MEMBRANE TREATMENT OF LIQUIDS CONTAINING THE COMPONENTS OF BIOLOGICAL ORIGIN

STRUCTURE OF THE LECTURE

-**Main terms of baromembrane separation;**

-**Fouling (scaling, organic fouling, biofouling) and strategy of its prevention;**

-**Membrane bioreactor;**

-**Membrane methods for wastewater treatment;**

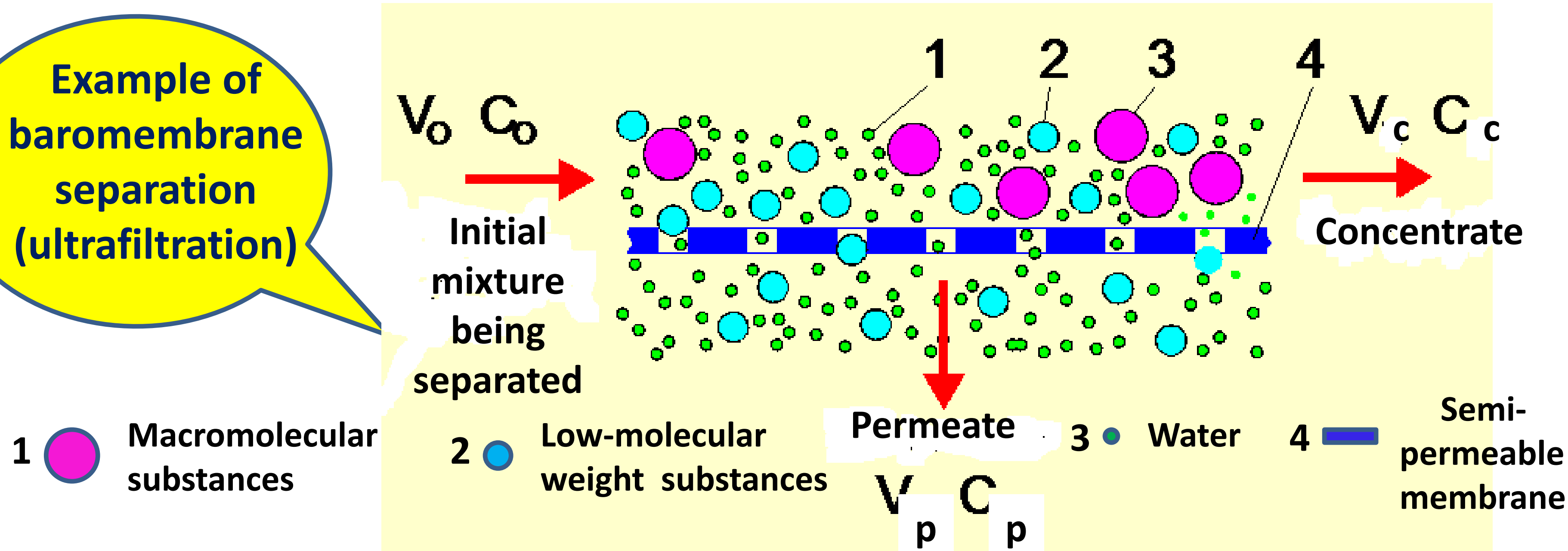
-**Membrane methods for water disinfection.**

MAIN TERMS OF BAROMEMBRANE SEPARATION

PRINCIPLES OF BAROMEMBRANE SEPARATION

Baromembrane process is the transfer of solvent through the semipermeable membrane affected by the pressure gradient. The principle of action is the rejection and concentration of valuable and unwished components.

Example of baromembrane separation (ultrafiltration)



Macromolecular substances are collected in concentrate, permeate is free of them.

If no deposition occurs on the membrane surface, following equality is valid both for macromolecular and low-molecular weight substances:

.

$$V_pC_p+V_cC_c=V_0C_0$$

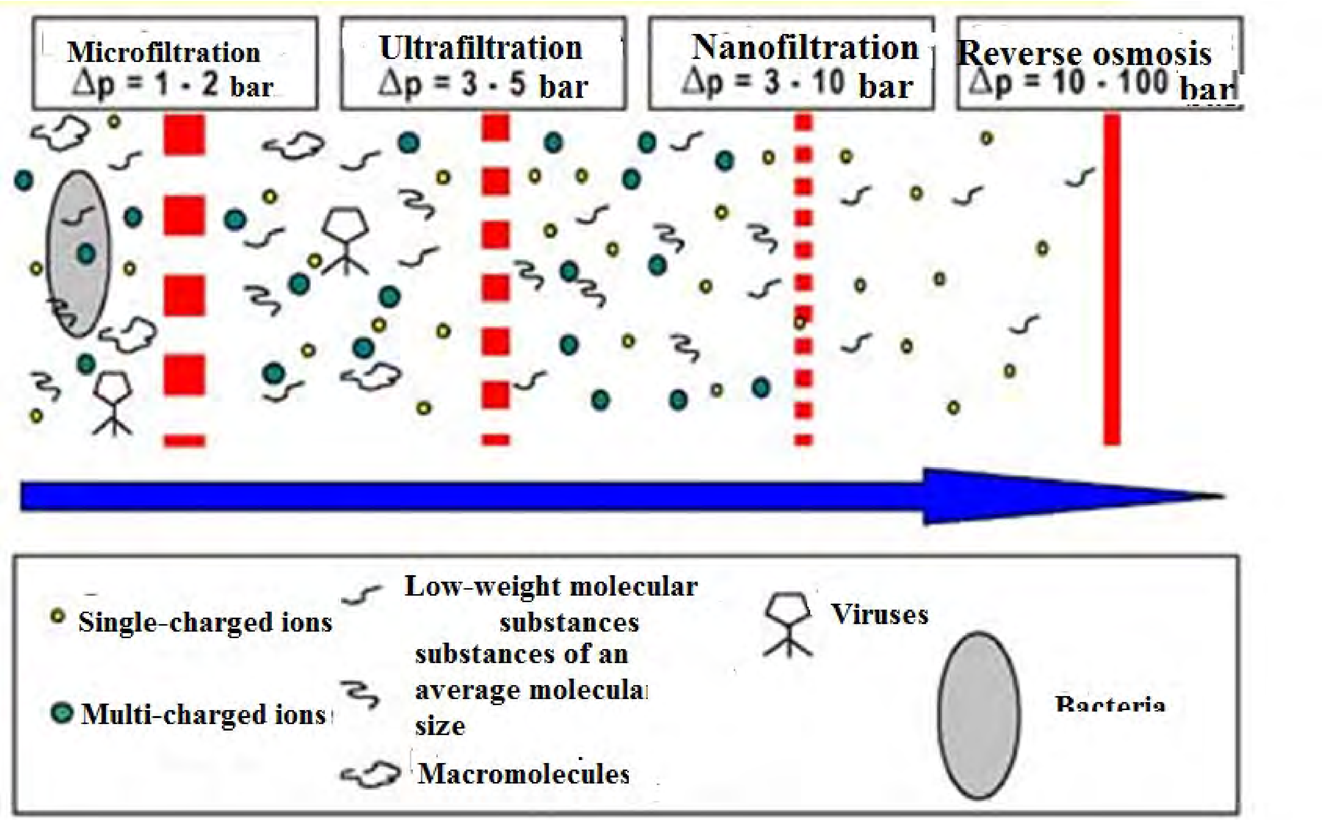
V – volume
C – concentration
VC – amount of substance

TECHNOLOGICAL POSSIBILITIES OF BAROMEMBRANE PROCESSES

Target products produced by baromembrane processes

Permeate – Wastewater treatment,

Concentrate – Food industry and biotechnologies



APPLICATION OF BAROMEMBRANE PROCESSES TO DIFFERENT SPECIES

Species	Size, nm	Method
Yeast, fungi	1000-10000	microfiltration
Bacteria	300-10000	micro-, ultrafiltration
Oil emulsions	100-10000	micro-, ultrafiltration
Solid colloidal particles	100-1000	Micro-, ultrafiltration
Viruses	30-300	Ultrafiltration
Proteins, polysaccharides	2-10	Ultra-, nanofiltration
Enzymes	2-5	Ultra-, nanofiltration
Antibiotics	0.6-1.2	Nanofiltration, reverse osmosis
Organic molecules	0.3-0.8	Reverse osmosis
Inorganic ions	0.2-0.4	Reverse osmosis
Water	0.18	

LIQUIDS OF BIOLOGICAL ORIGIN

Membrane methods, which allow us to save the chemical composition of components, are used for the treatment of following liquids:

- Liquid feedstock of food and pharmaceutical industry

(baromembrane and electromembrane methods, dialysis, diaultra- and diananofiltration);

Blood

(hemodialysis).

Destructive methods are applied to:

Communal wastewaters, wastewaters of hospitals, paper, leather food and agriculture industry;

(combined baromembrane and other methods).

MEMBRANE METHODS FOR THE TREATMENT OF BIOLOGICAL LIQUIDS

Main problems

Fouling **Biofouling**

- Fouling with inorganic substances (scaling)

Fouling with organic substances

Reversible

Cake on the membrane surface, partially deposit inside pores

Reversible fouling

Solution of the problem

Mechanical way,

Hydrodynamic pulsation,

Reverse permeate flow

Irreversible

Deposit inside pores

Reversible fouling

Irreversible fouling

Solution of the problem

Use of chemical reagents

FOULING OF MEMBRANES

Non-porous membranes (reverse osmosis) show cake formation.

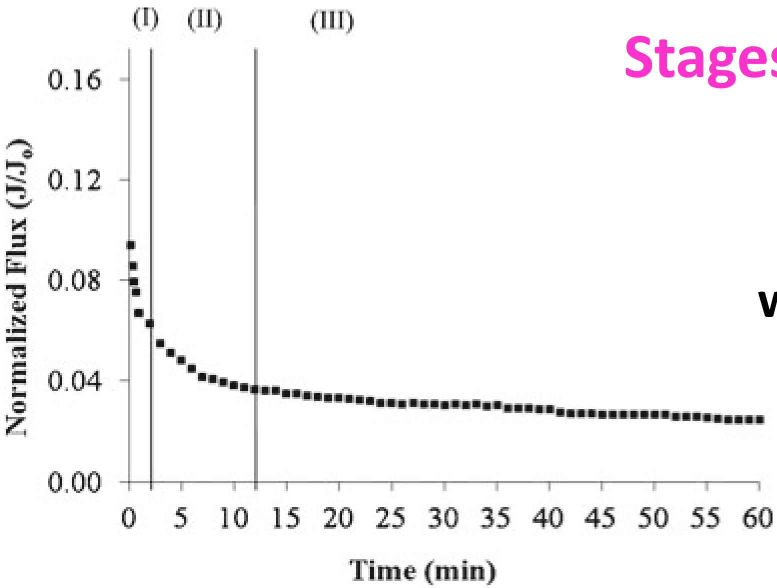
Porous membranes (micro-, ultra-, and nanofiltration) show both cake formation and precipitation in pores.

Stages of fouling. Precipitate location

I -pore blocking at the beginning of filtration (if particles are smaller than pores);

II - cake formation;

III - cake compression.



Stages of fouling. Compound solubility

I –Precipitation of insoluble compounds

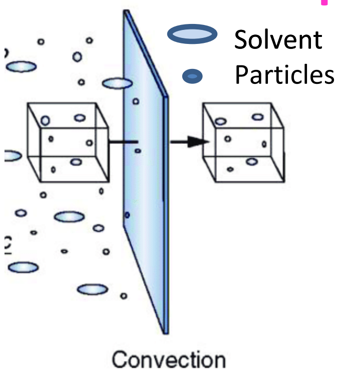
II – Precipitation of soluble compounds,

when the volume of concentrate becomes small.

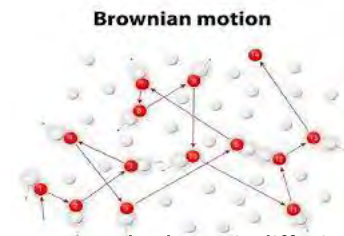
Three stages of flux decline: I, initial rapid drop; II, longer-term decline; and III, quasi-steady state period.

FOULING OF MEMBRANES

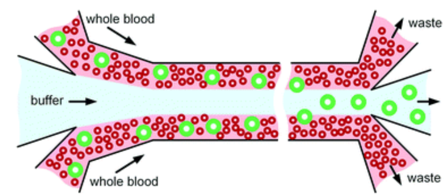
Transport mechanisms of substances to the membrane surface



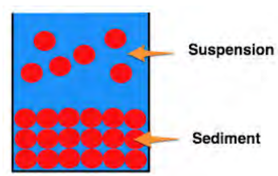
Convection,
Brownian diffusion,
Hydrodynamically induced diffusion (interaction of particles affected by flow),
Gravitation



Hydrodynamic diffusion



Gravitation



Effect of particle size

Unimportant for fouling - Particles, a size of which is larger than 450 nm.

Important for fouling – Particles with a size of 3-20 nm.

Factors affected fouling

- **Process conditions (pH, temperature, volume reduction factor (VRF), hydrodynamic conditions),**
- **Components of the liquid being treated (hydrophobicity, molecular shape, concentration),**
- **Membrane characteristics (surface chemistry, pore size, morphology, hydrophobicity, zeta potential).**

FOULING WITH INORGANIC SUBSTANCES (SCALING)

Why is it possible to precipitate inorganic substances on the membrane?

- **Considerable content of ions, which cause precipitation;**

Inorganic ions of waste waters of milk industry, which contribute to precipitate over ultrafiltration treatment

Cations	Anions			
	OH^-	CO_3^{2-}	SO_4^{2-}	PO_4^{3-}
Al^{3+}	$Al(OH)_3$	–	–	$AlPO_4$
Ca^{2+}	$Ca(OH)_2$	$CaCO_3$	$CaSO_4$	$Ca_3(PO_4)_2$
Fe^{3+}	$Fe(OH)_3$	–	–	$FePO_4$
Mg^{2+}	$Mg(OH)_2$	$MgCO_3$	–	$Mg_3(PO_4)_2$

- **Hydrolysis (Fe^{3+} and Al^{3+} ions);**

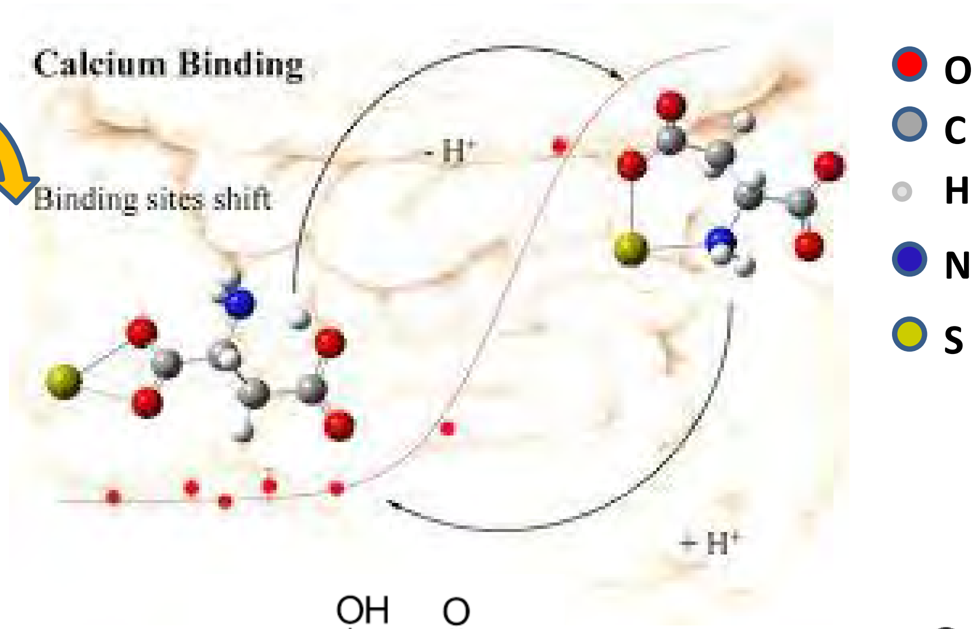
- **Concentrating of ions at the membrane surface, if the membrane can reject them. Ultrafiltration membranes partially reject di- and trivalent ions. Thus, their precipitation is possible. Nanofiltration membranes reject these ions practically completely. It means the most intensive precipitation of insoluble compounds.**

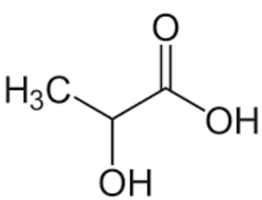
FOULING WITH INORGANIC SUBSTANCES (SCALING)

Inorganic ions in the liquids of biological origin

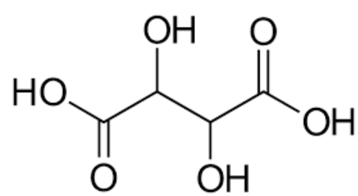
Juices and milky whey contain Ca^{2+} and Mg^{2+} and phosphate ions. They are bonded with proteins and aminoacids. Cations are also in a form of soluble lactates, tartarates, citrates etc.

Binding of calcium with aminoacids

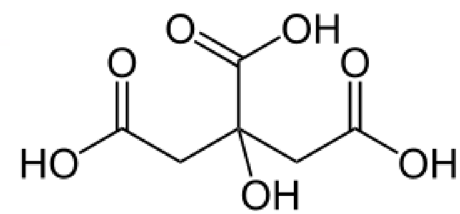




Lactic acid



Tartaric acid



Citric acid

FOULING WITH MOLECULAR ORGANIC COMPOUNDS

Dissolved organic substances can be classified into three different classes:

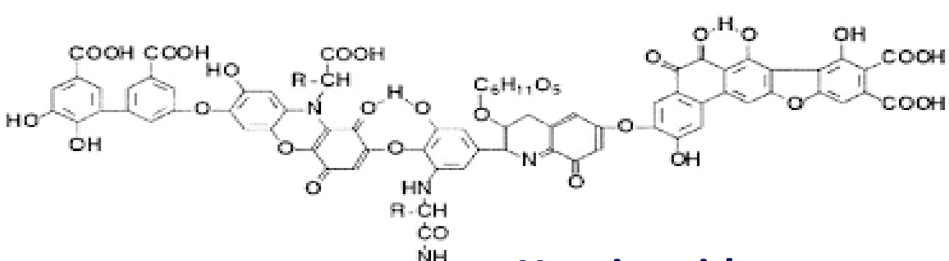
- **Natural organic compounds** derived from biological liquids (organic acids, particularly aminoacids, saccharides etc.);
- **Synthetic organic compounds** added by producers (stabilizers, dyes etc.);
- **Soluble microbial products** formed by microorganisms (polysaccharides etc.).

Natural organic substances (low and high molecular compounds)

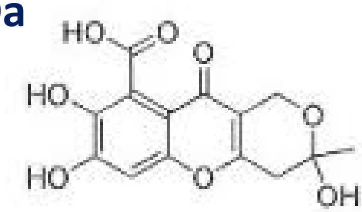
Most natural organic substances involve a range of compounds: from small hydrophobic acids, proteins and aminoacids to larger humic and fulvic acids (waste waters). In waste waters of plants, which use technical water, the considerable fraction of natural organic compounds is composed of humic substances, which comprise a large amount of the dissolved organic carbon, both aromatic and aliphatic components containing three main functional groups: carboxylic acids (COOH), phenolic alcohols (OH), and carbonyls (C=O).

The order of the **fouling potential** : hydrophilic neutral > hydrophobic acids > transphilic acids > hydrophilic charged.

1-100 kDa



Humic acid

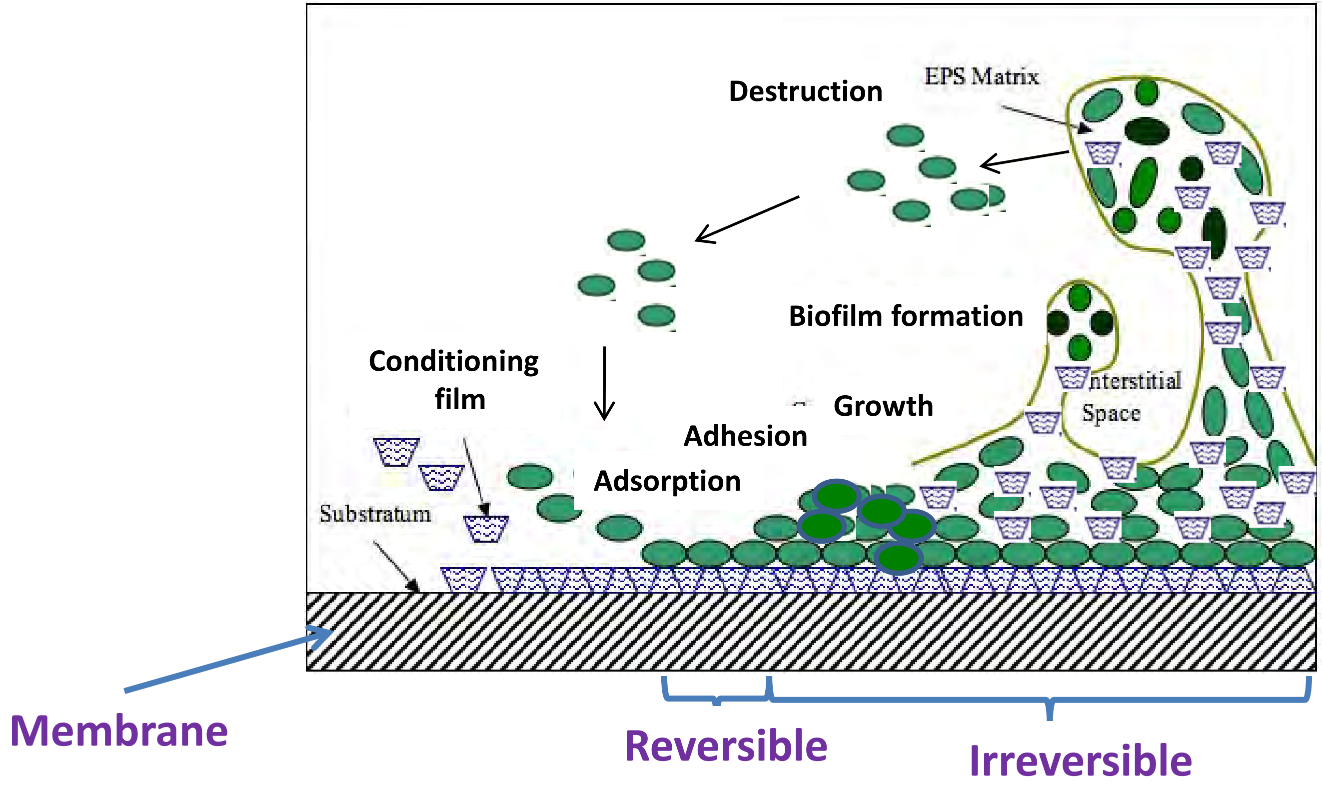


Fulvic acid

BIOFOULING

Stages of biofouling

- Formation of conditioning (nutrient) film;
- Adsorption of bacteria;
- Adhesion of adsorbed species,
-- Growth of bacteria layers,
-- Biofilm formation (microorganisms +exopolysaccharides),
- Splitting off, colonization of the new regions of membrane.



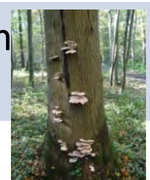
Biofilm

Bacteria in the matrix of ecopolysaccharides

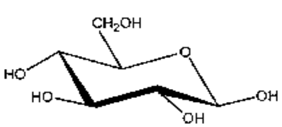
BIOFOULING. CONDITIONING LAYER

MAIN CONSTITUENTS - EXOPOLYSACCHARIDES

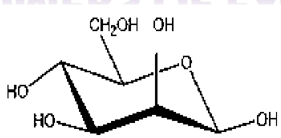
Bacteria or fungi	Media	Molecular mass	Constituents of polysaccharides
Weissella cibaria SJ14	Fermented cassava puree	71	Mannose, glucose, galactose, arabinose, xylose, and rhamnose. Hydroxyl, carboxyl and acetyl groups
Achromobacter piechaudii NRC2	Marine media	6	Arabinose, xylose, fructose, and galacturonic acid. Carbonyl, hydroxyl and carboxyl groups
Lactobacillus delbrueckii ssp. *Bulgaricus* SRFM-1	Milk media	3.97 × 105 397	Galactose, glucose and hydroxyl, sulfate and carboxyl groups
Aspergillus terreus	Fungus	19	Mannose and galactose
Pleurotus ostreatus	Mushroom	0.95	Fucose, rhamnose, arabinose, galactose, glucose, and xylose. Hydroxyl groups



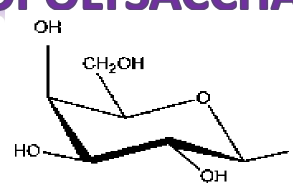
SOME MONOMERS OF EXOPOLYSACCHARIDES



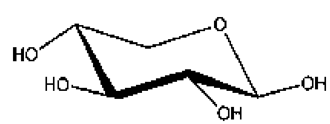
glucose



mannose



galactose

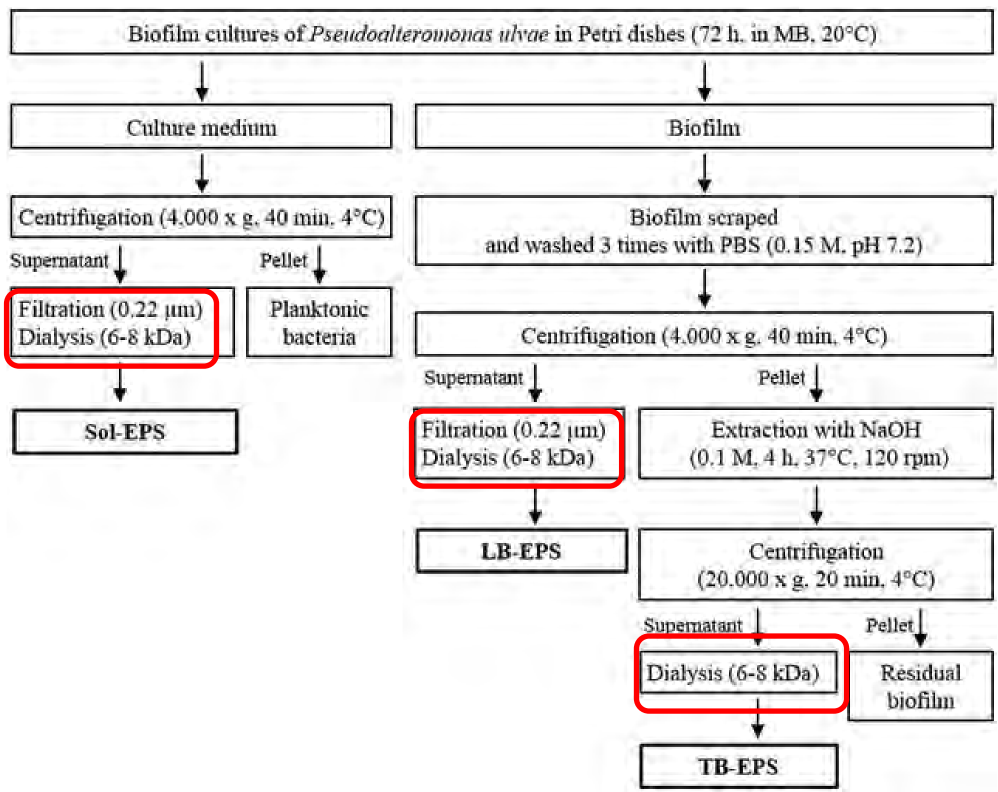


xylose

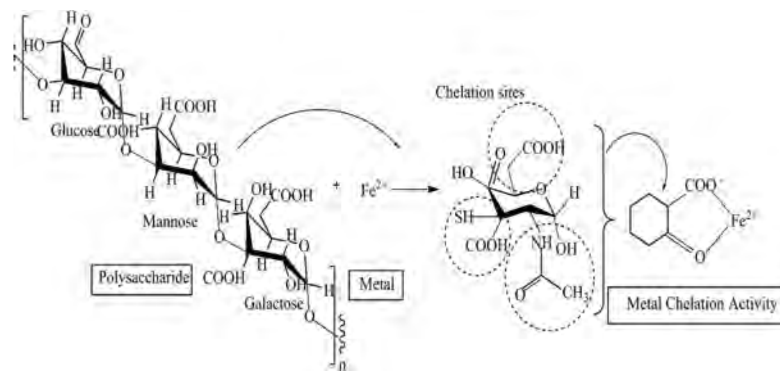
OTHER CONSTITUENTS ARE PROTEINS, NUCLEIC ACIDS, (POSPHO)LIPIDS AND HUMATES

EXOPOLYSACCHARIDES. ISOLATION AND PRACTICAL APPLICATION

Isolation



Bioadditives. Complex formation with Fe^{2+} ions (for anemia prevention)



Membrane method (dialysis) is used for the isolation of poltsaccharides.

EXOPOLYSACCHARIDES. PRACTICAL APPLICATION

Properties and functional attributes of some bacterial exopolysaccharides

Polysaccharide	Constituent	Molecular Weight, kDa	Applications	Bacteria strains
Dextran	Glucose	1000-1000000	Foods, pharmaceutialcs (blood volume expander), chromatographic media	*L. mesenteriodes*
Alginate	Guluronic acid, mannuronic acid	300-1300	Food hydrocolloid and medicine (surgical dressings, wound management, controlled drug release)	*P. aeruginosa and A. vinelandii*
Xanthan	Glucose, mannose, glucuronic acid	2000-50000	Foods, petroleum industry, pharmaceuticals, cosmetics	*Xanthomonas spp.*
Cellulose	Glucose	1000	Foods (indigestible fiber), biomedical (wound healing, tissue engineered vasculars)	*Acetobacter spp.*
Succinoglycan	Glucose and galactose	5-1000	Food, oil recovery	*Alcaligenes faecalis var. myxogenes*

BIOFOULING. BIOFILM

Stages of biofouling

-Formation of conditioning (nutrient) film

Conditioning layer is formed just after the contact of membrane with liquid. Hydraulic resistance of the biofilm on the membrane surface is mainly due to the conditioning layer. The layer is bonded with the surface by means of physical (adsorption), chemical (covalent bonds) and electrostatical interaction. The layer contains 50-90 % of organic carbon of the biofilm.

-Adsorption of bacteria

The mechanism of bacteria adsorption to the conditioning film is also physical and electrostatical (primary layer). Hydrate shells of the bacteria and conditioning film are saved.

-Adhesion of bacteria

Formation of covalent bonds between the conditioning film causes adhesion of bacteria to the membrane surface. The regions of hydrate shell between the bacteria and conditioning film are absent.

-Growth of the bacteria layer and biofilm formation

The growth of layer is due to dividing bacteria and also joining bacteria from the solution. Bacteria produce a exopolysaccharides, which fill space between them.

-Destruction of biofilm

Destruction is due to external influence, leakage of exopolysaccharides, degradation of enzimesand surface binding proteins etc.

FOULING MANAGEMENT STRATEGY

- **Process conditions** - All types of fouling

Hydrodynamics

Dead-end module

Flow module (prefarable)

Partial washout of the precipitate with water flow

Ionic strength

Decreasing the ionic strength of the solution enhances repulsion between bacteria and membrane preventing fouling. This approach is possible only for wastewaters.

pH

Decreasing the pH prevents inorganic and organic fouling. Alkaline media is against Biofouling.

Concentrate volume

$V_{concentrate}/V_{total}=0.1\text{-}0.25$

Decreasing the concentrate volume over filtration provides mainly reversible fouling due to formation of the solution, the concentration of which is close to saturated.

Temperature

Decreasing the temperature slows down biofouling and organic fouling. However, reversible inorganic fouling is possible due to the limitation of compound solubility.

In food industry, the operating temperature of membrane separation process is 10-12^{o}C

FOULING MANAGEMENT STRATEGY

Pretreatment of liquids

Biological and biochemical techniques

Organic and biofouling

Enzymes

Biofouling

Bacteriophages (viruses)

signalling molecules

Protozoas and metazoas

(mainly to clean membranes)

Coagulation-flocculation

Organic and biofouling, partially inorganic s

(adsorption of ions on particles)

$Al_2(SO_4)_3 \bullet 18H_2O$,

$Fe_2(SO_4)_3 \bullet 9H_2O$,

$FeSO_4 \bullet 7H_2O$,

$FeCl_3 \bullet 6H_2O$,

$Ca(OH)_2$,

polyamines

Solar disinfection

Biofouling

Two effects: thermal treatment and UV irradiation.

Bacteria fall at 60-100ºC.

Ultraviolet light

Biofouling

Main requirement: Liquids must be transparent.

Ultraviolet light combining with photocatalysis

Biofouling. Partially organics

TiO_2 (anatase)

Main requirement: Liquids must be transparent.

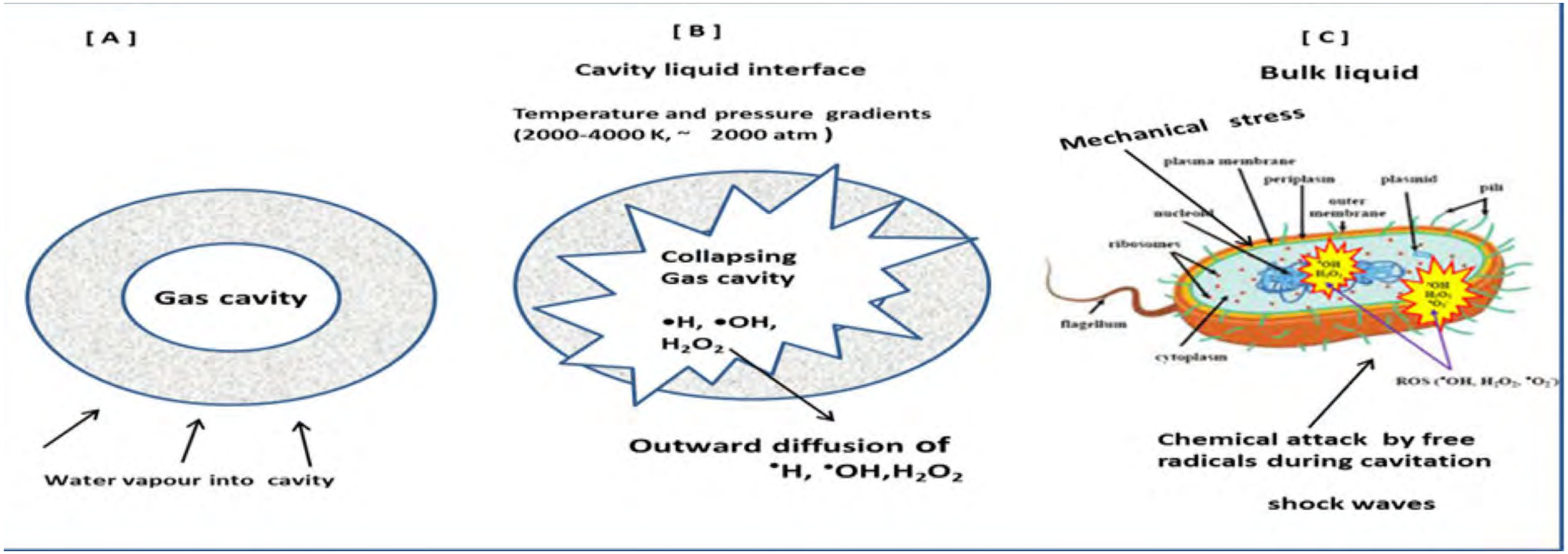
FOULING MANAGEMENT STRATEGY

Pretreatment of liquids

Ultrasound

Prevents biofouling

Mechanism of ultrasound effect on bacteria



1. Cavitation in liquid.
2. Chemical effects of cavitation: the generation of free radicals,
3. Heat effects caused by the generation of localized hot spots as a result of the rapid explosion of the bubbles.
4. Destruction of the cell membrane caused by chemical, thermal and vibration effects

FOULING MANAGEMENT STRATEGY

Pretreatment of liquids

Chemical oxidation

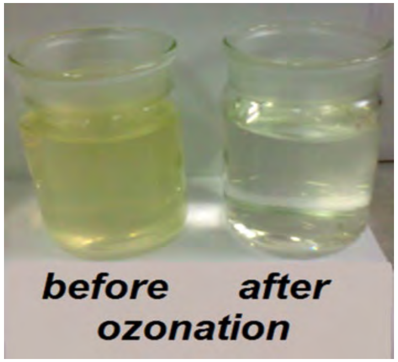
Prevents biofouling, partially organics

O_3, Cl_2, $NaClO$, ClO_2, NCl_3, $NHCl_2$, $NHCl$, H_2O_2.

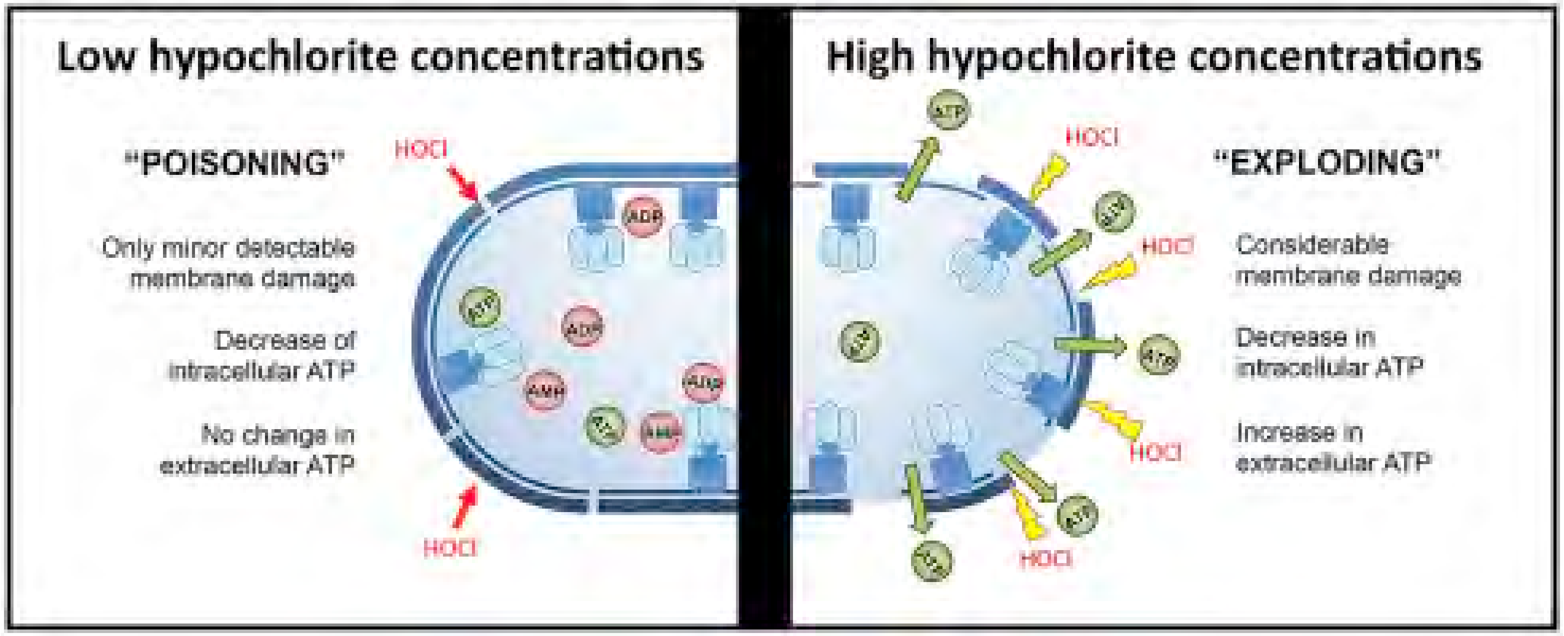
Fenton reagent

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^-$$

Nanofiltration permeate of milky whey



Mechanism of cell destruction



FOULING MANAGEMENT STRATEGY

Pretreatment of liquids

Electrochemical methods

Prevent biofouling, partially organics and inorganics

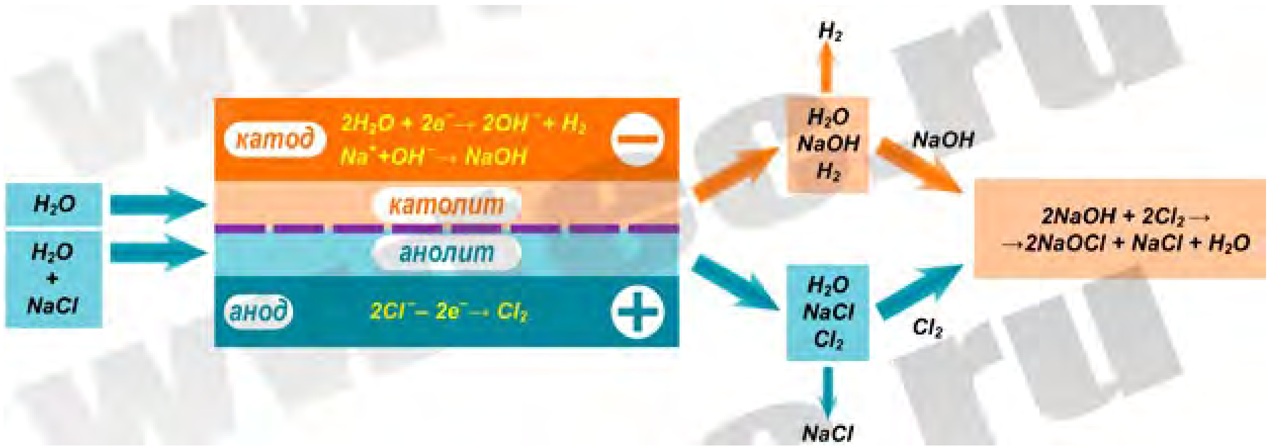
I. Electric pulsed field. Effect on cells

Theory of electroporation. The membrane cell acts as a capacitor and the exposure to an electric field can generate potential difference across the membrane. The increase in the potential results in the reduction of membrane thickness and its destruction.

Theory of electro-termoporation. The effect of electroporation is enhanced by heating.

I. Electrolysis of solution, to which NaCl was added

$$NaCl + H_2O \rightarrow NaClO + H_2.$$



FOULING MANAGEMENT STRATEGY

Adsorption with activated carbon

Prevents organic fouling, partially inorganic

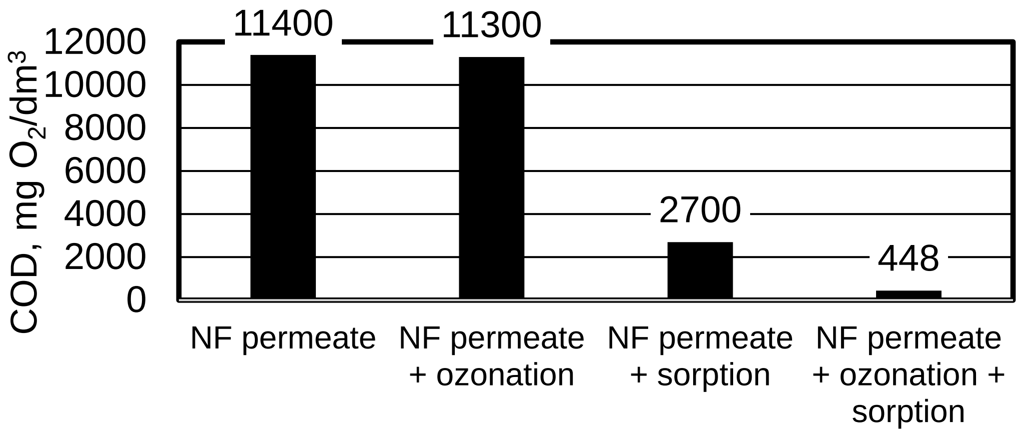
Adsorption with clays

Partially prevents organic and inorganic fouling

Ion exchange resins

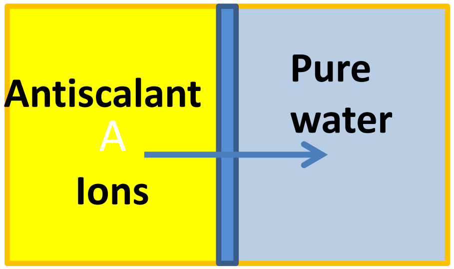
Partially prevents organic and inorganic fouling

Ozonation combining with adsorption
for reducing COD of nanofiltration permeate of milky whey



ANTISCALANTS FOR REVERSE OSMOSIS

Antiscalants are commercial products, they are added to the liquid being purified. They prevent mainly inorganic fouling and partially deposition of organic substances.



Antiscalant consists of a **base** (**soluble polymers like polyacryl acid**),

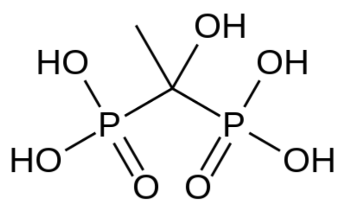
+

Surfactant

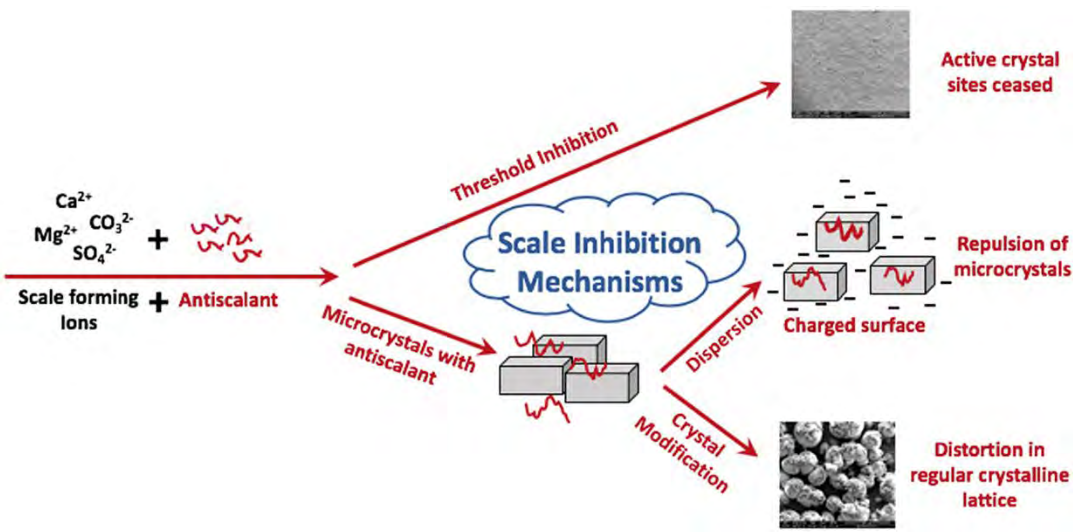
+

Complex forming agents

(phosphonic acids, for instance, hydroxyethylidene diphosphonic acid)



Mechanism of antiscalant action



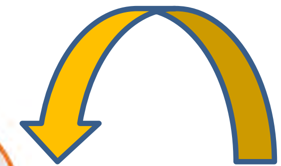
Threshold inhibition. Maintaining solutions in a supersaturated state.

Adsorption on small salt crystals providing their negative charge and enhancing repulsion.

Distortion of crystal lattice of salt facilitating destruction of crystals.

DISADVANTAGES OF PRETREATMENT METHODS

Solution of the problem



Combination of different pretreatment methods

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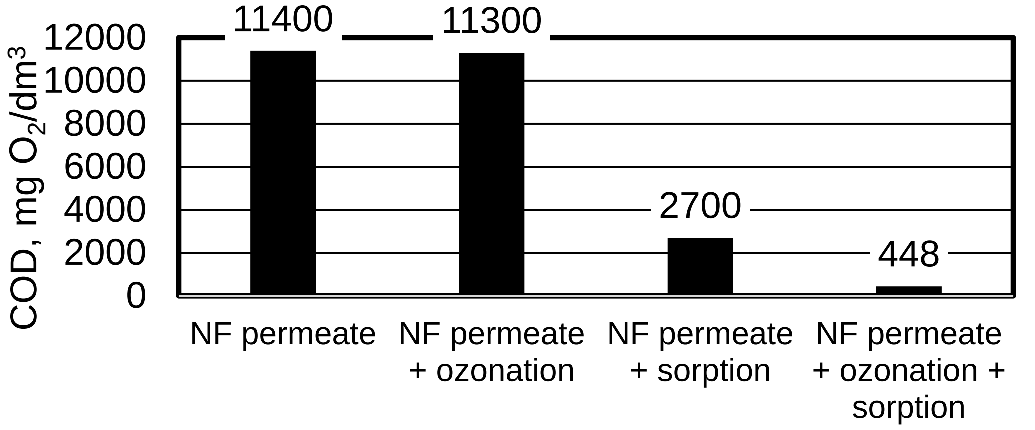
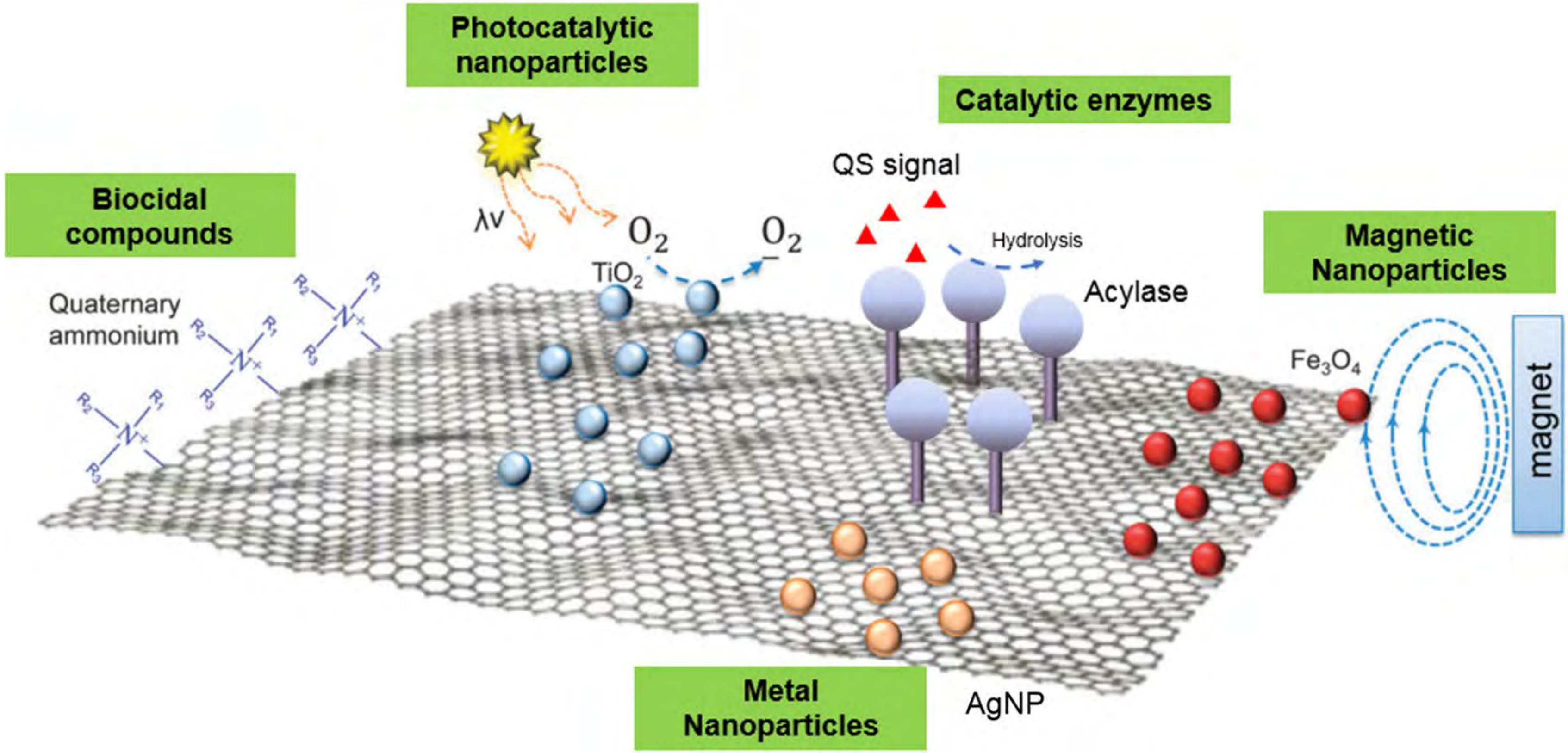


FOULING MANAGEMENT STRATEGY

Membrane materials



MEMBRANE BIOREACTOR.
A COMMON APPROACH TO THE TREATMENT OF WASTE WATER CONTAINING CONTAMINANTS OF BIOLOGICAL ORIGIN

MEMBRANE BIOREACTOR

Combining process

- **Biodegradation of organic compounds** + **Micro- or ultrafiltration**

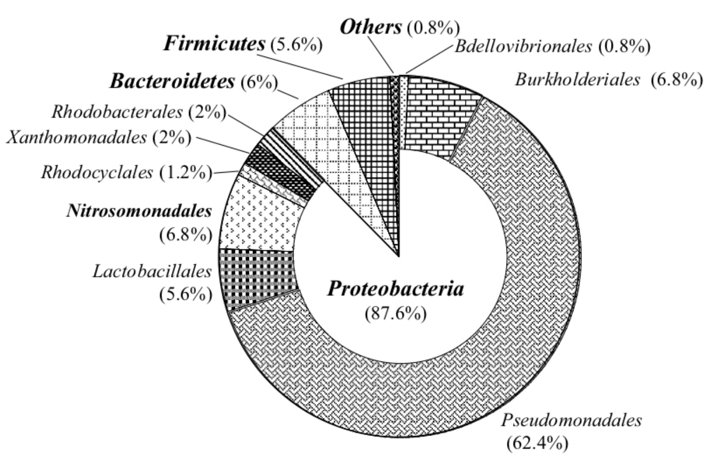
Constituents of bioreactor

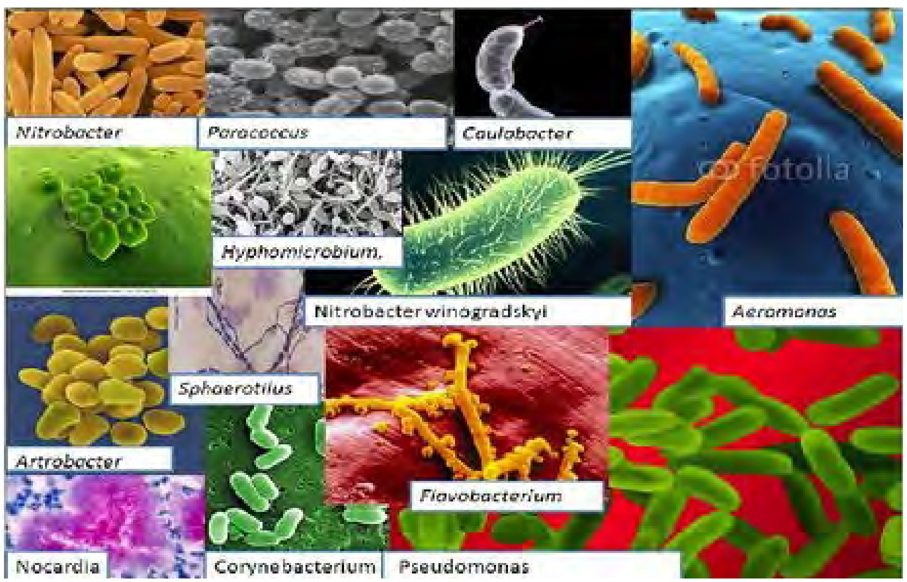
- **Activated sludge**
- **Membranes**

Activated sludge

Composition of activated sludge

Bacteria (95 %), protozoa (3 %), yeast, metazoa, fungi.

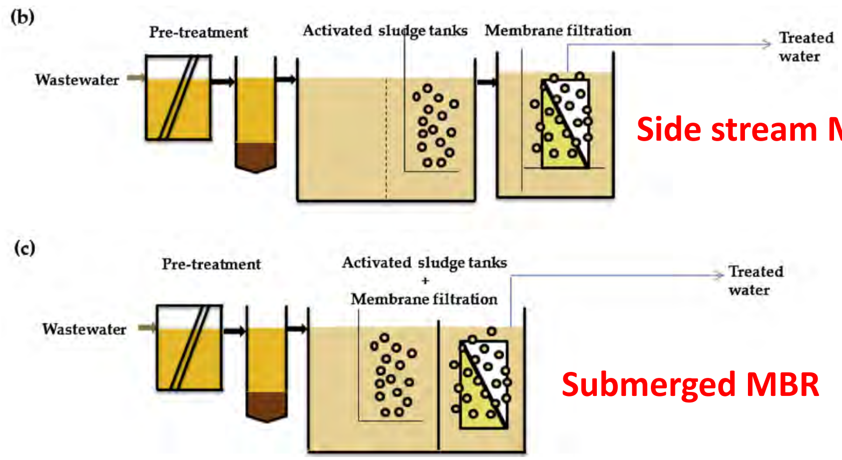




MEMBRANE BIOREACTOR

Classification of membrane bioreactors

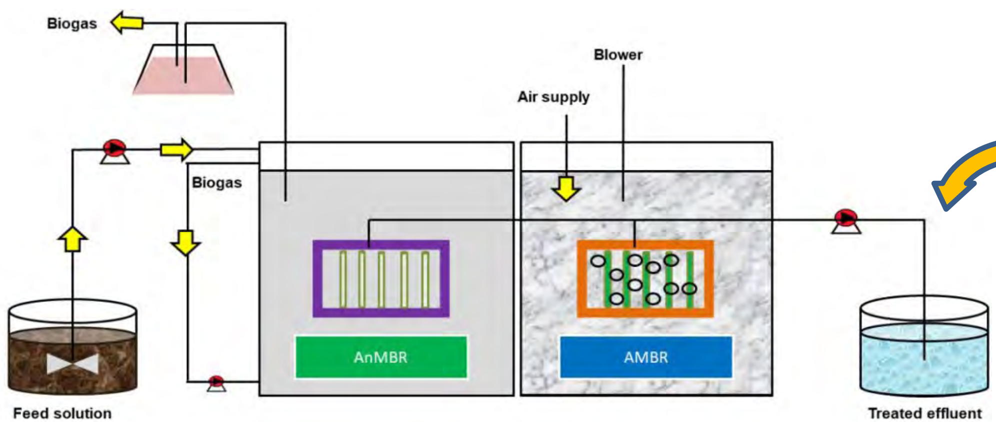
Membrane location



Side stream MBR

Submerged MBR

Final products



Advantages of membrane bioreactors over activated sludge

- Lower increase of organic wastes;
- Minimization of foaming;
- Higher quality of purified water.

Advantages over membrane filtration

-Higher quality of purified water.

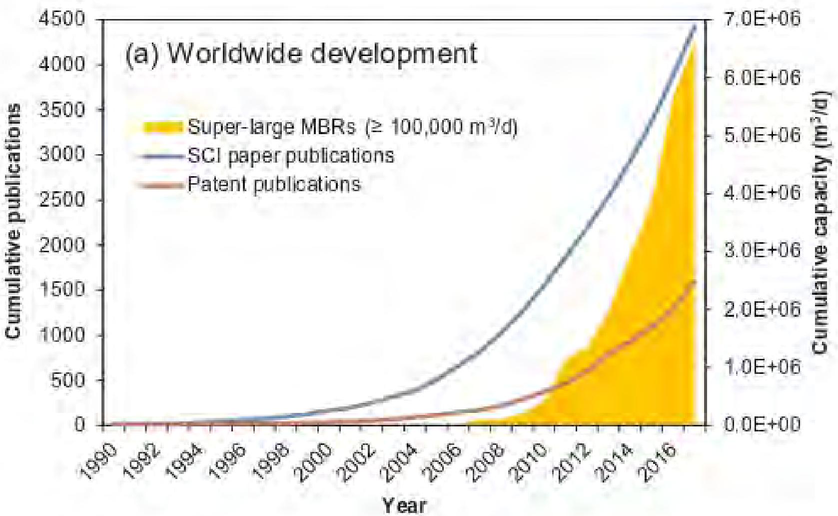
- Minimization of fouling with organic Substances

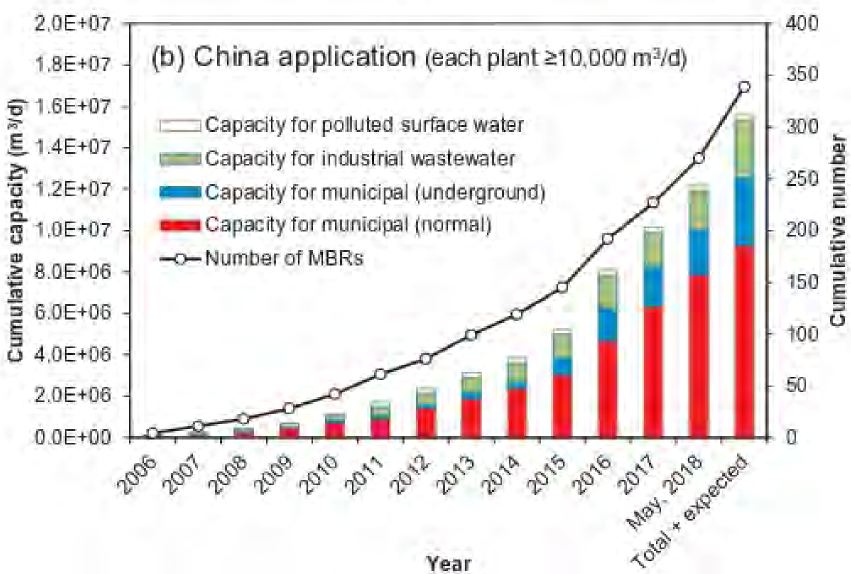
-NO PROBLEM OF CONCENTRATE!

Aerobic floc has a metabolic rate approximately ten times higher than anaerobic sludge. The time of aerobic treatment is 4-6 h.

MEMBRANE BIOREACTOR

MBR on a global scale





Modern tendency of MBR development

- Microbiology (development of sludge composition);

- Improvement of membrane device;

-- Optimization of operation conditions;

-- Development of membrane materials.

-- DEVELOPMENT OF HIGH-RETENTION MBR (HR-MBR):

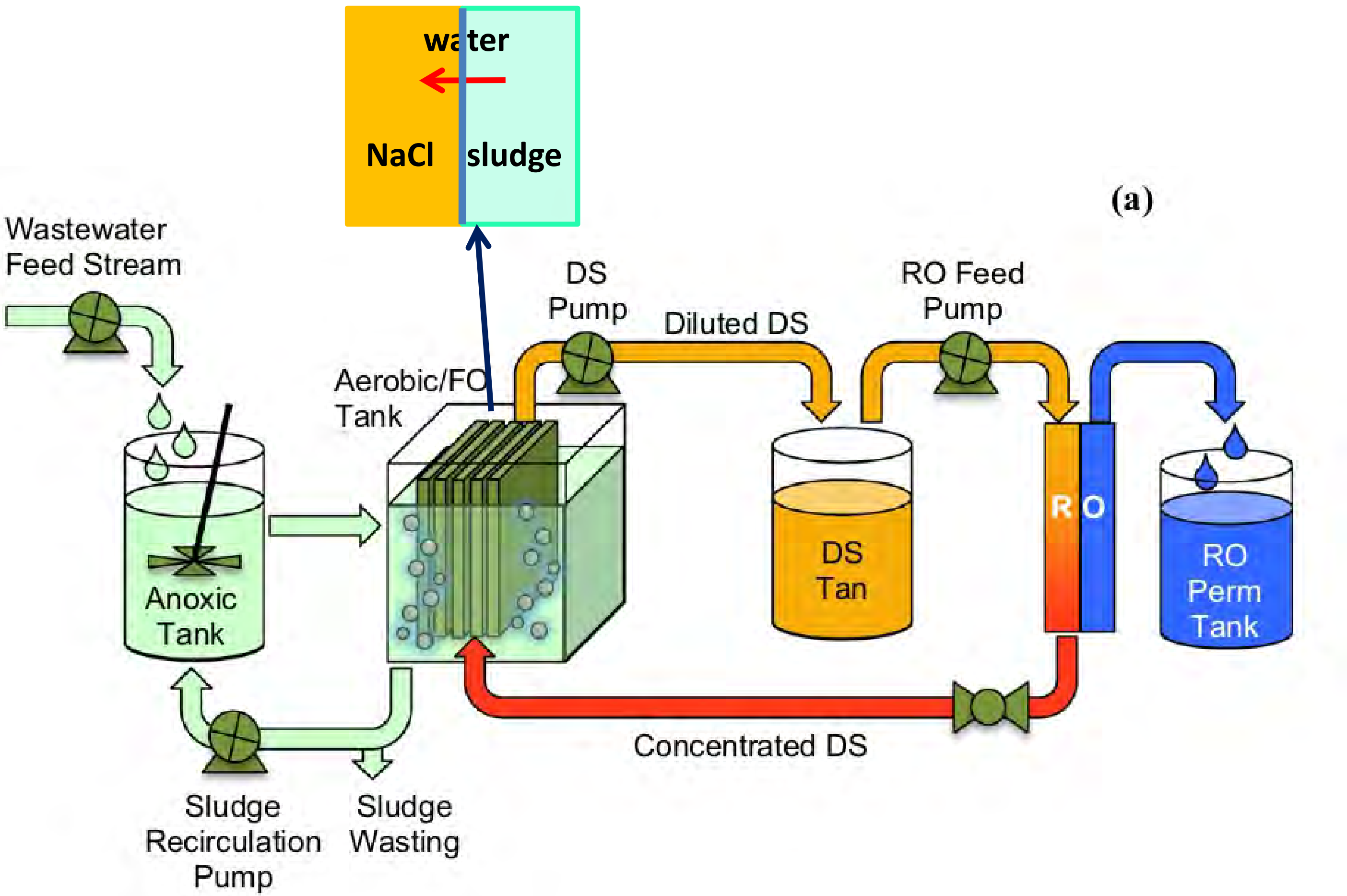
- Forward osmosis MBR,

- Nanofiltration MBR.

-Combination of MBR and HR-MBR with other membrane processes.

MEMBRANE BIOREACTOR

Forward osmosis-MBR combining with reverse osmosis



MEMBRANE TREATMENT OF WASTEWATERS

Main branches of industry developed in Brazil:

Leather

Textile

Food

Pulp and paper

WASTEWATERS TREATMENT

Typical origin of industrial wastewaters

Types of wastewaters	Formation	Contribution to total volume, %
Wastes of technological processes	Process effluents, washing equipment and production sites	82
Conditionally pure	Process water from equipment and machinery cooling	10
Household	Drains of bathrooms and laundries	5
Stormwater	Atmospheric precipitation, washout from the territory, vehicles, roads	3

Plants of food industry. As a rule, mainly biological method (activated sludge) is used.

Main requirement for membrane processes

The ratio of Biological oxygen demand (BOD)/Chemical oxygen demand (COD) must be 0.05-0.5.
Normally this ratio is >0.4-0.5.

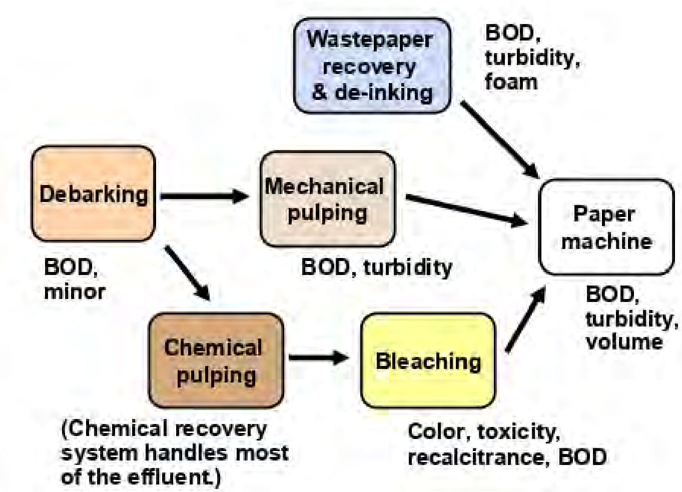
MAIN REQUIREMENT TO WATER TREATMENT IN PAPER AND LEATHER INDUSTRY

The process of water purification requires different approaches after each technological stage.

WASTE WATERS OF PULP AND PAPER INDUSTRY

Needs of paper industry 100 to 1000 l of water /ton of paper. Water is used from the initial stage of debarking up to pulping, washing, bleaching and papermaking.

Waste waters of paper industry **contain** cellulose fibers, paper particles, mineral fillers and dyes, glue particles, emulsions, latexes, lignin, monosaccharides, hemicellulose etc. The content of nitrogen and phosphorus is inconsiderable.



Main contaminant in wastewaters of paper industry

WASTE WATERS OF PAPER INDUSTRY

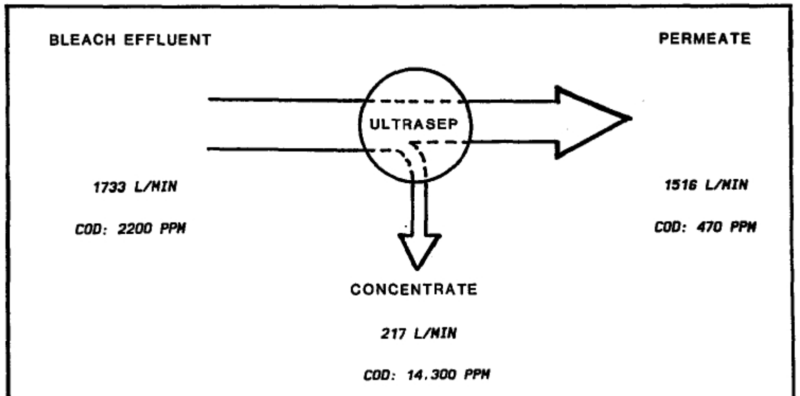
For primary stages of wood treatment, **chemical oxygen demand** is up to 3000 mg dm^{-3}. **Biological oxygen demand** is about 800 mg dm^{-3} . The BOD/COD ratio is <0.5. Thus, the pretreatment before the use of membrane methods is needed to decrease color and also the content of coarse and colloidal particles.

The commercial application of membrane technology in the pulp and paper industry consists less than 2% of the global membrane market.

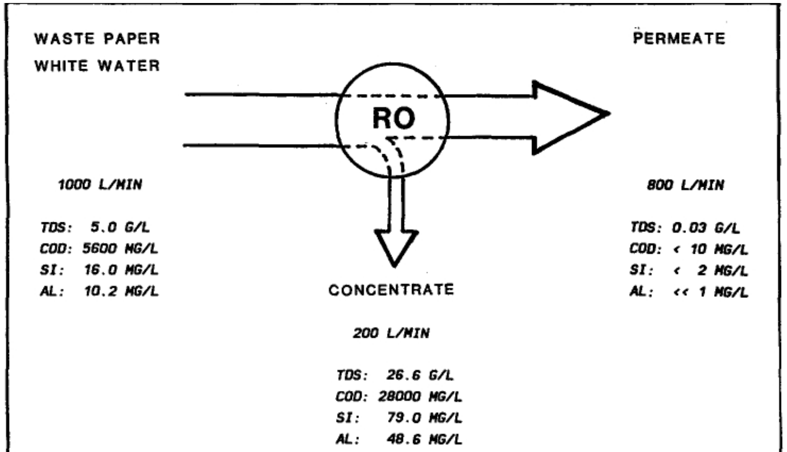
Membrane process	Areas of research/application
RO	Paper mill effluent, demineralisation of freshwater, pre-hydrolysis effluent treatment
MF	Deinking effluent, white water treatment, paper machine filtrate, paper mill effluent, kraft spent liquor, coating effluent, bleaching effluent
UF	Bleaching effluent, pre-hydrolysis effluent treatment, paper mill effluent, pulp mill effluent, paper machine filtrate, white water, coating effluent, black liquor treatment, deinking effluent
NF	Deinking, white water, bleach effluent, paper machine filtrate, paper mill effluent, black liquor treatment, pulp mill effluent
MBR	Paper mill effluent, white water, bleach effluent, condensate treatment

Summary of common membrane application

Results



Ultrafiltration



Reverse osmosis

WASTEWATERS OF PAPER INDUSTRY

Pretreatment of wastewaters is strictly required

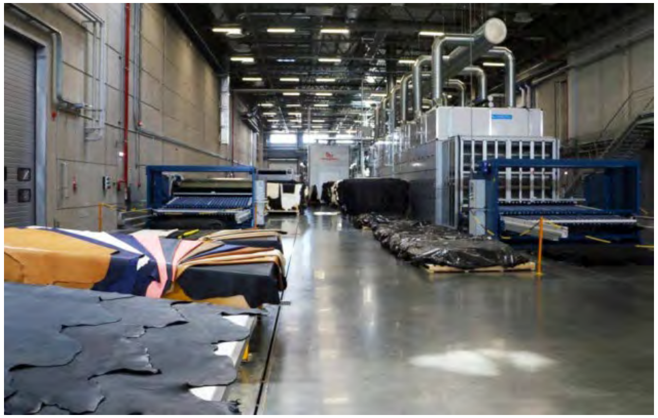
Strategies of fouling control over membrane treatment of waste water

Processed materials	Membrane	T, degree	ΔP, bar	Main foulants	Fouling control strategies
Prehydrolysis Liquors of Poplar Chips	MF/UF	20		High molecular weight lignin	NaOH addition + MF
Process Water from the thermomechanical pulping mill	MF, UF, NF 5/10	55	3-5	Degradation products of lignin	Combined physical and chemical
Process water from the thermomechanical pulping mill	Ceramic	50-80	6-20	Extractives and solids	Pretreatment with drum filter and MF
Paper wastewater	NF	25-30	8	Nonbiodegradable pollutants	Cross-flow velocity

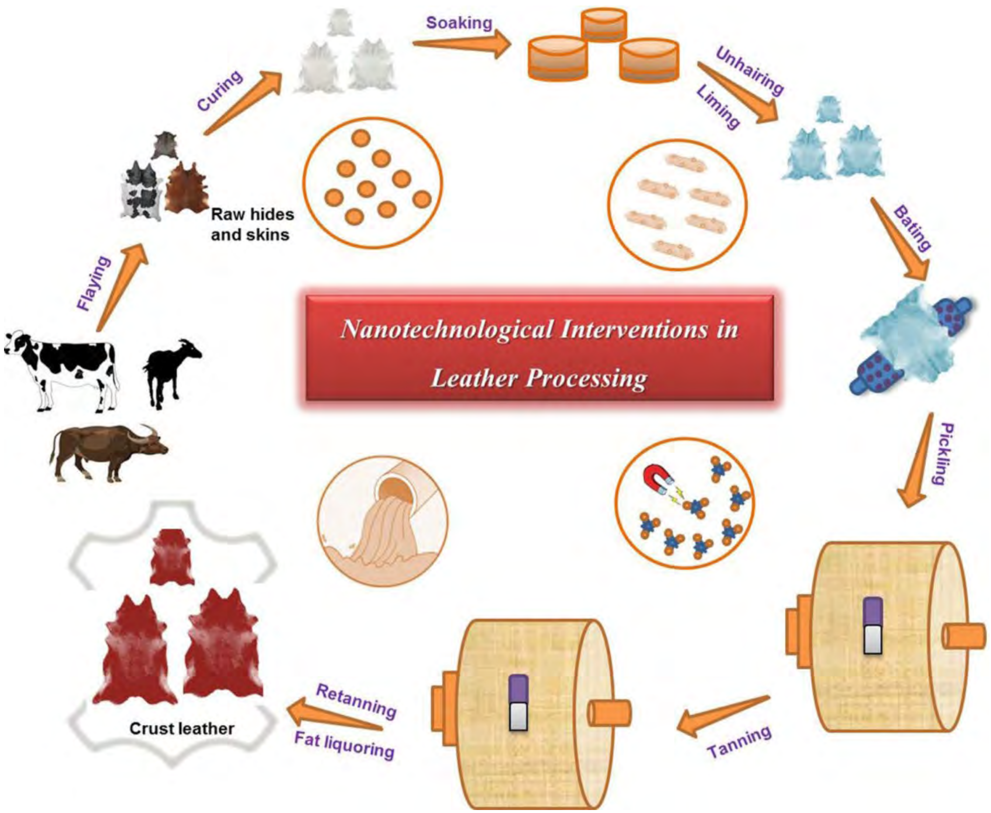
WASTE WATERS OF LEATHER INDUSTRY

Water consumptions – 1-1.5 m^3 per 1 skin.

Pretreatment is needed before membrane filtration.



Scheme of leather production



Membrane technologies allow us to purify water, which can be used repeatedly for technological processes of leather treatment. Purified water cannot be discharged to sewage, especially to water sources.

WASTE WATERS OF LEATHER INDUSTRY

- Water consumptions – 1-1.5 m^3 per 1 skin.

Pretreatment is needed before membrane filtration.

Characteristics of effluents

	Stage	Water volume, %	BOD, mg dm^{-3}	pH	Pollutants
UF	Soaking and unhearing	19	5000	6-7	Salts, wool, skin peaces, bristles, blood, fats, hairs, sand
UF	Liming	17	20000	13	Lime, Na_2S, hairs, dissolved organic substances
UF	Deliming	4	4000	11	Inorganic substances, mainly ammonia
RO	Pickling + Rinsing	34	1000	6-8	Inorganic substances, mainly ammonia
UF	Softening	3	5000	6-8	Dissolved organic substances
UF→NF	Tanning	2.5	1400	3	Dissolved organic substances, Cr(III) salts, bacteria
	Retanning	2.5	20000	3-6	Dissolved organic substances
	Dyeing	18	6000	5-6	Dissolved organic substances (dyes, polymers), organic solvents.

WASTE WATERS OF LEATHER INDUSTRY

Effect of membrane filtration on the chemical oxygen demand of the effluents

Testing ultrafiltration and nanofiltration (tanning)

Parameter	Feed	Ultrafiltration		Nanofiltration	
		permeate	concentrate	permeate	concentrate
COD, mg dm^{-3}	5960	5126→NF	6413	3315	7641

Unhairing-soaking-liming (UF)

Sample	COD, mg dm^{-3}
Initial bath	5673
Permeate	2163

Dyeing. Membrane reactor (UF)→ →reverse osmosis

Sample	Concentration, mg dm^{-3}
Initial bath	15000
Permeate	COD - 470
	Cr(III) – 0.4

Energetic analysis results for the unhairing-liming water →treatment using ultrafiltration

Benefits (EUR/year)	
Sulfide saving	38653.7
Auxiliary products saving	14725.2
Water saving	2284.1
Waste treatment cost saving	21691.2
Recovery proteins	4183.3
Costs (EUR/year)	
Electrical energy	722.9
Plants investment	38734.3
Pretreatment	309.9
Work	4067.1
Chemicals	826.3
Maintenance	3615.2
Economical balance (EUR/year) **175 000 R$**	33261.9
Primary energy saving (GJ/year)	358.9
Total substitution coefficient (MJ/kW h)	51.3

Wastewaters of food and beverage industry

Food industry is one of the major water consumers and for generating wastewater. Water consumption is needed for the processing of raw material and for washing, heating, and cooling stages. In a global scale, the **demands of food and beverage** industry were **127 000 000 000 m^3** in 2012.

The composition of wastewaters strongly depends on the branch of food industry.

Main components of wastewaters of food industry

Sources	Main Components of Wastewater	Characteristics
Dairy	Proteins, detergents, lactose, and lipids	BOD = 442 mg/L COD = 8960 mg/L TDS = 253.6 mg/L pH = 7.10
Olive mill	Phenols, pectin, sugars, fats, oil, salts and carbohydrates	BOD = 4426 mg/L COD = 55,730–156,000 mg/L Total phenol = 2439–8300 mg/L pH = 5.6
Slaughterhouse	Nitrogen, sodium, potassium, calcium and fats	BOD = 1209 mg/L COD = 4221 mg/L Total nitrogen = 427 mg/L pH = 6.95
Fruits	Carbohydrates, minerals, nitrogen phosphorus and salts	BOD = 860 mg/L COD = 919 mg/L Total nitrogen = 40 mg/L pH = 5.5–7.2
Seafood	Sodium chlorides, phosphorus, nitrogen, salts, fats and grease	BOD = 3250 mg/L COD = 13,180 mg/L Salts = 2–5% (*w*/*v*) pH = 5–7

Wastewaters of food and beverage industry

Type of Membrane Filtration	Source	Characteristics	Performance
MF	Dairy wastewater	BOD = 890 ± 92 mg/L COD = 3536 ± 328 mg/L Turbidity = 623 ± 140 NTU TSS = 1860 ± 220 mg/L pH = 7.3 ± 0.3	COD Removal (%) = 89 ± 2 Color Removal (%) = 93 ± 5 Turbidity Removal (%) = 98 ± 4
UF	Dairy wastewater	BOD = 890 ± 92 mg/L COD = 3536 ± 328 mg/L Turbidity = 623 ± 140 NTU TSS = 1860 ± 220 mg/L pH = 7.3 ± 0.3	COD Removal (%) = 95 ± 1 Color Removal (%) = 97 ± 6 Turbidity Removal (%) = 99 ± 5
NF	Restaurant wastewater	BOD = 816.17–1097.25 mg/L COD = 10,356.67–16,443.33 mg/L Turbidity = 402.67–1208 NTU TSS = 1860 ± 220 mg/L pH = 4.49–6.15	COD Removal (%) = 99.4 BOD Removal (%) = 86.8 Turbidity Removal (%) = 99.9
RO	Olive wastewater	Suspended matter = 14–16 mg/L COD = 120.5–226.6 mg/L	COD Removal (%) = 99.8

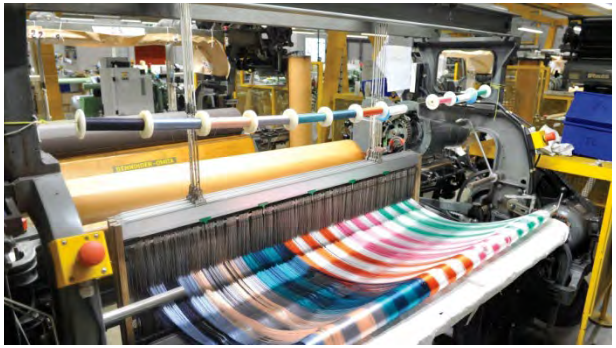
Practical use of nanofiltration permeate obtained from milky whey

permeate → Column filled with anion exchange resin → Alkaline solution for washing equipment

Column filled with anion exchange resin → Regeneration of resin with NH_4OH → NH_4Cl + NH_4OH → Neutralization with HNO_3 → $NaNO_3$ + KNO_3 NH_4NO_3

Fertilizer for alkaline soils

WASTE WATERS OF TEXTILE INDUSTRY



Water consumptions

Strongly depend on the type of textile material.

Acryl textile - 35 m^3 per 1 ton of textile,
Wool textile – 70 m^3 per 1 ton of textile,
Cotton textile -100 m^3 per 1 ton of textile.

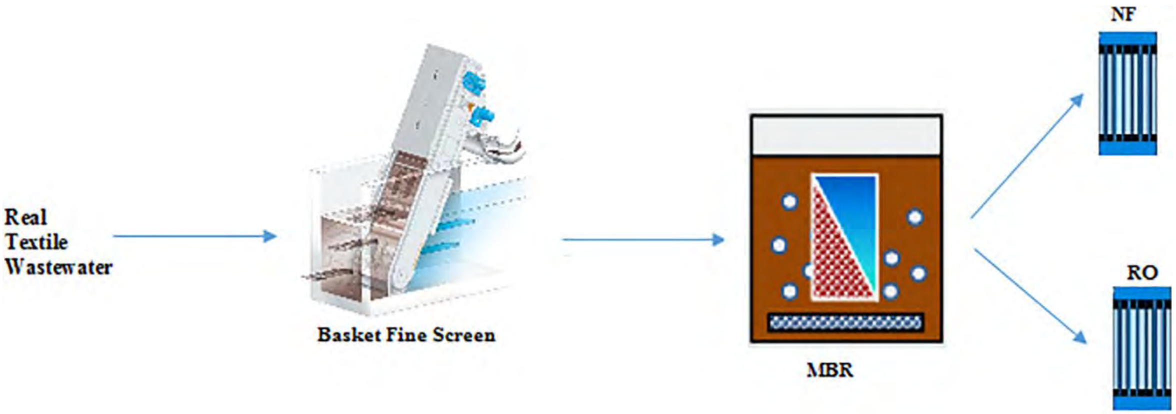
Composition of wastewaters

Fiber residues (for natural textiles), dirt particles, reagents, surfactants, dyes.

Pollutants of biological origin

COD is up to 1500 mg dm^{-3}.
BOD is up to 10 mg dm^{-3} . BOD<< COD

Scheme of wastewater treatment



WASTE WATERS OF TEXTILE INDUSTRY

Removal of COD using different filtration methods

Ultrafiltration

COD 64–76%

Nanofiltration

COD 90%

Membrane bioreactor

COD 75 %

Membrane bioreactor + nanofiltration

COD 97 %

Removal of color with nanofiltration using ceramic membranes

Color	Color removal. %	Residual COD, mg dm^{-3}
Blue	88	67
Red	95	61
Green	94	67
Black	89	59
Purple	89	48

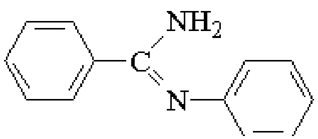
TREATMENT OF THE LANDFILL LEACHATE

A.V. Dumanskii Institute of Colloidal Chemistry and Water Chemistry
of the Natiional Academy of Science of Ukraine

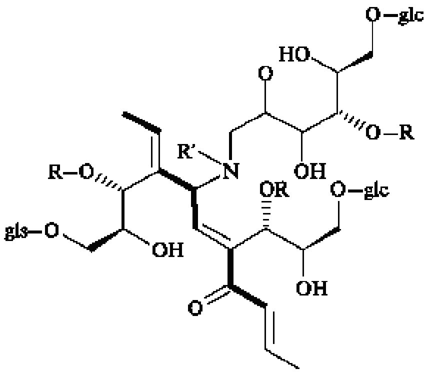
The leachate contains both inorganic and organic components. Many of them are biogenic origin.

COD is 2000-5000 mg dm^{-3}.

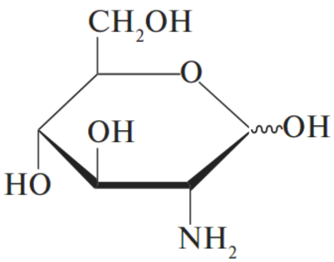
Organic components



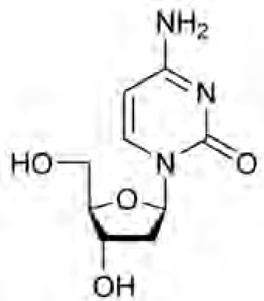
Guanidine



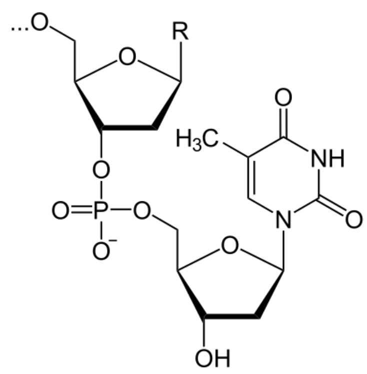
Melanoidine



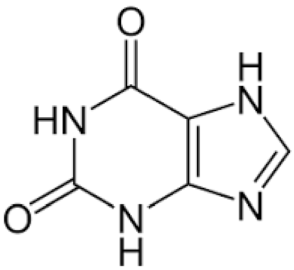
Aminosaccharides



Nucleosides



Nucleic acids



Xanthine

The leachate contains also proteins, fats, surfactants etc.

TREATMENT OF THE LANDFILL LEACHATE

I stage: Coagulation combining with UV irradiation. Reducing COD from 3400 to 1800-1500 mg dm^{-3} :

or electrocoagulation: Reducing COD from 3400 to 900 mg dm^{-3}.

or galvanocoagulation+ cathalytic oxidation: Reducing COD from 3400 to 1900 mg dm^{-3}.

II stage: Removal of Fe(III), Al(III) and COD with ultrafiltration involving ceramic membranes.

III stage: Removal of heavy metal ions with nanofiltration.

Removal of organic substances from the leachate

Sample	Amidines	Xanthines, Green meloidines	Red, yellow orange meloidines	Brown meloidines	Others
Initial leachate	Present	Present	Present	Present	Present
Galvanocoagulation	Present				
Galvanocoagulation+ + cathalytic oxidation	–	–	–	Present	Present
Nanofiltration	–	–	–	Present	–

IV stage: Bonding of ammonia to struvite ($MgNH_4PO_4 \bullet 6H_2O$).

V stage: Adsorption of organics with activated carbon.

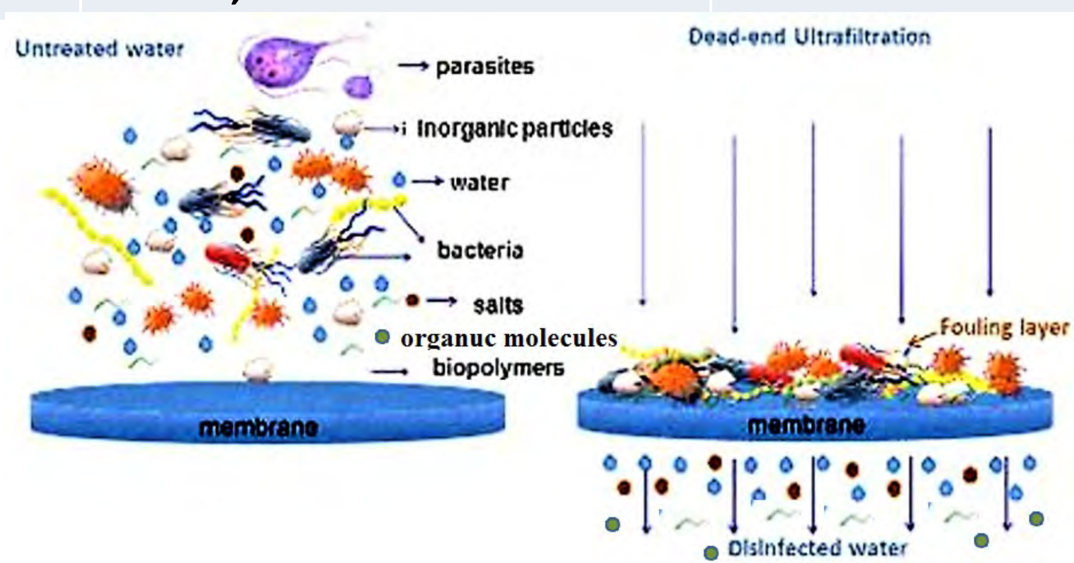
MEMBRANE METHODS FOR WATER DISINFECTION

MICRO- AND ULTRAFILTRATION. WATER DISINFECTION

Removal of pathogens from water

Species	Size, nm	Method	Pressure, bar
Helminth eggs	25000-55000	Macro-, microfiltration	0, 0.5-5
Fungi	8000-15000	Macro-, microfiltration	0, 0.5-5
Fungi spores	250-1000	Microfiltration	0.5-5
Eukaryotes, (protozoa)	10000-100000	Macro-, microfiltration	0, 0.5-5
Procaryotes (bacteria)	300-10000	Macro-, micro-, ultrafiltration	0, 0.5-10
Viruses	30-300	Micro-, ultrafiltration	1-10

Rejection of pathogens with a membrane



MICRO- AND ULTRAFILTRATION. WATER DISINFECTION

Dead-end module

Flow module

Partial washout of precipitate with water flow

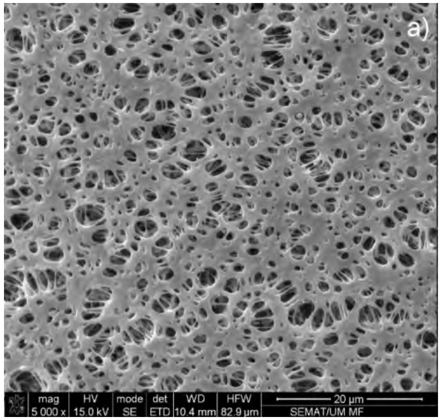
Removal of E-coli and mesophilic bacteria from water using different membranes

Membrane	Number of *E.coli* bacteria in 100 mL			The number of mesophilic bacteria, in 1 ml at 37°C/24h		
	Raw water	Permeate	R	Raw water	Permeate	R
Polymeric flat membrane						
PAN-13	63 (240)	0 (<5)	100	36	3	91.7
PAN-15	60 (240)	0 (<5)	100	205	1	99.5
PSf-13	45 (240)	0 (<5)	100	250	0	100
PSf-15	60 (240)	0 (<5)	100	320	4	98.75
PAN/PSf-15	30 (20)	6 (6)	80	60	6	90.0
Ceramic membrane						
MF – 0.1 µm	60 (240)	0 (<5)	100	205	1	99.5
MF – 0.2 µm	60 (240)	0 (<5)	100	220	2	88.9
UF – 15 kDa	30 (23)	0 (<5)	100	60	4	93.3
UF – 300 kDa	63 (240)	0 (<5)	100	36	4	88.9
Capillary membrane						
Polypropylene	86 (62)	0	100	24	0	100
Polysulfone	28 (23)	0	96.4	23	4	82.6

R – retention coefficient, PAN – polyacrylonitrile, PSf – polysulfone

Incomplete removal of bacteria

Heterogeneous pores size distribution



Secondary pollution of water
Due to biofouling

MICRO- AND ULTRAFILTRATION. WATER DISINFECTION

Advantages of membrane disinfection

- Production of water of a constant quality, which is free from pathogens ;
- Water of high quality from different water resources;
- Small addition of chemicals to raw water during the treatment process;
-- Low energy requirements for operation;
- Simple design and construction of a small scale system;
- Removal of a wide range of substances;
- Independency of removal efficiency from flow rate and pressure for particles larger than the membrane pore size;
- Formation of a depth filter by large particles on the membrane surface (dynamic membrane). This layer can retain particles smaller than the membrane pore size.

The disinfection can be carried out at low temperature (i.e. the method of "cold" sterilization). Thus, it can be applied to biological liquids.

MICRO- AND ULTRAFILTRATION. WATER DISINFECTION

Disadvantages of membrane disinfection

- **Increasing chlorine demand if the membrane filtration fails.**

- **Retention of small species (colloids, viruses, etc.) may not be complete and may depend on solution composition and operating conditions. Performance is not easily predicted.**

-**Filtration rate can be reduced due to membrane fouling. This is also not easily predicted**.

PROBLEMS OF CONCENTRATE

The volume of concentrate is less in 4-10 times than that of waste waters.

Sometimes it is possible to return the concentrate back to the process (tanning stage of leather industry, membrane bioreactor combining with forward and reverse osmosis).

The concentrate has to be treated with physical, chemical or electrochemical methods, after this it can be filtered again. Purified water can be used for technical purpose. Solid which is formed over the concentrate treatment can be burned or used as additions to paving slabs.

IN GENERAL, THE PROBLEM OF THE CONCENTRATE TREATMENT REQUIRES MORE SERIOUS STUDY, SINCE THE PAPERS AND PATENTS CONSIDER MAINLY FILTRATION PROCESSES.

CONCLUSIONS

Membrane technologies are promising to purify waste waters containing substances of biological origin, such as waste waters of textile, food, leather and paper industries, as well as leaching filtrate. Membrane can be effective for water disinfection.

Among filtration methods, membrane bioreactor looks very promising, since it provides biodegradation of pollutants.

Purified water can be discharged to sewage, sometimes it can be returned to the technological process. Nanofiltration permeate of milky whey can be transformed into mineral fertilizer.

Main problems of the membrane separation processes are fouling with organic and inorganic substances and also biofouling. The ways of the problem solution are optimization of the operation conditions, development of new membrane materials and solution pretreatment.

CONCLUSIONS

Type of fouling		Prevention
Inorganic fouling (scaling)	→	Operation conditions , partially solution pretreatment
Organic fouling	→	Operation conditions , solution pretreatment, membrane materials
Biofouling	→	Operation conditions , solution pretreatment, membrane materials