

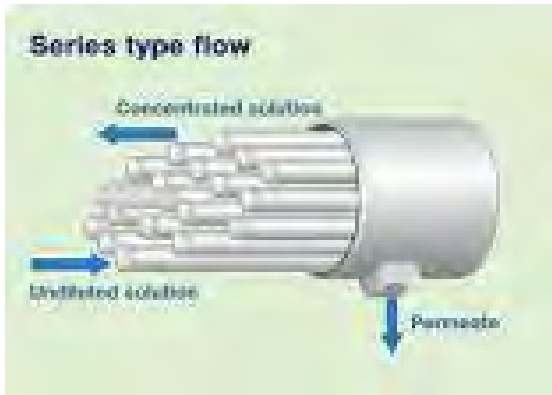
# **MEMBRANE PROCESSES FOR FOOD INDUSTRY AND BIOTECHNOLOGIES**

# STRUCTURE OF LECTURE

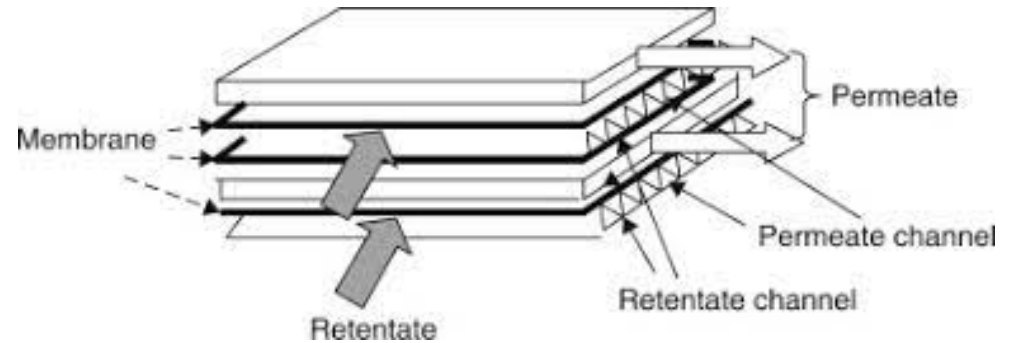
- **1. Conditions for membrane separation;**
- **2. Diafiltration;**
- **3. Affine ultrafiltration;**
- **4. Membrane separation for biotechnologies;**
- **5. Membrane separation for food industry.**

# MEMBRANE MODULES

## Tubular module

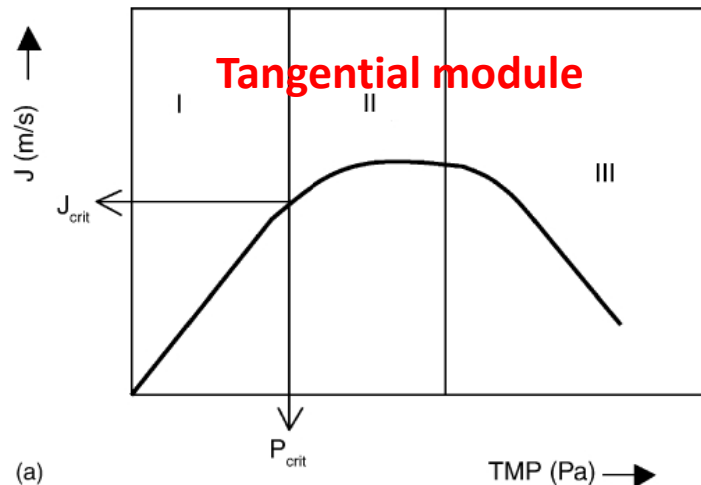


## Flat plate module



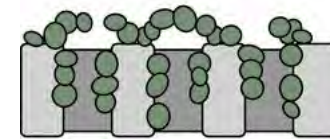
These cross-flow modules are traditionally used in food industry, since it is easy to clean them.

Typical effect of pressure on the permeate flux over filtration processes in dairy industry

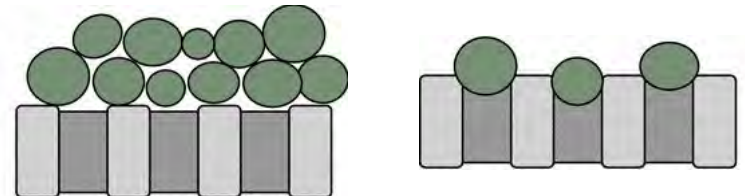


**Regime I.** No considerable fouling.

**Regime II.** Cake formation, pore constriction.



**Regime III.** Cake compaction, pore blockage



# **OPERATION CONDITIONS**

## **Time of the membrane separation**

The time of membrane separation is strictly regulated. Normally it is 10-20 h. Just after the finish, cleaning and disinfection of the membrane system must be performed.

## **Ionic strength**

Increasing ionic strength of the solution provides aggregation of colloidal particles, this facilitates their separation.

This approach is possible, when:

- No requirements to salt content in a target product,
- Desalination of the target product is possible and appropriate from the economical point of view.

## **Temperature**

- The temperature must be kept at the predetermined level.

As a rule, the temperature is about 10° C.

## **Pressure**

In the case of MF and UF processes, the pressure is about 0.5-1 bar to avoid polymerization of some compounds.

# STRATEGY OF FOULING CONTROL AND CLEANING MEMBRANES

**Fouling control for the membranes, which are used in food industry**

Method	Working principle	Possible disadvantages
High cross-flow velocity	Enhance transport by turbulent flow, low pressure	High power consumptions, high investment and operation costs
Spacers	Enhance transport close to membranes	Difficult cleaning, increased power consumptions
Backwashing	Remove cake by pressure reversing	High operation costs
Pulsating cross-flow	Velocity fluctuations in the feed	Difficult to control pressure waves in large systems
Air flow	Increase mixing close to membrane	Difficult to control air bubble size, foaming and denaturation
Cleaning particles	Increase mixing close to membrane	Run-out of membranes and pump
Sonication	Prevention of precipitation	Power consumption and heating, damage of sensitive compounds
Vibration modules	Increase mixing close to membrane	High investment cost
Electric field	Keeping charged particles far from membrane	Electrolysis, gas production, heating, power consumptions

# STRATEGY OF FOULING CONTROL AND CLEANING

## Fouling control for the membranes, which are used in food industry

**Cleaning** has a significant impact on process operations and the commercial viability of the process. It is accomplished by physically removing the gel layer and/or foulants, for example by backflushing, and/or by using a specific cleaning solution containing appropriate detergents and/or chemicals. The cleaning treatment must effectively remove and/or dissolve the gel layer and/or foulants while not exceeding the mechanical or chemical limits of the membrane.

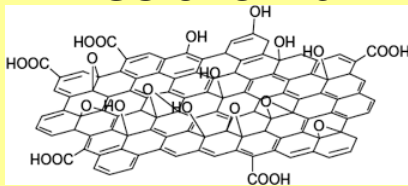
**Disinfection** is the necessary stage of cleaning.

## Requirements to membrane materials

- Chemical stability,
- No modifiers, which destroy the components of liquids of biological origin.

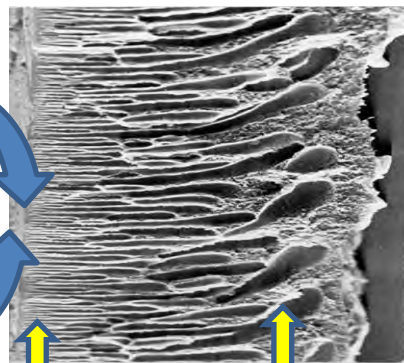
### MODIFIER

#### GO or CNDs



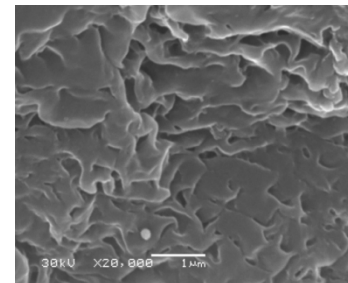
Inorganic  
ion-exchanger (binder)

### POLYMER FILTRATION MEMBRANE

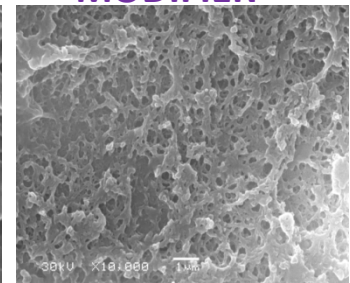


Active layer

Active layer



Active layer +  
MODIFIER



# SEPARATION OF PLASMID DNA FROM RNA BY ULTRAFILTRATION

## Needs of plasmid DNA

**Plasmids** are circular doublestranded extrachromosomal DNA that are produced by many bacteria and also by some eucaryotes, often at high copy numbers.

Gene therapy and preparation of DNA vaccines require large-scale production of highly purified plasmid DNA from fermentation broth. Plasmid DNA is isolated from the fermentation broth. Downstream purification is needed to remove cellular debris, host cell proteins, genomic DNA, RNA, and endotoxins.

Ion exchange chromatography are used extensively in current separation systems, these methods are expensive and time-consuming. **Membrane separation** is much more attractive.

$$M_{pDNA} = 130000 \text{ kDa}$$

$$M_{RNA} = 0.04-1 \text{ kDa}$$

$$M_{gDNA} \approx 1000 \text{ kDa}$$

**Membranes** can reject large plasmids.

## Problems of pressure-driven processes

**Elongation of plasmid molecules** → their leakage through the membrane →  
→ decrease of yield.

**Interaction of plasmid molecules with contaminants** → decrease of purification degree.

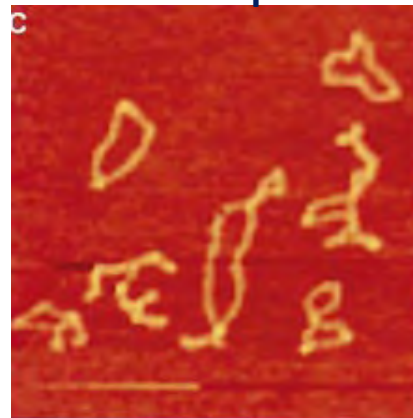
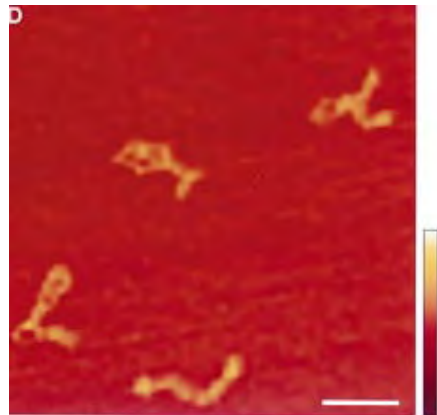
## Plasmid



# SEPARATION OF PLASMID DNA FROM RNA BY ULTRAFILTRATION

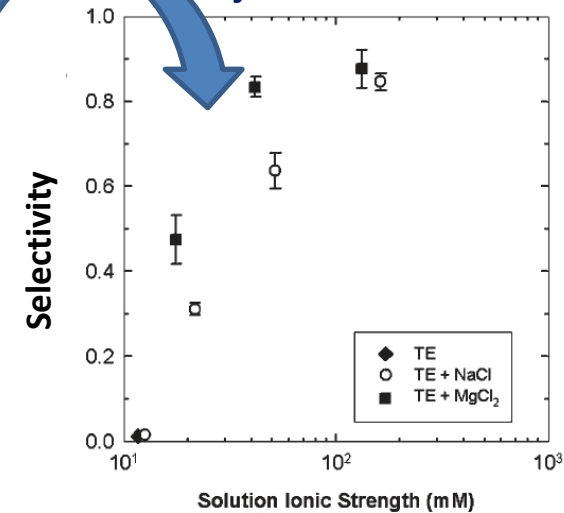
DNA show typical behavior for colloidal systems for instance, aggregation in salt solutions.

+MgCl<sub>2</sub>



Aggregation enhances pDNA rejection. The effect of double-charged ions is expressed.

Effect of ionic strength on pDNA rejection

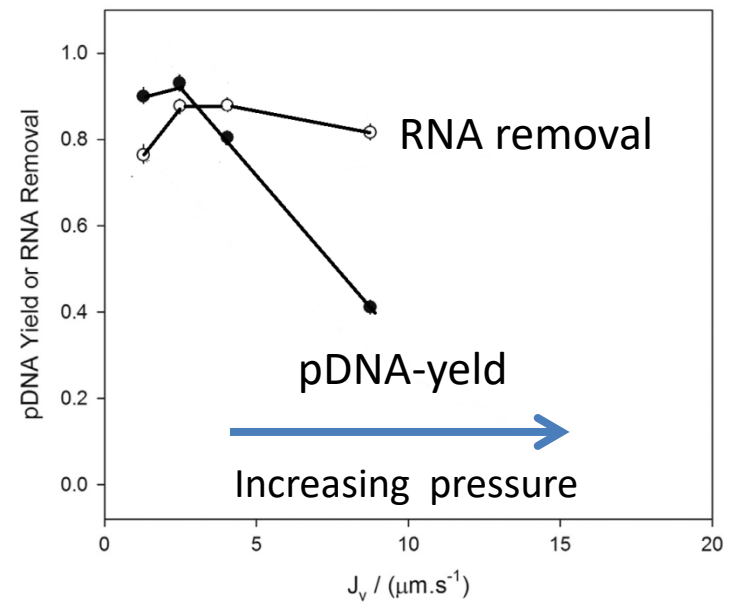


Key factors affected DNA-RNA separation

Pore size (25 nm is the optimal size)

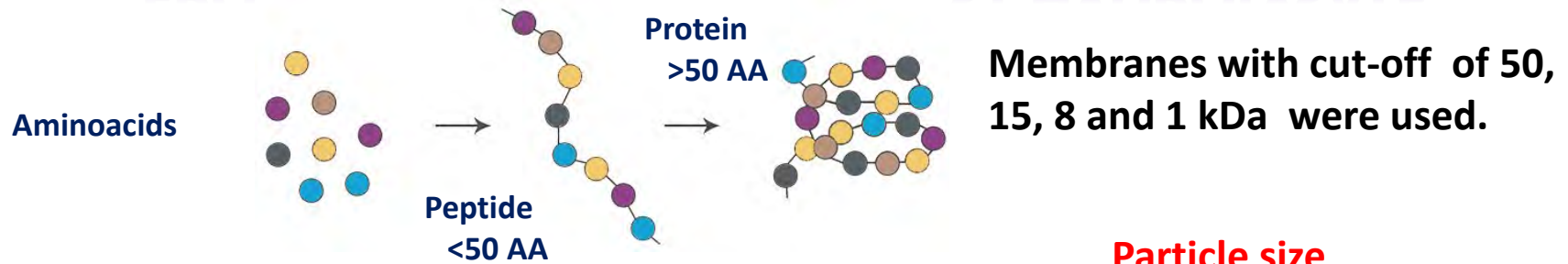
Pressure

Effect of pressure on pDNA-RNA separation

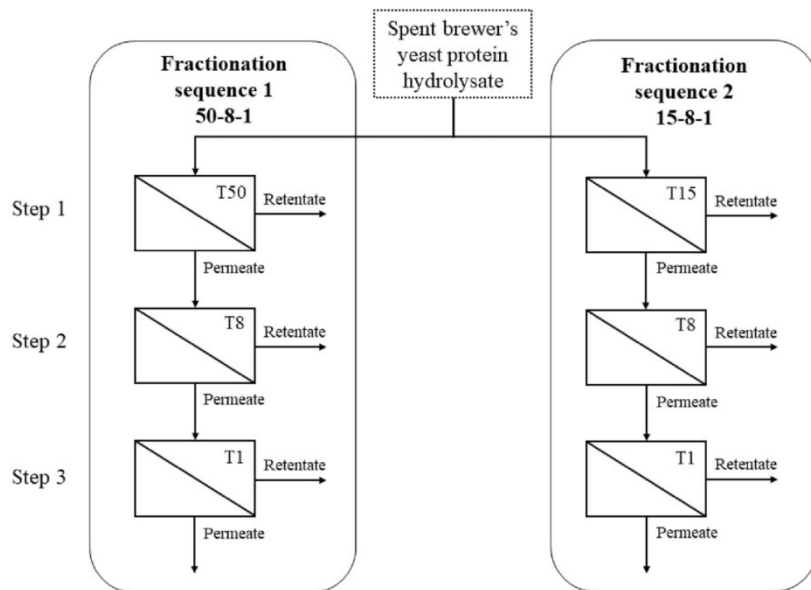




# SERIAL FRACTIONATION OF PEPTIDES FROM SPENT BREWER'S YEAST HYDROLYSATE



## Scheme of fractionation

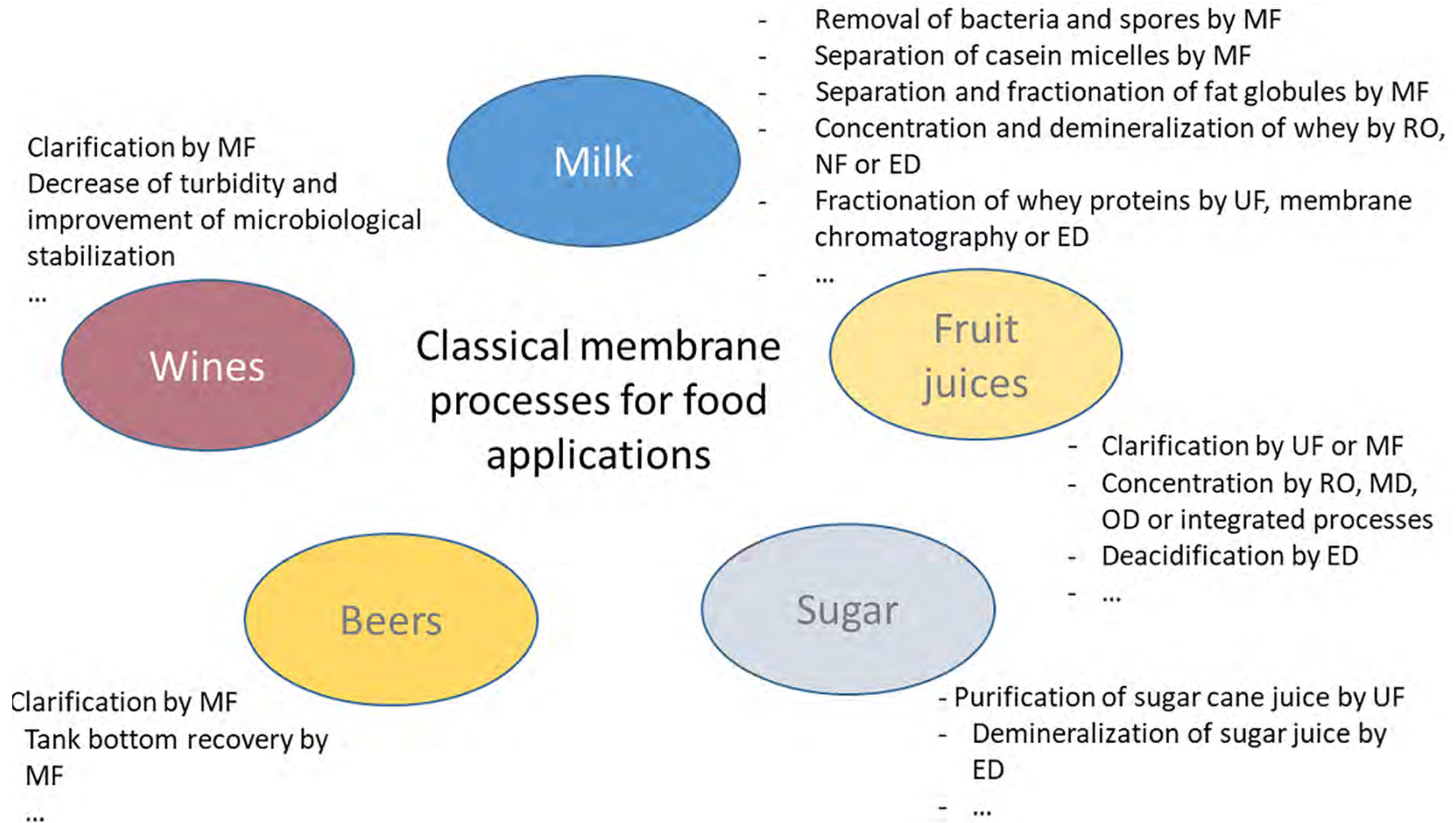


## Particle size

Sequence	MW<1	1<MW<7	MW>7
Initial	59.0	29.8	11.2
50-8-1			
Concentrate 1	50.0	30.8	19.2
Concentrate 2	62.3	29.6	8.1
Concentrate 3	79.0	19.0	2.0
Permeate 3	91.7	7.0	1.3
15-8-1			
Concentrate 1	51.0	32.2	16.8
Concentrate 2	66.0	28.7	5.3
Concentrate 3	80.3	17.1	2.6
Permeate 3	88.7	7.9	3.4

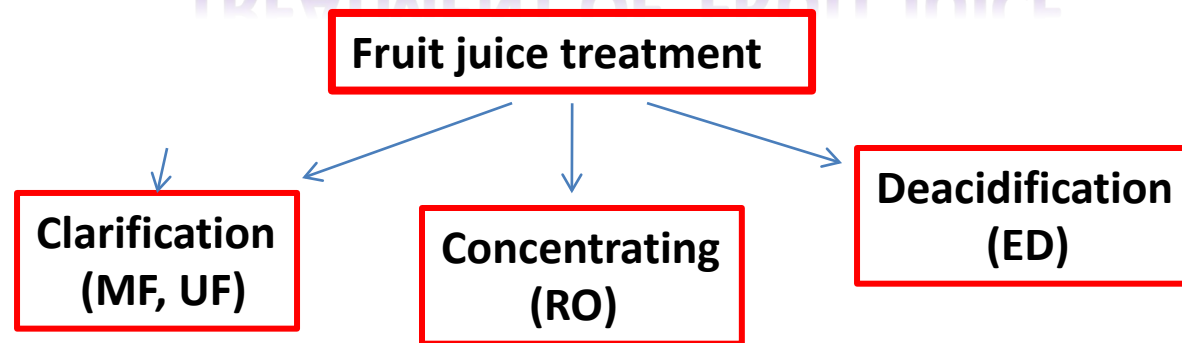
**Permeate 3 containing the smallest peptide particles can be used as food ingredient. Concentrate 2 contains the largest fraction of Bioactive peptides (5 kDa and smaller).**

# MEMBRANE PROCESSES IN FOOD INDUSTRY

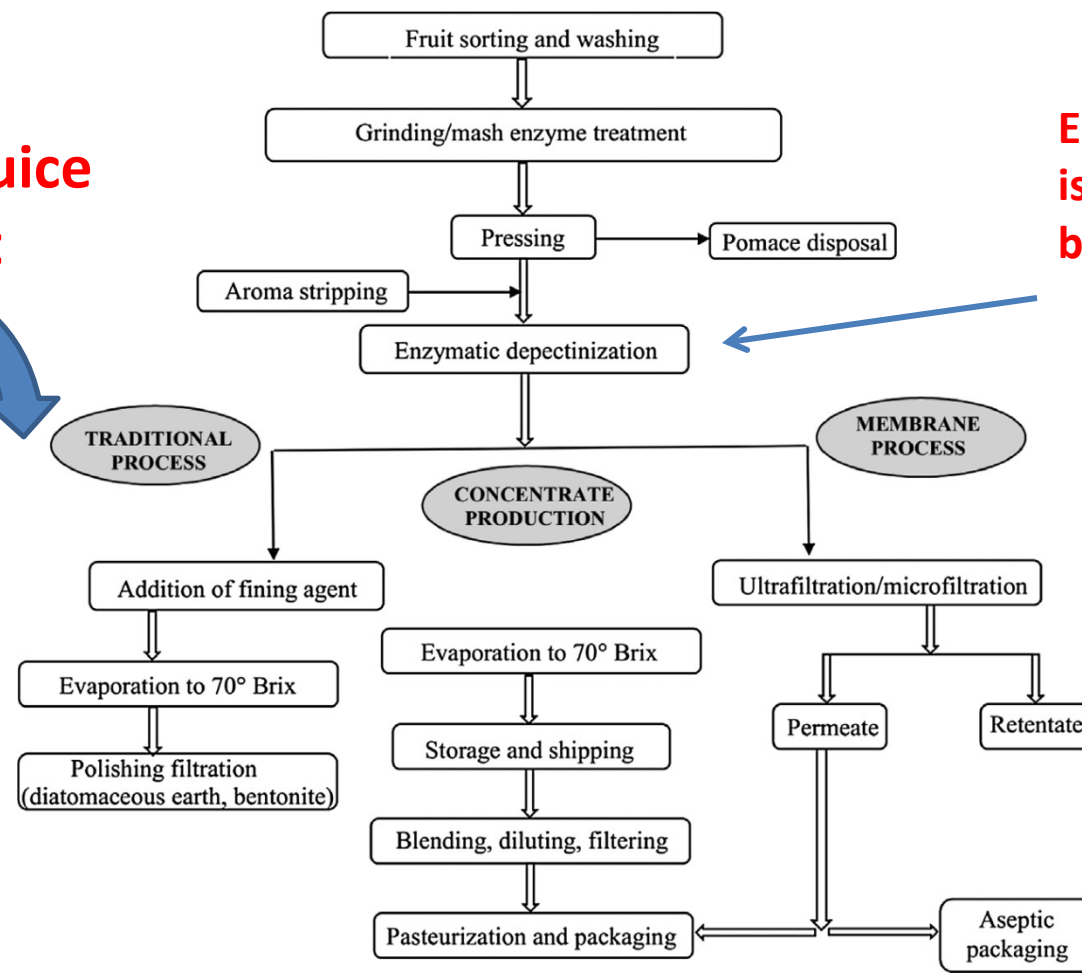


# TREATMENT OF FRUIT JUICE

## Scheme of juice treatment



Enzymatic pretreatment is a mandatory stage before the membrane treatment



# TREATMENT OF FRUIT JUICE

## Membrane materials

**Citrus juices** can be very aggressive to some membrane materials (polyamide, polysulfone polyacrylonitrile) . Poly(vinylidene fluoride) membranes are recommended.

## JUICE CLARIFICATION

Fruit juices are characterized by **natural turbidity** due insoluble substances, such as pectin, starch, and cells from the juice. Depending on the application of the fruit juice, **clarification process is required**. For example, clarified fruit juices are needed for the production of clear beverages (soft drinks, natural aromatic waters, alcoholic beverages, cold teas, etc.), candies (melting products), and pastries (natural essences, translucent fruit sauce).

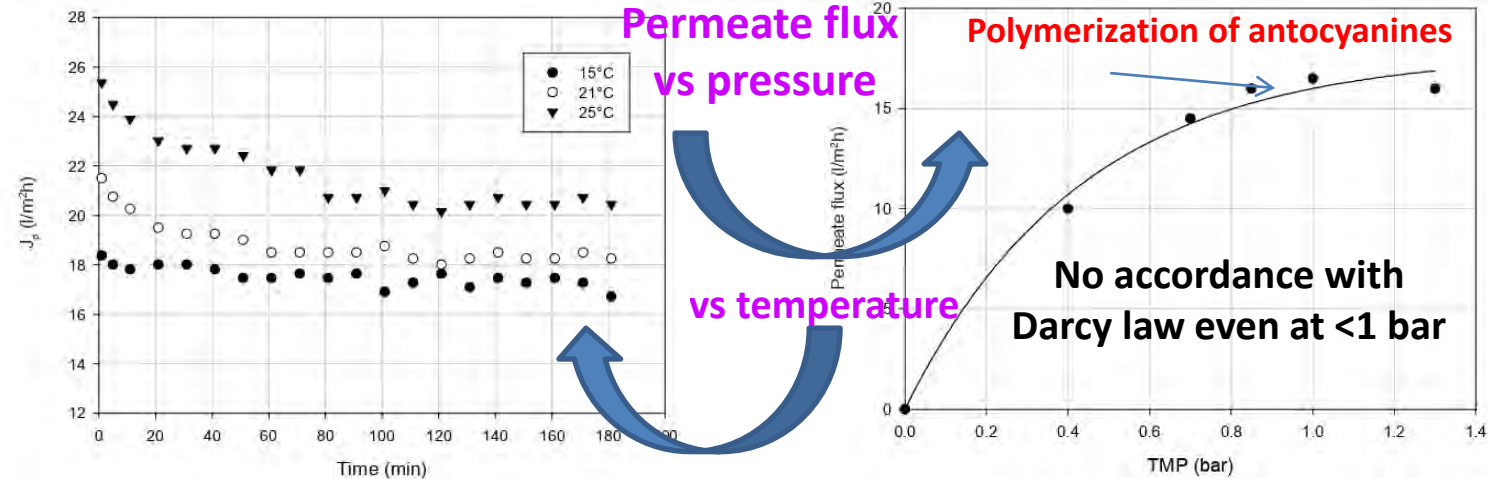
**Conventional clarification** usually involves batch processes, such as enzymatic pretreatment, clarification with bentonite, gelatin or diatomaceous earth, and pasteurization.

MF and UF are alternatives to traditional clarification techniques. The **advantages of MF and UF** are increased juice yield, possibility of operating in a single step, fevrease of enzyme consumption, decrease of operating times, elimination of needs for pasteurization, and production with a continuous process.

# ORANGE JUICE CLARIFICATION



Commercial product

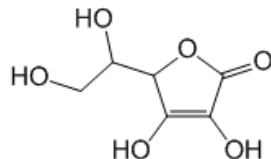
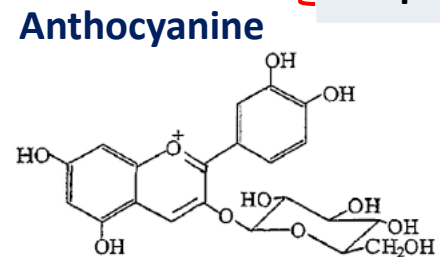


Composition of orange juice

Substance	Feed	Permeate	Concentrate	Balance, %
Total soluble solids, g/ 100 g	12.0	11.2	13.5	100.0
Suspended solids, %	10	0	>50	91.6
Ascorbic acid, mg l <sup>-1</sup>	701	642	640	98.5
Anthocyanins, mg l <sup>-1</sup>	60.4	54.7	60.6	92.0
Narirutin, mg l <sup>-1</sup>	46.7	46.7	46.7	100.0
Hesperidin, mg l <sup>-1</sup>	33.9	33.6	31.1	99.7

Flavonoids

Ascorbic acid



Ascorbic acid and anthocyanines are partially adsorbed by membrane.

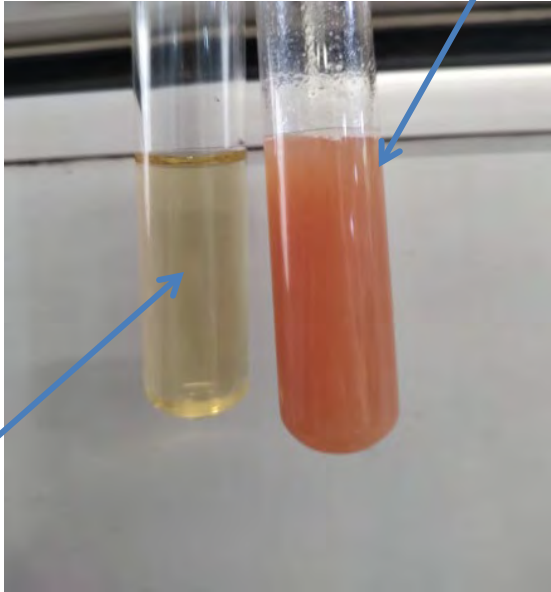


Cyanidin-3-O-glucoside chloride

# GUAYAVA JUICE CLARIFICATION

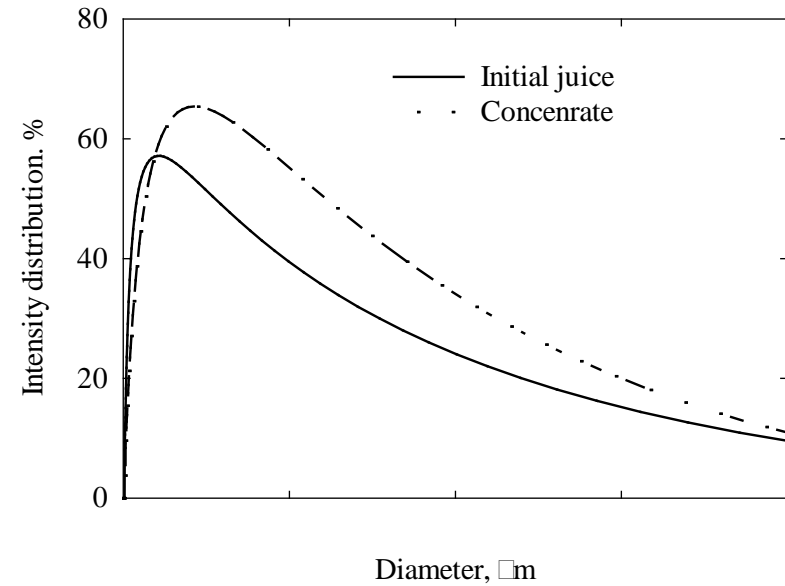


Pristine juice



Clarified  
juice

## Effect of pressure on the particle size



**Selectivity of the modified MF membranes is 33-73%.**

**The concentrate can be used for the production of confectionery**



# CONCENTRATING FRUIT JUICE

**Fruit juices** are usually **concentrated** to allow easier and cheaper storage, transportation, and distribution, as well as better conservation. The classical methods of juice concentration, such as thermal evaporation, usually employ high temperatures to remove water. However, heat can cause undesirable changes in the product sensory and nutritional properties, such as color and flavor changes, and reduction in the nutritional value. **Membrane concentration processes are alternatives** to thermal evaporation. They are able to concentrate juices at room temperature, causing little or no damage to the product.



## Concentrating apple juice using reverse osmosis

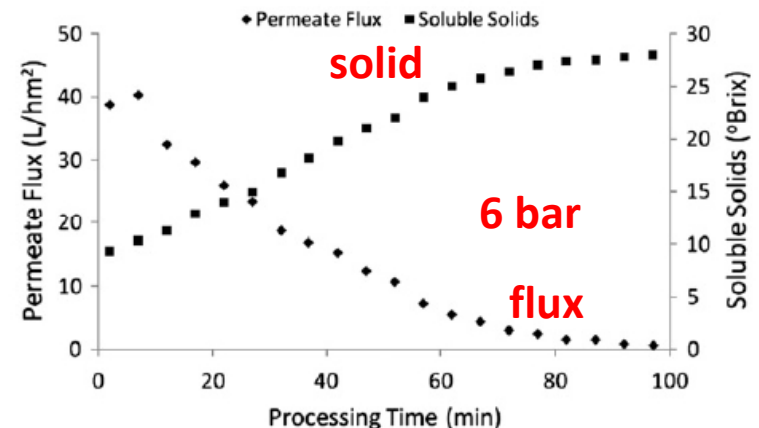
Juices are concentrated in 3-4 times.



### Physico-chemical characteristics of apple juice

Analysis	Feed	Reverse osmosis
pH	3.83 <sup>a</sup>	3.79 <sup>b</sup>
Soluble solids (°Brix)	8.7 <sup>c</sup>	28.1 <sup>b</sup>
Total solids (g kg <sup>-1</sup> )	92.2 <sup>c</sup>	291.1 <sup>b</sup>
Titrateable acidity (g kg <sup>-1</sup> )	20.2 <sup>c</sup>	64.4 <sup>b</sup>
(g kg <sup>-1</sup> dry matter)	219.1 <sup>a</sup>	221.2 <sup>a</sup>
Total phenolics (mg GA kg <sup>-1</sup> )	495.3 <sup>c</sup>	1393.7 <sup>b</sup>
(mg GA kg <sup>-1</sup> dry matter)	5372.0 <sup>a</sup>	4787.7 <sup>b</sup>
Antioxidant activity (mmol TE g <sup>-1</sup> )	5.9 <sup>c</sup>	13.2 <sup>b</sup>
(mmol TE g <sup>-1</sup> dry matter)	57.4 <sup>a</sup>	45.3 <sup>b</sup>

### Permeate flux and content of solids in apple juice

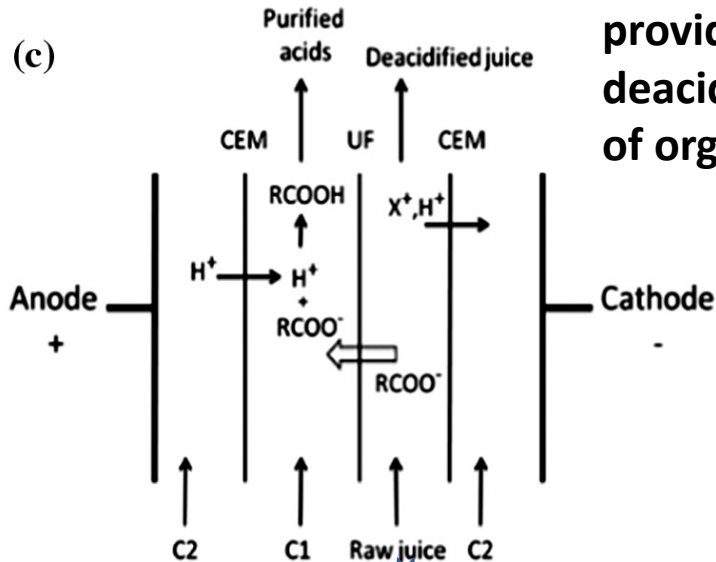


# ELECTROMEMBRANE PROCESSES FOR PH CORRECTION.

## Example. Cranberry juice deacidification



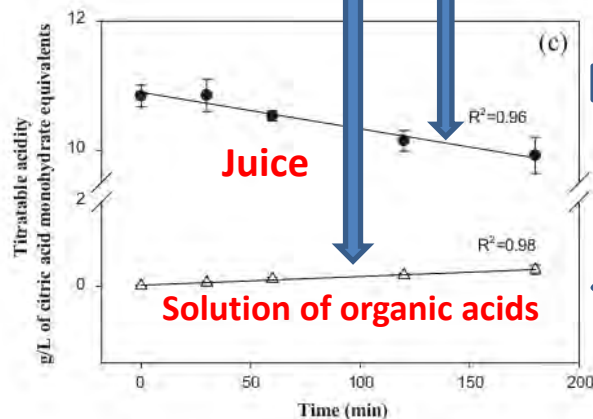
### Ion transport through membranes



**Advantage.** The method provides not only juice deacidification, but also recovery of organic acids.

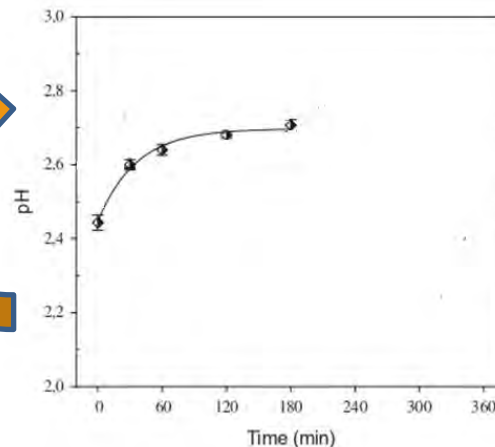
Several configuration of membrane system are used. The system can involve cation-exchange, anion exchange, bipolar membranes, as well as a membrane, which possesses no ion exchange properties, for instance, ultrafiltration separator.

**Disadvantage.** Low efficiency of the method. Theoretically it is possible to intensify the process by increasing current. In this case, juice



Change of total acidity

Change of pH



is acidified, since migration of  $H^+$  ions from the concentrating compartment to "juice" compartment is more intensive.



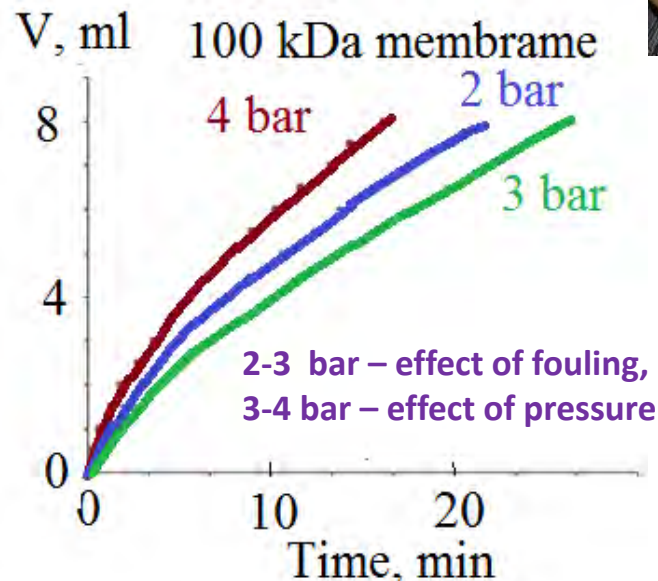
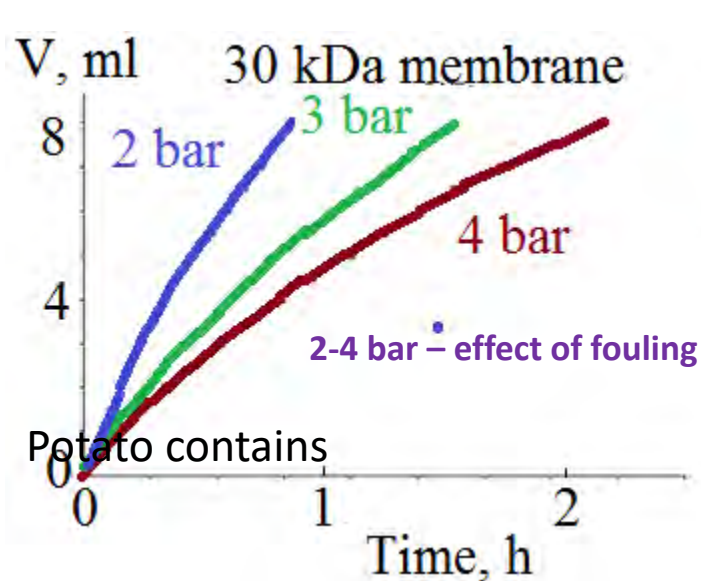
# SEPARATION OF PROTEINS FROM POTATO JUICE



Potato's protein (patatin, 39-45 kDa) is effective for muscles, it supports the body's metabolism and lowering blood pressure. One medium-sized potato contains about 4 g of protein (2.2 g/100 g) and 80% of liquid.



## Effect of membrane material on filtration of potato juice



Fouling of the membrane with smaller pores (30 kDa) enhances with increasing pressure (from 2 to 4 bar). Regarding the membrane with larger pores (100 kDa), the effects of both pressure and fouling are expressed.

## Recovery of proteins from potato juice



	Feed	100 kDa		30 kDa	
		Permeate	Concentrate	Permeate	Concentrate
Protein, $\mu\text{g ml}^{-1}$	535	420	830	5	1010

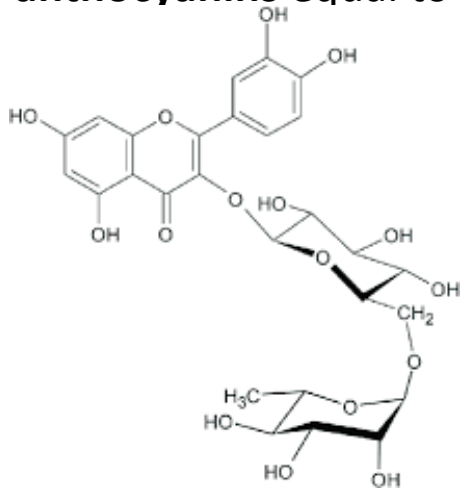
# MEMBRANE TREATMENT OF OLIVE RESIDUES

## Recovery of anthocyanines

The biophenols and other compounds present in the olive derived products are associated with effective antioxidant properties. Their antiaging effect and their associated prevention against cardiovascular diseases and neoplasia processes have also prompted a high interest in applying these bioactive compounds in the pharmaceutical and cosmetic fields.

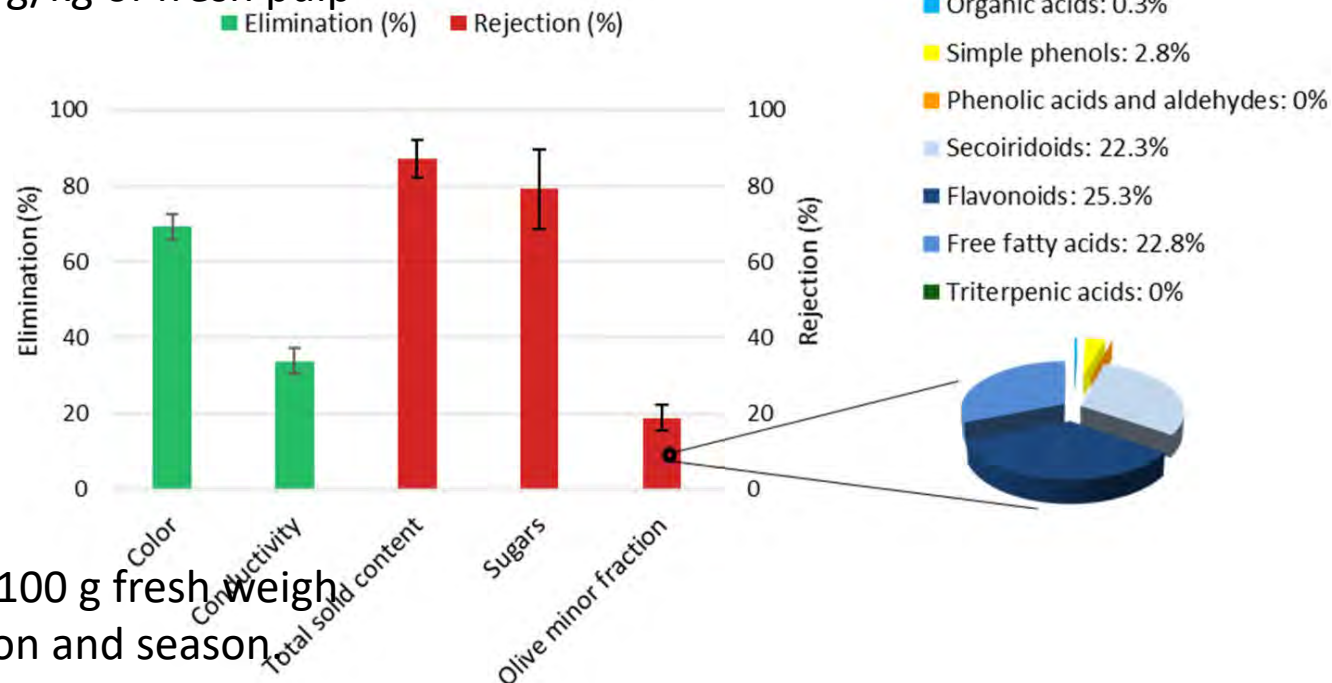


**anthocyanins** equal to 1.25 g/kg of fresh pulp



Que-3-rutinoside

Its content is 24-93 (mg per 100 g fresh weight)  
 Depending on the kind, region and season  
 The maximal content is in December (ripe fruits)



# AFFINE ULTRAFILTRATION. METHOD FOR ENZYME PURIFICATION

## World market of technical enzymes

12 billions USD (2022) only for technical enzymes

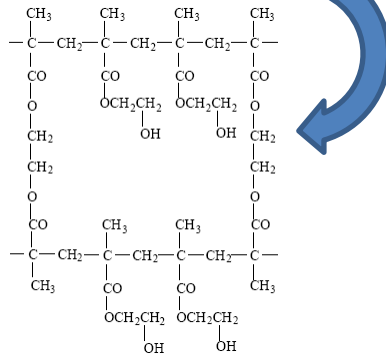
## Requirements for enzymes

- Selective concentrating of the target protein being purified in one phase, additions must be in the second phase,
- Mechanical separation of two phases,
- Recovery of the target protein from the enriched phase,
- Regeneration at least one of the phase for repeated usage.

## Solution of problem

**Affinity chromatography**- is a separation method based on a specific binding interaction between a immobilized ligand, which is attached to solid (immobile phase), and protein.

**Adsorbent matrix** – silica, toyopearl



**Ligands** – The ligands used in affinity chromatography are obtained from both organic and inorganic sources. Examples of **biological sources** are serum proteins, lectins and antibodies. **Inorganic sources** are moronic acid, metal chelates and triazine dyes.

# **AFFINE ULTRAFILTRATION. METHOD FOR ENZYME PURIFICATION**

## **Disadvantage of affine chromatography**

**Too expensive for industrial application**

**The adsorbents containing ligands can be unstable**

## **Solution of problem is affine ultrafiltration**

**Affinity-membrane separation is based on the ability of many biologically active compounds, including enzymes, to selectively and reversibly bind with some substances, which are commonly called ligands or affinity ligands.**

**Ligands can be high-molecular water-soluble polymers or small solid particles (starch granules, inactivated yeast cells, etc.), which can be easily separated from unbound proteins by ultra- or microfiltration.**

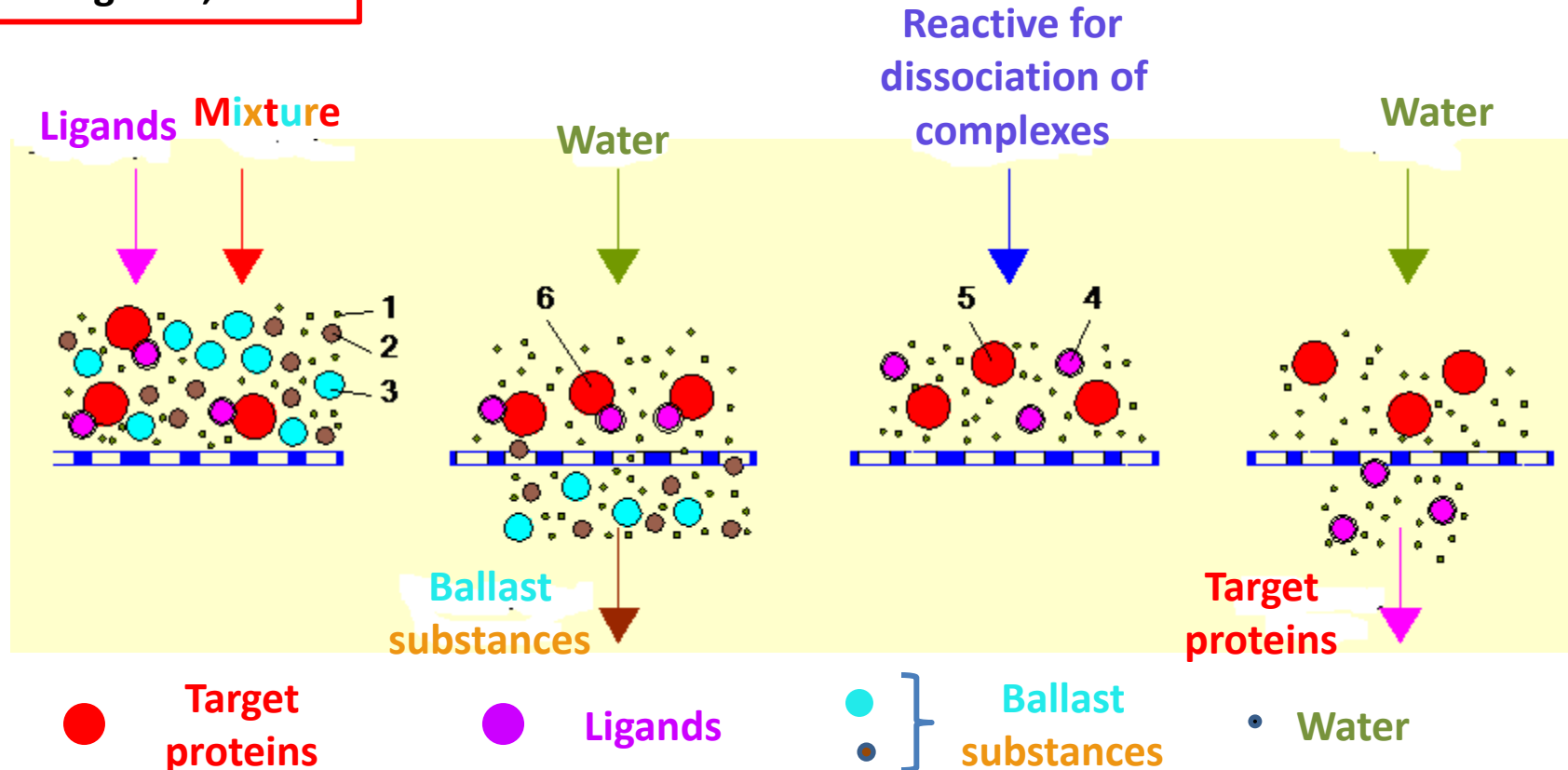
# PRINCIPLES OF AFFINE ULTRAFILTRATION.

– Insertion of ligands into the mixture and formation of complexes of target proteins with ligands;

– Diafiltration:  
Washout of ballast compounds from the mixture with water

– Dissociation of complexes

– Separation of target proteins from ligands



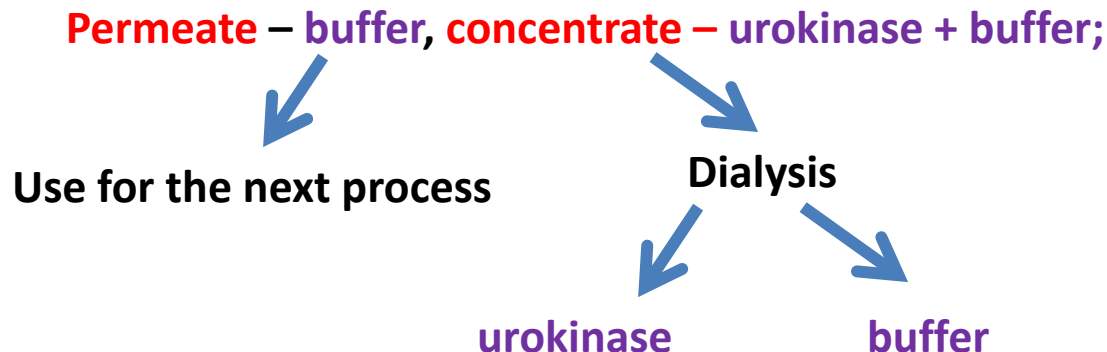
# EXAMPLE OF AFFINE ULTRAFILTRATION

## Ultrafiltration of urokinase from human urine

1. Bonding the enzyme with polymerized N-acryloyl-rn-aminobenzamidine.
2. Destroying the complex with a buffer containing 0.1 M NaCl and 0.1 M benzamidine. Ultrafiltration of the mixture simultaneously with washing out of ballast substances. The membrane of 100 kDa cut-off was used;

**Permeate** – urokinase+ buffer, **concentrate** – ligand + buffer+ballast

3. Ultrafiltration of the permeate. The membrane of 10 kDa cut-off was used; **Per**



# **ADVANTAGES OF AFFINE ULTRAFILTRATION**

**The possibility of purification of target protein products from all ballast impurities without exception;**

**Intensification of the process of isolation and purification of protein products;**

**The possibility of highly efficient continuous purification of protein products in a on an industrial scale;**

**Shortage of technological stages;**

**Lower consumption of chemical reagents;**

**Increase in the yield of target protein products.**

# **DISADVANTAGE OF AFFINE ULTRAFILTRATION**

**Perhaps the only difficulty in the implementation of affinity ultrafiltration is the need for individual selection of a ligand for a specific protein product and determination of the conditions for complexation and dissociation of complexes.**



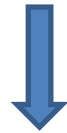
# SEPARATION OF IMMUNOGLOBULIN FROM EGG YOLK BY ULTRAFILTRATION



EGG YOLK IS A GOOD SOURCE OF SPECIFIC ANTIBODIES, which may be used in therapy. For the wide utilization of yolk immunoglobulin (IgY), a large-scale production of IgY with high purity and recovery from egg yolk is necessary. Such separation process should be simple and economical requiring few chemicals for food applications.

## Isolation of immunoglobuline

1. Diluted with water → filtration .



water soluble fraction

2. Purification using a freezing-thawing method,
3. Alkalization up to pH 9,
4. Ultrafiltration.

These procedures yielded 74-99% pure immunoglobuline with 72-85% recovery.



# MEMBRANE TECHNOLOGIES FOR WINE PRODUCTION

## Average composition of wine

Components	Concentration, g l <sup>-1</sup>		
Water		750-900	
Ethanol		69-121	
Glycerol		5-20	
Organic acids		3-20	
Minerals		0.6-2.5	
Nitrogen (amino-acids, proteins)		0.5-5	
	White wine		Red wine
Phenolic compounds	0.1-0.3		1.5-6
Polysaccharides		0.4-0.7	

## Wine colloids

Polyphenols, polysaccharides, proteins.

## Red wine

Anthocyanins, tannins.

## White wine

Hydroxycinnamic acids

## Polysaccharides

Grape polysaccharides: pectins, pectin substances,  
Yeast polysaccharides,  
Fungi polysaccharides: beta-glucan.

## Wine proteins

Grape proteins and minor extent proteins from autolyzed yeast 10–500 mg/l).

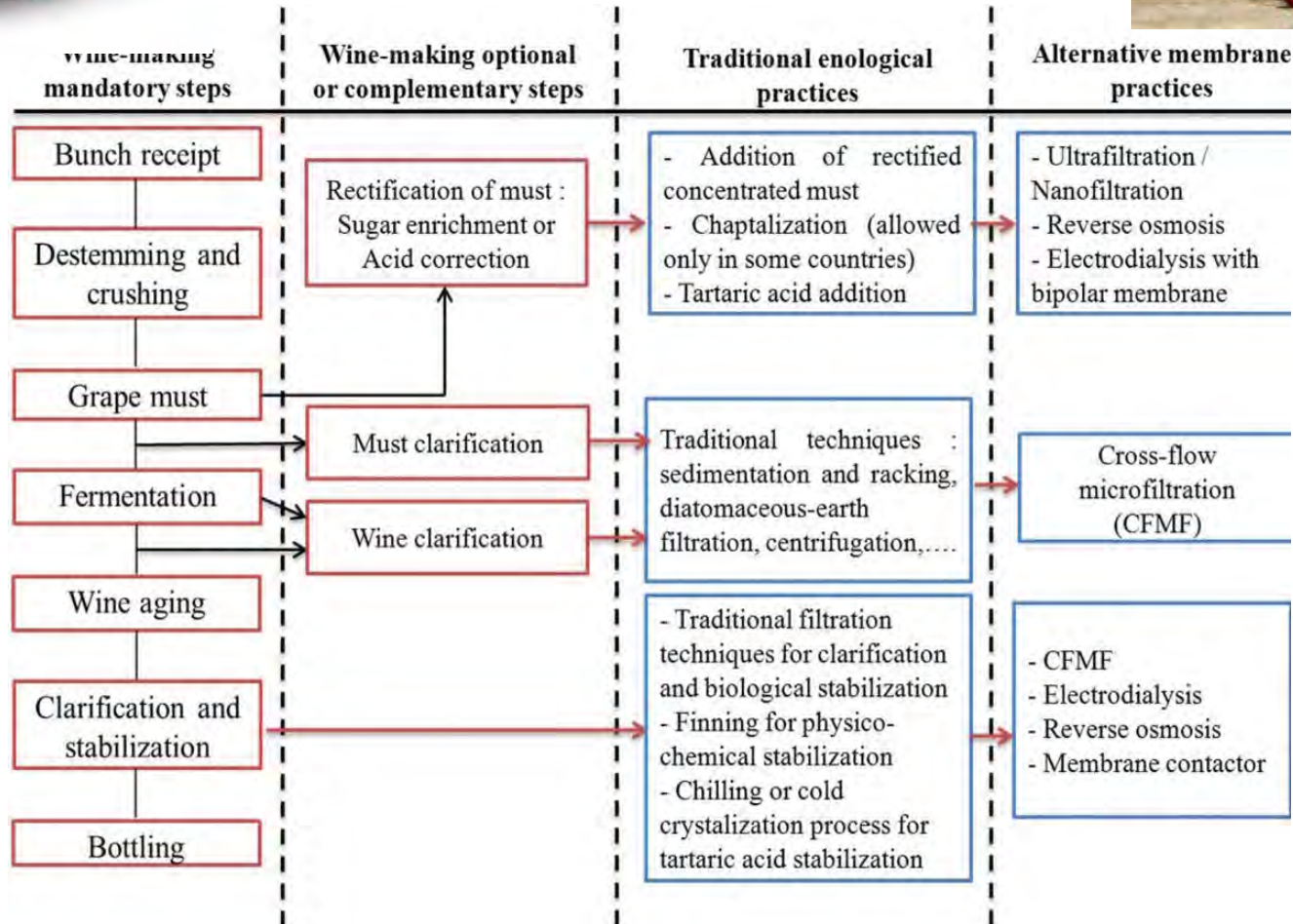
## Tasks of filtration

In the overall production process, wine filtration is used to decrease turbidity and improve microbiological stabilization. Turbidity is due to macromolecules and particles in suspension

# MEMBRANE TECHNOLOGIES FOR WINE PRODUCTION



## Stages of wine production: with and without membranes



# MEMBRANE TECHNOLOGIES FOR WINE PRODUCTION

## Grape Must (mosto) Concentration

**Must** is freshly crushed fruit juice (usually grape juice) that contains the skins, seeds, and stems of the fruit.

## Methods

Reverse osmosis, nanofiltration

## Pretreatment

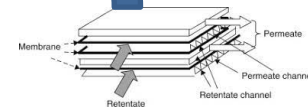
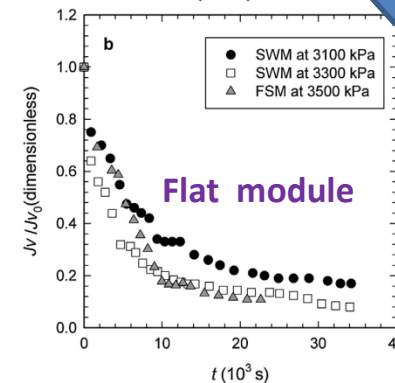
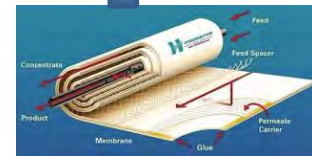
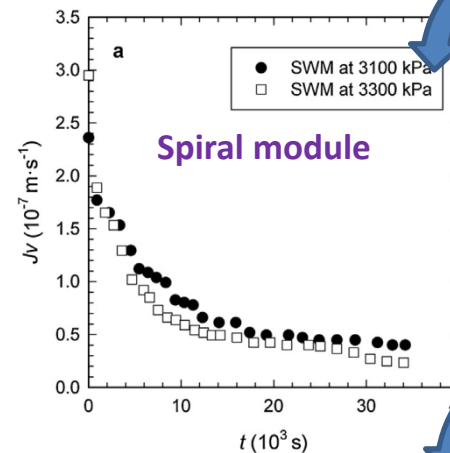
Removal of solids

## Comparison of two methods

Parameter	Unit	40 bar	Wine enriched by <sup>a</sup>	
		NF	RO	
Alcohol	% vol	11.9	11.9	
Dry extract	g l <sup>-1</sup>	23.2	21.6	
Reducing sugars	g l <sup>-1</sup>	0.7	0.6	
Ashes	g l <sup>-1</sup>	2.35	2.20	
Alcalinity	meq l <sup>-1</sup>	8.5	8.2	
pH	—	3.14	3.09	
Titrate acidity	g l <sup>-1</sup>	6.5	6.2	
Tartaric acid	g l <sup>-1</sup>	2.15	2.20	
Malic acid	g l <sup>-1</sup>	4.10	3.90	
Total polyphenols	mg l <sup>-1</sup>	129	94	
DO at 420nm	AU	0.11	0.09	
Sulphates	mg l <sup>-1</sup>	40	41	



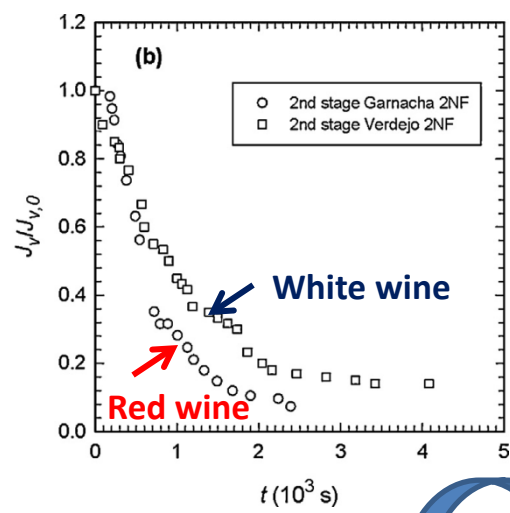
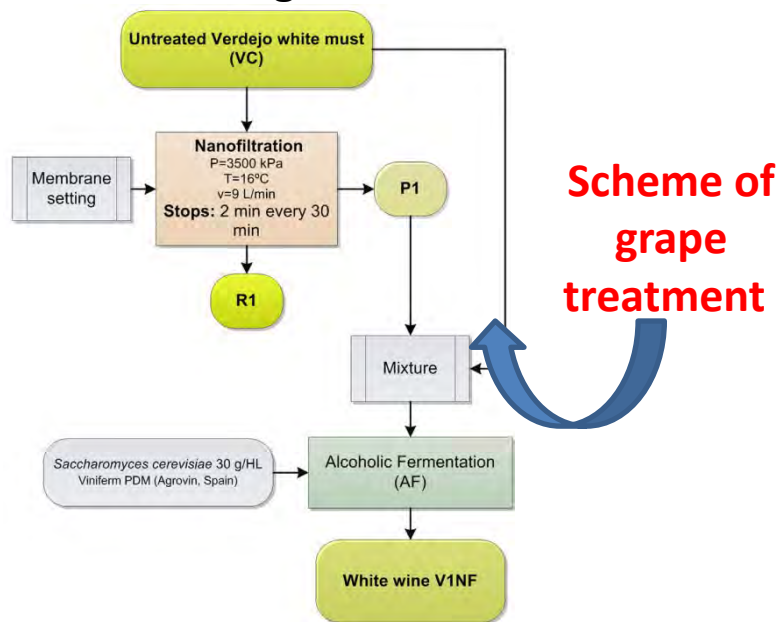
## Use of different membrane modules



**Spiral module is preferable due to optimal hydrodynamic conditions.**

# REDUCING ALCOHOL CONTENT. REMOVAL OF SUGARS FROM THE MUST

An excess of alcohol must be removed from the must, since it complicates fermentation. Meanwhile, consumers show preference and demand wines with less alcohol content (between 9 and 13%). The way to reduce the content of alcohol is to decrease the sugar content from the must.



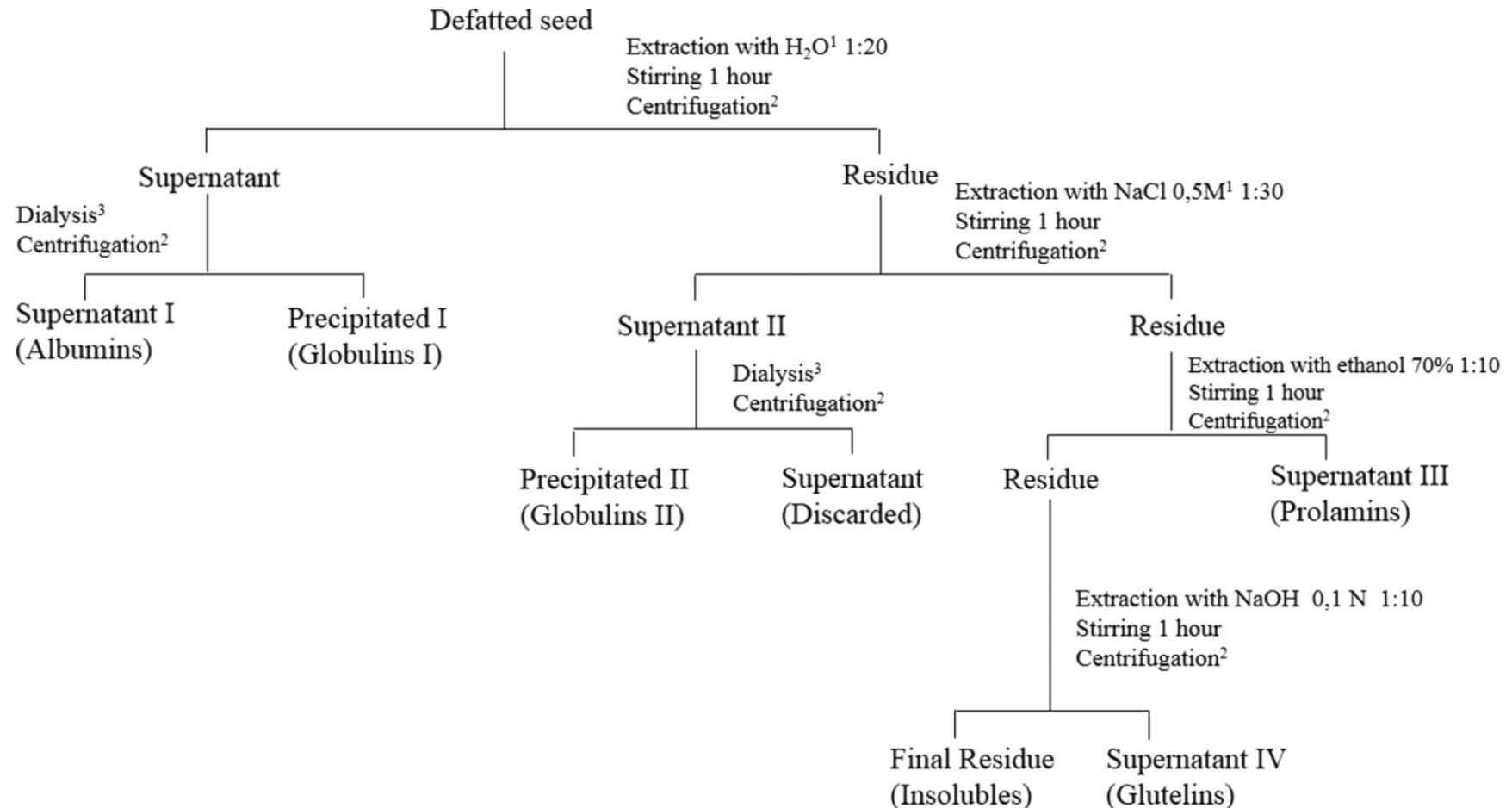
**Flux as a function of time**

**Initial and final content of components in wine**

Component	Red grape			White grape		
	Initial must	Must after NF	Wine	Initial must	Must after NF	Wine
Glucose (g/L)	105	90		117	105	
Fructose (g/L)	106	93		120	106	
Alcoholic degree , %	12.5	10.9	11	13.9	12.5	14
Anthocyanins (mg/L)	371		278	4.4		2.2

# PROTEIN FRACTIONATION OF SEEDS OF MORINGA OLEIFERA

The extract of the seeds of *Moringa oleifera* is recommended as a coagulant for water treatment. the concentration 0.2 lg/IL of *Moringa oleifera* seed extract recommended to treat water for humans





# ULTRAFILTRATION FOR BEER PRODUCTION

## MALT



**Malt** is germinated cereal grain that has been made by soaking in water and dried under elevated temperature or roasted.

Separation of flavor from color by ultrafiltration

## MALT treatment

Speciality Malt

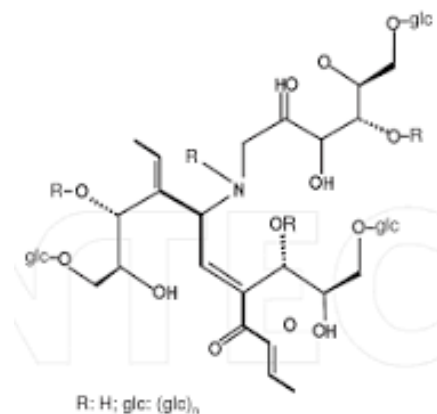
Mill

Aqueous Extraction

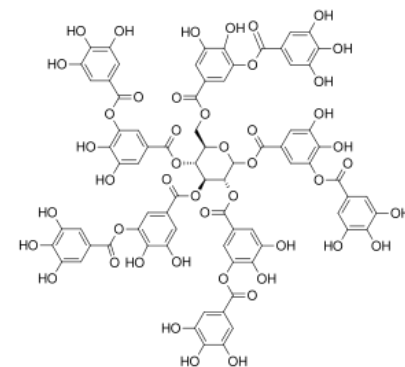
Ultrafiltration

Low MWt  
Flavor Extract

High Mwt  
Color Extract



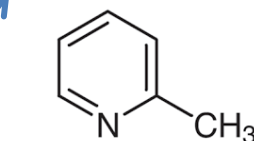
Melanoidine



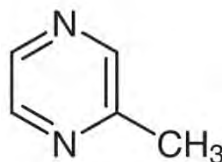
## Flavor compounds

Compound	Flavor	Color
2-Methylpyridine	100	0
2-Methylpyrazine	98	2
2,5-Dimethylpyrazine	94	6
2-Ethylpyrazine	80	20
2,3,5-Trimethylpyrazine	98	2
Maltol	98	2

1 kDa



2-methylpyridine



2-methylpyrazine

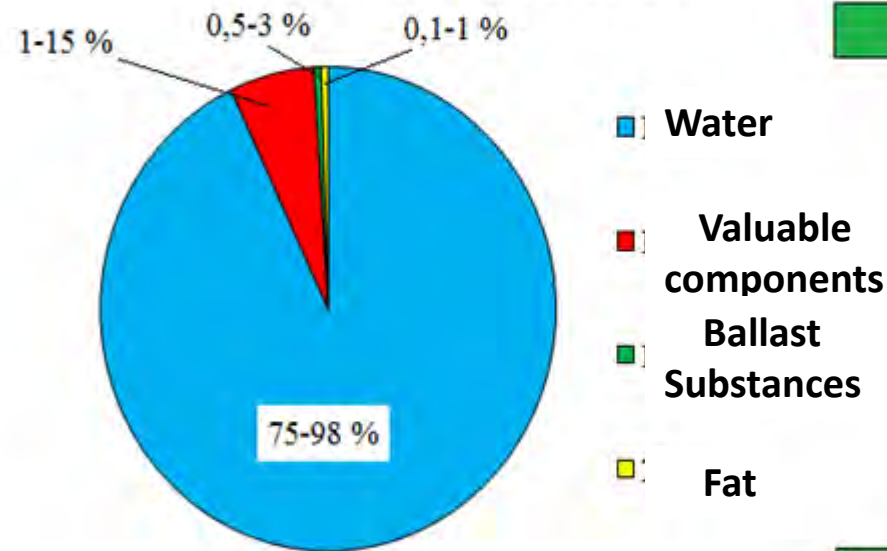
10-100 kDa

Color is due to polyphenols and melanoidines

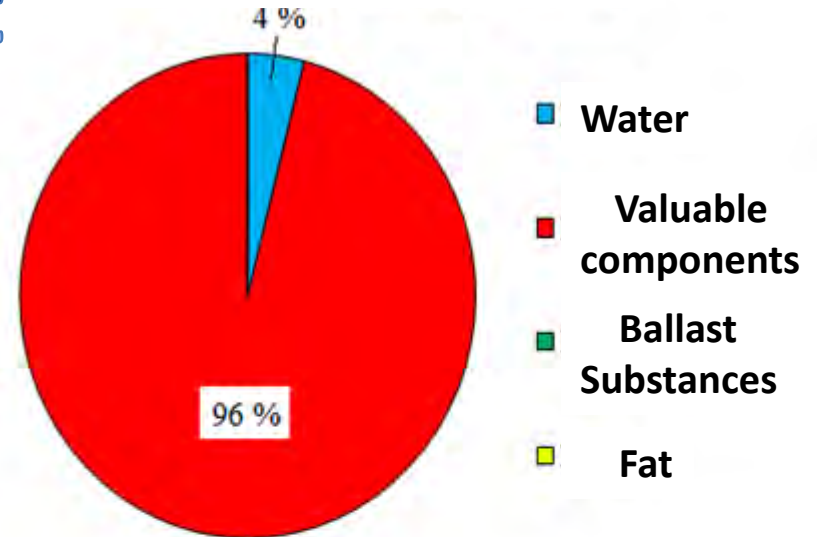
Further the extracts are used for the enhancement of flavor and color.

# Solution → Dry product

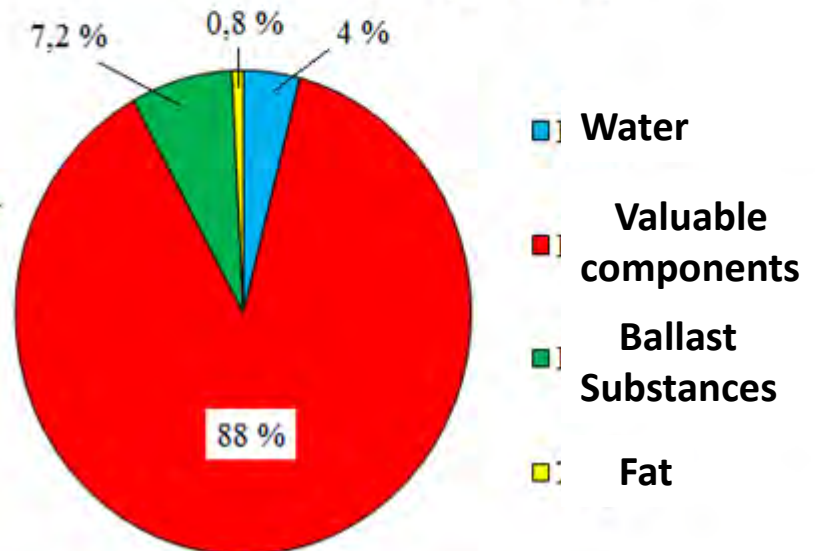
Average values of the composition of solutions  
In food industry



Ideal composition of the target  
dried product



Real composition of values of the  
target dried product



# DIAFILTRATION

Liquid of biological origin

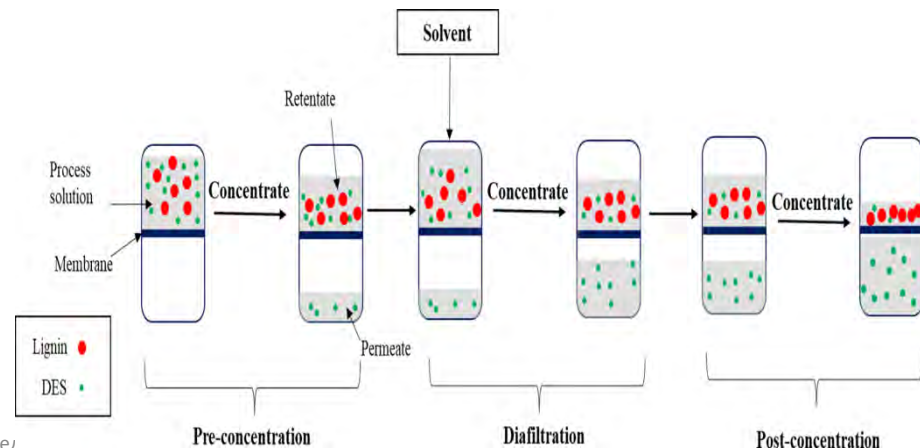
Valuable product  
(High-molecular compounds )

Ballast substances  
(low-molecular compounds )

Similarly to electrodialysis, **DIAFILTRATION** allows us to remove ballast (low-molecular) substances.

**Diafiltration** is the membrane filtration, which involves dilution of concentrate with deionized water. Simultaneously with the removal of permeate from the solution being purified, water is added to the concentrate. Ballast low-molecular compounds are washed from the concentrate by this manner.

**Separation over diafiltration** is based on different selectivity of membranes to highly- and low-molecular compounds. Membrane rejects highly-molecular compounds, low-molecular compounds are passed through the membrane to the permeate





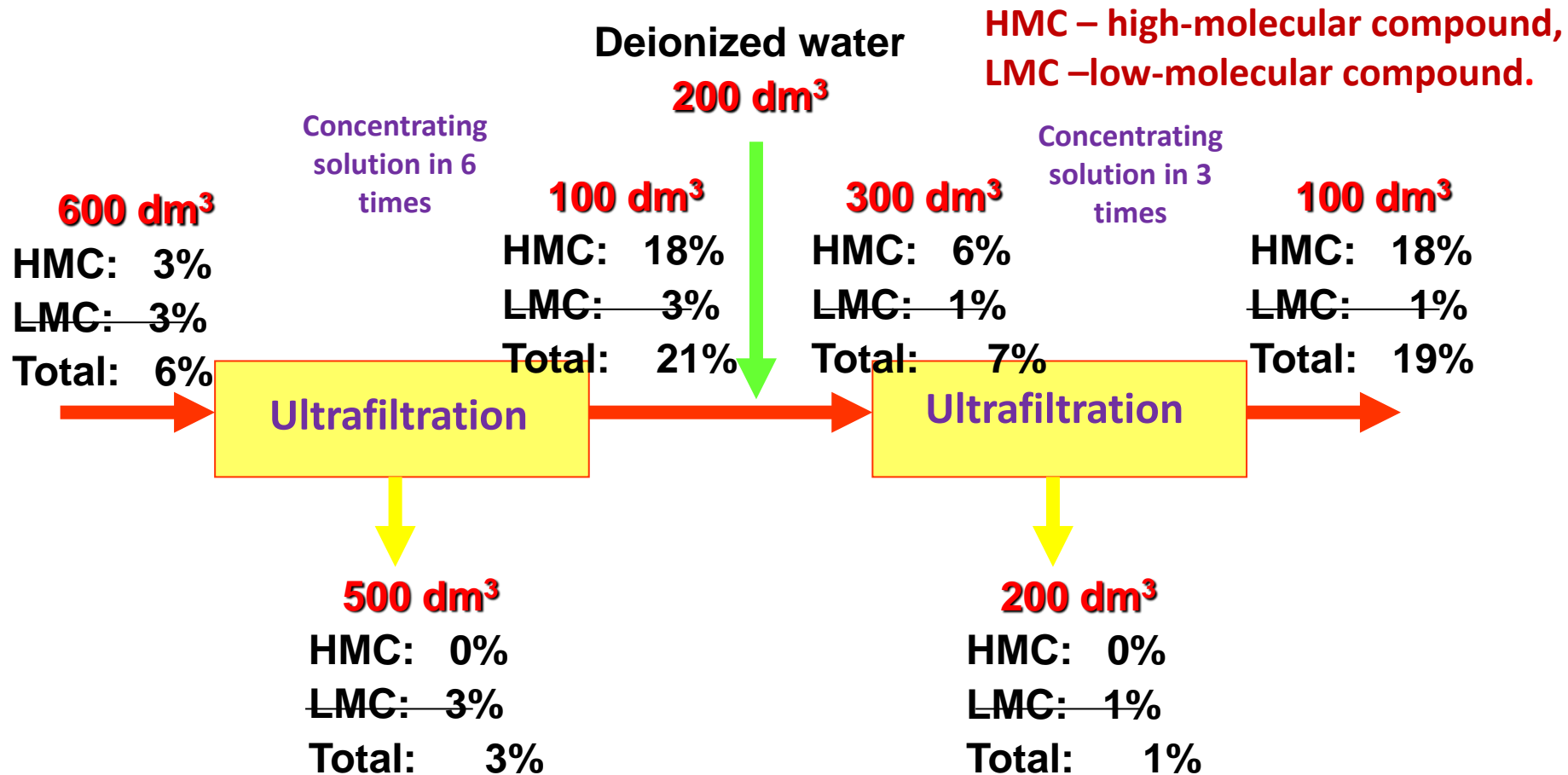
# EXAMPLE OF DIAFILTRATION

(for ideal membrane system)

**Ideal membrane,  
Ideal apparatus;  
No fouling**

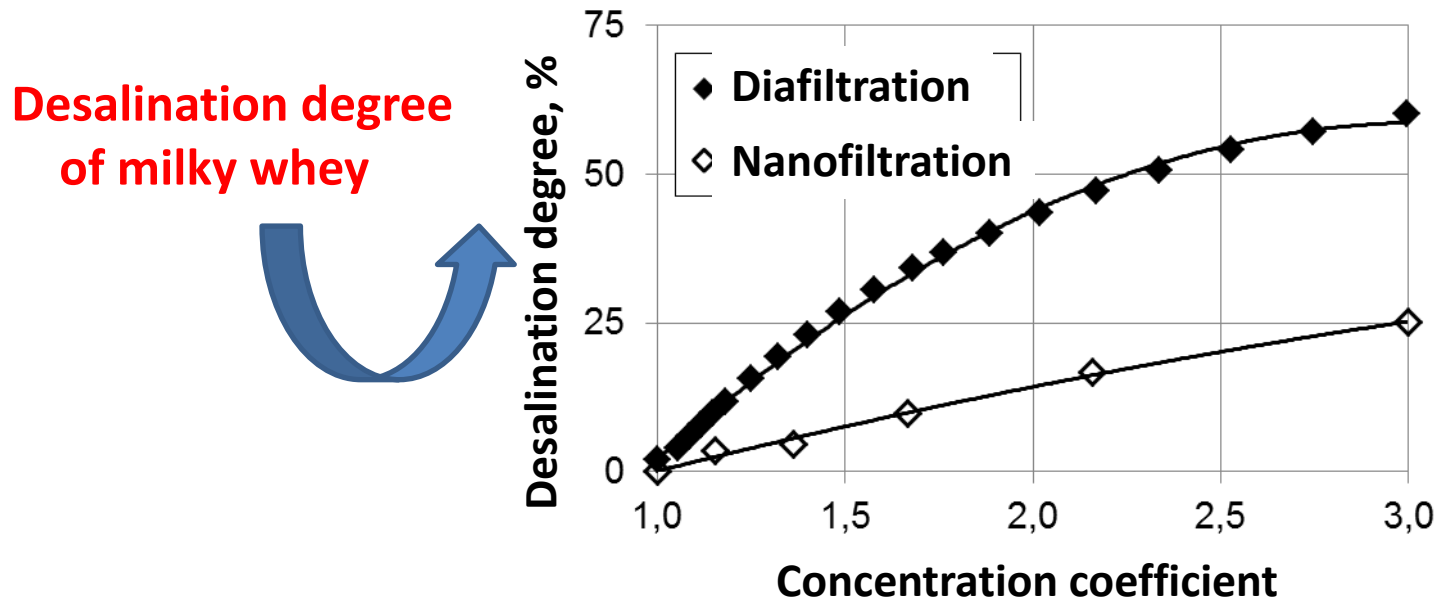
The parameter, which reflects the efficiency of diafiltration is the ratio of the contents of ballast compounds in the HMC solution before and after the process. **This ratio is 3 for the example.**

Other parameters are the ratios of concentrations of HMC and LMC before and after the process. **These ratios are 3 (before) and 18 (after).**



# TECHNOLOGICAL POSSIBILITY OF DIAFILTRATION

- It is possible to purify high-molecular compounds only from low-molecular additions, molecular mass of which is sufficiently different (the order of magnitude) from the molecular mass of high-molecular compounds (target product).
- High-molecular ballast additions are also concentrated over diafiltration. In other words, it is impossible to remove them using this method.



# COMPARISON OF DIFFERENT SEPARATION METHODS

## Desalination of milky whey

Parameter	Nanofiltration	Diananofiltration	Electrodialysis
Demineralization, %	25-30	50-60	50-60
Energy consumptions, kW m <sup>-3</sup>	5,2	15,6	3,4-4,2
Water consumptions, m <sup>3</sup> m <sup>-3</sup>	-	1,5-3	Closer to 0,5
Concentrating dry substances	in 2.5-3.5 times	in 2,5-3,5 times	-
Lactose losses, %	2-4	6-8	3-4
Losses of lactic acid, %	до 10	20-30	33-45

## Problems of diafiltration. What is unknown?

The efficiency of diafiltration depends on a number of conditions:

- The composition of the solution being desalinated?
- What is a volume of the solution before adding water?
- What is a volume of deionized water?
- And so on...

# MEMBRANE SEPARATION IN DAIRY INDUSTRY

## Composition of cow milk

	Concentration in whole milk (g/L)	Size range and average (at weight average)
Water	87.1	
Fat globules	4.0	0.1–15 $\mu\text{m}$ , average 3.4 $\mu\text{m}$
Casein (in micelles)	2.6	20–300 nm, average 110 nm
Serum proteins	0.7	3–6 nm
$\alpha$ -lactalbumin	0.12	14 kDa
$\beta$ -lactalbumin	0.32	18 kDa
BSA	0.04	66 kDa
Proteose-peptone	0.08	4–40 kDa
Immunoglobulins	0.08	150–900 kDa
Lactoferrin	0.01	86 kDa
Transferrin	0.01	76 kDa
Others		
Lactose	4.6	0.35 kDa
Mineral substances	0.7	
Organic acids	0.17	
Other		

Membrane processes  
for needs of dairy  
industry

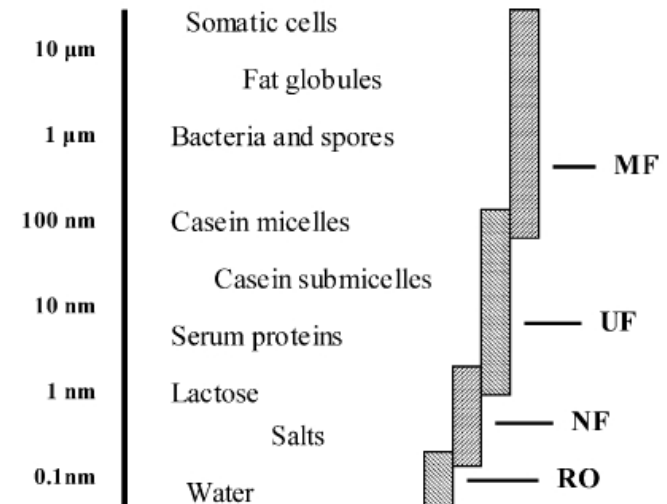
Removal of Bacteria and Spores from Skim Milk (Cold Pasteurization)

Separation of Casein Micelles from Soluble Proteins

Separation and Fractionation of Fat Globules from Whole Milk

Concentration and Demineralization of Whey and Milk Ultrafiltration Permeate

Fractionation of Whey Proteins

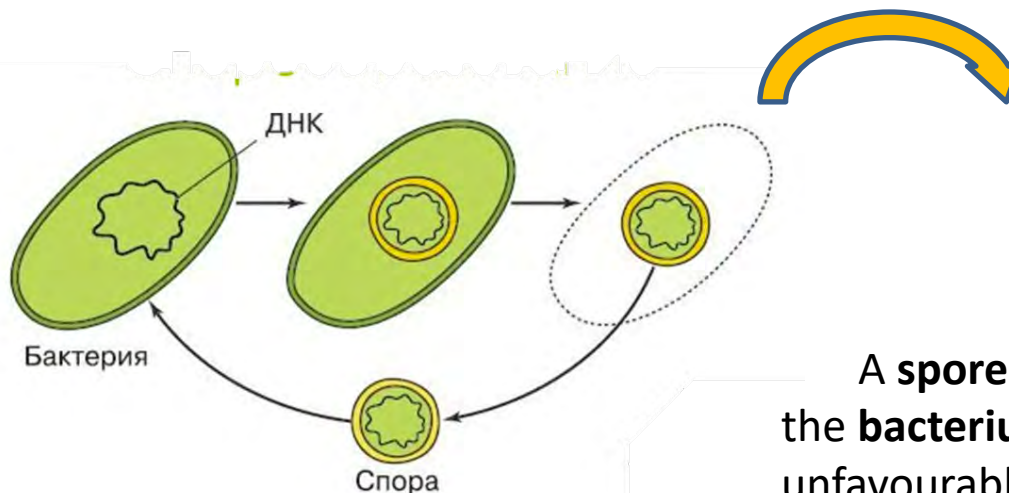


# REMOVAL OF BACTERIA AND SPORES FROM SKIM MILK (COLD PASTEURIZATION)

## Removal of pathogens from milk

Collected milks by the dairy plant present the risk of containing pathogenic bacteria for human such as *Listeria*, *Brucella*, *Mycobacterium*, or *Salmonella*. Therefore, the reduction of bacteria and spores has to be achieved, without changing the functionality of the milk proteins, especially when the milk has to be used for cheese production. The growth of unwanted bacteria and spores can spoil the cheese by a late blowing during ripening.

### Spore formation



A **spore** is a dormant stage in which the **bacterium** can survive despite unfavourable external conditions.

As opposed to plant or fungi, bacteria **spores are only for survival**, not for reproduction.

# REMOVAL OF BACTERIA AND SPORES FROM SKIM MILK (COLD PASTEURIZATION)

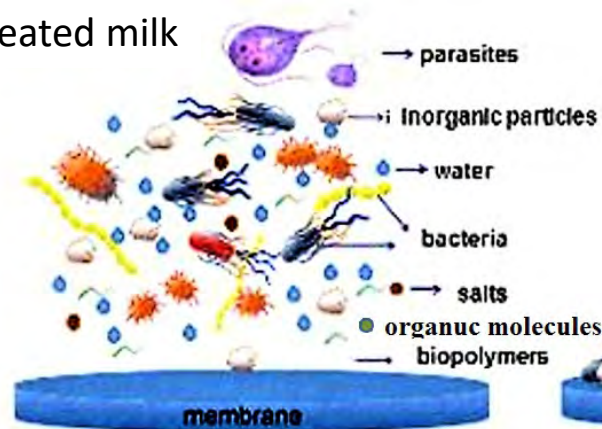
## Typical pathogens in skim milk

Species	Size, nm	Method	Pressure, bar
Helminth eggs	25000-55000	Macro-, microfiltration	0, 0.5-5
Eukaryotes, (protozoa)	10000- 100000	Macro-, microfiltration	0, 0.5-5
Procaryotes (bacteria)	300-10000	Macro-, micro-, ultrafiltration	0, 0.5-10
Bacteria spores	800-1200	Micro-, ultrafiltration	0.5-10

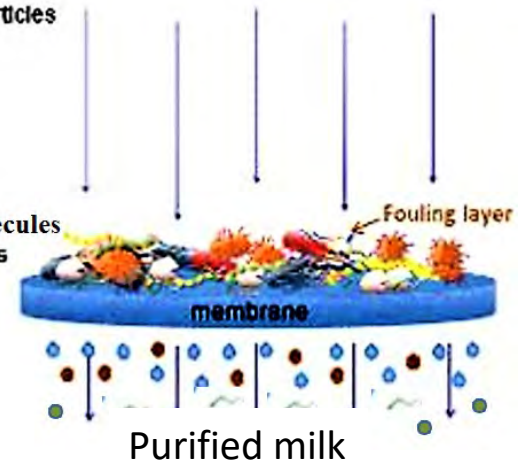
**Rejection of  
pathogens with a  
membrane**



Untreated milk



Dead-end Ultrafiltration





# REMOVAL OF BACTERIA AND SPORES FROM SKIM MILK

A commercial MF process for the reduction of bacteria and spores from milk is available under the name Bactocatch (Tetra Laval Co.)

The **pressure** is about 0.5 bar.

**Pore size** of 1.2  $\mu\text{m}$  is preferable. Smaller pore size causes casein rejection.

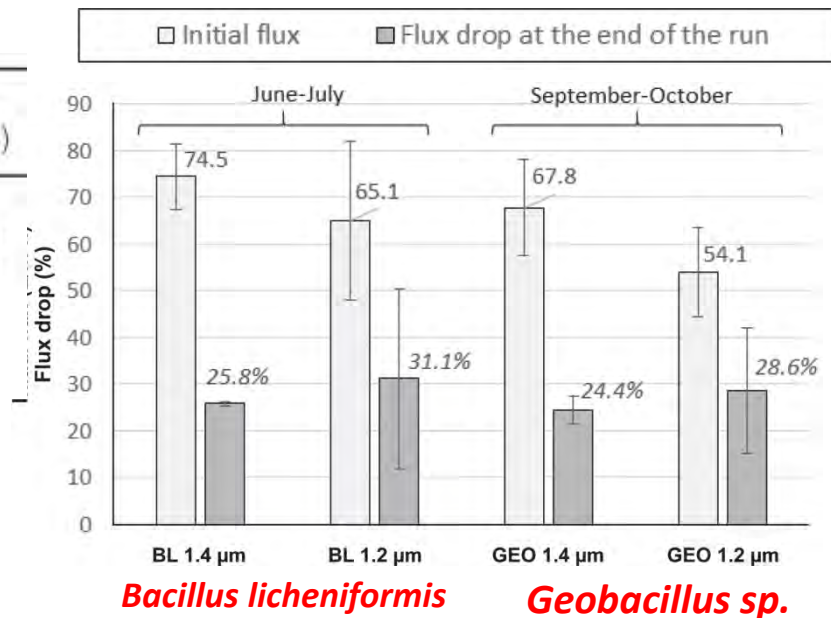
**Strategy of fouling control:**

To minimize the formation of the fouling layer, high cross-flow velocities (4–8 m/s) or backflushing techniques have to be used.

## Removal of bacteria spores

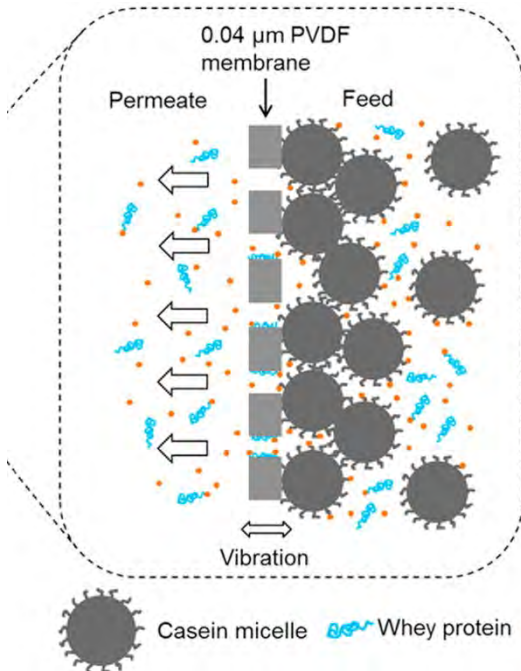
Challenge study	Initial load (log cfu/mL)	After MF (log cfu/mL)
<i>Bacillus licheniformis</i>		
1.4- $\mu\text{m}$ MF membrane	$6.11 \pm 0.53$	$3.94 \pm 0.13$
1.2- $\mu\text{m}$ MF membrane	$6.98 \pm 0.08$	$2.41 \pm 0.15$
<i>Geobacillus</i> sp.		
1.4- $\mu\text{m}$ MF membrane	$6.56 \pm 0.29$	ND <sup>†</sup>
1.2- $\mu\text{m}$ MF membrane	$6.38 \pm 0.24$	ND

## Removal of bacteria spores



# SEPARATION OF CASEIN MICELLES FROM SOLUBLE PROTEINS

Casein micelles (30-400 kDa) are not in the concentrate, they are deposited on the membrane. Lactose is partially associated with casein. Soluble whey proteins (albumins and globulins) pass through the membrane, the pore size of which is 40 nm.



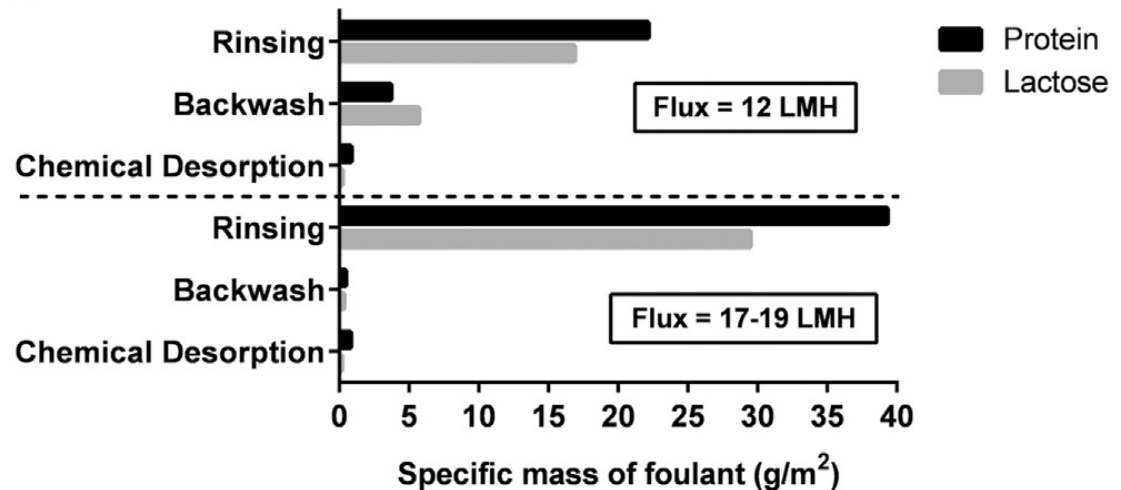
- Loose foulant layer consisting of both protein (mainly casein) and lactose
- Approximately 70% of resistance can be recovered by rinsing

(b)

Casein is **removed** by washing (about 70 %).

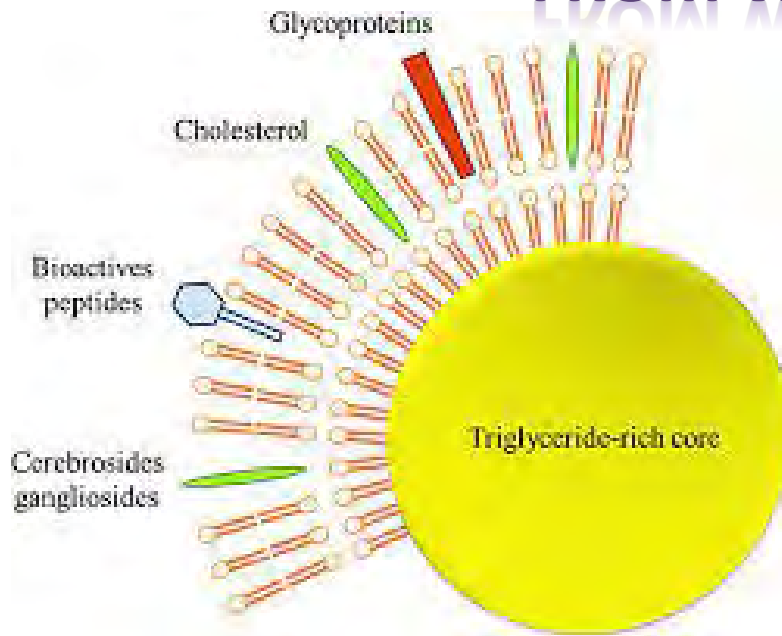
**Fouling control** – vibration of membrane module.

**Removal of deposit**



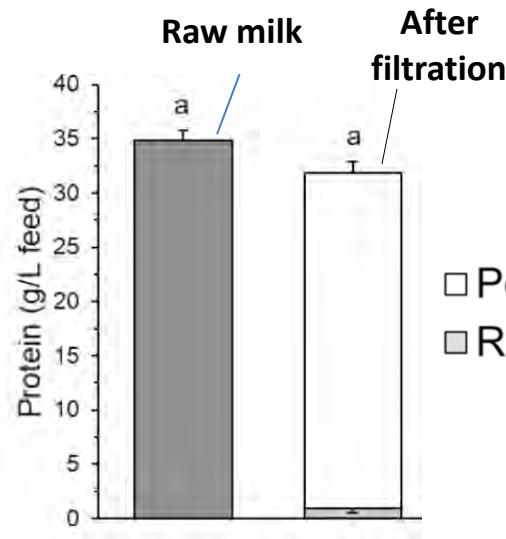
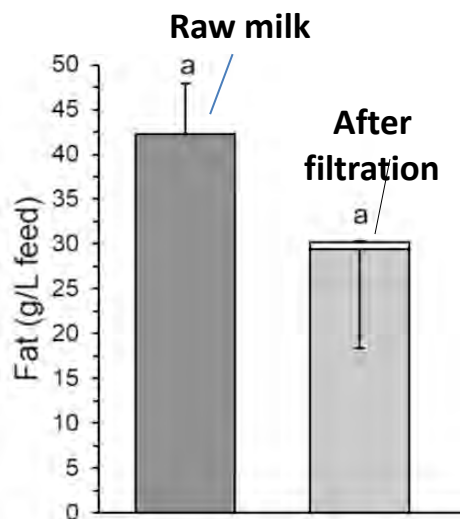


# SEPARATION AND FRACTIONATION OF FAT GLOBULES FROM WHOLE MILK



Milk fat mainly consists of dispersed fat globules, with diameter between 0.1 and 15  $\mu\text{m}$ . Their integrity is maintained by a thin membrane surrounding their internal core. The number of fat globules per milliliter is between  $10^{10}$  and  $10^{11}$ .

MF is known for not damaging the fat globules membranes.



□ Permeate  
□ Retentate

Ceramic membranes with pore size of **0.8-1.4  $\mu\text{m}$**  were used. Pressure is 0.5 bar.

**Disadvantage** – casein particles are also rejected.

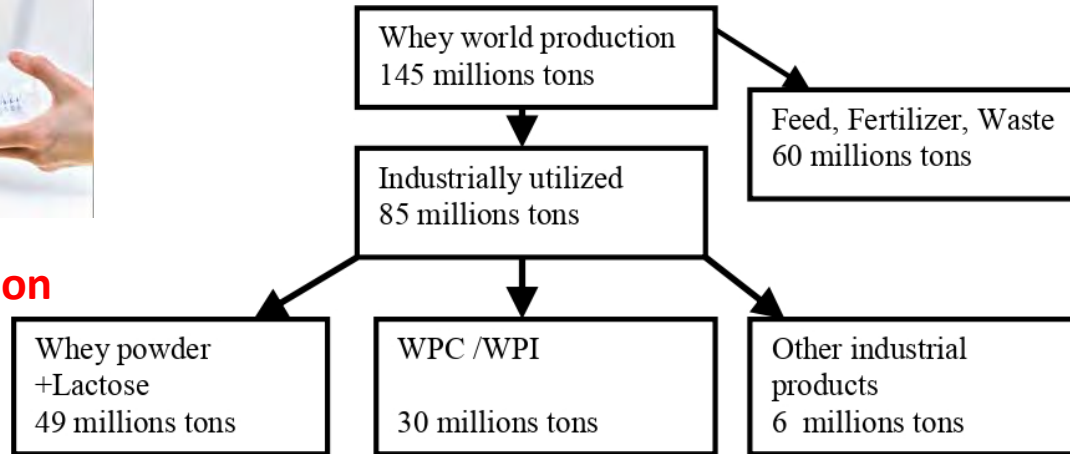
**Final product is skimmed milk.**

# MEMBRANE TREATMENT OF MILKY WHEY

## Milky whey in a global scale



### Infant nutrition



### Sport nutrition

## Composition of milky whey

S.No	Constituent	Unit	Sweet whey	Acid whey
1	Water	%	93-94	94-95
2	Dry matter	%	6-6.5	5-6
3	Lactose	%	4.5-5	3.8-4.3
4	Lactic acid	%	traces	up to 0.8
5	Total protein	%	0.8-1.0	0.8-1.0
6	Whey protein	%	0.6-0.65	0.6-0.65
7	Citric acid	%	0.1	0.1
8	Minerals	%	0.5-0.7	0.5-0.7
9	pH		6.4-6.2	5.0-4.6
10	SH Value		about 4	20-25

## Mineral composition of milky whey

K – 36 mmol dm<sup>-3</sup>

Na– 16 mmol dm<sup>-3</sup>

Ca – 24 mmol dm<sup>-3</sup>

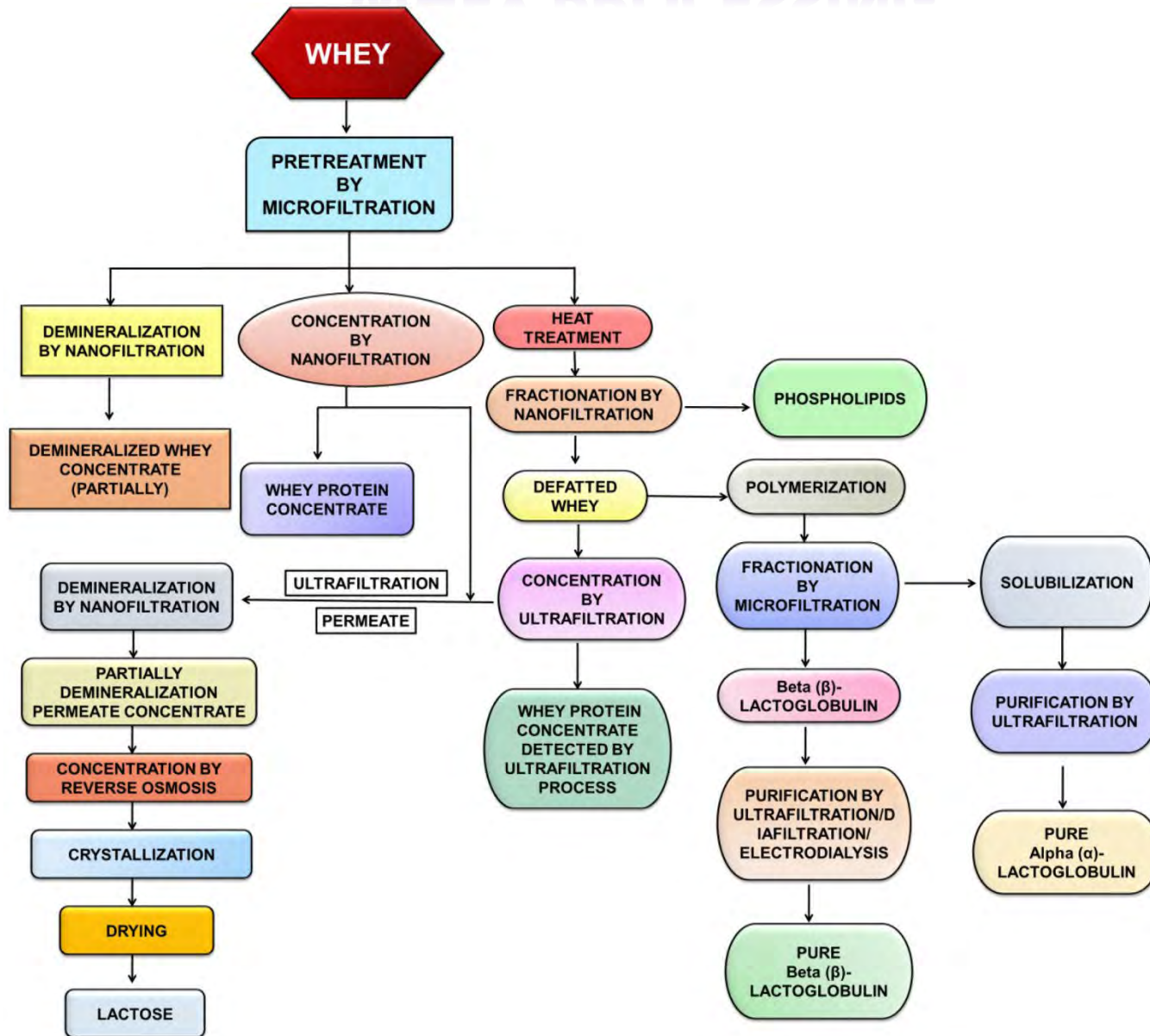
Mg – 4.3 mmol dm<sup>-3</sup>

P – 30 mmol dm<sup>-3</sup>

Cl – 51 mmol dm<sup>-3</sup>

Source : [www.dairyforall.com](http://www.dairyforall.com)

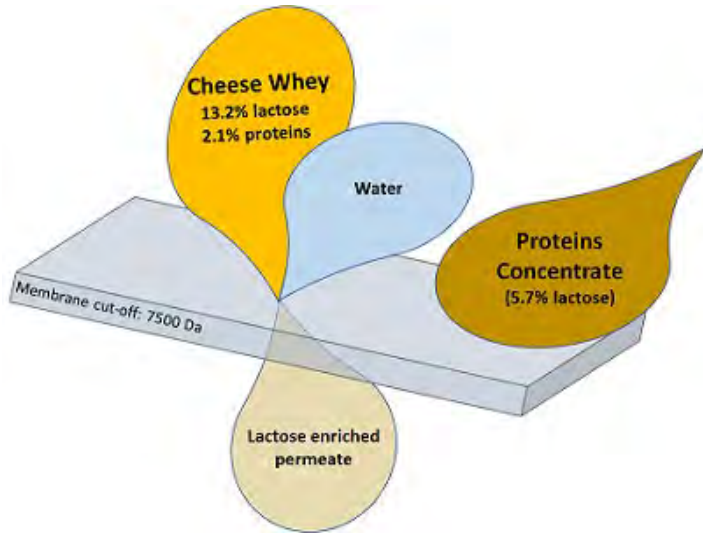
# WHEY PROCESSING



# WHEY PROCESSING

## Ultra- or nanofiltration

Target product is mineralized protein concentrate



**Key field of investigations** is the development of membranes with antifouling properties.

## Modifying microfiltration membranes

- transformation of microfiltration membranes to ultrafiltration separators.

## Advantages over microfiltration membranes

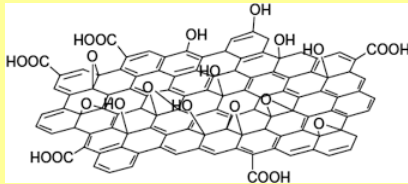
Rejection of colloidal particles.

## Advantages over ultrafiltration membranes

Higher mechanical stability.

## MODIFIER

### GO or CNDs

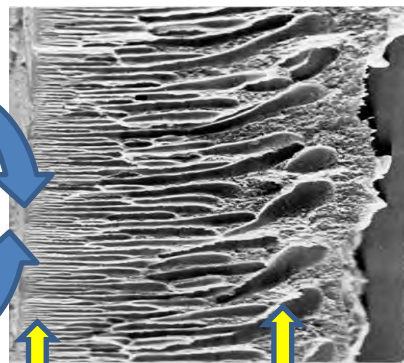


Inorganic ion-exchanger (binder)

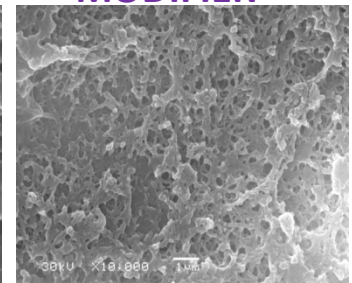
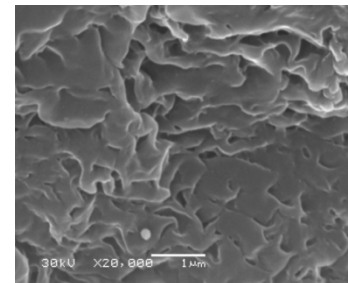
## POLYMER FILTRATION MEMBRANE

Active layer

Active layer +  
MODIFIER

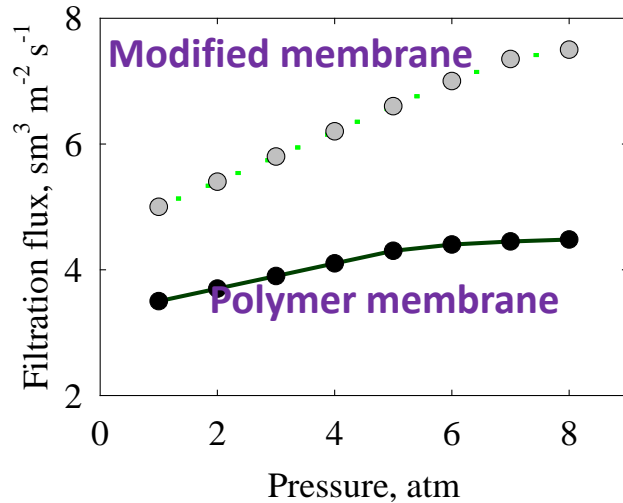


Active layer



# WHEY PROCESSING

## FILTRATION OF MILKY WHEY



## Typical vitamin content

Vitamin	Whey mg/kg	WPC <sup>b</sup> mg/kg
Thiamine	.31	.32
Folic acid	.07	.11
Niacin	1.18	1.28
Riboflavin	.16	.20
Choline	108.00	136.00
Pantothenic acid	3.94	4.43

Initial whey

Concentrate

## Typical whey composition before and after concentrating

Fraction	% Water removed (volume reduction)			
	0	80	90	95
Total solids	6.60	9.50	13.00	18.00
Lactose	4.80	5.50	5.60	5.80
Protein	.67	2.85	5.50	9.54
Ash	.74	.79	.77	.75

The problem of concentrate is high salt content



# TREATMENT OF ULTRAFILTRATION PERMEATE

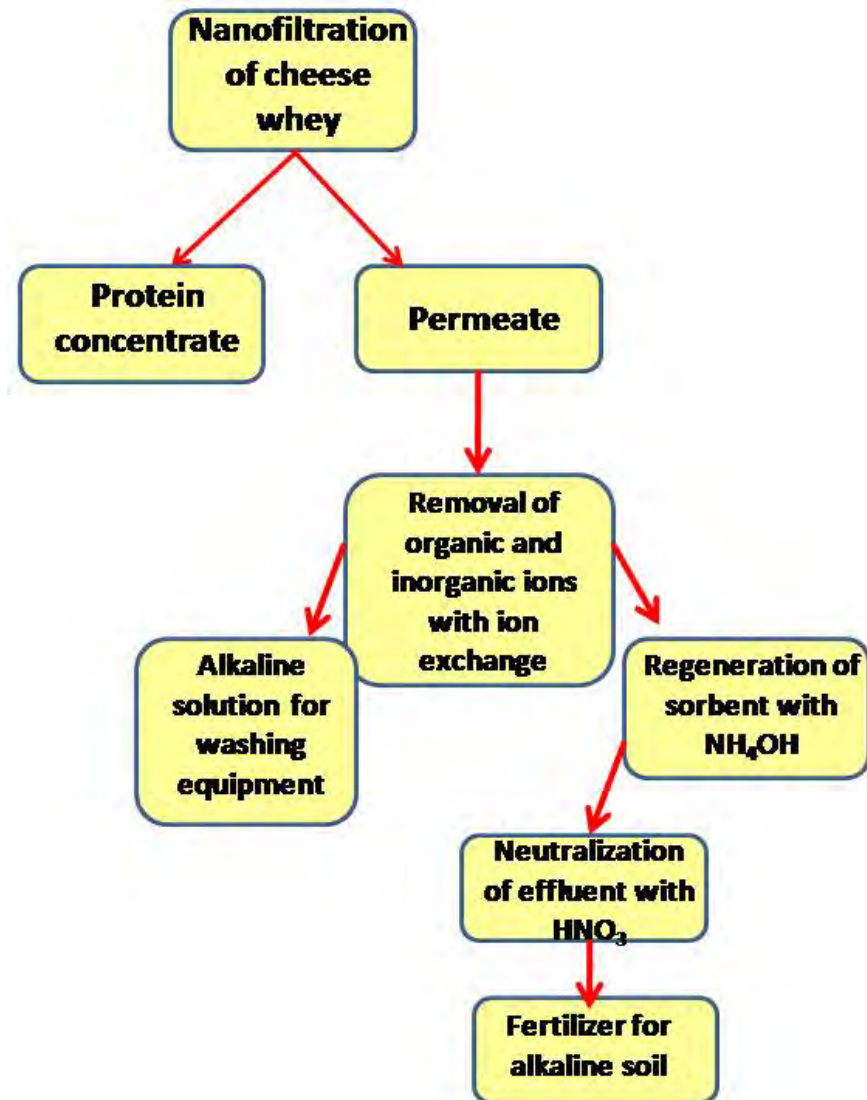
## Ion exchange method



Where  $\text{An}^-$  is  $\text{Cl}^-$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , Tartrates, citrates, lactates, lactic acid, aminoacids .

Alkaline solution is formed at the outlet of the column. It could be used for washing equipment. Amino acids substances are removed during the treatment with ion-exchanger, therefore the alkaline soluble has no an unpleasant smell. The spent regenerating  $\text{NH}_4\text{OH}$  solution is used to obtain nitrogen fertilizer.

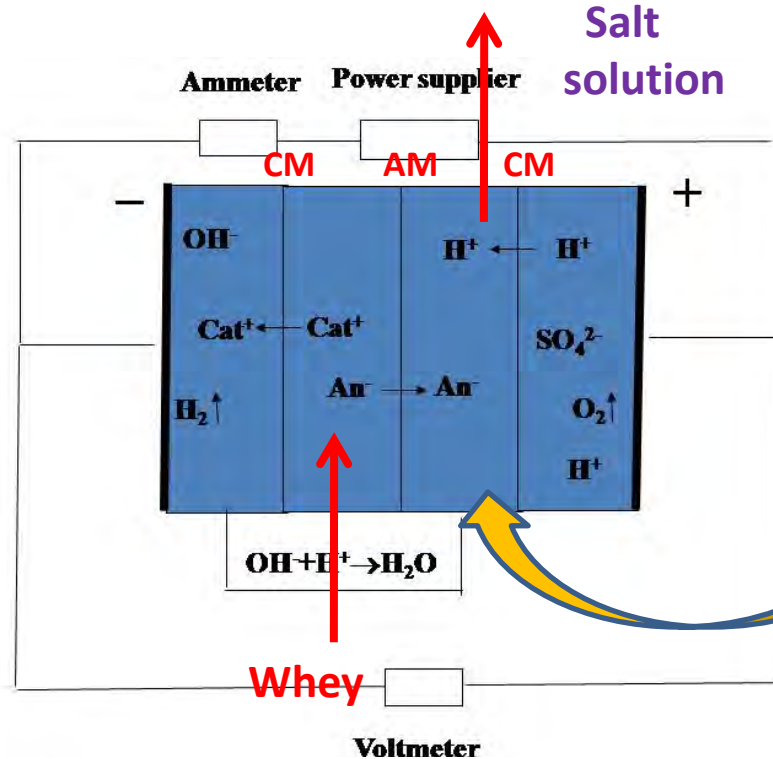
### Scheme of the permeate treatment





# Electrodialysis of milky whey

## Experimental set-up



Complication of electrodialysis module (additional camera, to which anions are moved) is to prevent whey acidification due to the acid leakage through the membrane from the anodic side.

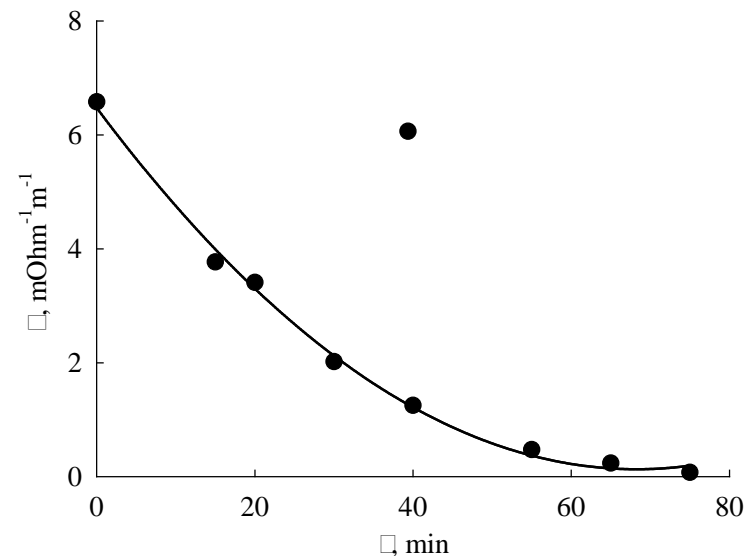
Chlorides, (di)hydrophosphates, sulfates, Lactates, tartrates, citrates, aminoacids.

Decrease of salt content  
Decrease of salt content

The energy consumptions of 2.4 kWh per 1 kg of salts,. For water treatment, it is typically 1 kWh per 1 kg.

Possible directions to decrease energy consumptions

Change of module configuration and geometrical parameters → difficult passage of liquids,



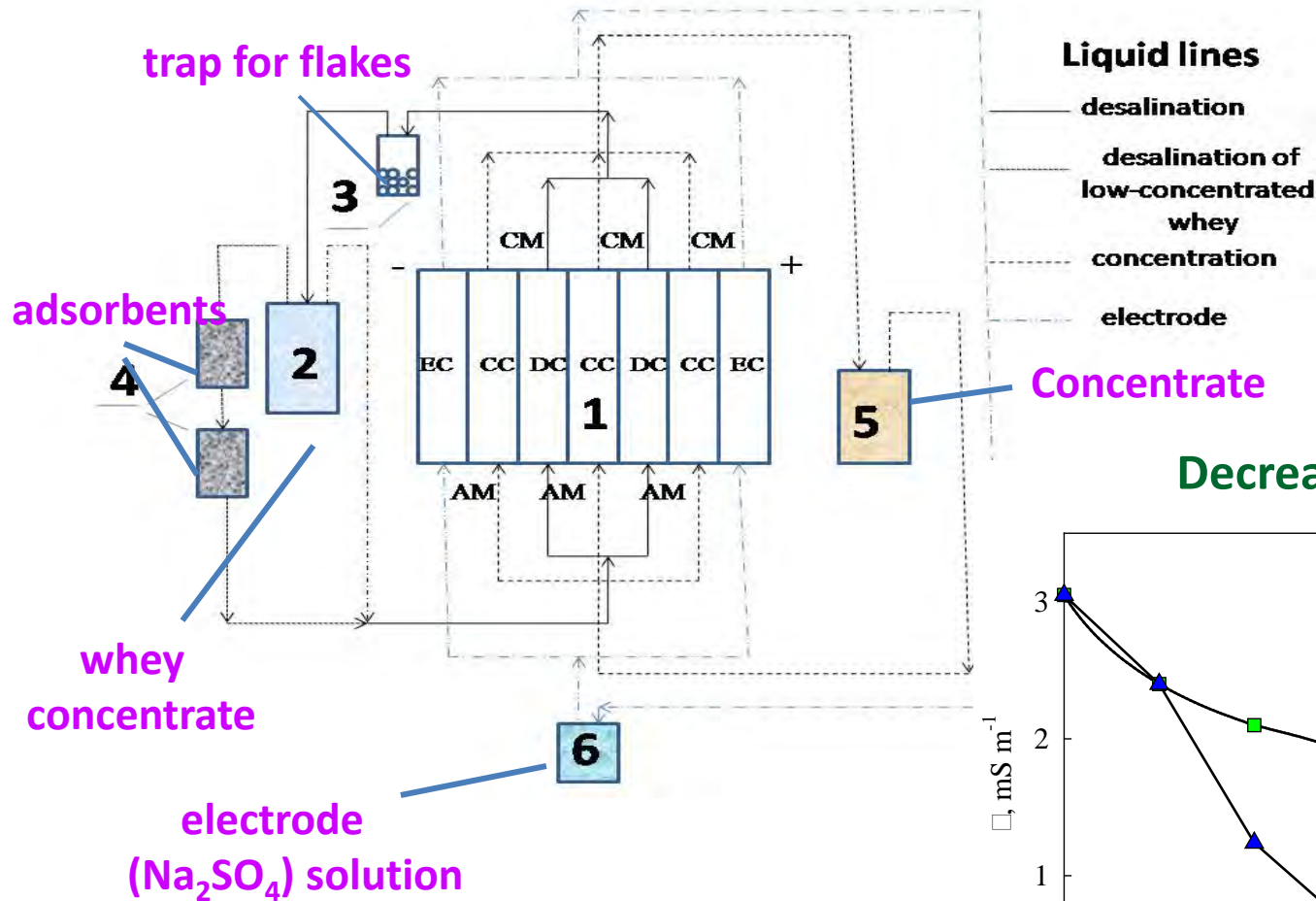
# Electrodialysis of whey concentrate

## Experimental set-up

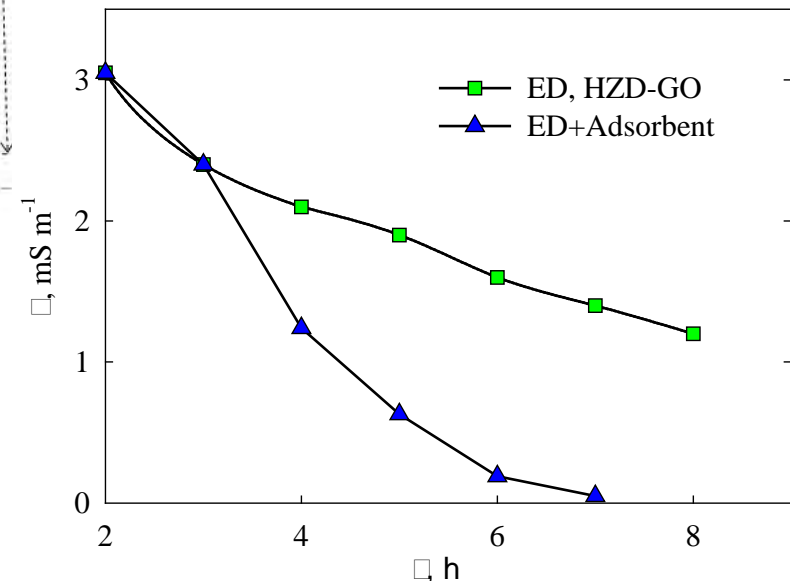
Adsorbents are integrated into the membrane set-up.

Why is it necessary?

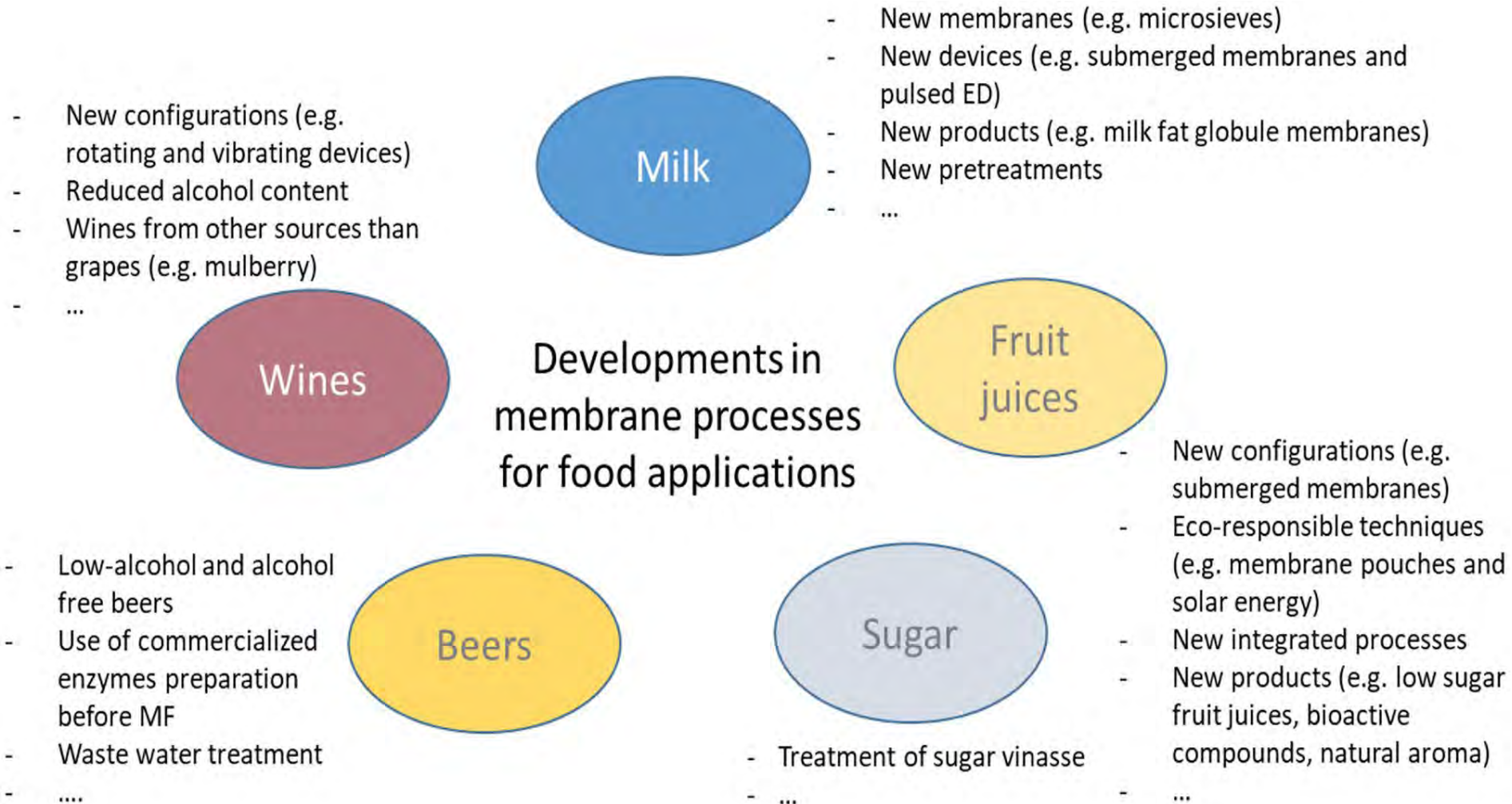
Too high salt content



Decrease of salt content



# DEVELOPMENT IN MEMBRANE PROCESSES FOR FOOD APPLICATIONS



# Conclusions