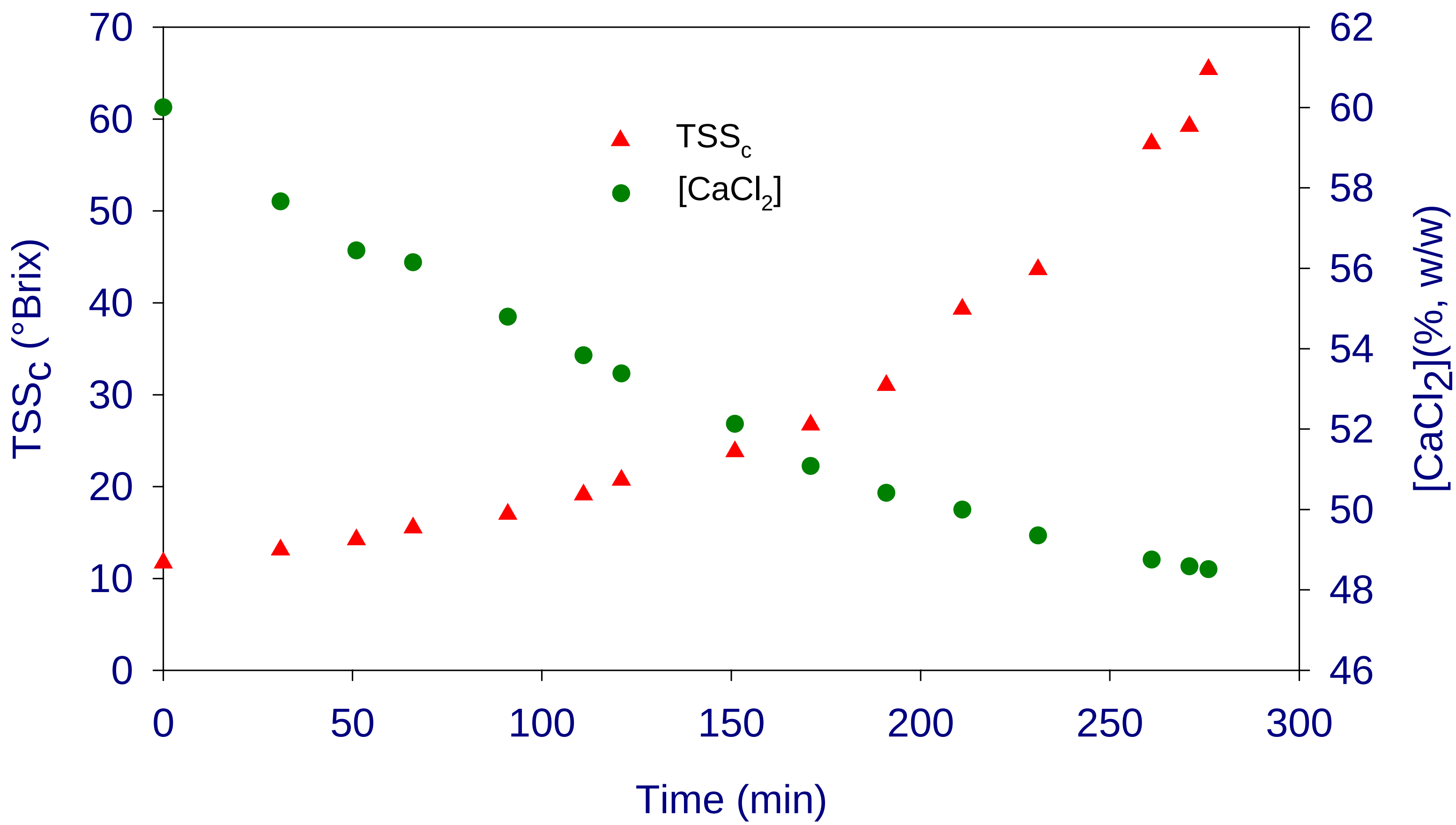
UF of kiwifruit juice. Time course of permeate flux and VRF
(batch concentration mode; T = 25 °C; TMP = 0.85 bar; Qf = 800 l/h)



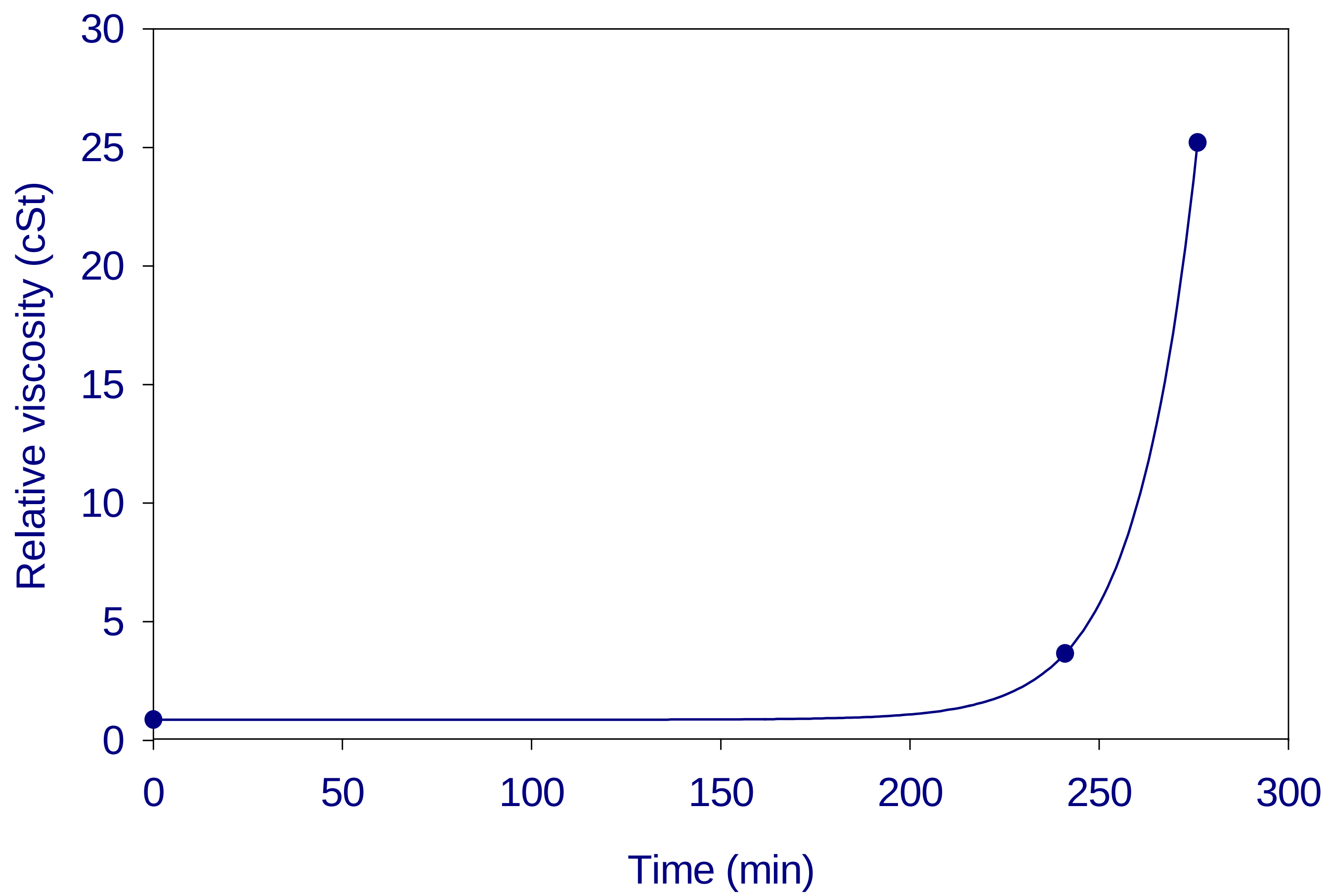
Measurement of the water flux in UF membrane module



OD of clarified kiwifruit juice. Time course of evaporation flux



OD of clarified kiwifruit juice. Time course of TSS and brine concentration



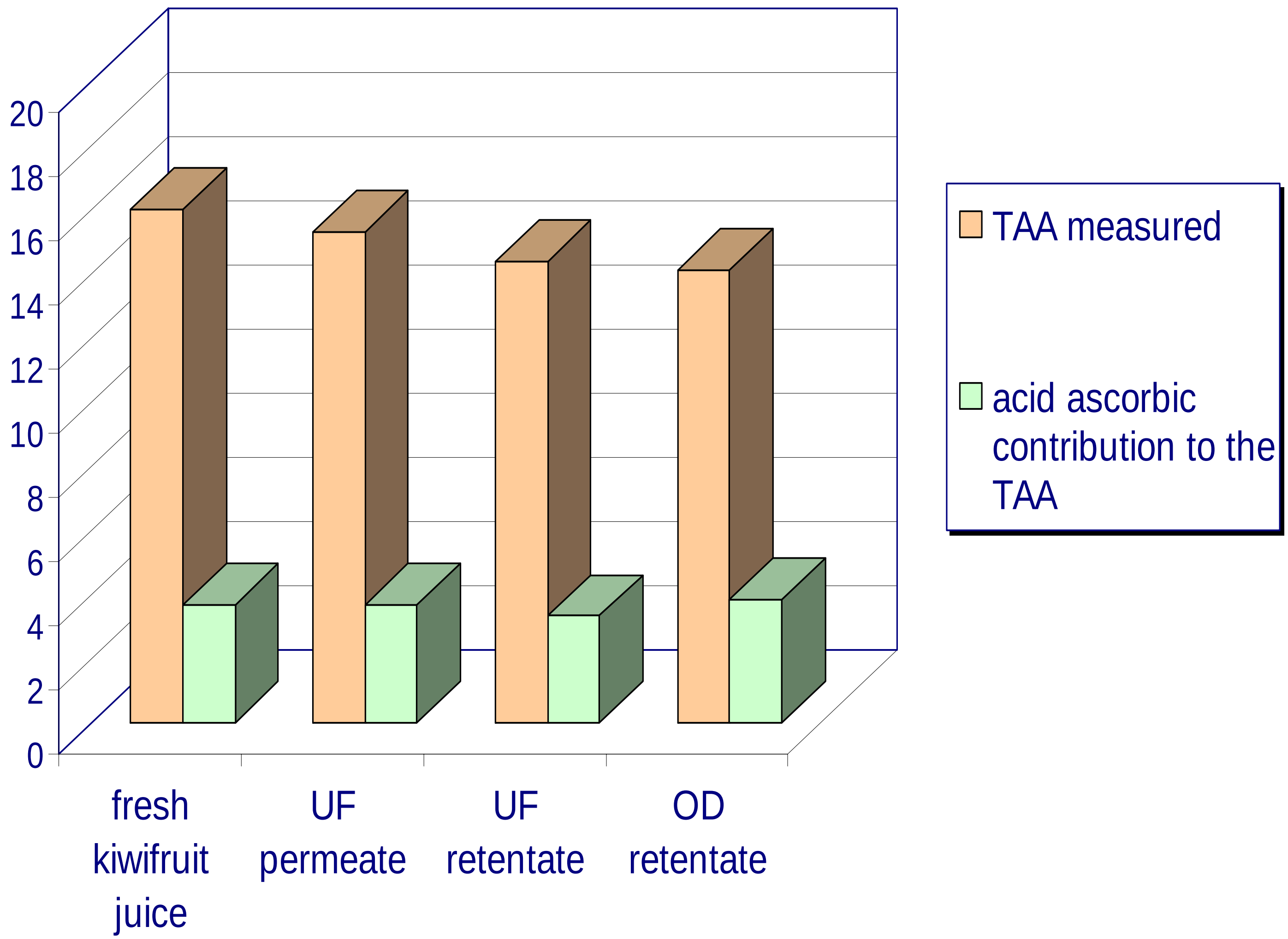
OD of clarified kiwifruit juice. Time course of the viscosity

At low TSS evaporation flux seems to depend mainly on brine concentration. At concentration values higher than 40 °Brix evaporation rate depends mainly on juice viscosity (viscous polarization) and, consequently, on juice concentration.

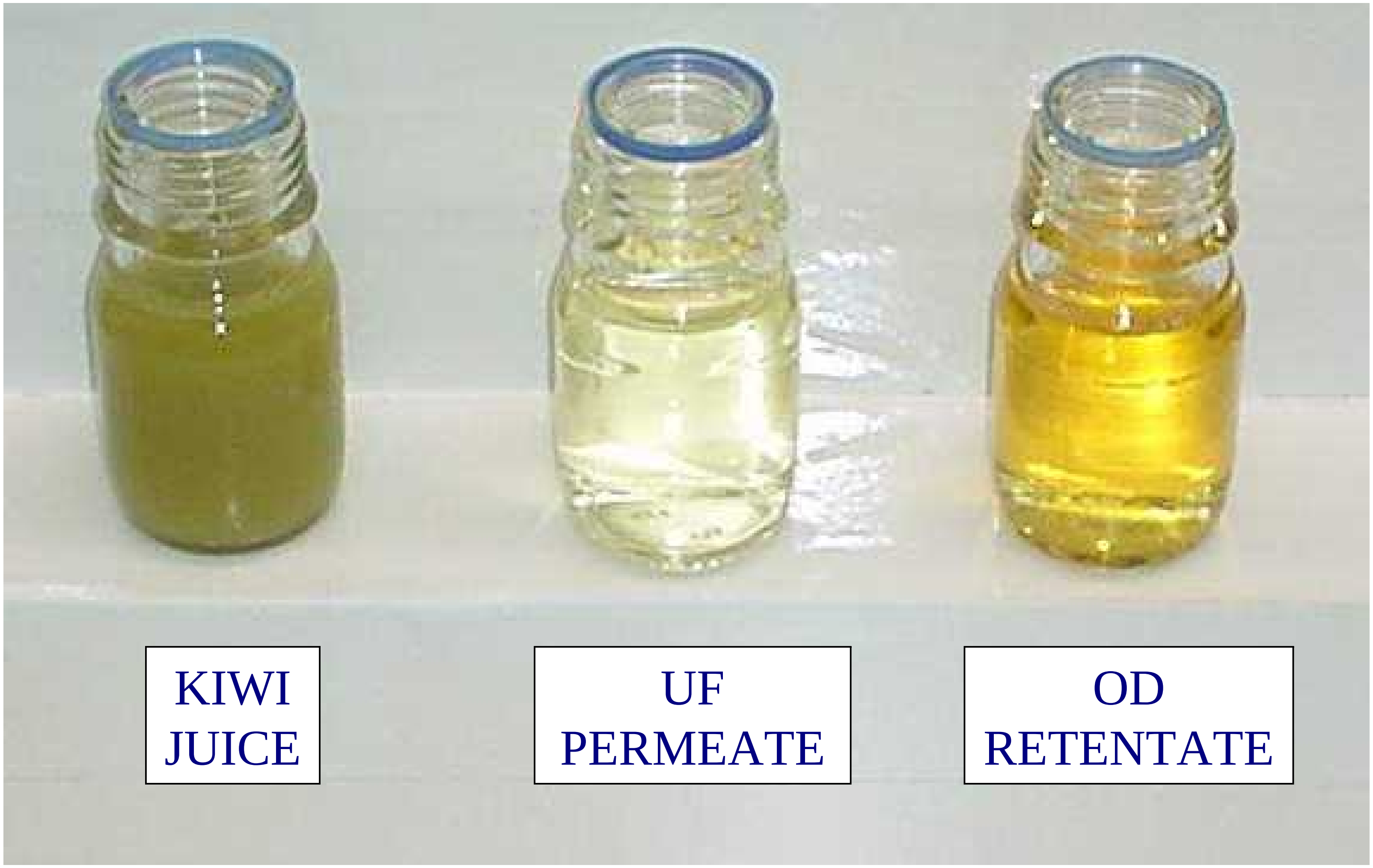
Analytical measurements on samples coming from treatment of kiwifruit juice by UF and OD

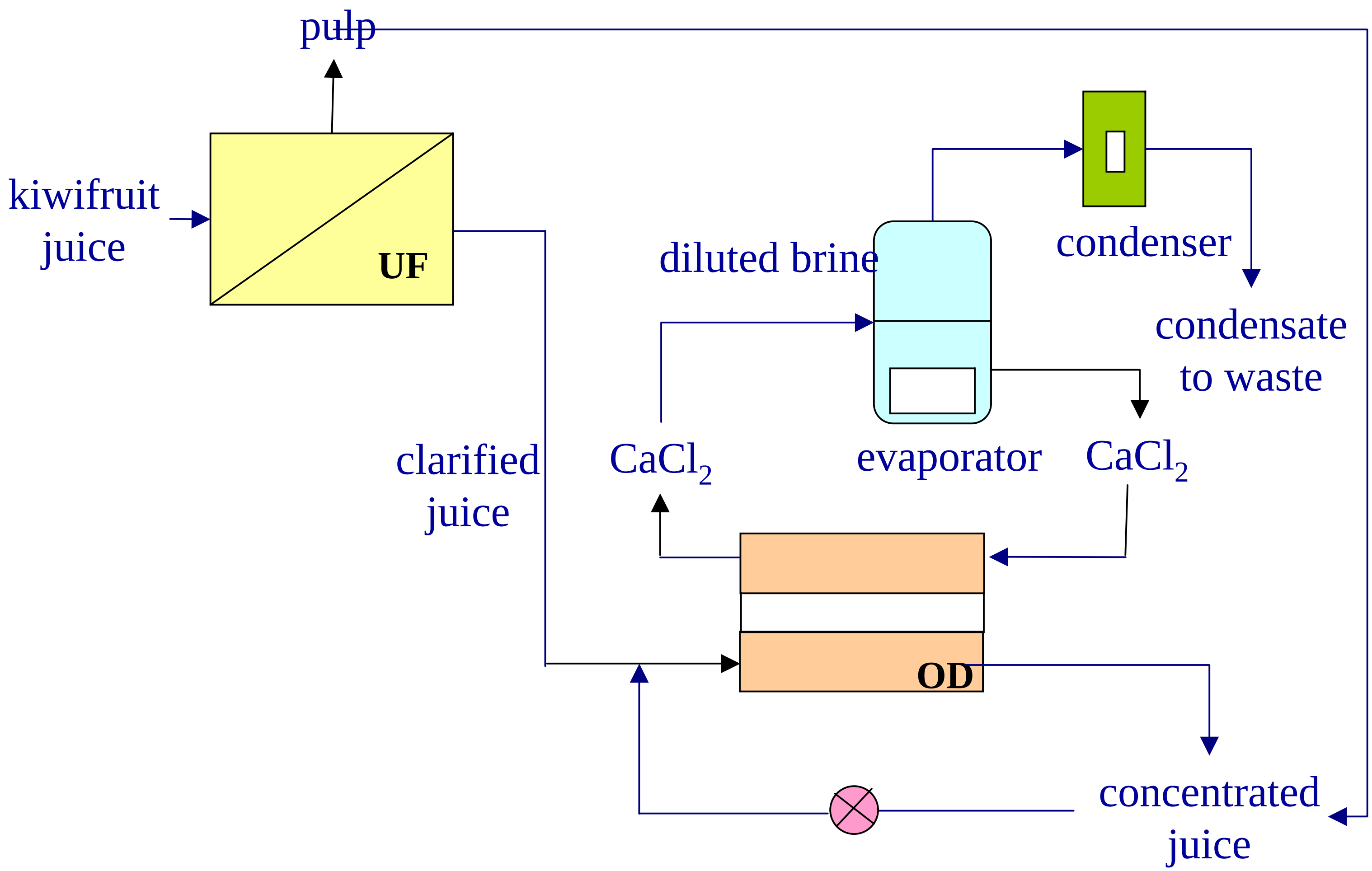
Sample	*Total Soluble Solids (°Brix)*	*pH*	*Suspended Solids (% w/w)*	*Turbidity (NTU)*	*Viscosity (cSt)*	*Ascorbic acid* (mg/100 g)*	*TAA* (mm trolox)*
Fresh juice	12.5	3.58	5.16	299.5	1.30	69.6	16.0
UF permeate	12.1	3.60	0	0	0.87	69.3	15.3
UF retentate	13.5	3.58	51.5	1336.7	-	62.8	15.6
OD retentate	65.8	3.40	0	0	25.2	69.6	14.1

** values referred to 12.5 °Brix*



Total antioxidant activity in samples of kiwifruit juice coming from UF and OD processes


KIWI
JUICE
UF
PERMEATE
OD
RETENTATE



Integrated membrane process for the production of concentrated kiwifruit juice

CONCLUSIONS

- The introduction of membrane technologies in the industrial transformation cycle of the fruit juices is one of the technological answers to the problem of the **production of juices with high quality**, **natural fresh taste** and **additive-free**

- The possibility to realise integrated membrane systems in which all the steps of the productive cycle are based on molecular membrane separations can be considered a valid approach for a **sustainable industrial growth** within the **process intensification** strategy. The aim of this strategy is to introduce in the productive cycles new technologies characterised by **low encumbrance volume**, **advanced levels of automatisation capacity**, **modularity**, **remote control**, **reduced energy consumption**

- The new membrane-based integrated process for the concentration of blood orange juice is very efficient in **preserving the antioxidant activity** of the final product even at high concentration (60°Bx).

- The blood orange concentrated juice retains its **bright red colour** and its **pleasant aroma**, which is on the contrary completely lost during thermal concentration so this product is more similar to a fresh orange juice

- The different membrane treatments were performed on different pilot plants, with freezing and defreezing steps to preserve the juice. So that even better results could be obtained on a **fully integrated pilot plant**

- Advantages of the proposed integrated membrane system are in terms of: **reduction of clarification times**, **simplification of the clarification process**, **increasing of clarified juice volumes**, **possibility to operate at room temperature** preserving the juices's freshness, aroma and nutritional value, **improvement of the quality of the final product** and **improvement of the productive processes**