



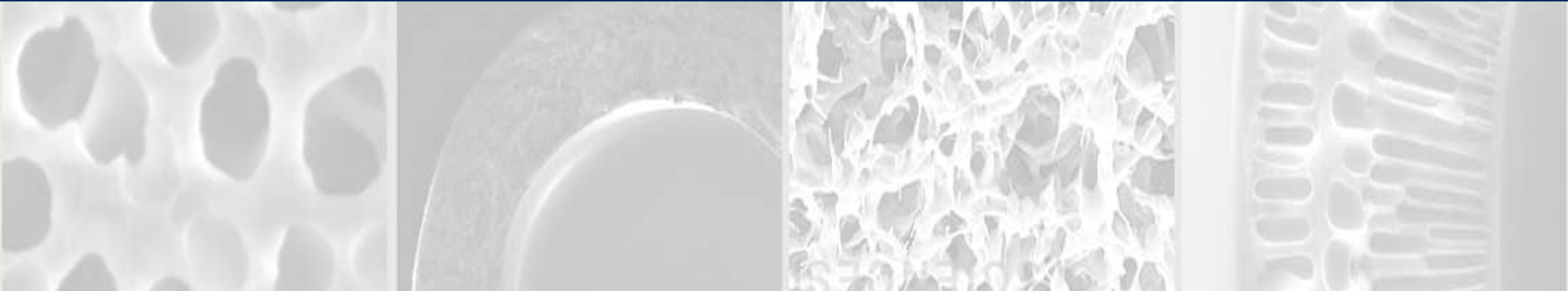
Istituto per la Tecnologia  
delle Membrane  
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Palermo, 16-17 maggio 2024

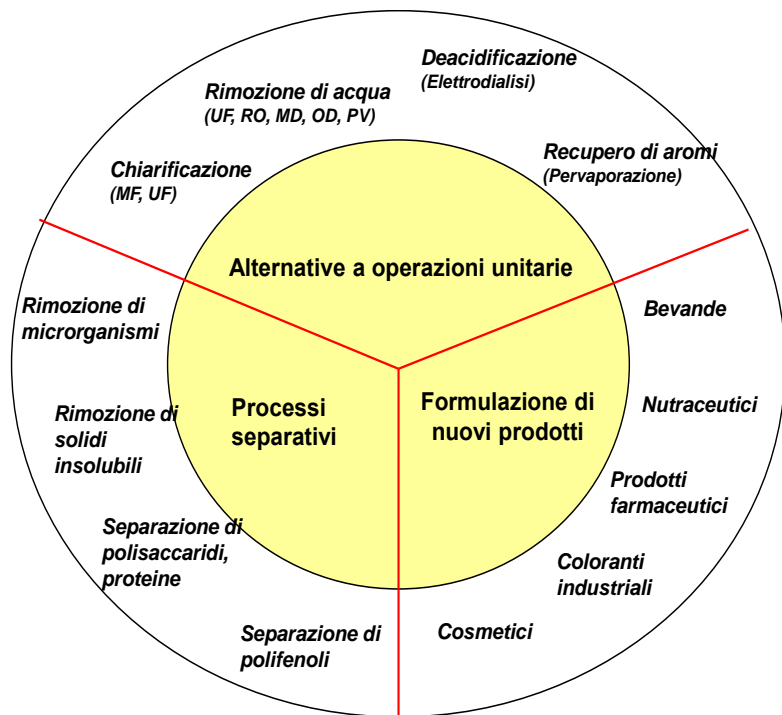


# Recupero di polifenoli da sottoprodotti della produzione agroalimentare mediante sistemi a membrana

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# Processi a membrana

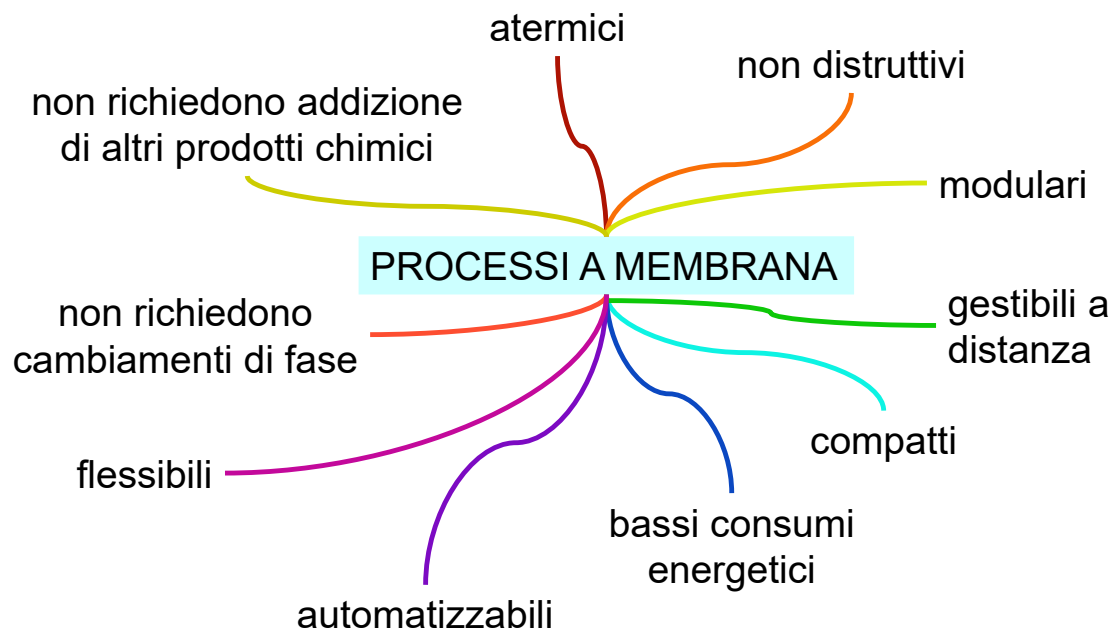


Estimation of global market of membranes in food and beverage processing in 2024



**US\$ 8.26 Billion**

growing at a CAGR of 6.8% over the forecast period (2019–2024)



## Miglioramento della qualità alimentare

chiarificazione e concentrazione di succhi e bevande, innovazione nell'industria lattiero-casearia ed enologica, rimozione di pesticidi

## Biorefinery

separazione e purificazione di sostanze ad alto valore aggiunto dagli scarti della produzione alimentare

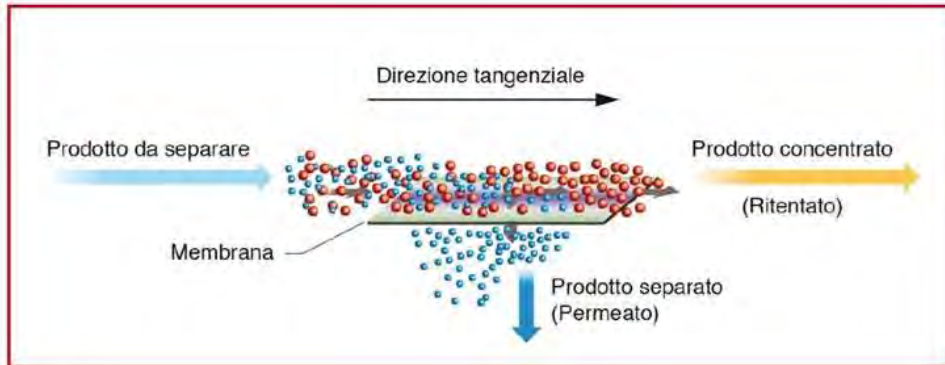
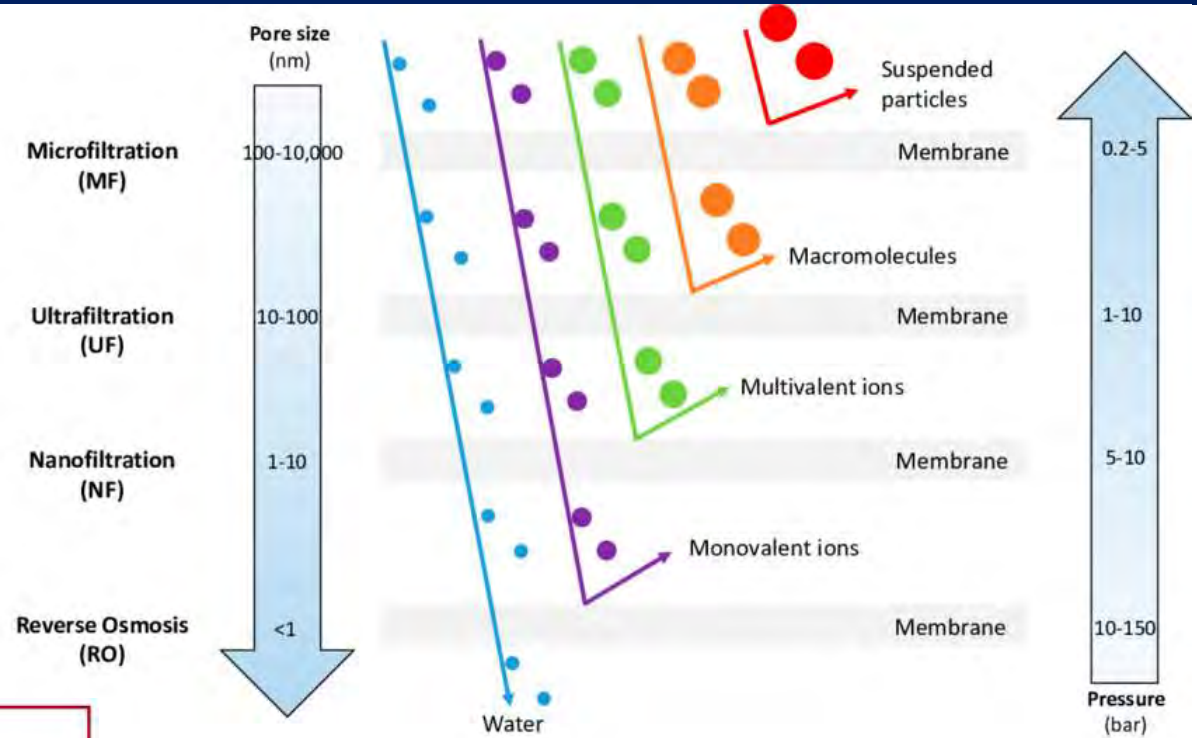
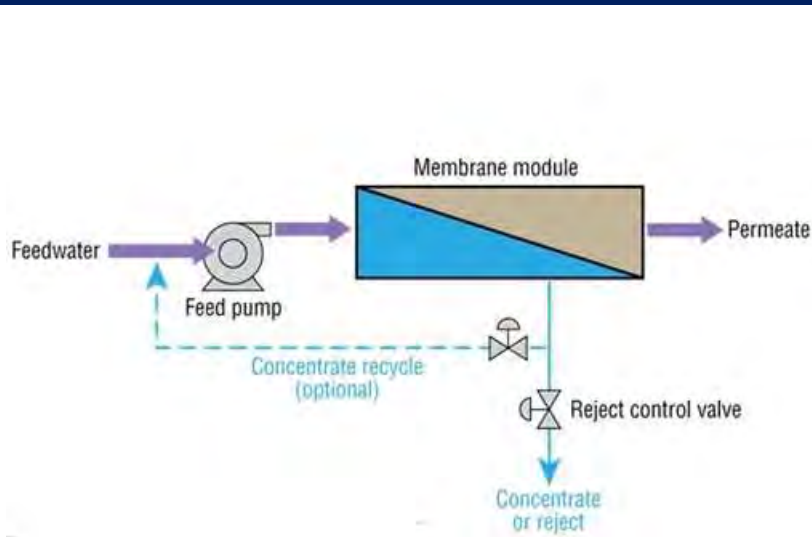
## Efficiente gestione della risorsa idrica

standardizzazione della qualità dell'acqua nelle fasi di approvvigionamento e smaltimento

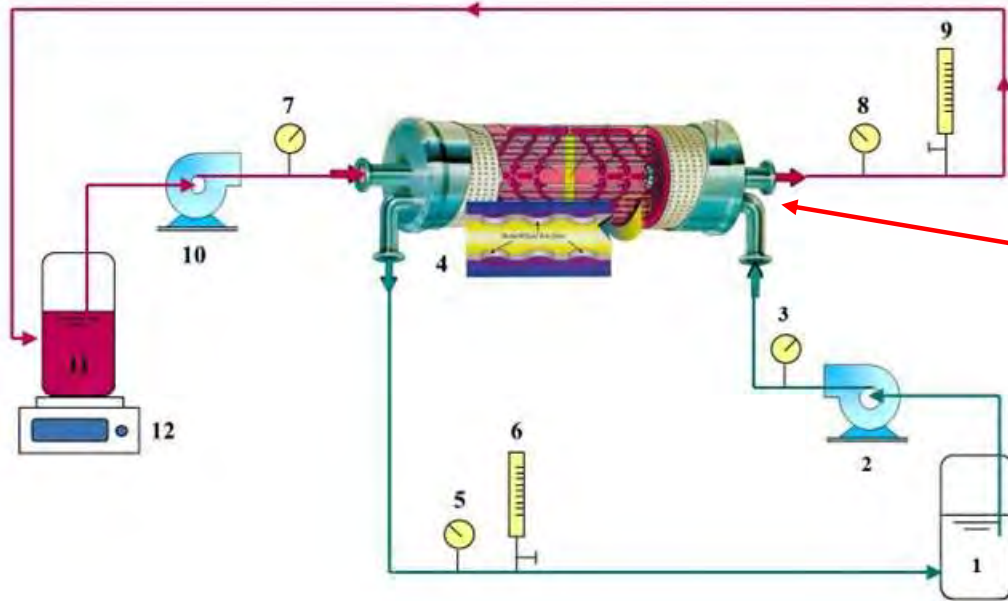
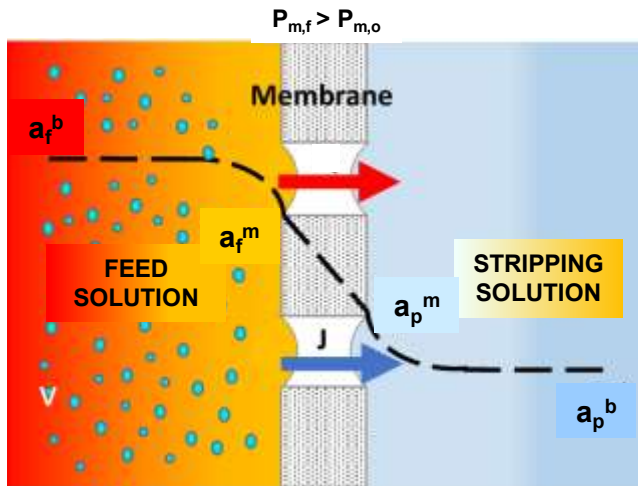
## Razionalizzazione del ciclo produttivo

innovazione dei cicli di trasformazione, valorizzazione della produzione e trattamento dei sottoprodotti

# Pressure-driven membrane operations



# Distillazione osmotica

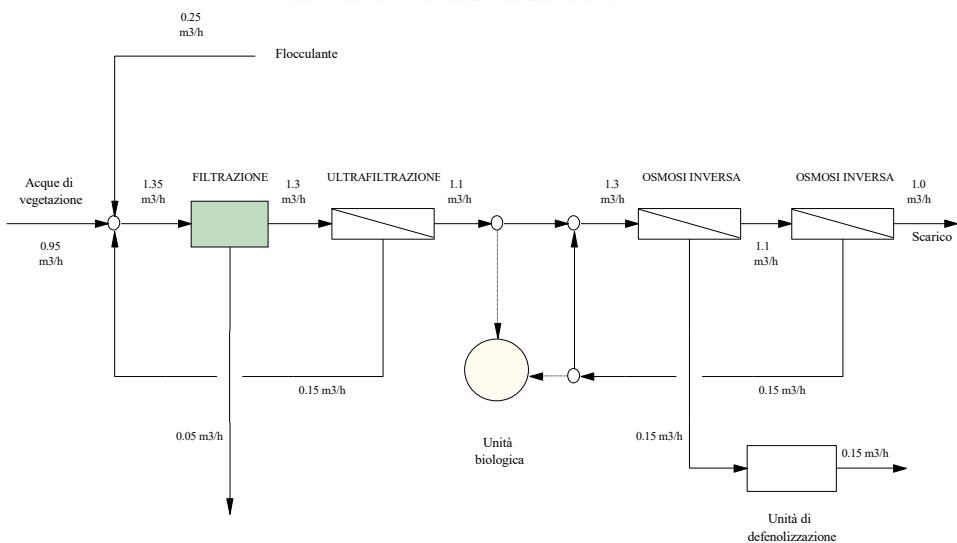


# Acque di vegetazione

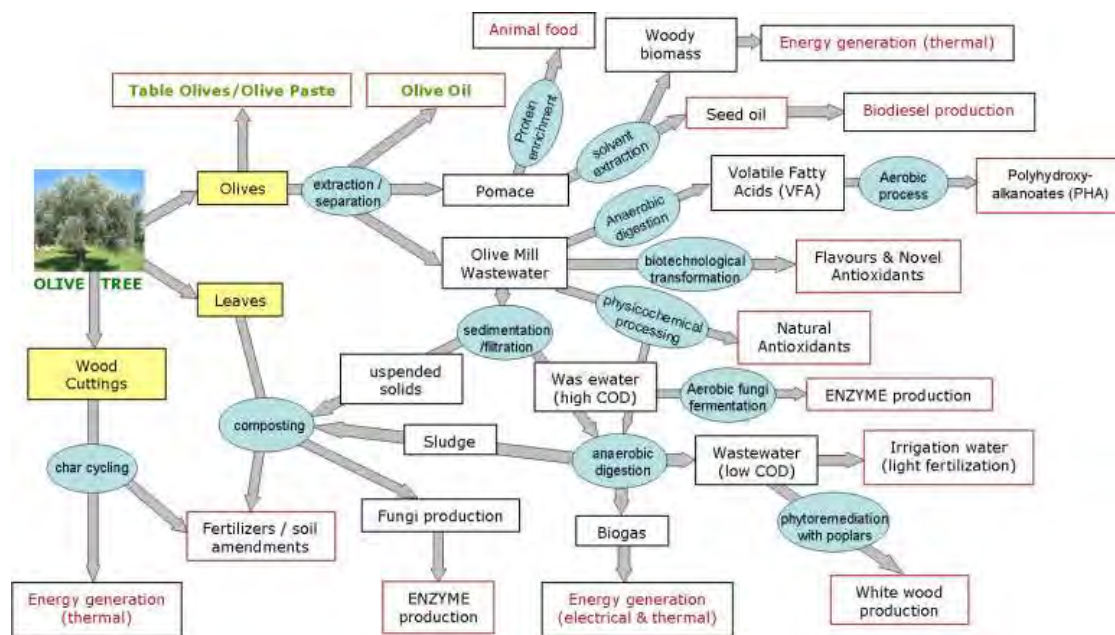


100 kg olive > fino a 110 kg di AV  
 $BOD_5$  1 m<sup>3</sup> = 100–200 m<sup>3</sup> di acque reflue urbane

	AV	Limiti per smaltimento in fogna (D. Lgs. 152/2006)
pH	4-5	5.5-9.5
COD	100-190 g/L	500 mg/L
BOD <sub>5</sub>	50-140 g/L	250 mg/L
Fenoli	3-10 g/L	1 mg/L

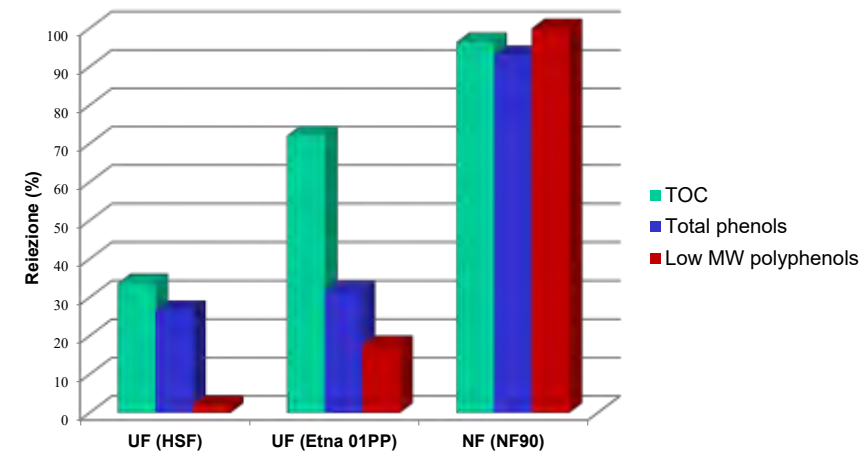
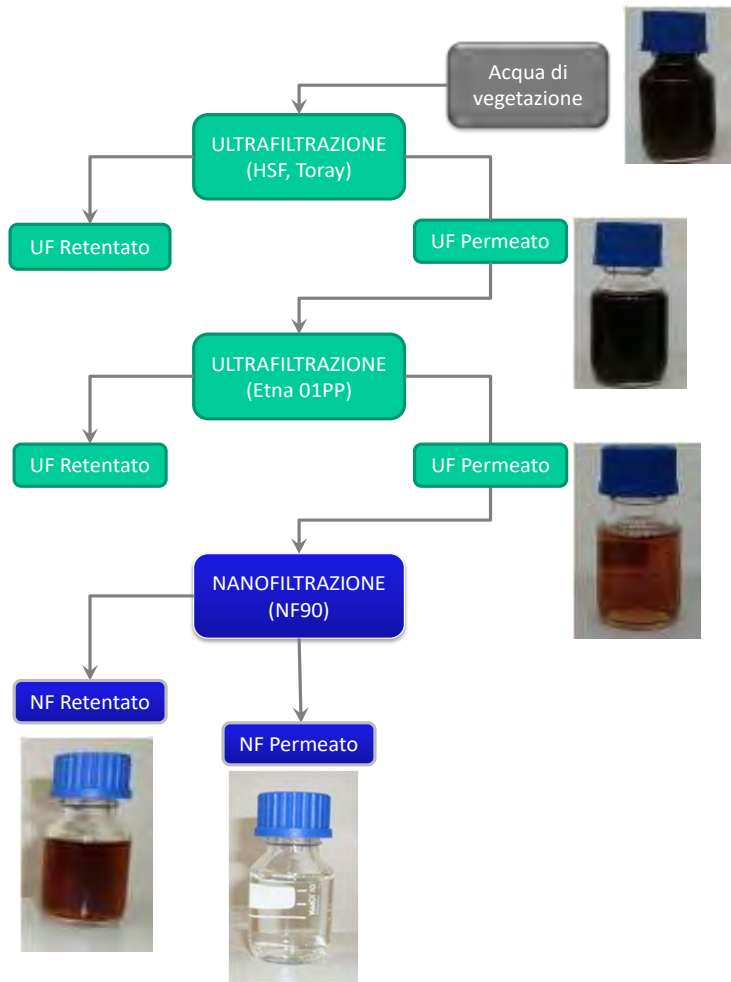


Schematic of an integrated process UF/RO for the treatment of OMWs realised in Spain by Separem (Biella, Italy)



The 'olive tree biorefinery' with the associated OMW processes, by-products and waste valorisation and disposal (Federici et al., *J Chem Technol Biotechnol*, 2009, 84: 895–900)

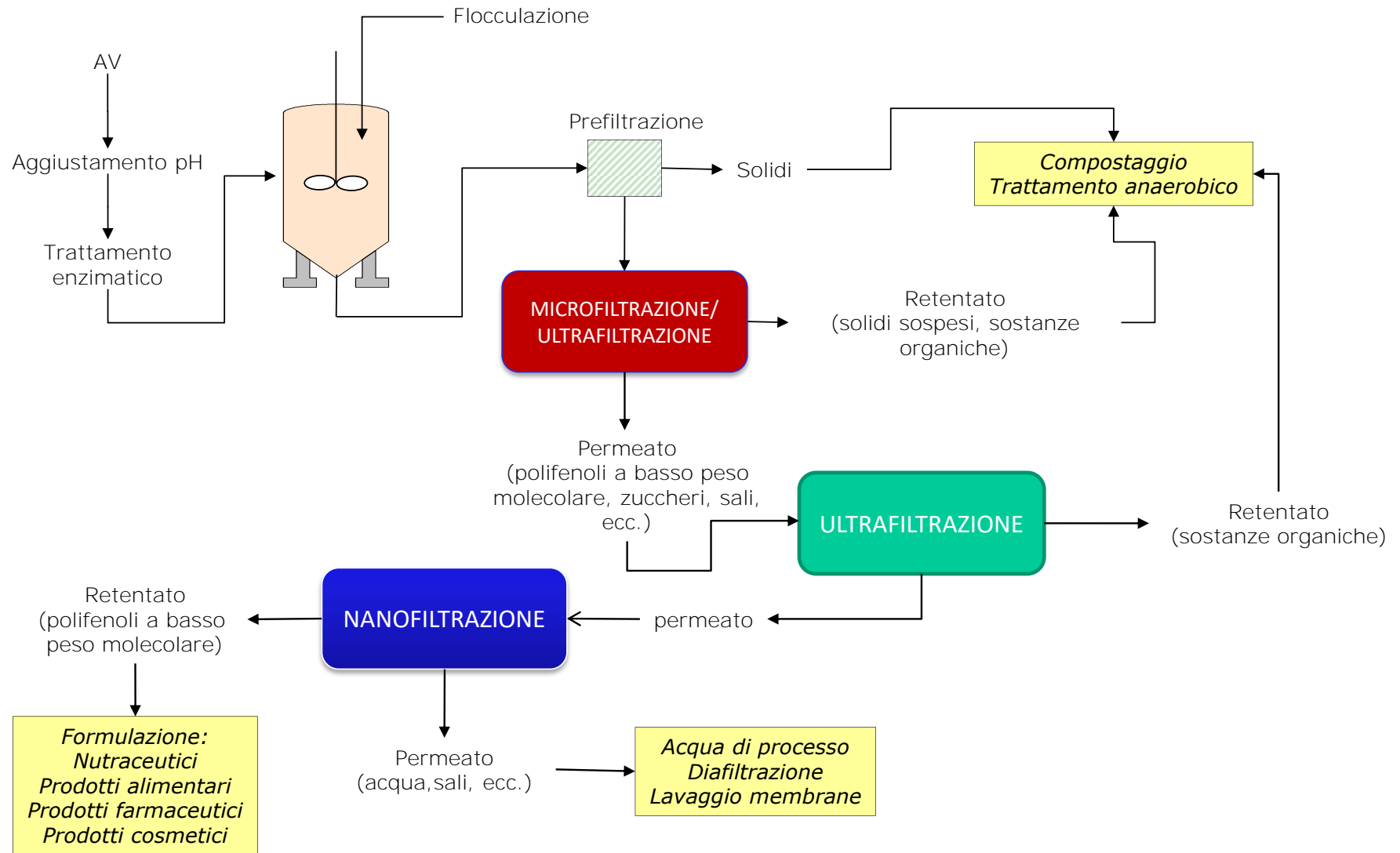
# Acque di vegetazione: sistema integrato MF-UF-NF



Retenzioni del TOC, fenoli totali e polifenoli a basso peso molecolare misurate in campioni di AV trattate mediante processo integrato a membrana (UF-UF-NF)

Processo	Campione	Idrossitiroso (mg/L)	Acido protocatecuico (mg/L)	Catecolo (mg/L)	Tiroso (mg/L)	Acido caffeico (mg/L)	Acido p- cumarico (mg/L)	TOTALE (mg/L)	R (%)
UF (HFS)	Feed	3.8	25	7.5	39	5	1	81.3	
	Permeato	3.72	24	7.12	38.74	4.98	0.97	79.53	2.1
	Retentato	3.9	24.5	7.2	39.6	5.2	0.9	81.3	
UF (Etna 01PP)	Feed	3.5	27	6	34.2	4	0.8	75.5	
	Permeato	3	20.6	5	30	3	0.6	62.2	17.6
	Retentato	3.8	26	6.2	36	4.4	1	77.4	
NF (NF 90)	Feed	3.2	22	5.5	31	3.2	0.7	65.6	
	Permeato	-	-	-	-	-	-	-	100
	Retentato	4	30	7.5	40	3.7	1	86.2	

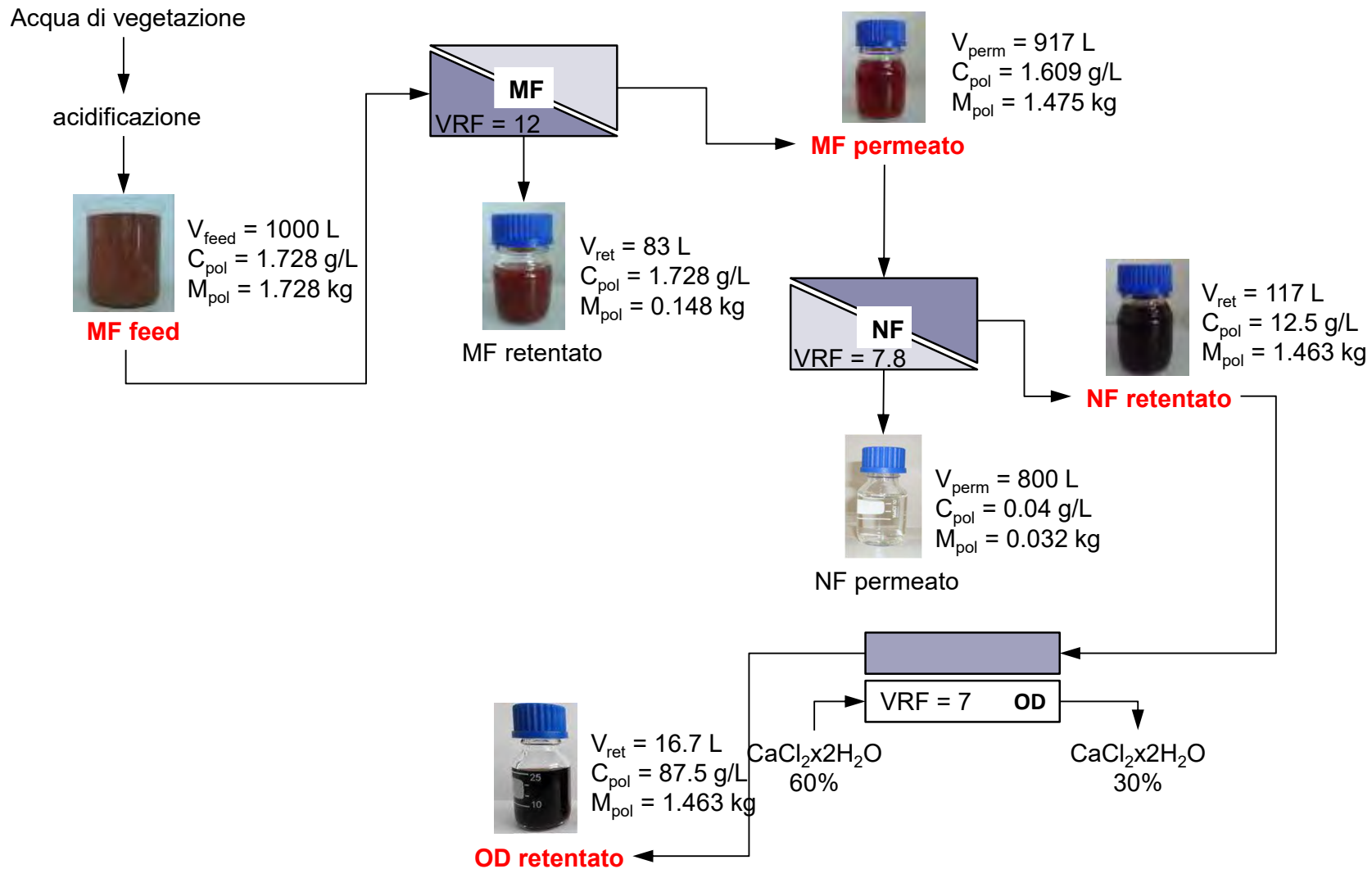
# Acque di vegetazione: sistema integrato MF-UF-NF



# Prototipo UF-NF acque di vegetazione



# Acque di vegetazione: sistema integrato MF-NF-OD



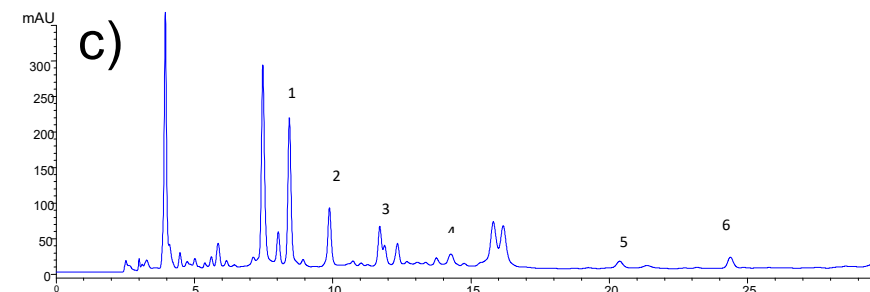
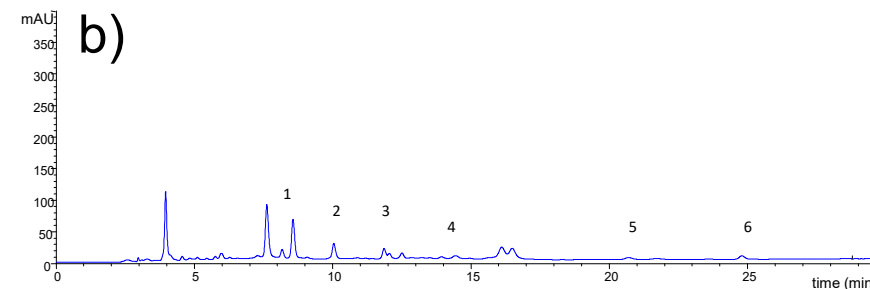
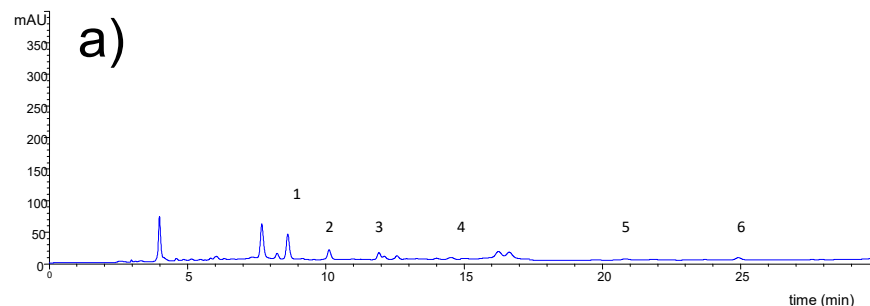
# Acque di vegetazione: sistema integrato MF-NF-OD

Low molecular weight biophenols detected in samples of OMWWs processed with NF90 membrane

	Feed (mg/L)	Permeate (mg/L)	Rejection (%)
Cathecol	36.7±1.8	1.9±0.1	94.9
Hydroxytyrosol	44.4±2.2	7.7±0.4	82.7
Tyrosol	195.9±9.8	17.7±0.9	90.9
Caffeic acid	4.9±0.2	0.080±0.004	98.4
Vanillic acid	0.56±0.03	0.030±0.015	94.7

Low molecular weight biophenols detected in samples of NF retentate processed by OD

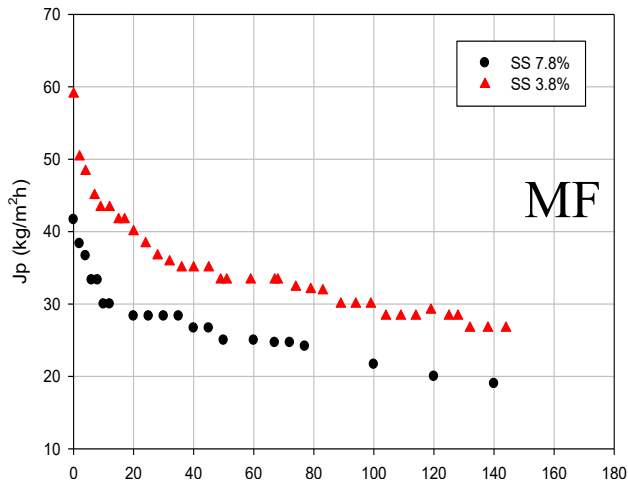
	Feed (mg/L)	Retentate (mg/L)
Cathecol	54.1±2.7	362.67±18.13
Hydroxytyrosol	60.7±3.0	406.89±20.34
Tyrosol	266.4±13.3	1785.08±89.25
Caffeic acid	7.3±0.4	49.04±2.45
Vanillic acid	1.00±0.05	6.7±0.33



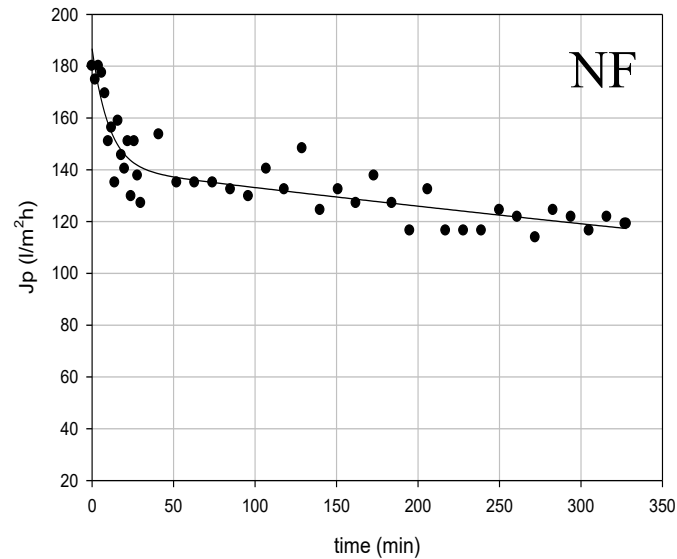
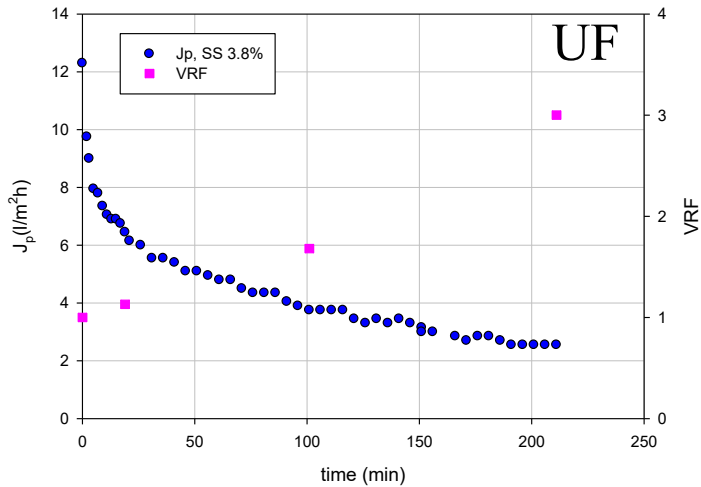
HPLC chromatograms of the polyphenols in OD retentate after a) 60 min, b) 120 min and c) 200 min.

1: Hydroxytyrosol; 2: Protocatechin acid; 3: Tyrosol; 4: Caffeic acid; 5: P-Coumaric acid; 6: Oleuropein.

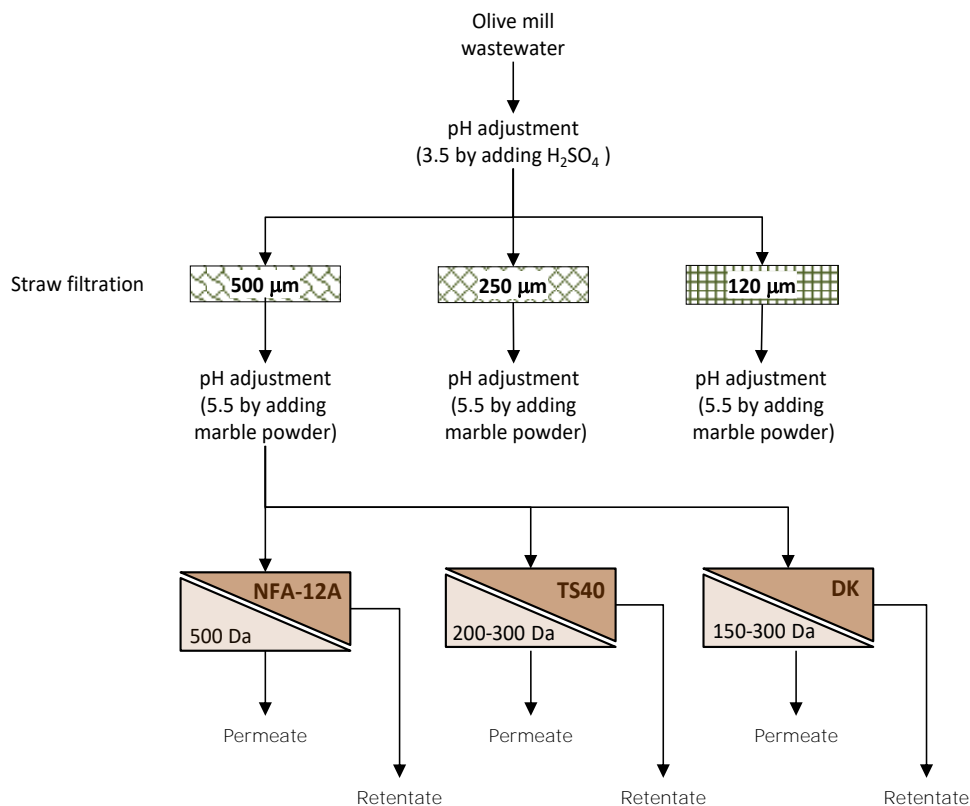
# Membrane fouling



Membrane type	WP <sub>0</sub> (l/m <sup>2</sup> hbar)	WP <sub>1</sub> (l/m <sup>2</sup> hbar)	I <sub>f</sub> (%)
MF (MD 020 TP-2N)	628.62	65.24	89.6
UF (HFS)	218.07	13.82	93.6
NF (NF PES 10)	8.83	6.081	31.1
NF (N 30F)	3.55	2.84	20.0
UF (Etna 01PP)	22.47	17.72	21.1



# Acque di vegetazione: sistema integrato MF-NF



Experimental filter for the removal of suspended solids from vegetation water: A) hydraulic valve connecting the lower chamber with a vacuum pump; B) filtered water drain valve. Right: Top vision of the filter before adding the layer of straw filtering material: C) the support technical sheet.

ID	Description	Filtration rate (mL/min)	COD (mg O <sub>2</sub> /L)	pH
US	OMW unaltered state	-	70000 ± 3500	4.80 ± 0.24
S120	Acidified OMW filtered with 120μm straw	23.7	22300 ± 1115	3.5 ± 0.17
S250	Acidified OMW filtered with 250μm straw	69.2	24650 ± 1232	3.5 ± 0.16
S500	Acidified OMW filtered with 500μm straw	112.5	18700 ± 935	3.5 ± 0.17

# Acque di vegetazione: sistema integrato MF-NF



# Nanofiltrazione delle acque di vegetazione



Impianto da banco di nanofiltrazione: 1. Bombola di azoto; 2. Manometro per la misura della pressione in ingresso; 3. Cella in acciaio inox contenente la membrana; 4. Tubo collettore per la raccolta del permeato; 5. Bilancia digitale; 6. Agitatore magnetico

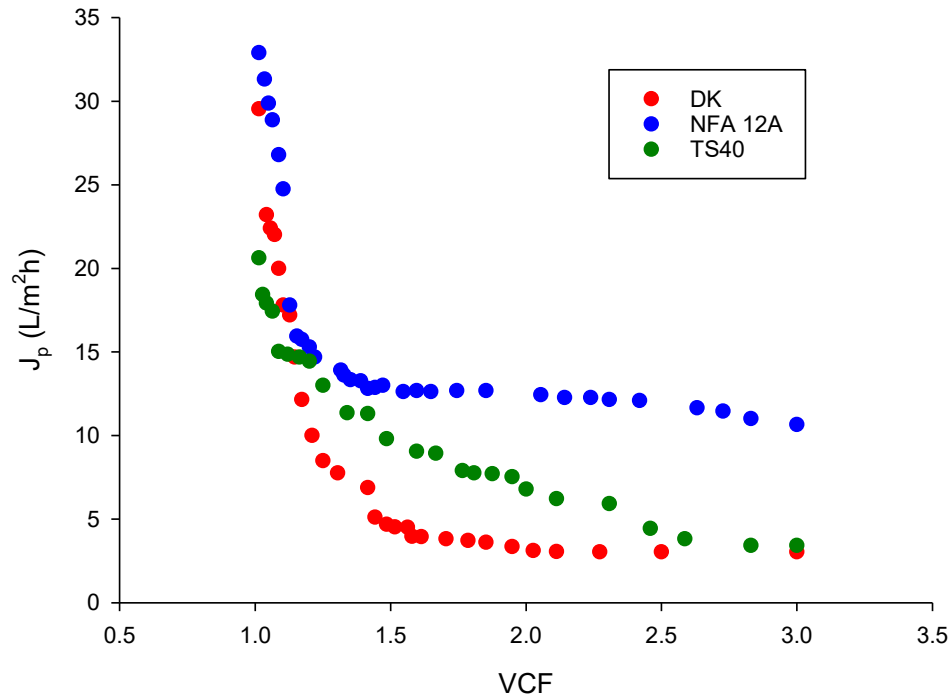


Caratteristiche delle membrane utilizzate

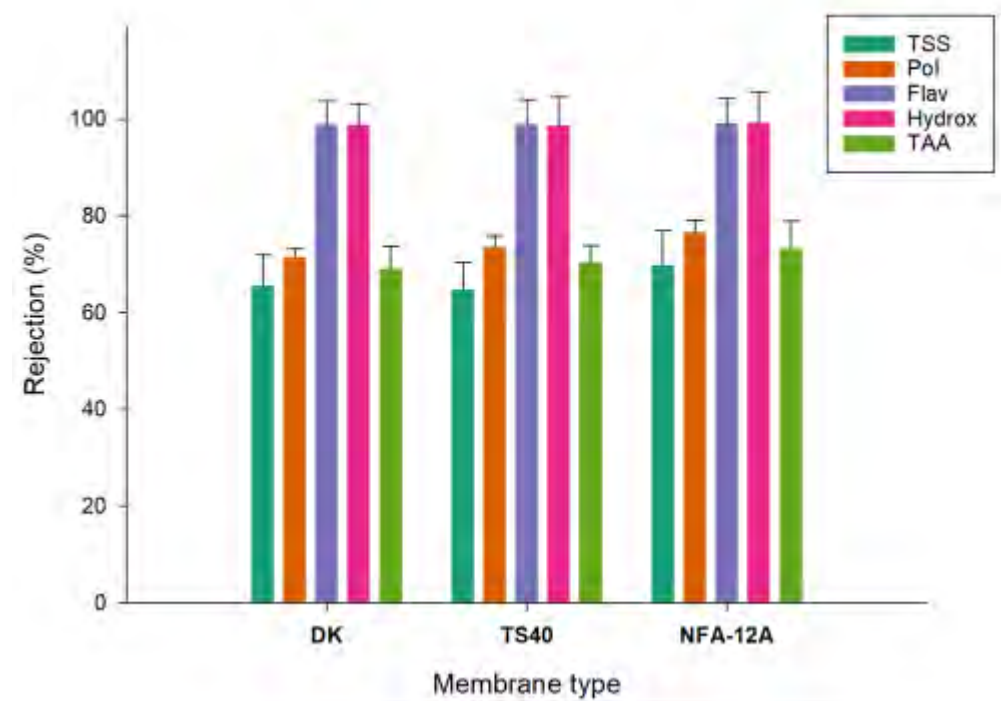
Tipo di membrana	NFA-12A	TS40	DK
Produttore	Parker	Microdyn-Nadir	GE Osmonics
Materiale di membrana	PA-TFC	PA-TFC	PA-TFC
Configurazione	piana	piana	Piana
Taglio molecolare (Da)	500	200-300	150-300
pH operativo	3-11	1-12	3-9
Max. temperatura operativa (°C)	63	50	50
Max. pressione operativa (bar)	30.6	41	41
Angolo di contatto (°)	10	30	41
Permeabilità all'acqua (18±1 °C) (L/m <sup>2</sup> hbar)	9.2	8.60	3.64



# Acque di vegetazione: sistema integrato MF-NF



Nanofiltration of clarified OMWs. Permeate flux as a function of VCF for selected membranes. Operating conditions: TMP, 20 bar; temperature,  $24 \pm 2$  °C.

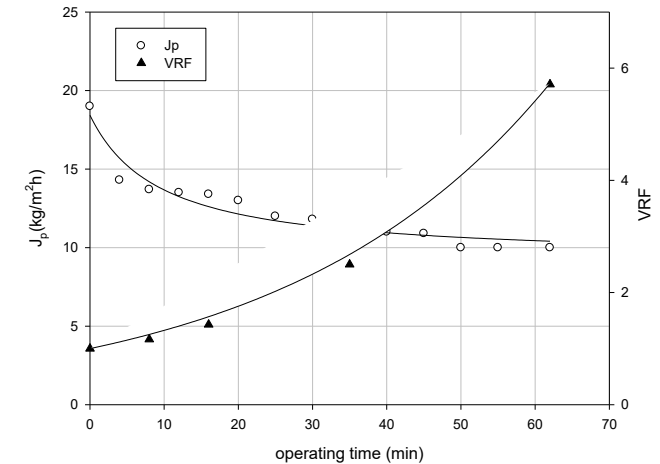


Rejections of NF membranes towards specific compounds (TSS, Total Soluble Solids; Pol, total Polyphenols; Flav, Flavanols; Hydroxy, Hydroxycinnamic acid derivatives; TAA, Total Antioxidant Activity).

# Estratti del carciofo: sistema integrato UF-NF-NF



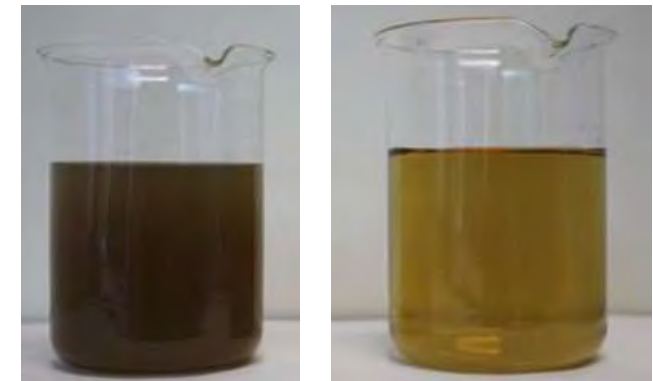
Membrane type	DCQ III-006C
Configuration	Hollow fiber
Material	polysulphone
NMWCO (Da)	50,000
Membrane surface area (cm <sup>2</sup> )	1.2



Chemical composition of artichoke extract before and after UF treatment

Parameters	Feed	Permeate	Retentate	R (%)
Suspended solids (%)	2.5±0.10	n.d.	2.43±0.10	100.0
TSS (°Brix)	3.05±0.05	2.94±0.065	3.11±0.07	3.6
Glucose (mg/L)	960±1	958±0.93	966±0.66	0.2
Fructose (mg/L)	837±1.07	830±2.5	840±1.70	0.8
Sucrose (mg/L)	1050±0.41	1040±0.49	1055±0.6	0.9
TAA (mM Trolox)	8±0.042	7.9±0.04	8.2±0.3	1.2
Chlorogenic acid (mg/L)	251±2.64	245±4.6	250.6±1.52	2.4
Cynarin (mg/L)	164.7±1.41	161±1.1	162.6±1.52	1.8
Apigenin-7-O-glucoside (mg/L)	101±2	100±4.5	100.4±2.9	0.9

Ultrafiltration of artichoke wastewater. Time course of permeate flux and VRF (TMP, 0.31 bar; Q<sub>f</sub>, 556 L/h; T, 24±2° C)

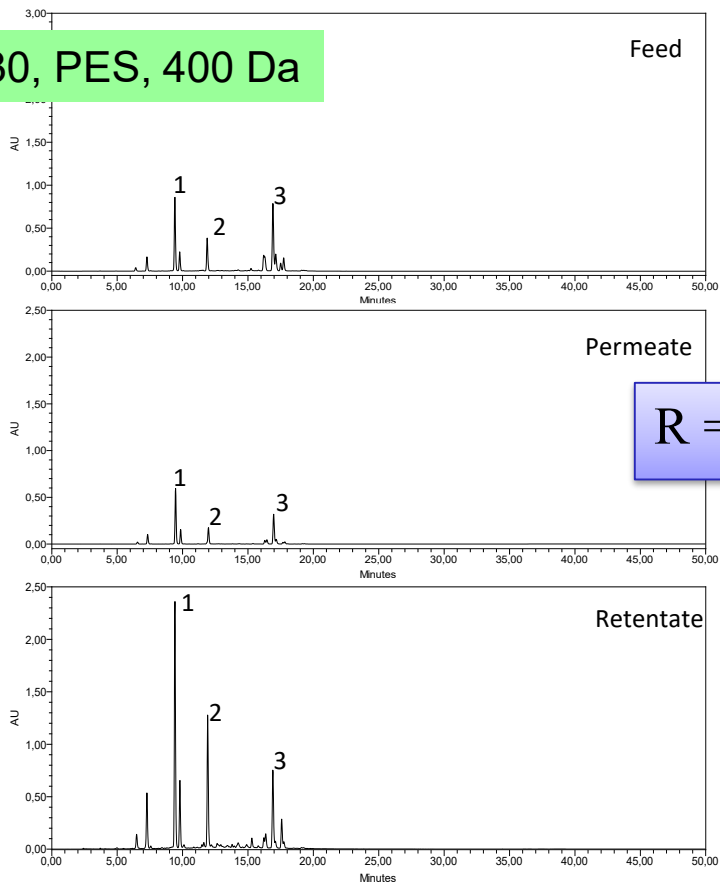


FEED

UF PERMEATE

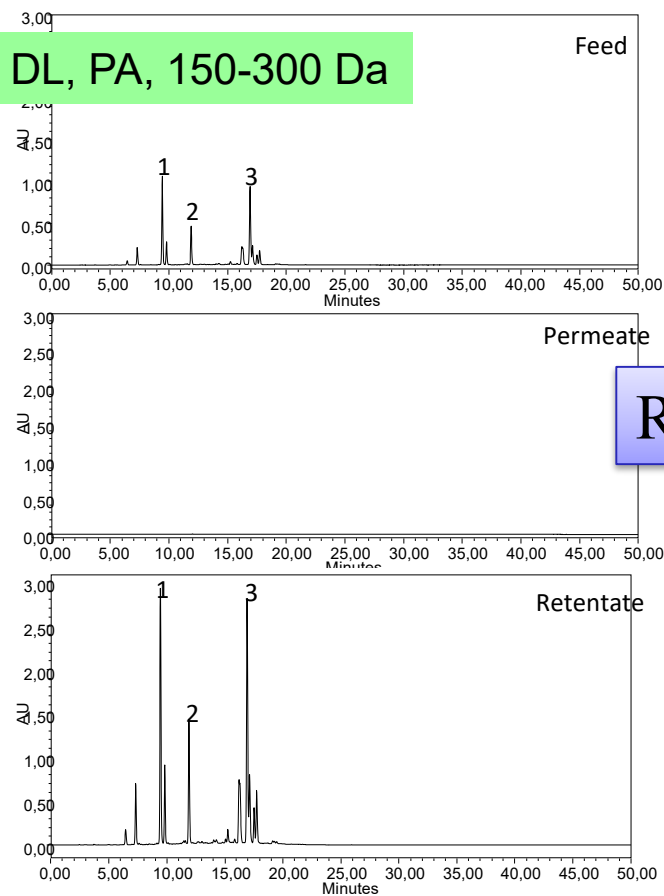
# NF di estratto di carciofo: analisi di composti fenolici

NP030, PES, 400 Da



R = 82-95%

Desal DL, PA, 150-300 Da



R = 100%

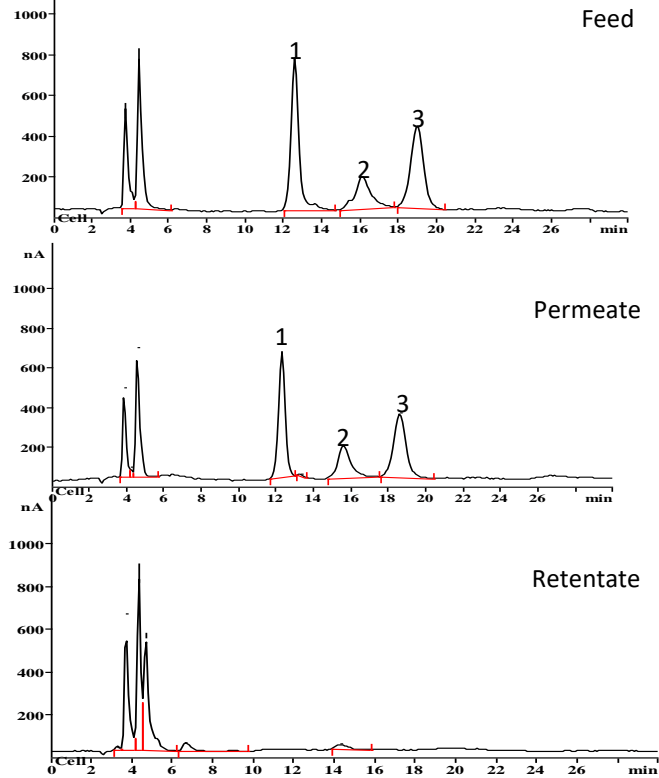
HPLC chromatograms of phenolics compounds detected in feed, permeate and retentate samples coming from the NF process with the NP030 and Desal DL membranes (VRF=5). Peak 1: chlorogenic acid; 2: cynarin; 3: apigenin-7-O- glucoside.

Sample	Cynarin (mg/L)	Chlorogenic acid (mg/L)	Apigenin-7-O-glucoside (mg/L)
Feed	158 ± 2.3	246.5 ± 1.7	100.2 ± 2.9
Permeate	14 ± 1.0	10 ± 1.74	18 ± 2.1
Retentate	412 ± 2.8	612 ± 2.4	400 ± 2.6

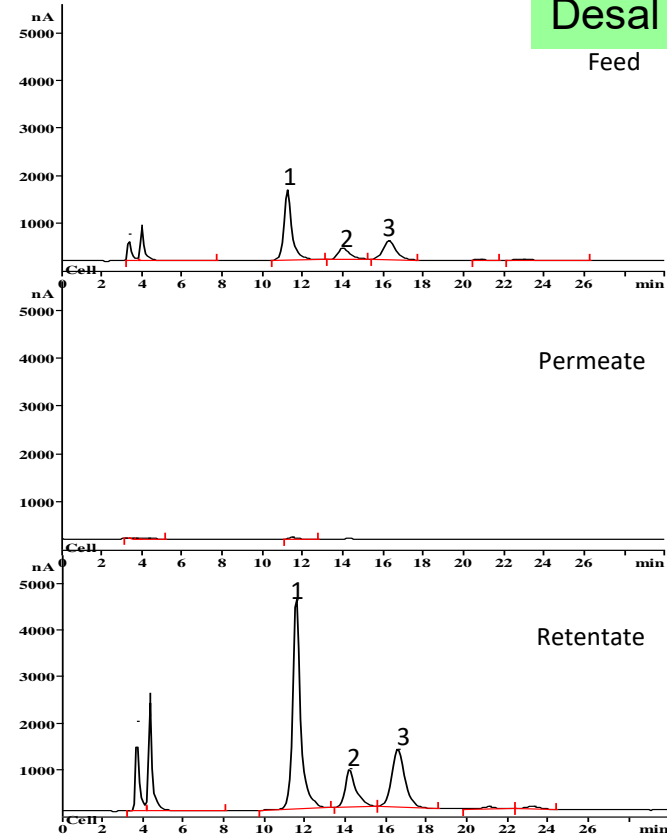
Sample	Cynarin (mg/L)	Chlorogenic acid (mg/L)	Apigenin-7-O-glucoside (mg/L)
Feed	158 ± 2.5	240 ± 2.15	100.6 ± 3.10
Permeate	n.d.	n.d.	n.d.
Retentate	450 ± 5.88	700 ± 1.70	480 ± 2.55

# NF di estratto di carciofo: analisi degli zuccheri

NP030, PES, 400 Da



Desal DL, PA, 150-300 Da

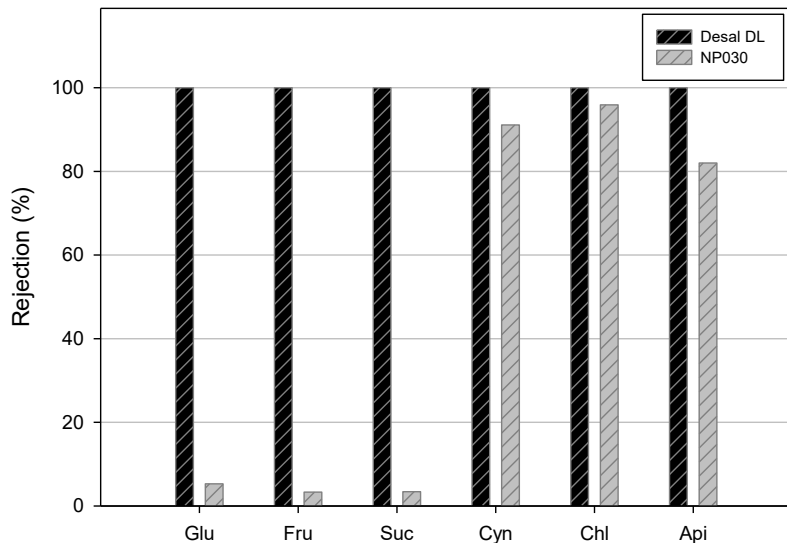


HPAEC chromatograms of sugars detected in feed, permeate and retentate samples coming from the NF process with the NP030 and Desal DL membranes. Peak 1: glucose; 2: fructose; 3: sucrose.

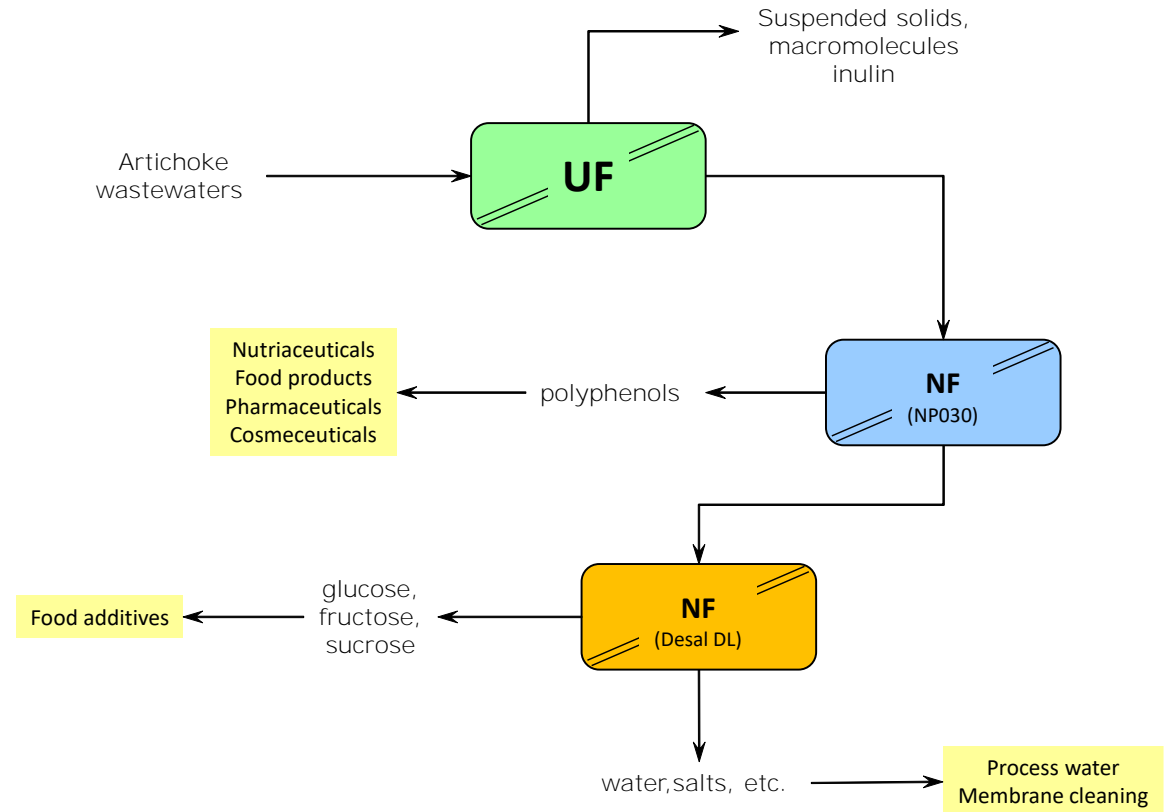
Sample	Glucose (mg/L)	Fructose (mg/L)	Sucrose (mg/L)
Feed	940±0.01	813± 0.1	1038±2
Permeate	890±1	786±0.05	1002±6.2
Retentate	200±1	256±0.5	112±2.4

Sample	Glucose (mg/L)	Fructose (mg/L)	Sucrose (mg/L)
Feed	920±2	810±0.02	1020±0.1
Permeate	n.d	n.d	n.d.
Retentate	3937 ±0.2	2877±6	4382±0.05

# Estratti del carciofo: sistema integrato UF-NF-NF

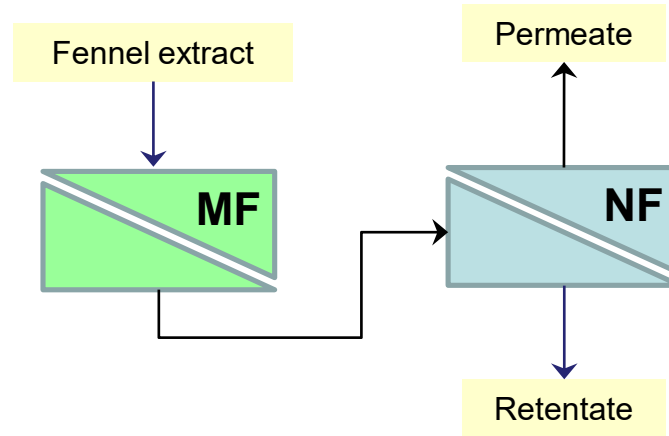


Rejections of NF membranes towards sugars and phenolic compounds (glu: glucose; fru: fructose; suc: sucrose; chl: chlorogenic acid; cyn: cynarin; api: apigenin- 7-O-glucoside)



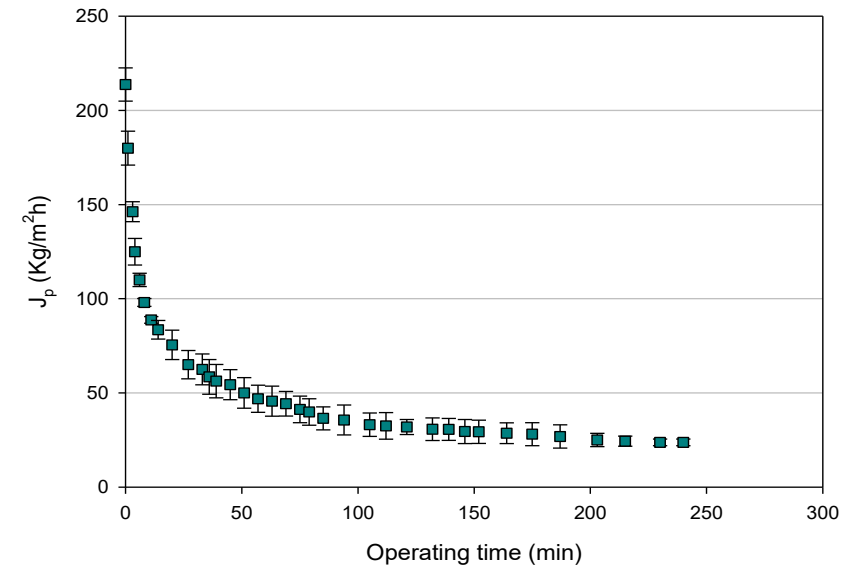
Conceptual process design for the treatment of artichoke wastewaters based on UF and NF operations

# Estratti di finocchio: sistema integrato MF-NF

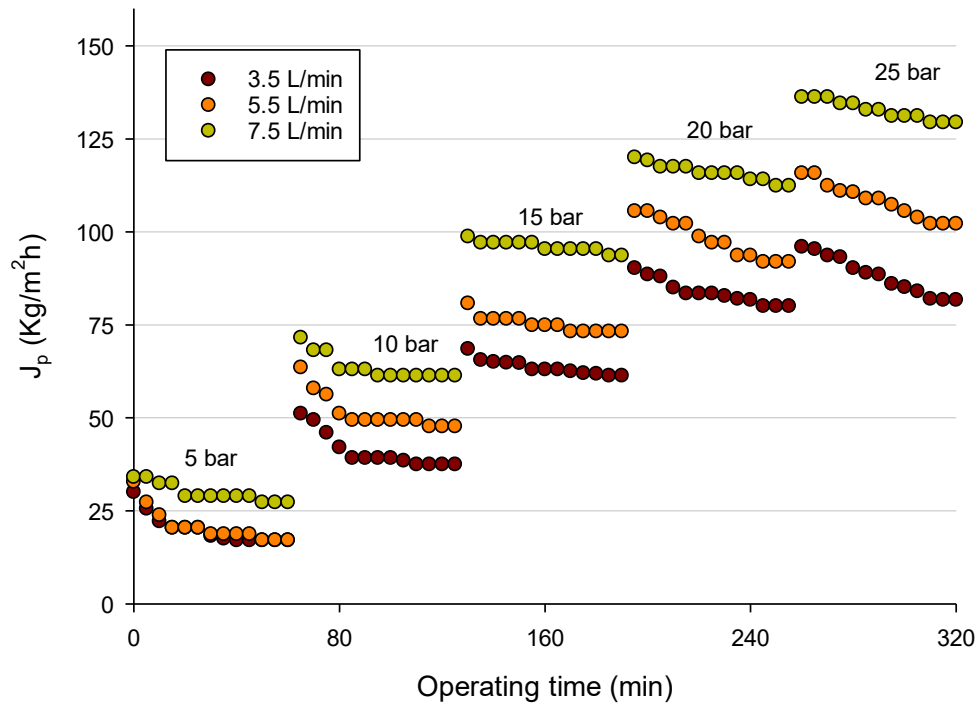


Chemical composition of fennel extract before and after the MF process

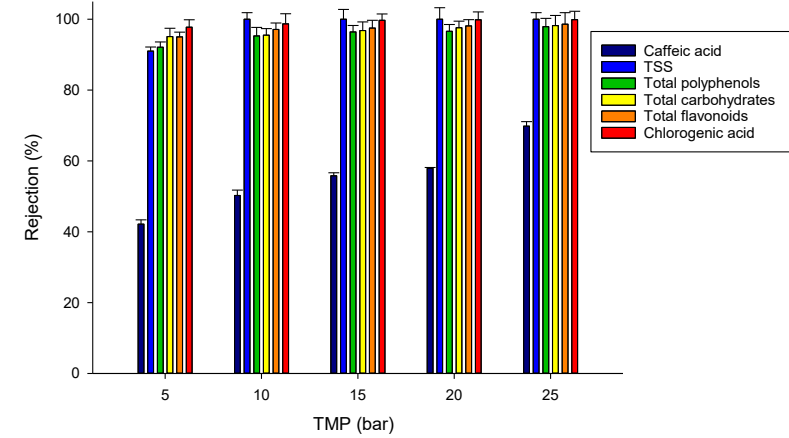
Parameters	Feed	Permeate
Total suspended solids (%)	3.0	-
TSS (°Brix)	3.2 ± 0.2	3.1 ± 0.2
Total polyphenols (mg GAE/L)	2196.1 ± 10.2	2152.9 ± 0.12
Total flavonoids (mg/L naringin)	391.0 ± 0.14	358.83 ± 0.9
Total carbohydrates (g/L glucose)	22.2 ± 0.4	19.7 ± 0.18
TAA (mM Trolox)	7.5 ± 0.02	7.3 ± 0.1
Caffeic acid (mg/L)	17.4 ± 0.12	16.8 ± 0.5
Chlorogenic acid (mg/L)	76.2 ± 0.5	73.4 ± 0.65



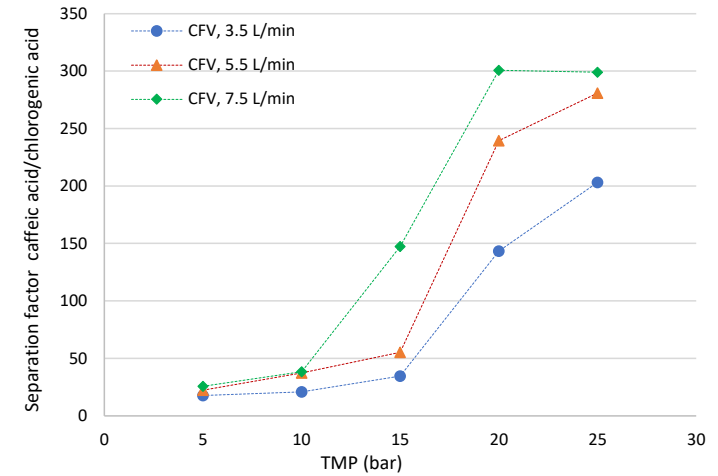
Treatment of fennel aqueous extract with MF ceramic membrane. Time course of permeate flux (TMP, 1 bar;  $Q_p$ , 200 L/h; T, 25 °C)



Time course of permeate flux at different cross-flow velocities and transmembrane pressures (Total recycle mode, T, 25 °C)

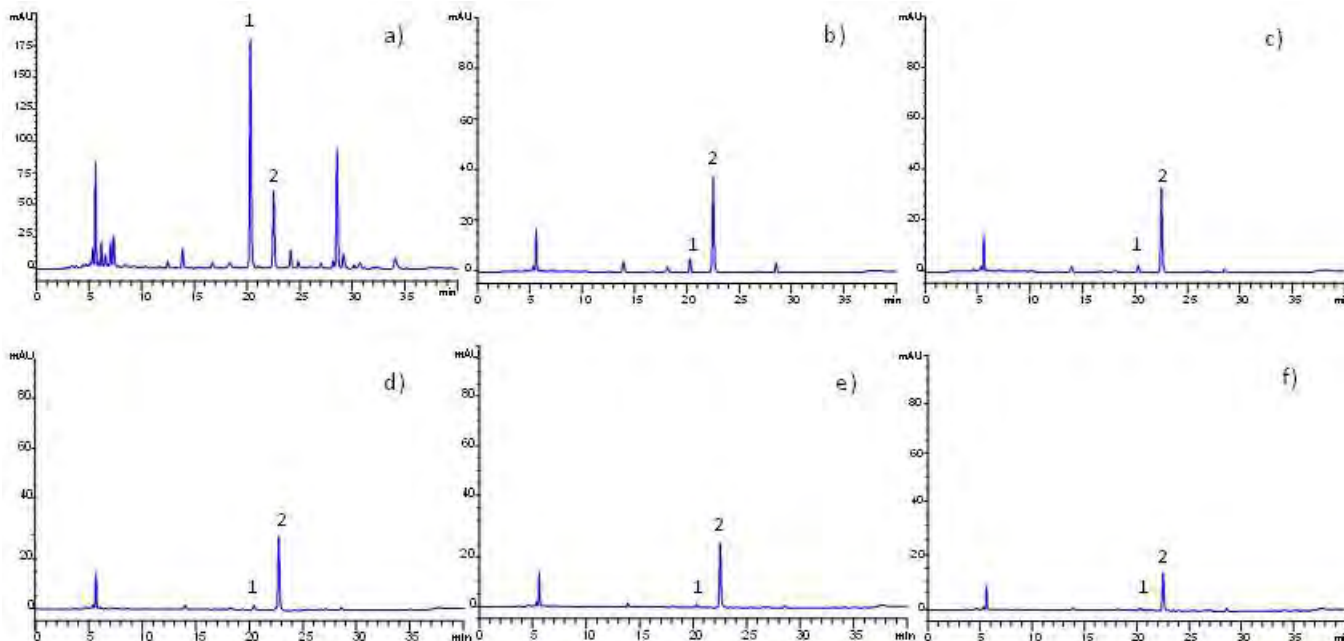


Effect of TMP on the rejection of the membrane towards analyzed compounds. CFV, 7.5 L/min

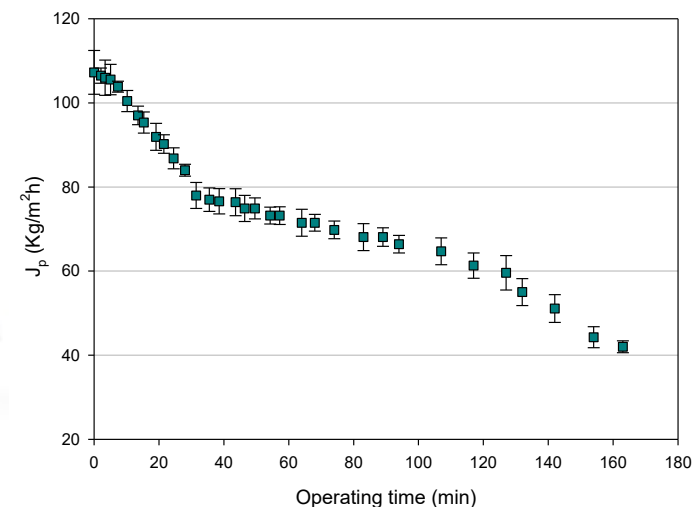


NF of clarified extract: effect of TMP and CFV on separation factor: a) caffeic acid/chlorogenic acid

# Estratti di finocchio: sistema integrato MF-NF



HPLC chromatograms of polyphenols of Feed NF (a) and permeate fractions at different TMPs: b) 5 bar; c) 10 bar; d) 15 bar; e) 20 bar; f) 25 bar. (CFV, 7.5 L/min). Peaks: 1: chlorogenic acid (354.3 g/mol); 2: caffeic acid (180.16 g/mol)



NF of clarified extract. Evolution of permeate flux as function of the operating time. (Batch concentration mode, TMP, 20 bar, CFV, 7.5 L/min, T, 25 °C)

Sample	Feed	Permeate	Retentate	Rejection (%)
TSS (°Brix)	3.4 ± 0.02	0.2 ± 0.01	5.6 ± 0.1	94.17
Total polyphenols (mg GAE/L)	2920.2 ± 30.2	160.07 ± 0.12	5000 ± 0.4	94.52
Total flavonoids (mg/L naringin)	435.16 ± 0.14	18.83 ± 0.02	722.66 ± 0.11	95.7
TAA (mM Trolox)	6.5 ± 0.02	1.5 ± 0.1	8.6 ± 0.4	76.92
Caffeic acid (mg/L)	14.8 ± 0.12	8.75 ± 0.8	15.01 ± 0.45	39.2
Chlorogenic acid (mg/L)	74.2 ± 0.02	0.2 ± 0.07	130.3 ± 0.8	99.73

# Conclusioni

- ✚ I risultati sperimentali dimostrano l'elevata potenzialità dei processi studiati per il recupero di composti bioattivi da sottoprodotti dell'industria agro-alimentare, unitamente alla possibilità di ridurre il carico inquinante di tali reflui.
- ✚ La combinazione di operazioni a membrana in definiti e validati schemi di processo permette di razionalizzare i cicli di produzione tradizionali dell'industria agroalimentare nella logica del 'zero discharge approach'.
- ✚ La selezione di specifici materiali, configurazione e taglio molecolare delle membrane impiegate e l'ottimizzazione delle condizioni operative e fluidodinamiche del processo sono fattori chiave per migliorare l'efficienza dei processi in termini di produttività e selettività nei confronti delle specie di interesse attraverso il controllo dei fenomeni di polarizzazione per concentrazione e fouling.
- ✚ La possibilità di realizzare sistemi integrati in cui tutte o alcune delle fasi del processo di produzione sono basati su separazioni molecolari a membrana può essere considerata un valido approccio per una crescita industriale sostenibile nell'ambito della *process intensification strategy*.