MODIFICATION OF MEMBRANES FOR PRESSURE-DRIVEN SEPARATION

PLAN OF THE LECTURE

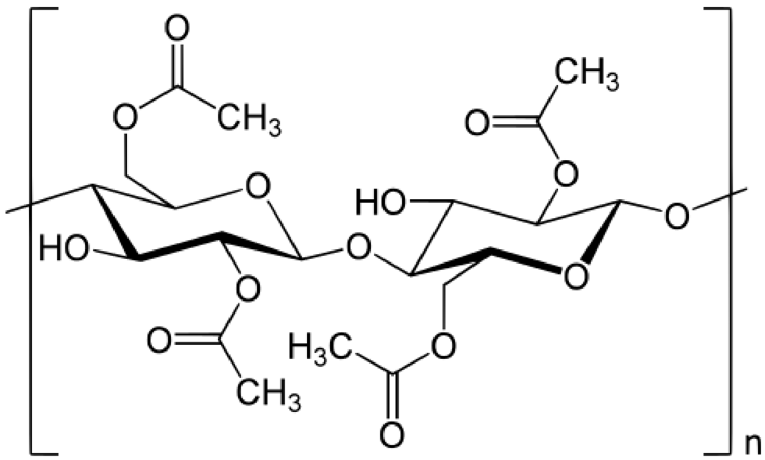
1. Polymers for filtration membranes,
2. Formation of membranes from polymers;
3. Modifying procedures;
4. Organic, inorganic and biological materials for membrane modifying.

COMMERCIAL MEMBRANES

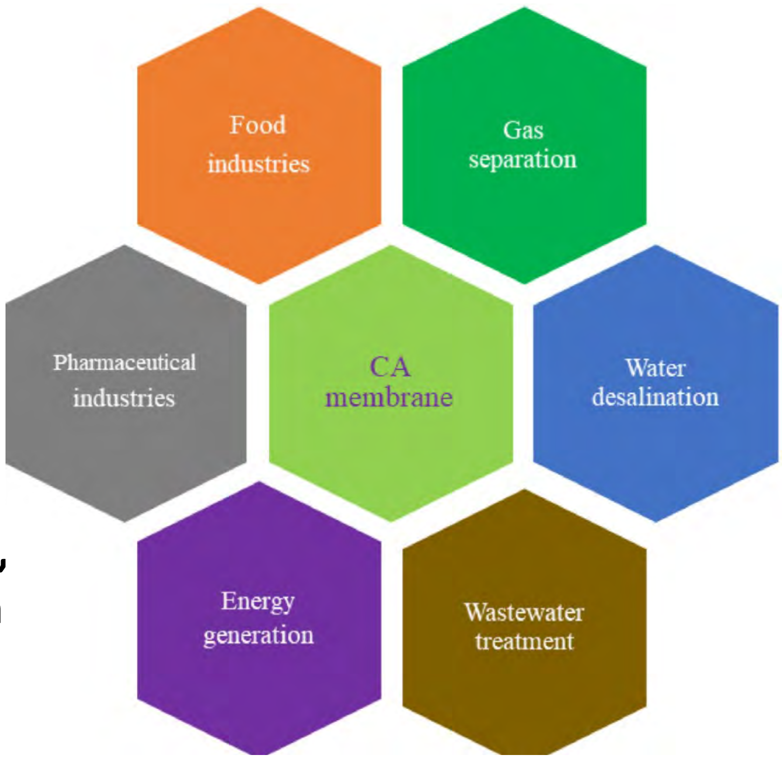
Most often used membranes

Cellulose acetate membrane

Cellulose acetate was first obtained from cotton in 1894 in UK. This method was rather expensive. Later this polymer was obtained from wood, the technique was much cheaper.



Application fields



Molecular mass of this polymer is 25-115 kDa. Acetylcellulose is soluble in acetic acid, CH_2Cl_2, $CHCl_3$, dichloroethane, aniline, pyridine. Cellulose oxidation started from 190° C, destruction is since 230° C.

The operating temperature is up to 45-50° C.

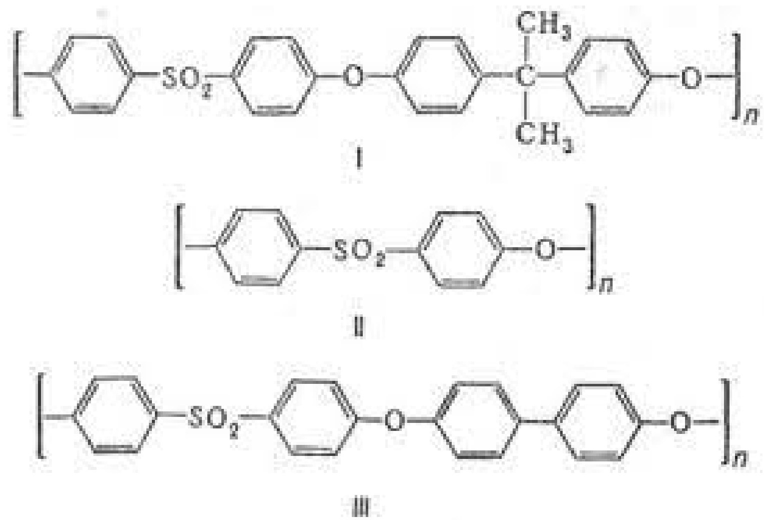
COMMERCIAL MEMBRANES

Most often used membranes

Polysulfone

Industrial production of aromatic polysulfone was started from 1965 in the USA.

Polysulfone



$-SO_2-$ groups are in the main chain

Aromatic polysulphones are thermoplastic polymers, Mw=3-230 kDa depending on the synthesis method. Polysulphone, which are used for the membrane preparation, are dissolved in aromatic non-polar aromatic solvents, DMFA, DMSO, pyridine, aniline. They are stable against strong acids and alkalies. Polysulphones are stable up to 400º C.

Aliphatic polysulhones are not produced by industry.

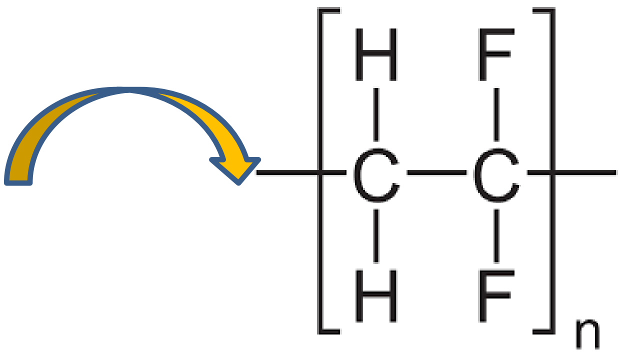
COMMERCIAL MEMBRANES

Most often used membranes

Polyvinylidene fluoride

The development of fluorine-containing polymers started since 1938 in the USA (DuPont), where fluoropolyethylene has been developed. The annual market of these polymers is 2 500 000 000 USD. Since their synthesis is complex, fluorine-containing polymers are produced in highly developed countries.

Polyvinylidene fluoride



PVDF is a very pure polymer; unlike other plastics, it does not contain residues of the catalytic system, thermal and UV stabilizers, lubricants, plasticizers, flame retardants. Polyvinylidene fluoride is chemically inert, it is not biodegradable. Maximal operation temperature is 150^{o} C.

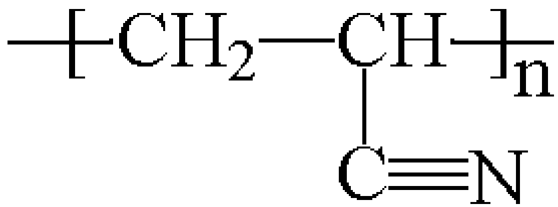
COMMERCIAL MEMBRANES

Most often used membranes

Polyacrylonitrile

Polyacrylonitrile was discovered in France in 1893.

Polyacrylonitrile



Polyacrylonitrile is an amorphous polymer, molecular mass of which is 30-100 kDa. It is softened only at 230-250°C.

Polyacrylonitrile is insoluble in hydrocarbon solvents and alcohols. It is dissolved in DMFA and DMSO, and also in highly concentrated solutions (50-70 %) of NaSCN, KSCN, NH_4SCN, LiBr, $ZnCl_2$.

Nitrile group is hydrolised in the solutions of strong acids:

$$R{-}C{\equiv}N + HCl + 2H_2O \rightarrow R{-}COOH + NH_4Cl$$

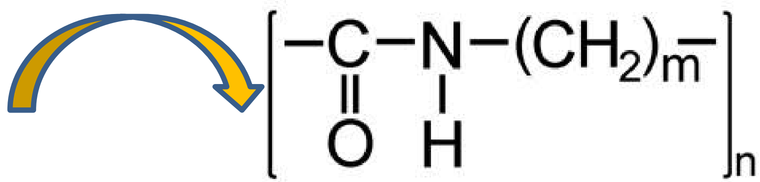
COMMERCIAL MEMBRANES

Most often used membranes

Polyamide

First polyamide was synthesized in 1938 in Germany. Now its main application field is textile industry, but it is partially used for the membrane preparation.

Polyamide



Molecular mass of synthetic polyamide is 10-35 kDa, melting point is slightly higher than 200ºC. The temperature of operation is up to 140ºC.

Polyamide is soluble in DMFA, tetrachloroethane (TCE), DMSO and H_2SO_4.

CONCLUSION

Thermal and chemical stability of polymers must be taken into consideration over membrane modifying.

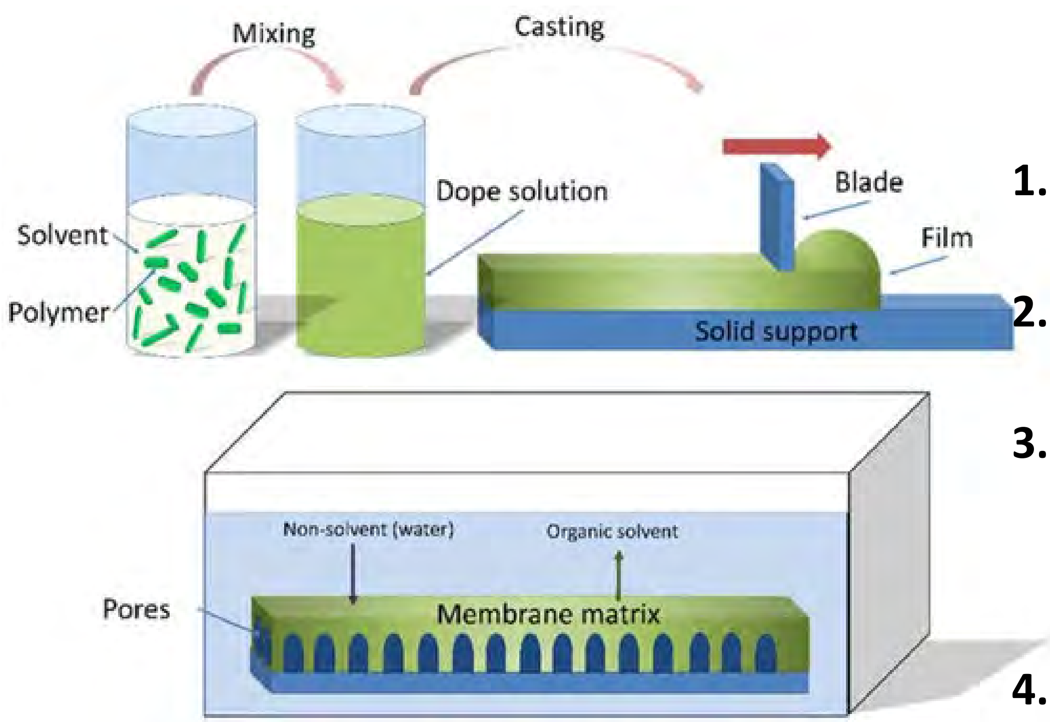
OBTAINING POROUS MEMBRANES

Phase inversion

Phase inversion is the most known method for obtaining polymer membranes.

Phase inversion is a phase separation process. A polymer is transformed from a solution or melt to a solid state in a controlled manner. The process of solid phase formation is often initiated by a change of one liquid, where the polymer is dissolved, to other one, where the polymer is insoluble. As a result, a solid phase of the polymer is formed.

Casting membranes



1. **Polymer is dissolved in a non-polar solvent;**
2. **The solution of polymer is discharged into the solid support;**
3. **The support with a polymer film is inserted into a bath filled with water, the solvent is exchanged into water;**
4. **Asymmetric membrane is formed by this manner.**

REQUIREMENTS TO POLYMERS FOR BAROMEMBRANE PROCESSES

Mechanical durability

Mechanical characteristics of commercial membranes

Microfiltration
- Elongation at break - 16-50 %,
- Tensile strength– 2.5-10.7 MPA.

Ultrafiltration
- Elongation at break – 3.2-10 %,
- Tensile strength – 4-44 MPa

Nanofiltration
- Elongation at break – 2-4 %,
- Tensile strength –13-60 MPa

Unfortunately the mechanical properties of the membranes are not indicated by the producers. It is, first of all, due to the lack of unification of methods and devices.

Chemical stability. The membranes must be stable against strong acids and bases as well as against oxidizers. Namely these reagents are used for the membrane cleaning.

Thermal stability. The membranes must be suitable for operation under elevated temperatures (separation and cleaning).

REQUIREMENTS FOR MODIFYING

- **The modifying procedure must cause no deterioration of mechanical durability, chemical and thermal stability.**

- **In the best case, these properties should be improved.**

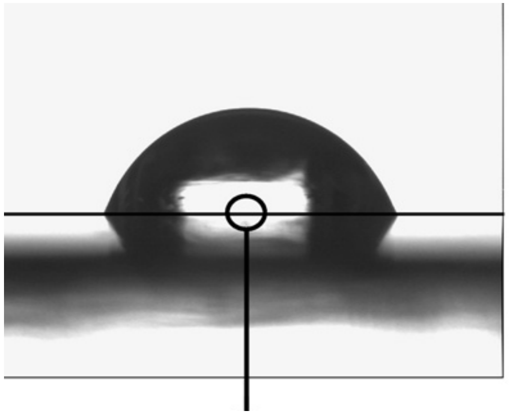
COMMERCIAL MEMBRANES

Main disadvantage

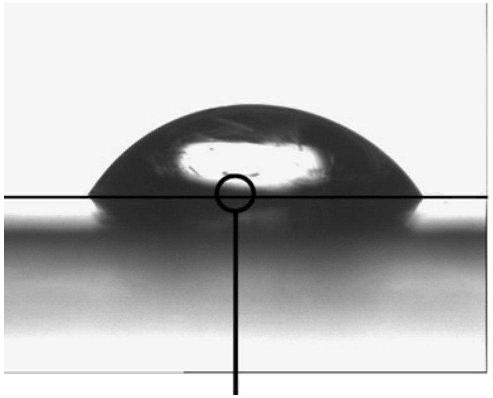
Hydrophobicity

Polyamide membrane

Water drop



Octane drop

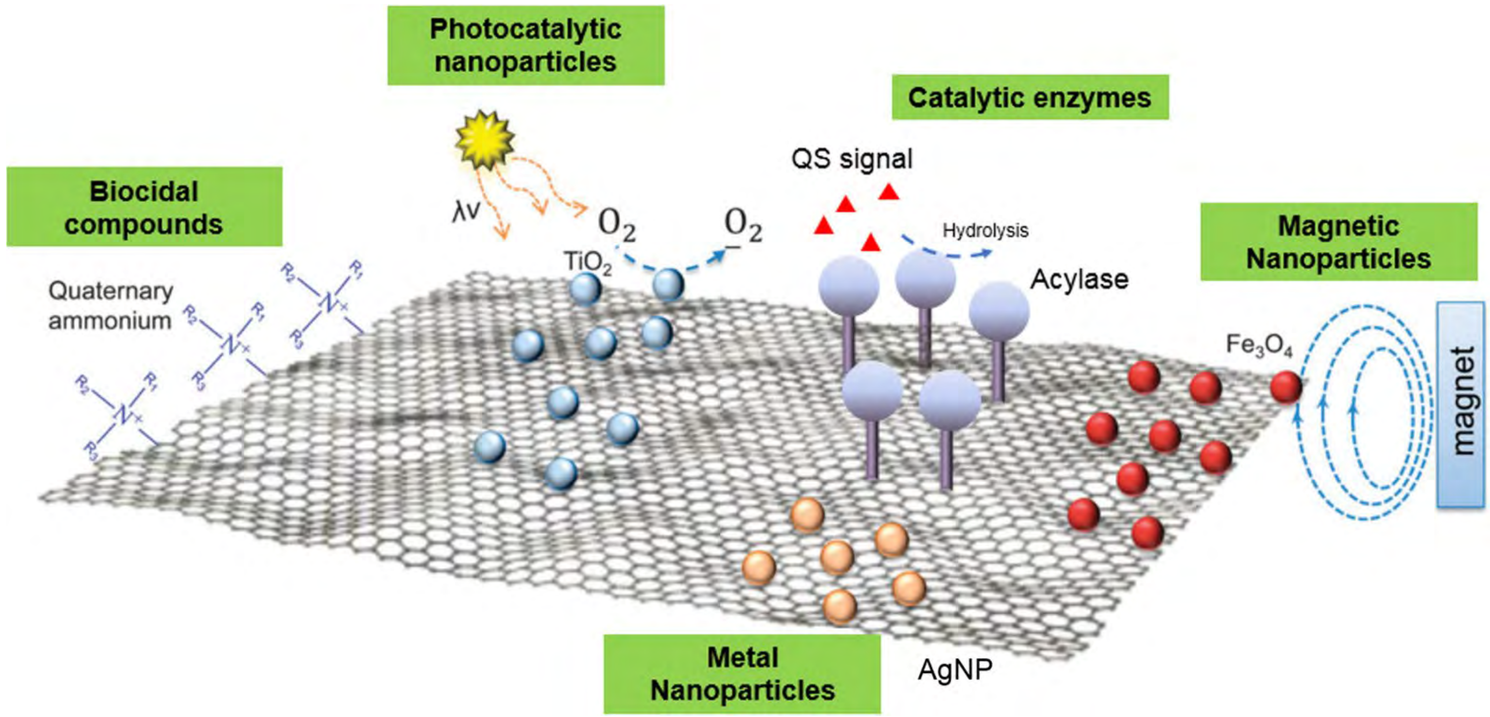


Hydrophobicity provides fouling with organic substances and biofouling.

Strategy for preventing fouling is hydrophilization of membranes or modifying them with substances, which destroy organic substances or bacteria.

FOULING MANAGEMENT STRATEGY

Membrane materials: modifiers for prevention biofouling



Additional modifiers (for hydrophilization)

Hydrophilic polymers;

Natural and synthetic inorganic ion exchangers;

Mxenes;

Advanced carbon nanomaterials

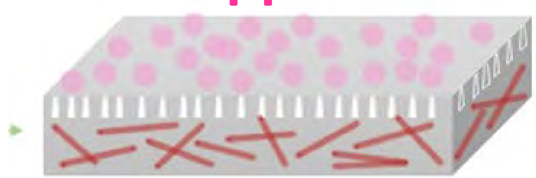
MAIN APPROACHES TO MODIFYING

Supporting matrix → Composite ← Active component

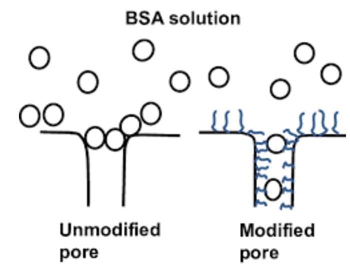
Supporting matrix provides separation.

Main approaches to modifying

1. Bulk modifying



2. Pore modifying

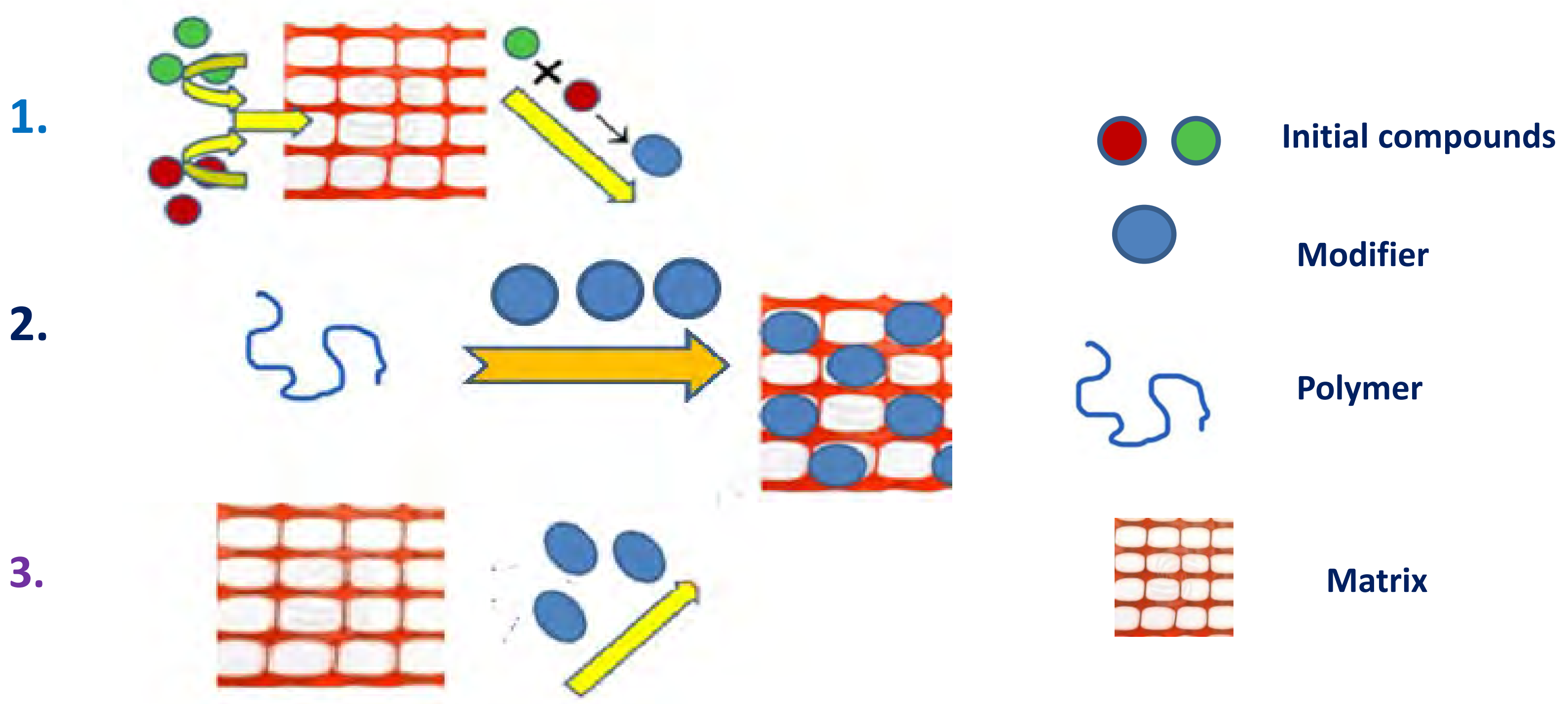


3. Modifying of outer surface

Separate fragments

Coating with polymer or GO film

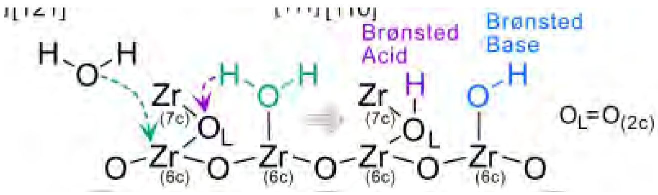
MAIN APPROACHES TO MEMBRANE MODIFYING



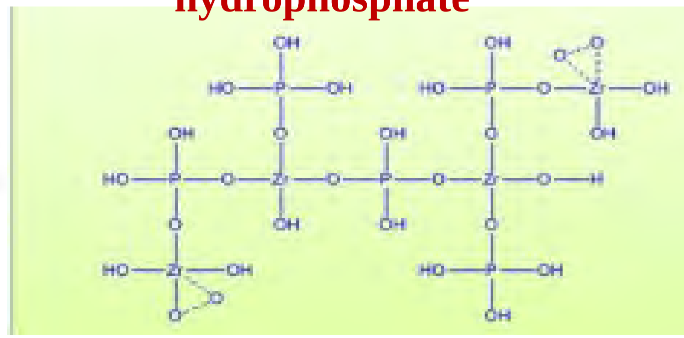
- 1. Synthesis of active components in previously formed matrix or on its surface (inorganic ion-exchangers, Ag and magnetic nanoparticles).
- 2. Reinforcement of preliminarily formed active component with matrix (clay, zeolites, GO)
- 3. Insertion of preliminarily formed active component unto the matrix or coating its surface (enzymes, biocidal compounds, hydrophilic polymers, advanced carbon nanomaterials. TiO_2).

INORGANIC ION-EXCHANGERS

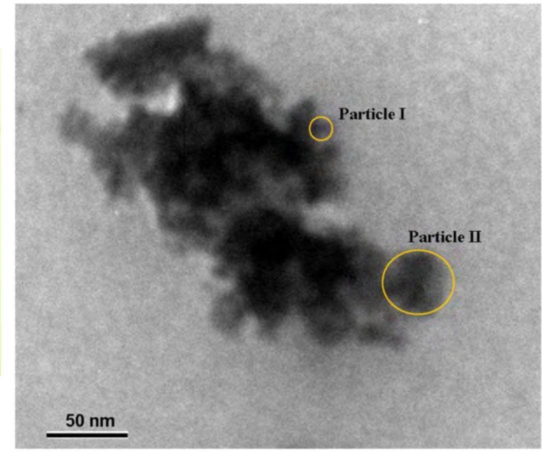
Hydrated zirconium dioxide



Zirconium hydrophosphate



Particles in membrane



Hydrophilicity is caused by functional groups

Hydrated oxides of multivalent metals

$$\equiv Zr{-}OH \leftrightarrow \equiv Zr{-}O^{-} + H^{+}$$

$$\equiv Zr{-}OH + H^{+} \leftrightarrow \equiv Zr{-}OH_2^{+}$$

Hydrophosphate of multivalent metals

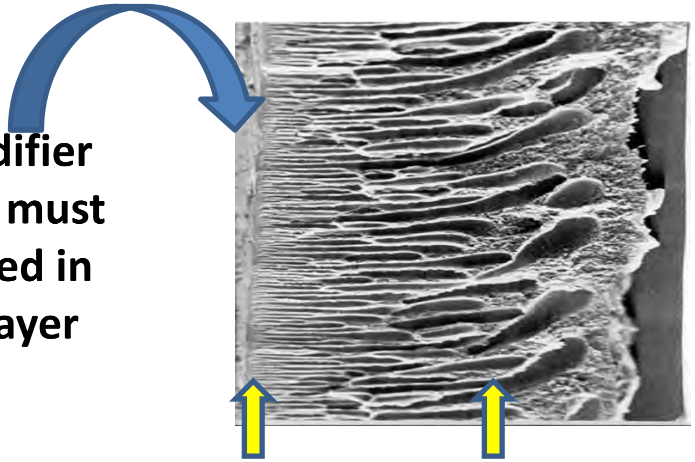
$$\equiv Zr{-}O{-}PO_3H_2 \leftrightarrow \equiv Zr{-}O{-}PO_3^{2-} + 2H^{+}$$

$$\begin{matrix}\equiv Zr{-}O\\ \equiv Zr{-}O\end{matrix}\Big\rangle PO_2H \leftrightarrow \begin{matrix}\equiv Zr{-}O\\ \equiv Zr{-}O\end{matrix}\Big\rangle PO_2^{-} + H^{+}$$

INORGANIC ION-EXCHANGERS

SEM image of filtration membrane

The modifier particles must be located in active layer



How is it possible to control the particle size in practice?

Formation of particles of predetermined size

Theoretical approach (adapted from Ostwald-Freundlich equation)

$$r = -\frac{\beta v_m \sigma \cos\varphi}{RT\left[\ln K_s - \ln[Cat_{\infty}^{z+}] - z_{Cat}\ln\left(C_{pr} - \frac{V_{pol}(z_{Cat}\overline{C}_{Cat})}{V_{pr}}\right)\right]}$$

Here r – particle radius, β – shape factor, V_m – molar volume, σ – surface tension, φ – wetting angle, R - gas constant, T – temperature, K_s – solubility product, $C_{Cat,\infty}$ - concentration of cation hydroxocomplexes in saturated solution, z – charge. Cpr- concentration of precipitator, $\overline{C}_{Cat}$ concentration of cations in polymer, V_{pol} – polymer volume, V_{pr} – precipitator volume.

To choose modifier (smaller particles are formed for less soluble compound),

Decrease of solubility in the range of hydrated oxides:

(Fe(III)>>Ti(IV) >Zr(IV)=Sn(IV)

to vary temperature,

to vary concentration of precipitator and salt of multivalent metal,

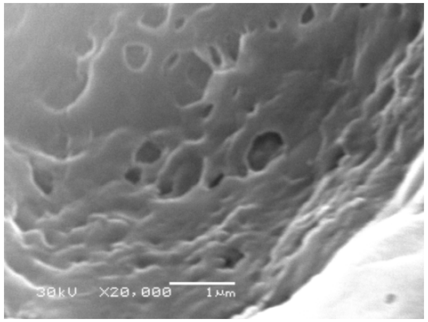
to vary volumes of membrane and precipitator.

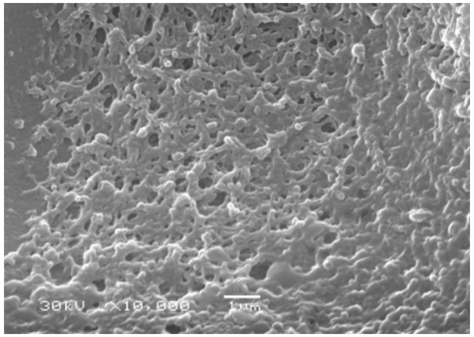
Practical application of theoretical approach

Formation Materials for baromembrane separation

Active layer of asymmetric membrane

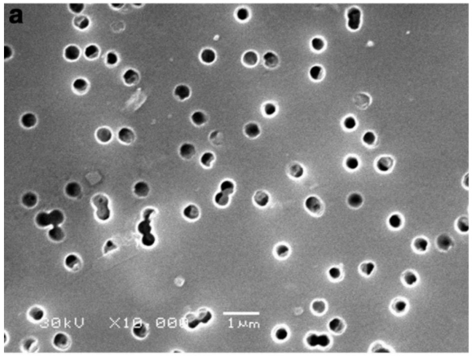
pristine membranes | composite membrane

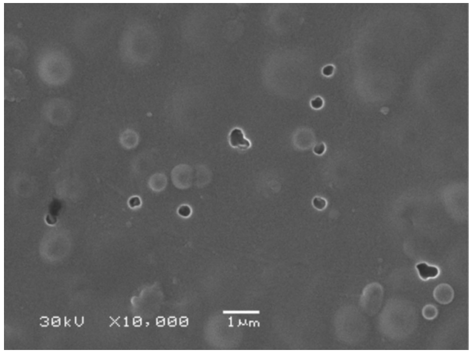




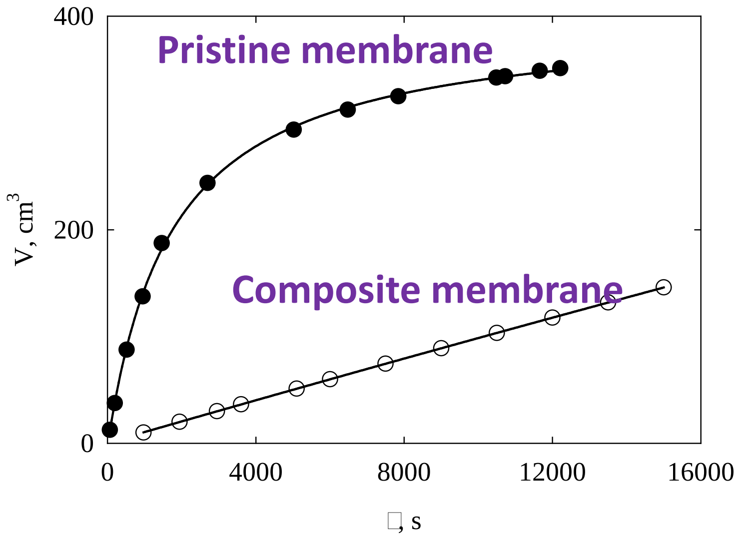
Symmetric membrane

pristine membranes | composite membrane





Filtration of milky whey



Selectivity of the composite membrane/ calibration

Bovine serum albumin (70 kDa) – 90%
Polyethylene glycol (40 kDa) – 10 %

Size of pores, which determine rejection ability

Pristine membrane – 300 nm
Composite – 14-18 nm

FUNCTIONS OF INSERTED ION-EXCHANGERS

Hydrophilisation of membranes

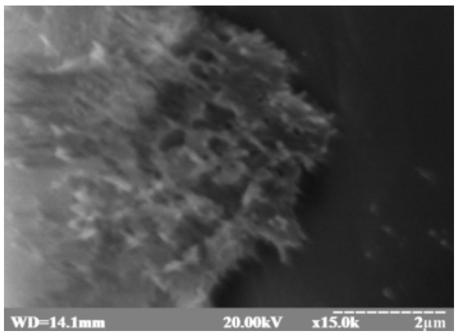
Stability against fouling with organic substances and biofouling

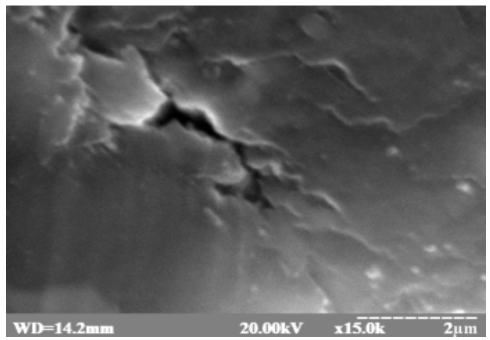
Asymmetric membrane

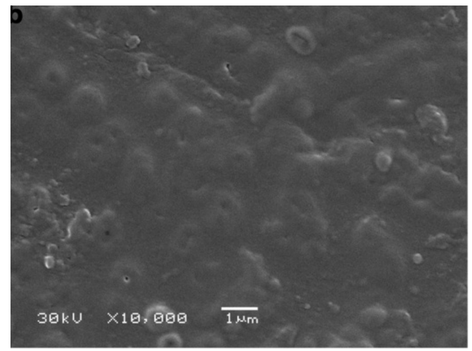
pristine membranes — composite membrane

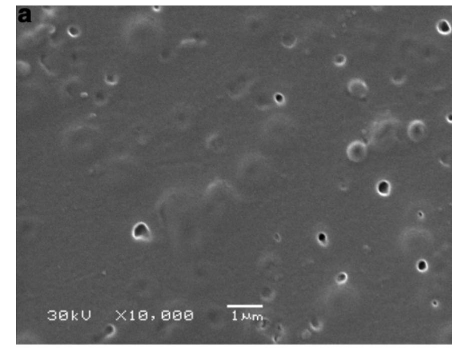
Symmetric membrane

pristine membranes — composite membrane









Transformation of microfiltration membranes into ultrafiltration

Rejection of colloidal particles (up to 90 %)

Partial rejection of Ca^{2+} and Mg^{2+} ions (up to 20 %)

Inorganic modifier is localized in pores

↓

Stability of modifier against mechanical action: flow of liquid, removal of precipitate.

STABILITY OF INORGANIC MODIFIER IN MEMBRANE PORES

PROBLEMS OF INORGANIC ION-EXCHANGERS

Disaggregation of oxide modifier in aqueous media

Dissolving oxide modifier in acidic media

Disaggregation of oxide and phosphate modifier under high pressure

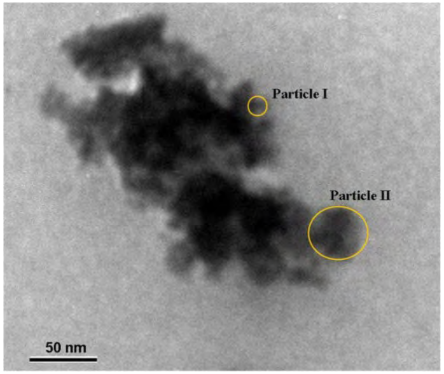
Leakage of modifier

Impossible to struggle

It is difficult to fill large pores with inorganic ion-exchanger

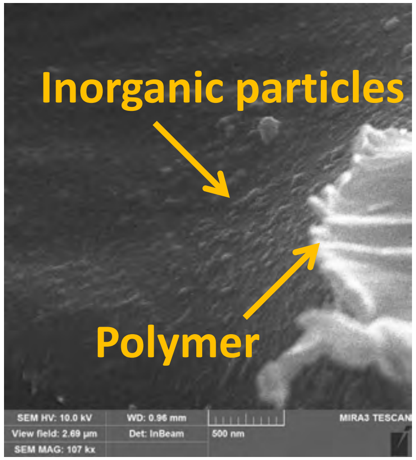
PARTIAL SOLUTION OF PROBLEMS

Roughness of aggregates



Fixing inorganic particles due to polyacrylonitrile etching during the modifying procedure

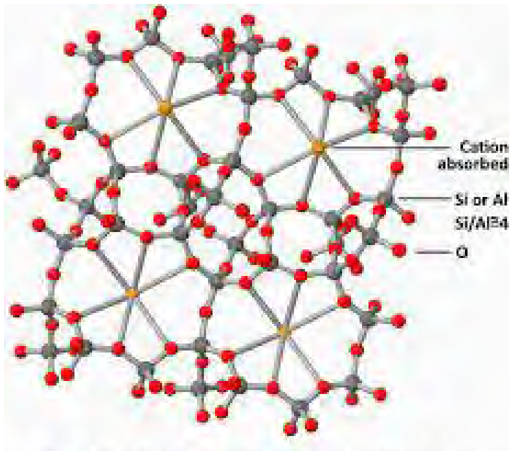
$$R{-}C{\equiv}N + HCl + 2H_2O \rightarrow R{-}COOH + NH_4Cl$$



MEMBRANES MODIFIED WITH ZEOLITE

$M^{n+}{}_{1/n}(AlO_2)^-(SiO_2)_x \cdot yH_2O$

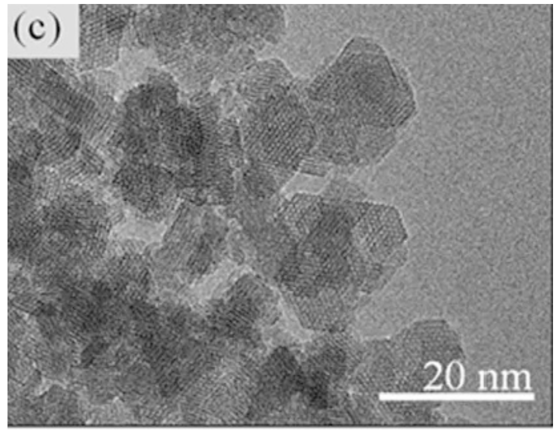
M is usually H^+ or Na^+



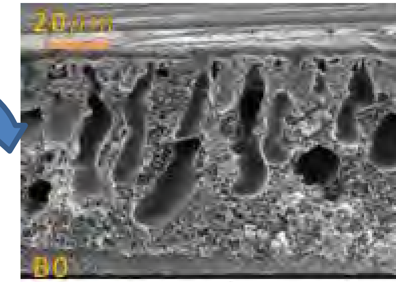
The Tetrahedral Framework of Clinoptiloite

Synthetic zeolites are used since they can be obtained in a form of nanoparticles.

Zeolite nanoparticles

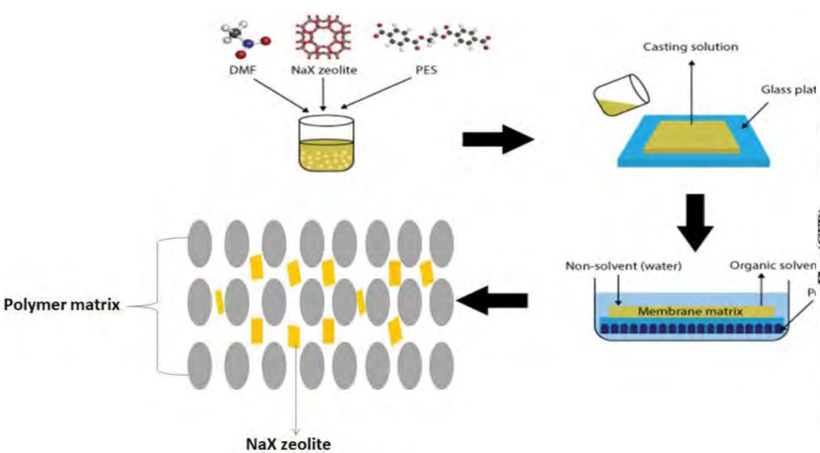


Polymer membrane



Zeolite-containing membrane

Synthesis of membranes
(phase inversion)



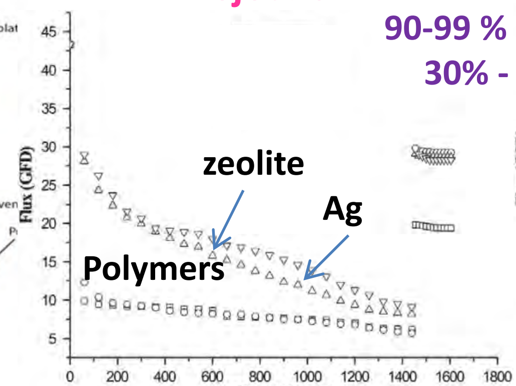
Filtration rate through polymer and membranes modified with zeolite and Ag

Flux of protein solution

Rejection

90-99 % - modified

30% - pristine

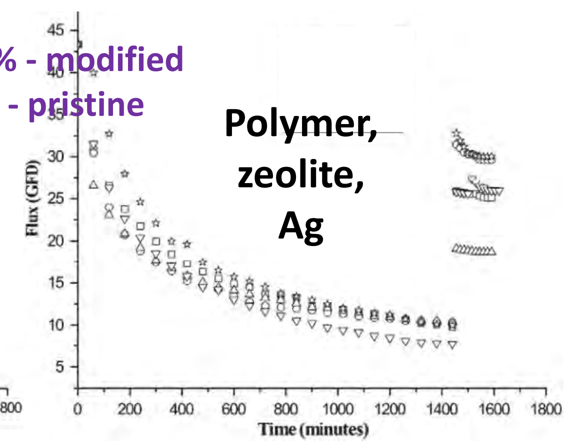


zeolite

Ag

Polymers

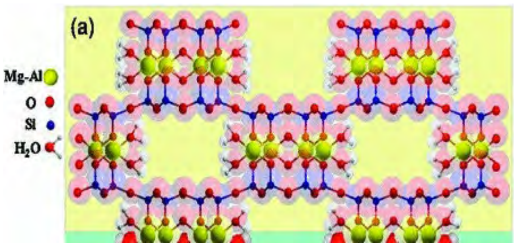
Flux of bacteria-containing solution



Polymer, zeolite, Ag

MEMBRANES MODIFIED WITH NATURAL CLAY MATERIALS

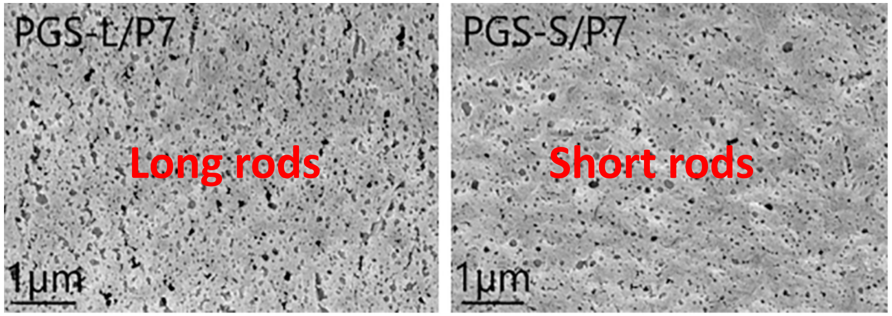
Palygorskite

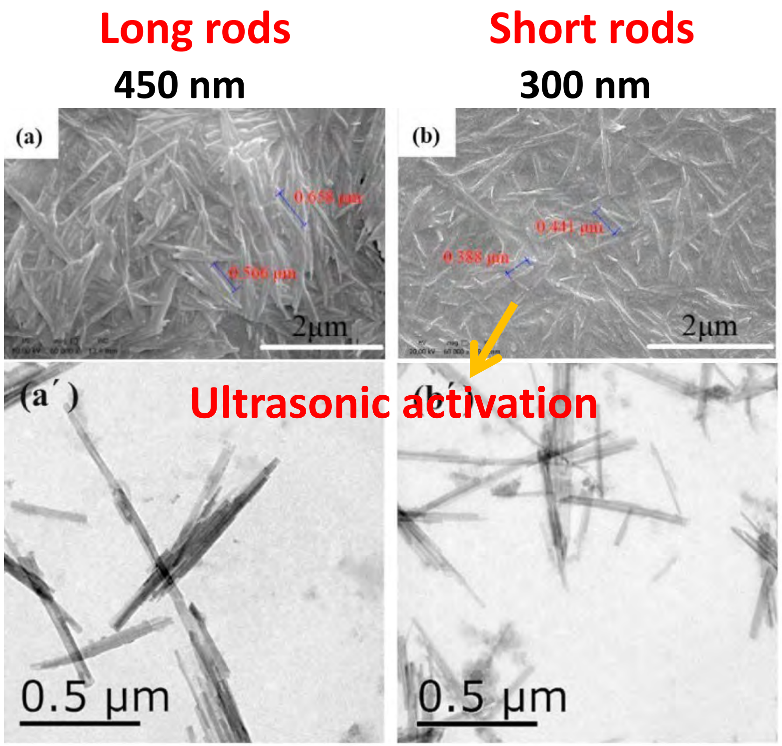


$(Mg,Al)_2Si_4O_{10}(OH)\cdot 4H_2O$

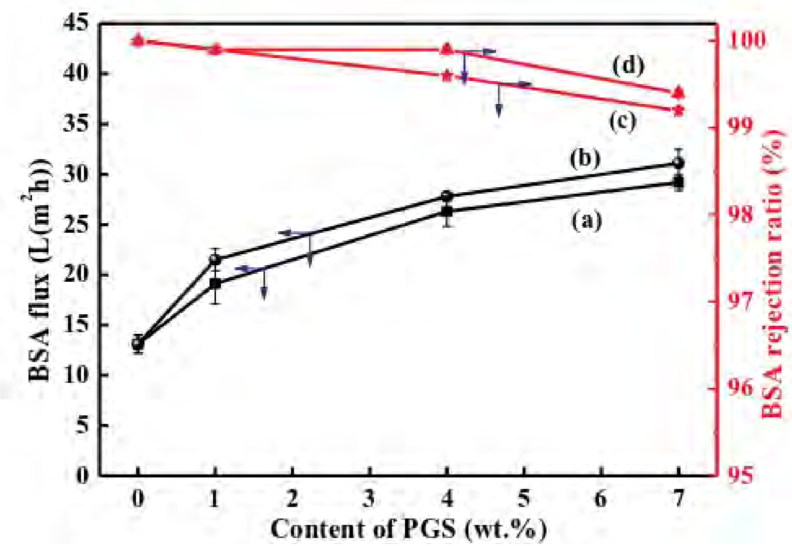
The Indians used palygorskite to make dyes.

SEM images of membranes





Filtration of the solution of protein calibrant



1. No sufficient effect of particle length on filtration
2. Increasing the clay content deteriorates selectivity.

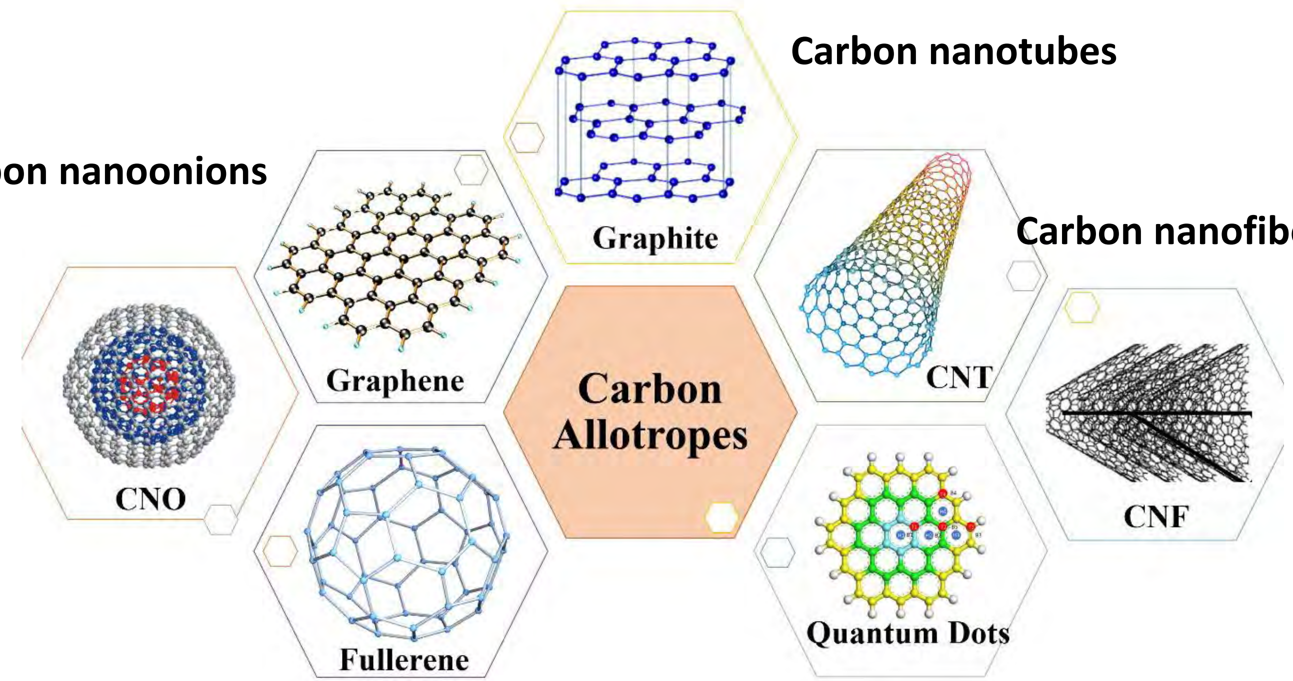
MEMBRANES MODIFIED WITH ADVANCED CARBON NANOMATERIALS

Carbon allotropes

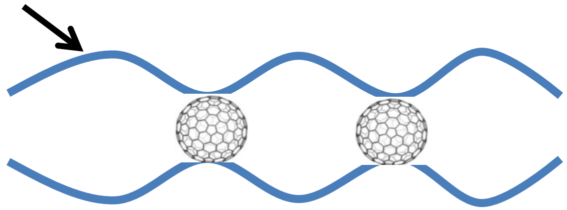
Carbon nanotubes

Carbon nanoonions

Carbon nanofibers



MEMBRANES MODIFIED WITH FULLERENES



Literature sources contain practically no information about filtration membranes modified with fullerenes, since they are hydrophobic.

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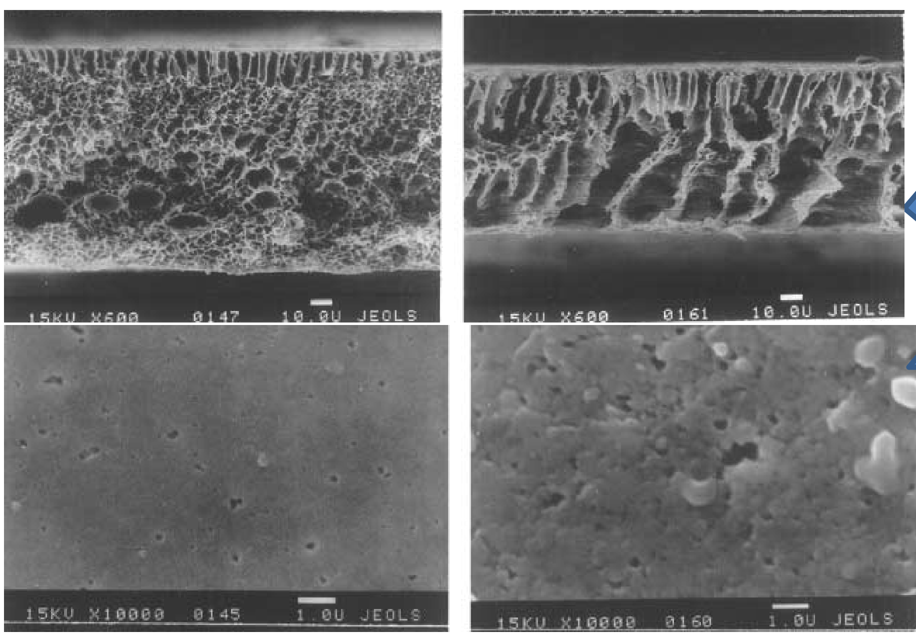
Their function is the cross-linkage of polymer chains → enhancement of the membrane durability. Other function is the pore ordering → facile liquid transport.

Polymer

Polymer + fullerene

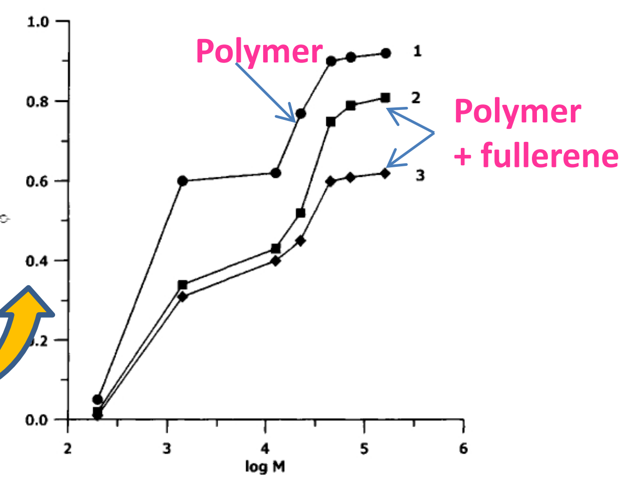


Disadvantages

Enhancement of hydrophobicity → fouling

Enlargement of pores → decrease of selectivity

Rejection of proteins of different mass



Possible solution of the problem:

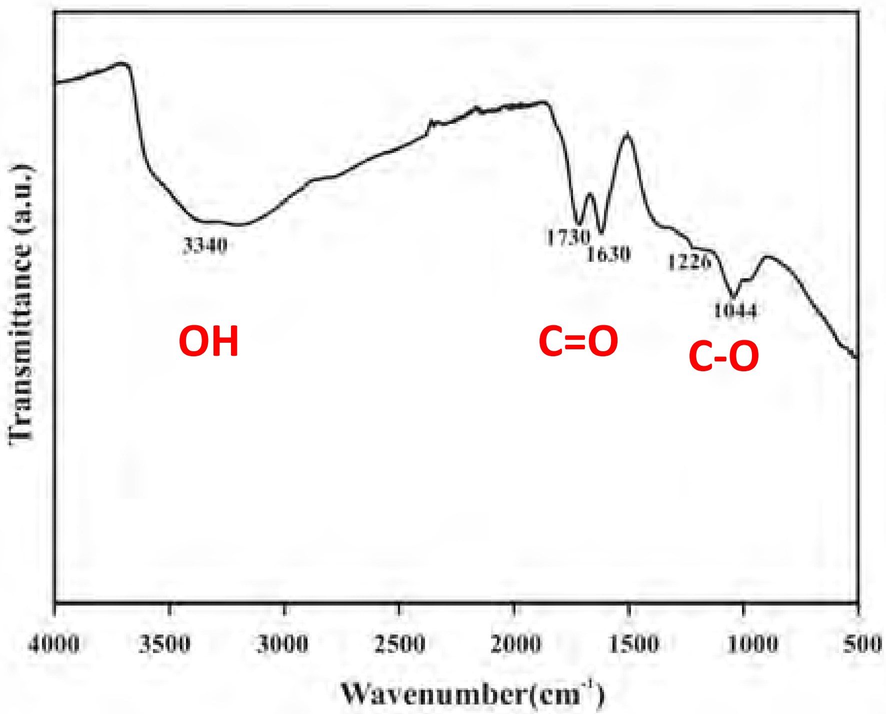
Use hydrophilic modifiers!

HYDROPHILICITY OF CARBON NANOMATERIALS

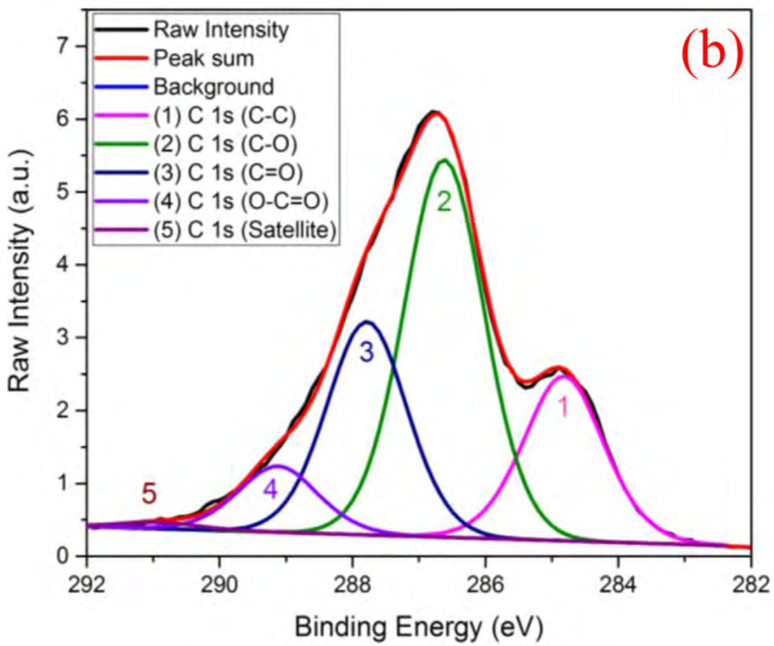
- -COOH and OH groups are formed over the synthesis procedure.
- Special approaches are used to obtain N-containing nanomaterials. N-containing groups (pyridine, pyrolidone, amine etc. also provide hydrophilicity).

Graphene oxide

IR spectroscopy

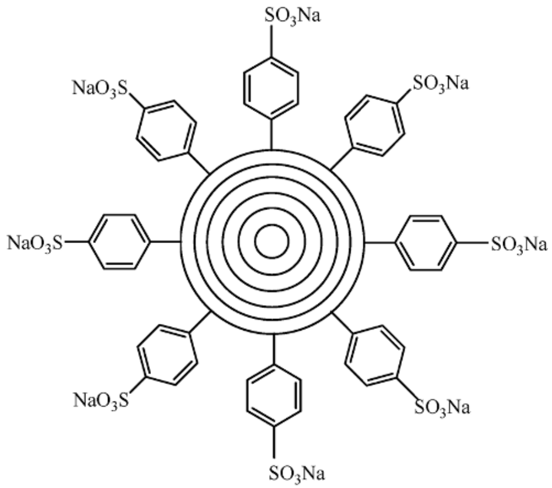


X-ray photoelectron spectroscopy

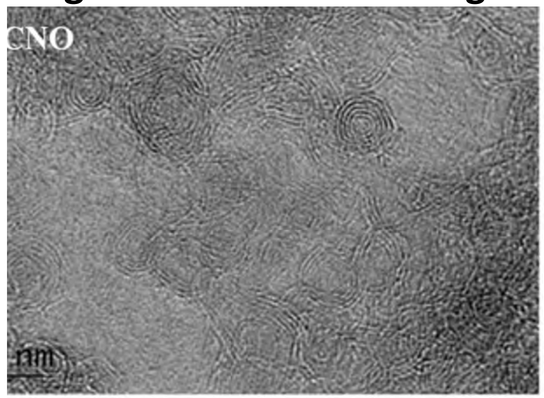


MEMBRANES MODIFIED WITH CARBON NANOONIONS

Functionalized carbon nano onions



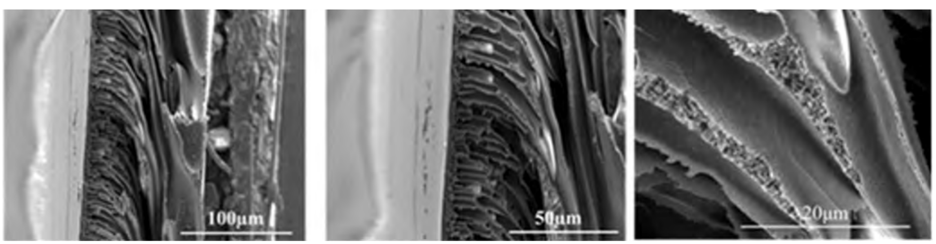
High-resolution TEM image



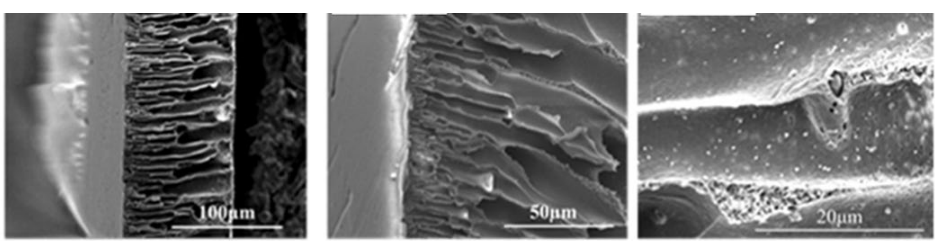
Contact angle

Amount of nano-anions, %	Contact angle, degree
~	88
0.5	49
1	38
1.4	31

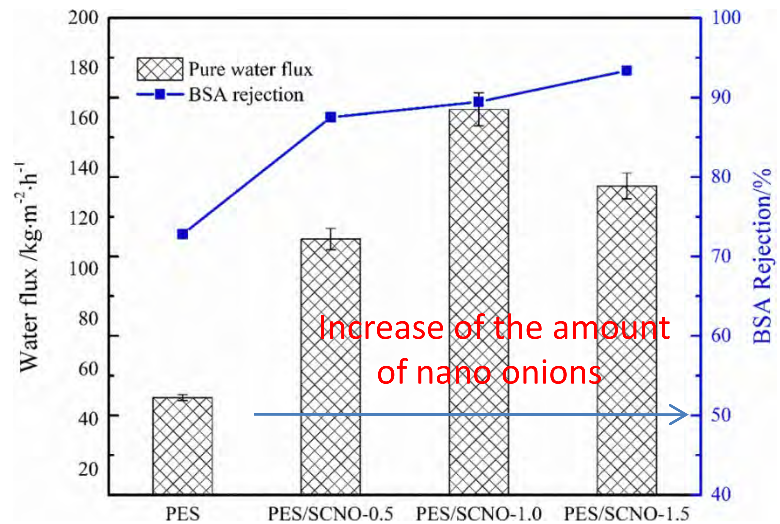
Polymer



Modified membrane



Filtration of the solution of protein-calibrant



Nano onions provide straight. pores of polyethersulfone. This differs modified membrane from the pristine material, which contains tortuous pores. Liquid transport is faster namely in straight pores.

MEMBRANES MODIFIED WITH CARBON NANOFIBERS

Production of carbon nanofibers

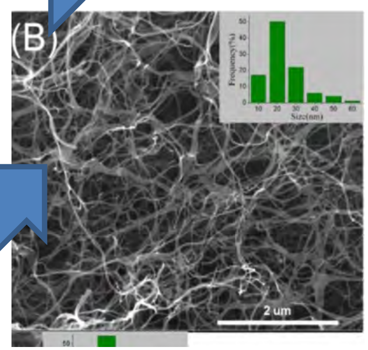
Bacteria cellulose

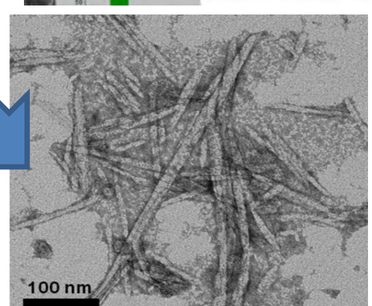
Simple purification procedure → **Gel preparation followed by drying using freezing supercritical conditions** → **Carbonization**

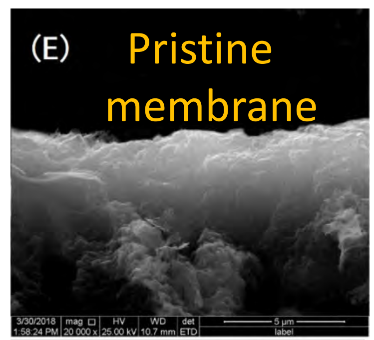
Carbon NF are deposited on the membrane surface

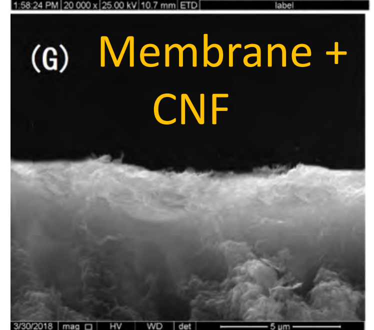
BC is produced by both Gram-positive and Gram-negative bacteria: Gluconoacetobacter xylinum, Agrobacterium etc.

Final product
Carbon aerogel



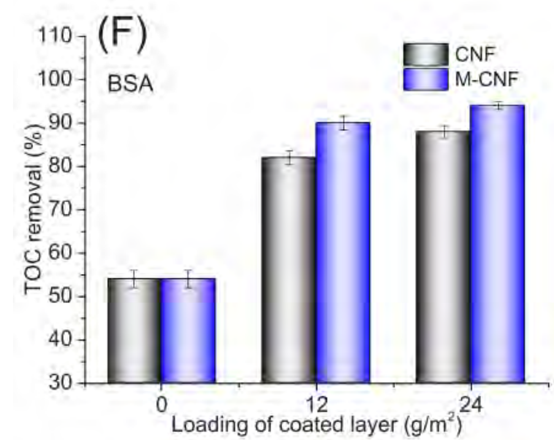






Membrane modified with CNF

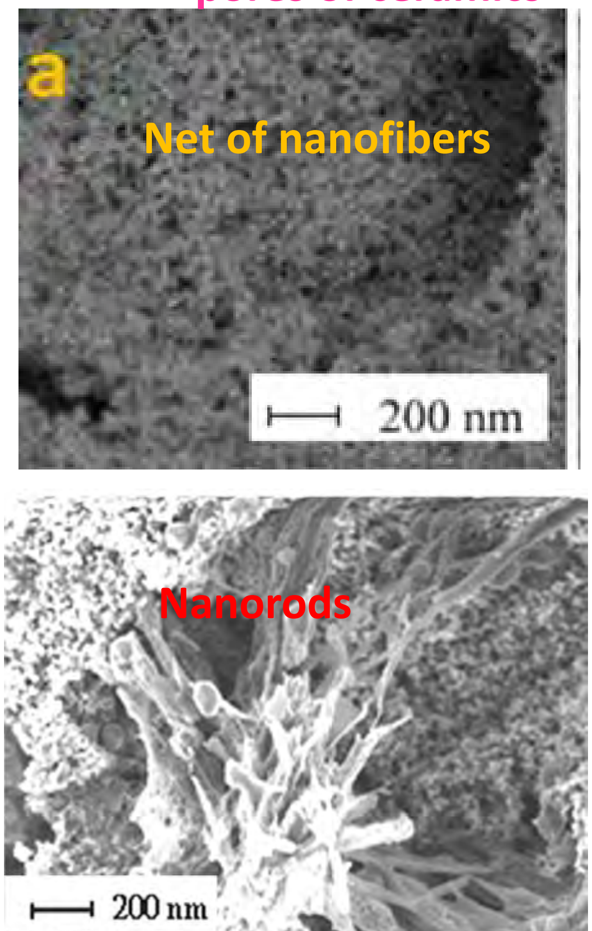
Filtration of bowine serum albumine



MODIFYING CERAMIC MEMBRANES WITH CARBON NANOMATERIALS

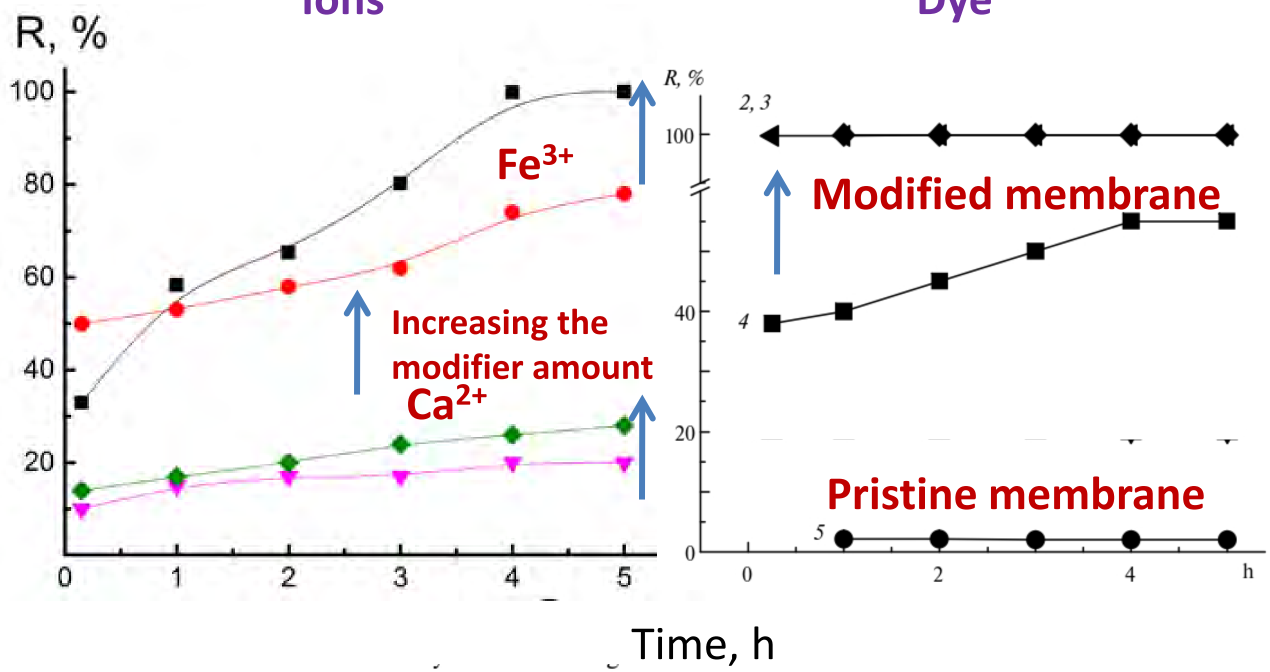
The approach is carbonization of polysaccarides inside pores of microfiltration ceramic membranes. Carbon nanofibers as well as nanorods are formed by this manner.

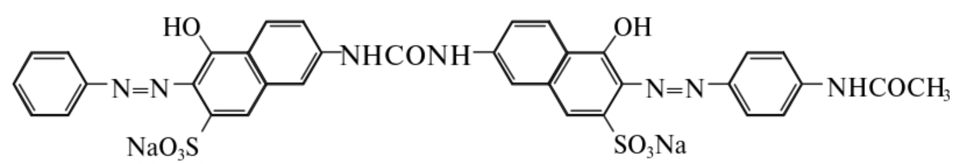
Carbon nanofibers inside pores of ceramics



Desalination and decontamination of water

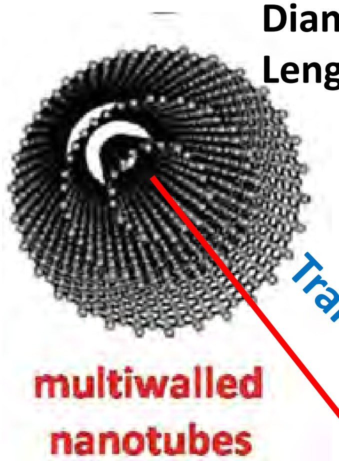
Ions **Dye**





Direct scarlet dye.

MEMBRANES MODIFIED WITH CARBON NANOTUBES

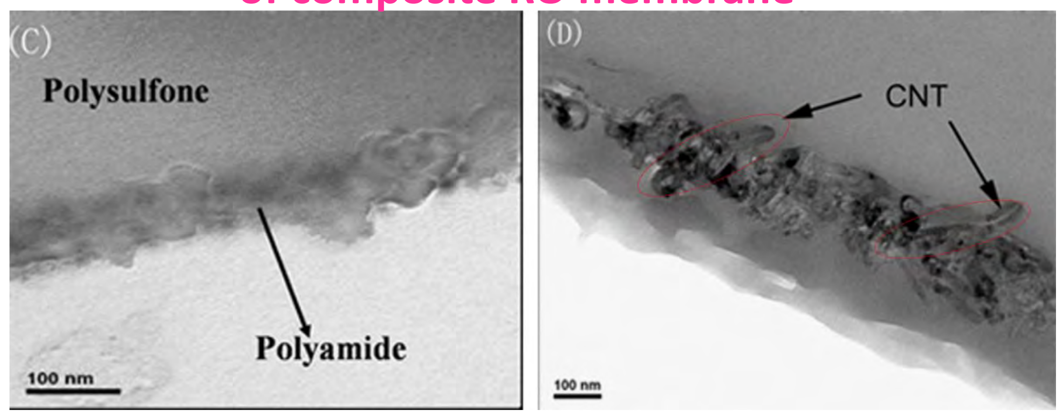


Diameter - <1 nm-50 nm.
Length – several microns

Transport

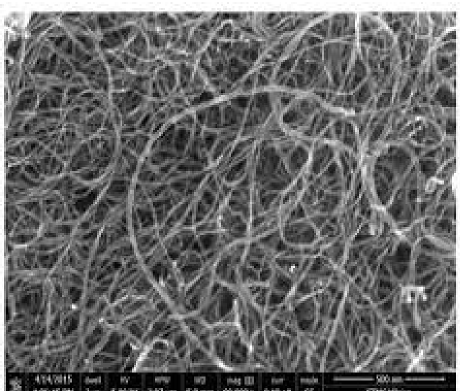
+ Polymer solution → **Phase inversion** → **Membrane**

MWCNT incorporated into polyamide active layer of composite RO membrane



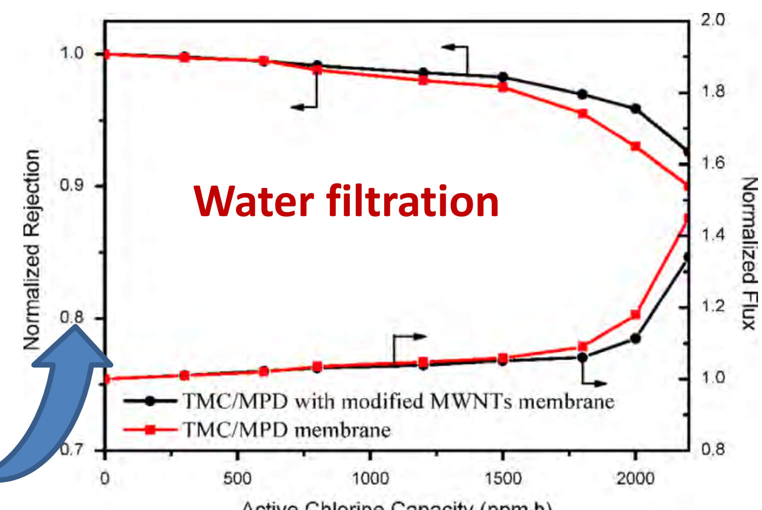
Disadvantage of approach

Twisting of nanotubes

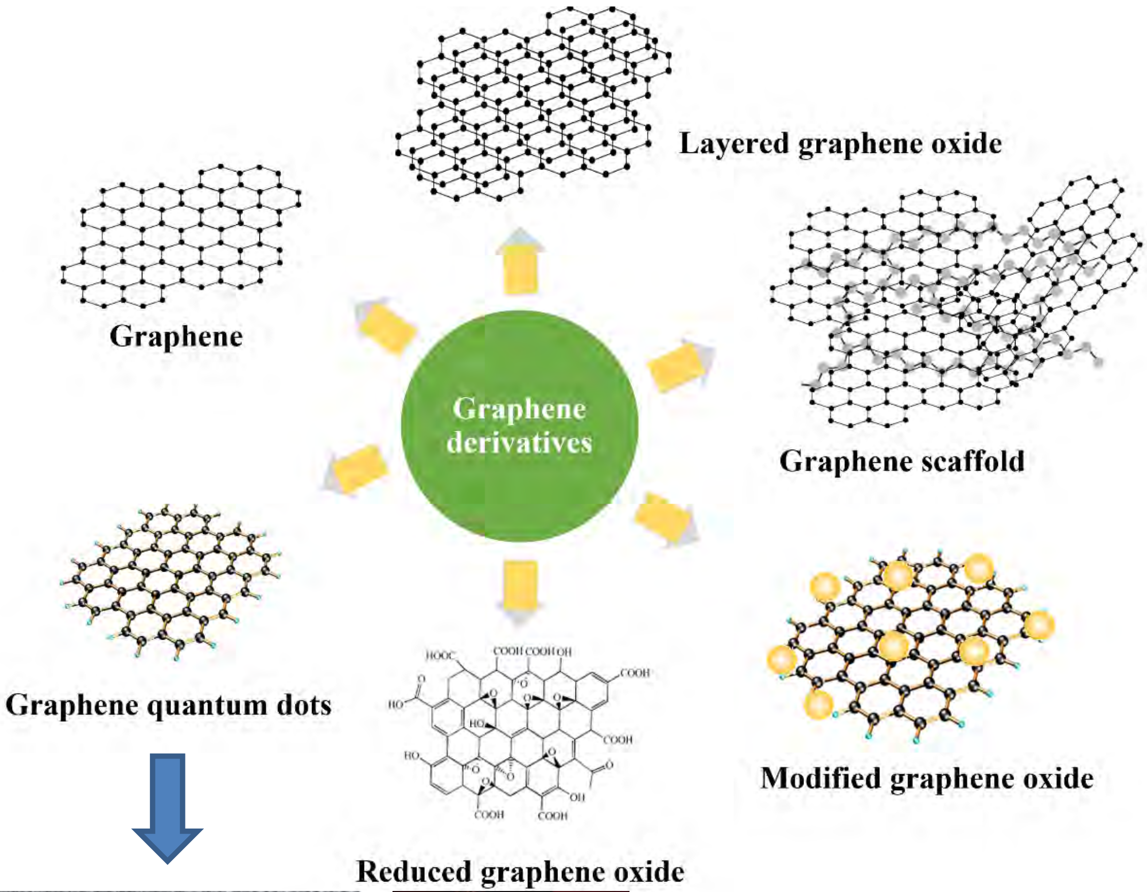


Tortuosity of pores → Difficult mass transport

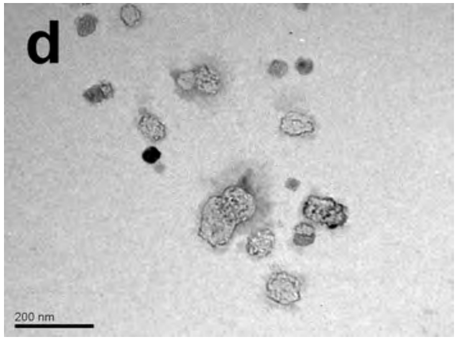
The effect of nanotubes on salt rejection is inconsiderable

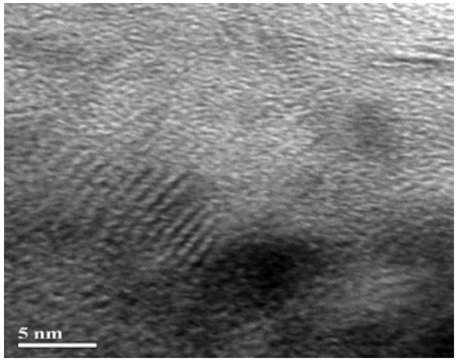


2D AND 0D CARBON NANOMATERIALS

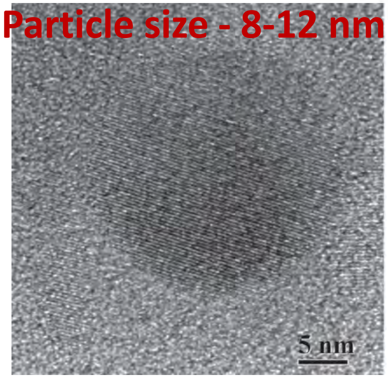


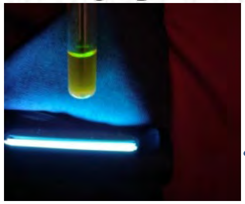
Graphene

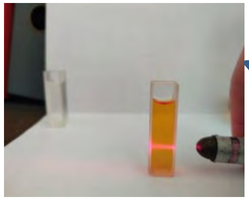




Particle size - 8-12 nm







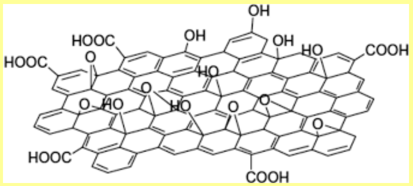
Tyndall effect

Luminescence
Affected by UV

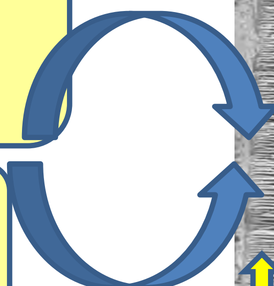
GRAPHENE OXIDE AND CARBON NANODOTS INSERTED INTO PORES OF POLYMER

MODIFIER

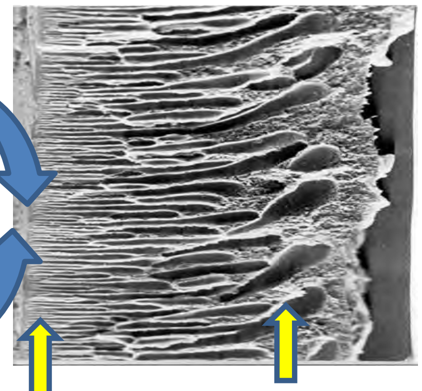
GO or CNDs



Inorganic ion-exchanger (binder)



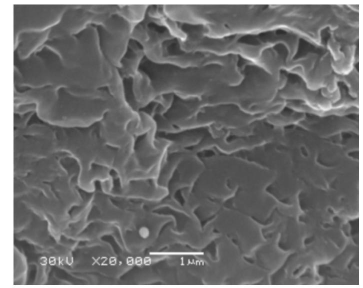
POLYMER FILTRATION MEMBRANE



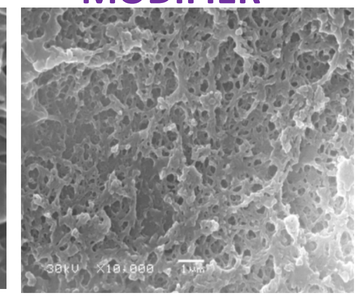
Active layer

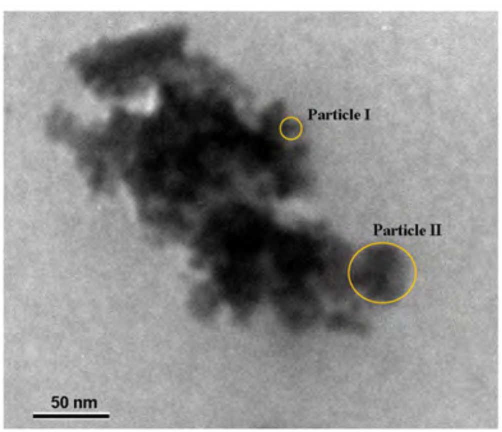
Macroporous basis matrix

Active layer

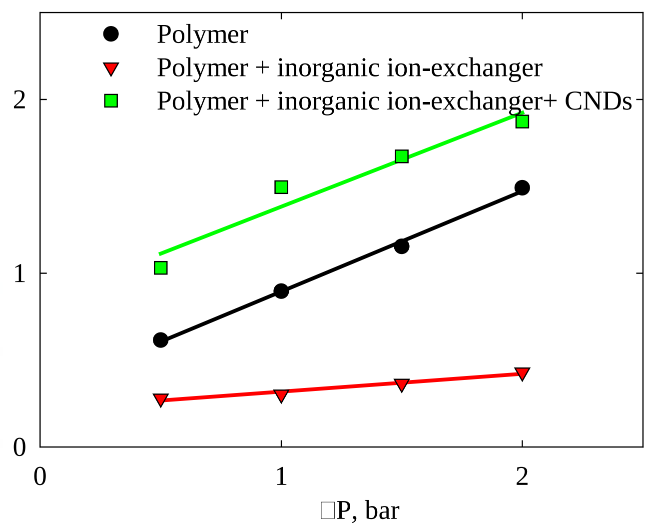


Active layer + MODIFIER

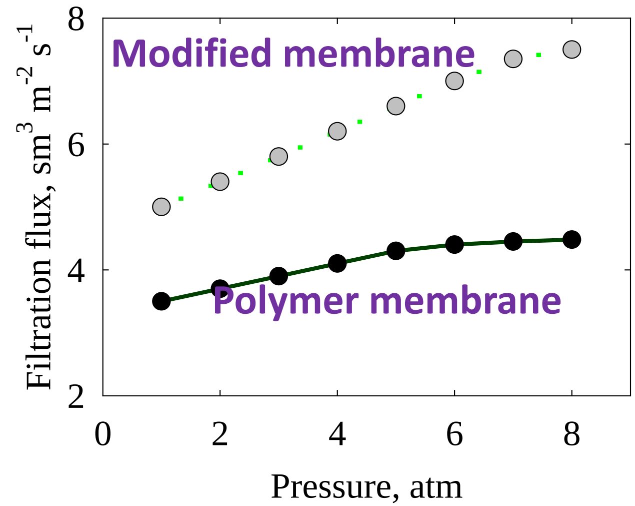




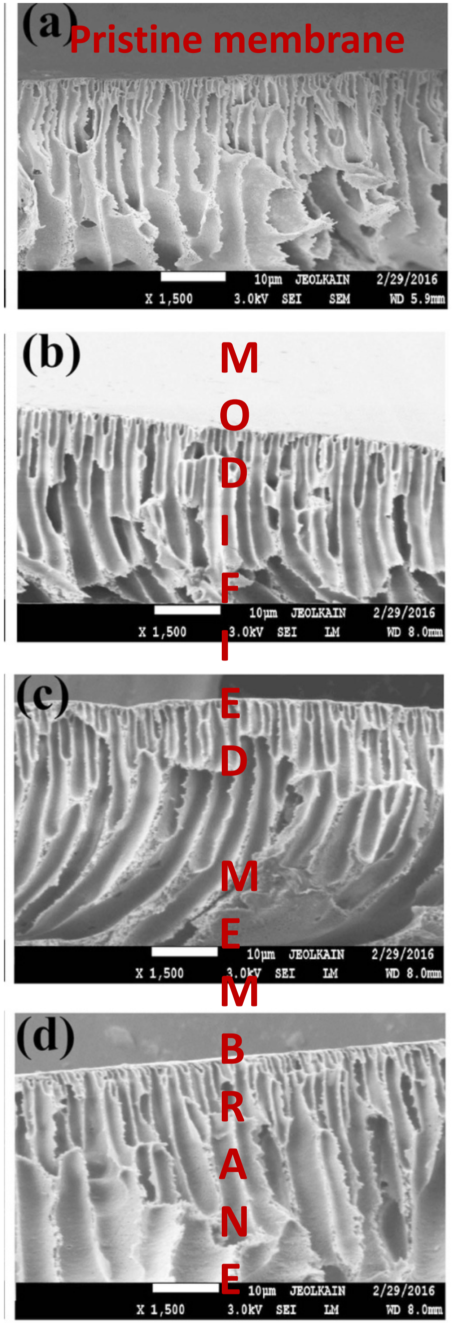
Membranes obey the Darcy law



FILTRATION OF MILKY WHEY



GRAPHENE OXIDE IN THE BULK OF POLYMER

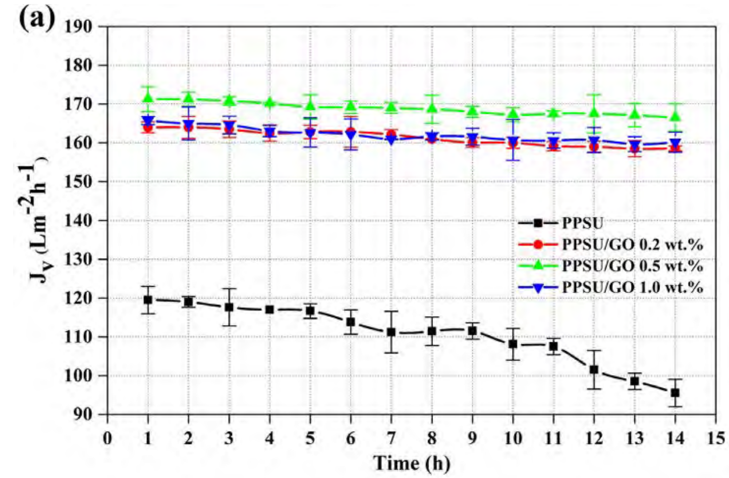


Increasing GO amount

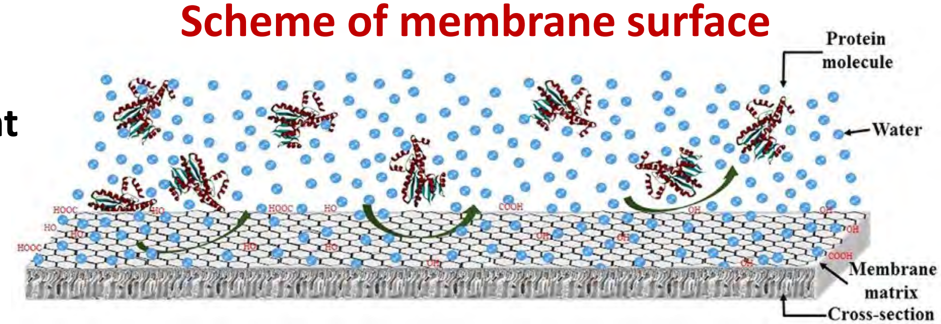
Enhancement of tortousity

Pore straightening

Filtration of the solution od bowine serum albumin



Scheme of membrane surface

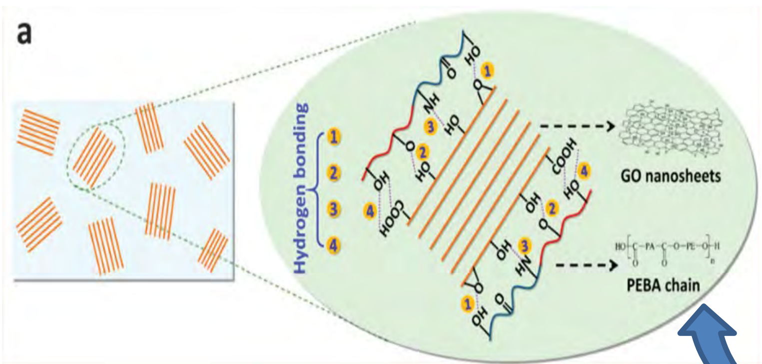


Rejection of BSA and pepsine

GO amount. %	BSA	Pepsine
-	97	93
0.2	95	91
0.5	94	88
1	95	90

GRAPHENE OXIDE ON THE OUTER SURFACE OF MEMBRANE

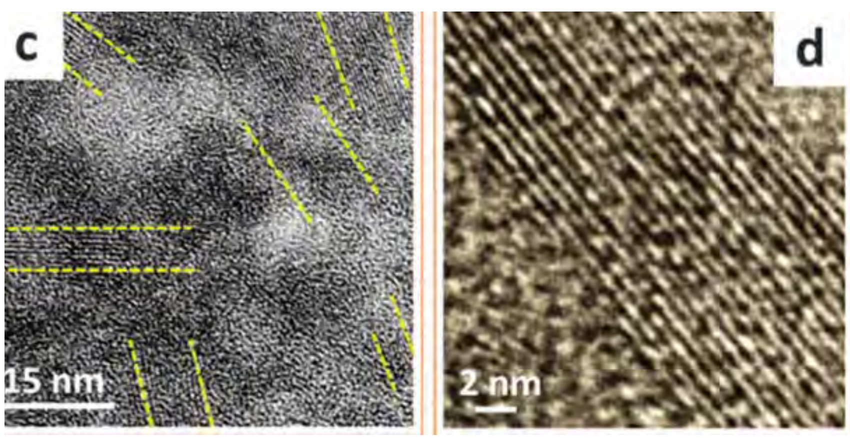
Main idea: **the thickness of graphene layer is one atom. It means, the monolayer can be applied to the substrate forming ultrathin active layer. This monolayer would provide low operation pressure of reverse osmosis.**



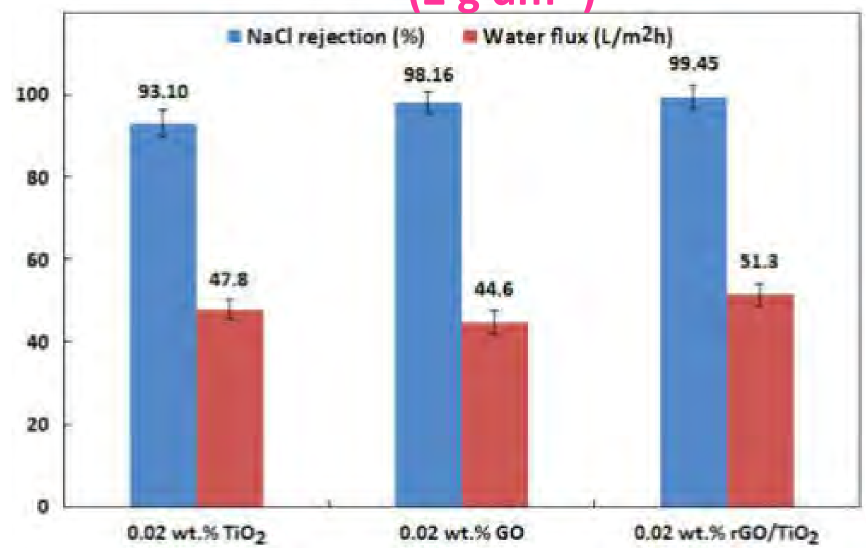
Problems:

1. Multilevel graphene can be obtained during chemical synthesis;
2. Aggregation of graphene flakes;
3. Polymer must be used for the graphene fixing on the support.

Graphene layer on the membrane surface

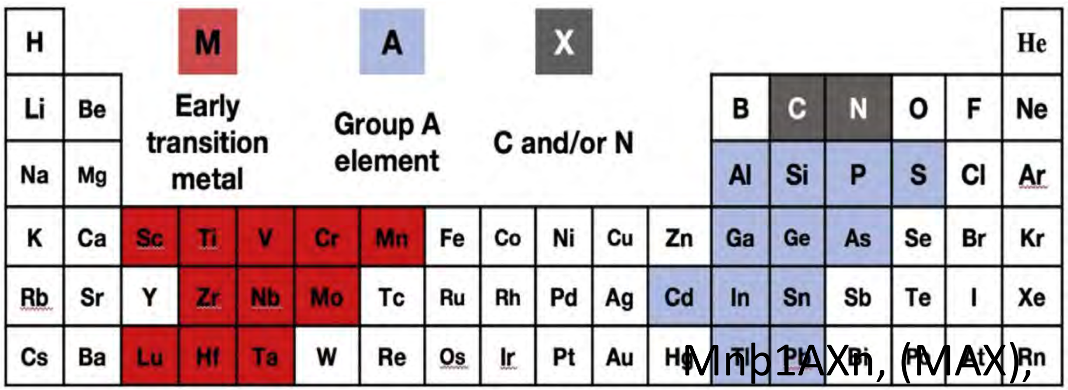


Desalination of NaCl solution ($2\ g\ dm^{-3}$)



MXenes - 2D Inorganic Modifiers for Filtration Membranes

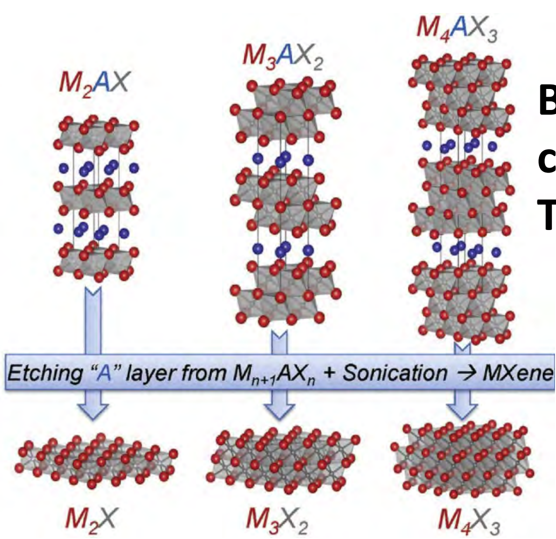
MXenes are originated from 3d MAXene compounds of $M_{n+1}AX_n$, for instance Ti_3SiC_2, V_2AlC, Ti_2SnC.



Yurii Gogotsi
A.J.Drexel Nanomaterials Institute

3d MAXens —etching→ 2d MXens

Usually HF is used for etching.



Besides M and X elements, MXenes contain surface functional groups, T. They are usually –F, =O or –OH.

In fact, the MXene formula is

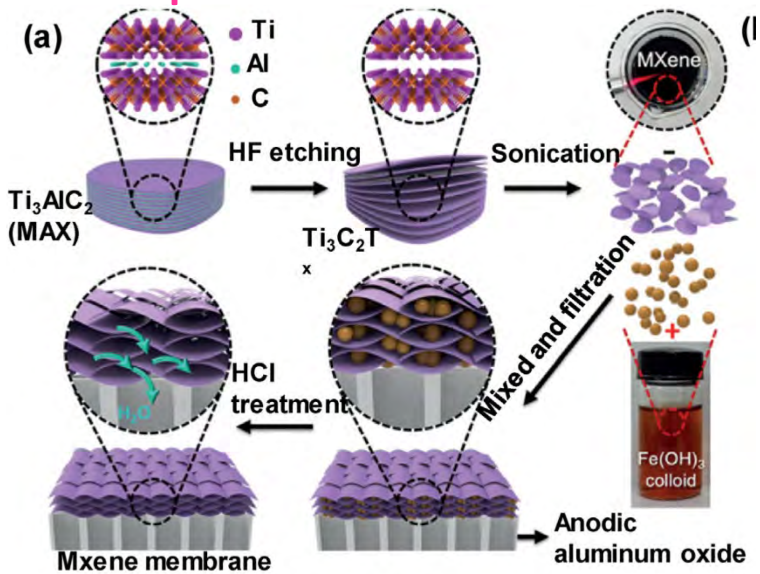
$$M_{n+1}X_nT_x.$$

–OH groups provide hydrophilicity of MXenes. This, and also 2d structure give a possibility to use MXenes for modifying membranes.

MXenes - 2D Inorganic Modifier for Filtration Membranes

Main idea: the thickness of MXene layer is one atom. It means, the monolayer can be applied to the substrate forming ultrathin active layer. This monolayer would provide low operation pressure of reverse osmosis.

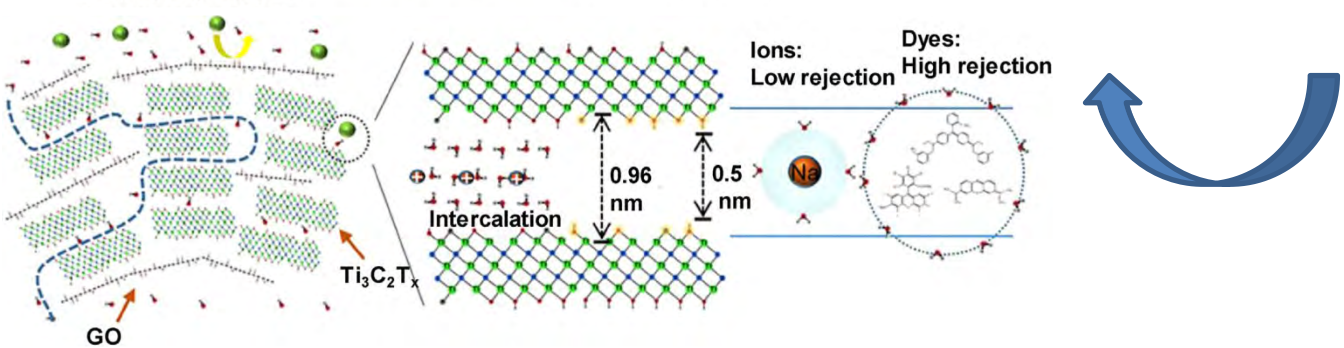
Membrane formation by Mxene deposition on the substrate



Problem:

1. Aggregation of MXene flakes;
2. Fixing of MXene on the support.

The most suitable way is the insertion of Mxene flakes into the bulk of polymer. In this case, Mxene has no advantages over other modifiers.



Combination of Mxenes with graphene oxide

MEMBRANES MODIFIED WITH SILVER NANOPARTICLES

Deposition of Ag nanoparticles inside membranes

I Citrate method (under heating)

$$Na_3C_6H_5O_7 + AgNO_3 + H_2O = Ag + CH_2O + CO_2 + NaNO_3$$

II Tetrafluoroborate method (under cooling)

$$2AgNO_3 + 2\mathbf{NaBH_4} \rightarrow 2Ag + H_2 + B_2H_6 + 2NaNO_3$$

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

II Aldehyde method (can be realized under ambient conditions or under slight heating)

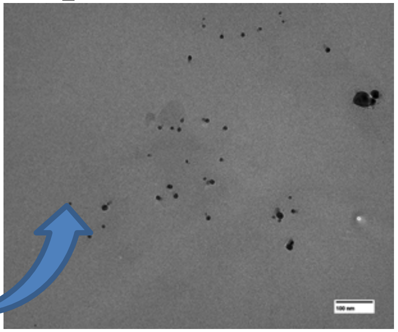
$$2[Ag(NH_3)_2]OH + R\text{-}CHO \rightarrow R\text{-}(COONH_4) + 2Ag\downarrow + 3NH_3 + H_2O$$

$$Na_3C_6H_5O_7 + AgNO_3 + H_2O = Ag + CH_2O + CO_2 + NaNO_3$$

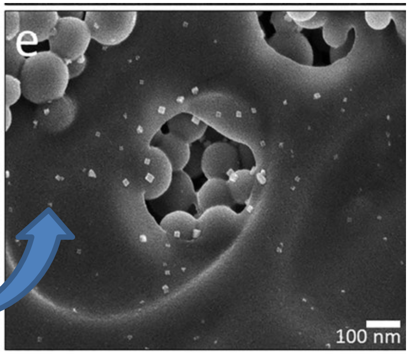
Reducing agents for obtaining Ag nanoparticles

Reducing reagent	Temperature, °C	Rate
Alcohols, flavonoids	>70	Slow
Aldehydes, sugars	<50	Moderate
Citrate	>70	Moderate
Hydrasine, H_2SO_3, H_3PO_2	Ambient	Fast
$NaBH_4$, boranes	Ambient	Very fast

Silver nanoparticles



Silver nanoparticles in membrane



MEMBRANES MODIFIED WITH SILVER NANOPARTICLES

Membrane performance. Disinfection

Membrane	Target Microbes	Disinfection Efficiency
Ceramic	*E coli*	100 %
Cellulose paper	*E coli*	100 %
Blotting paper	*E coli, Enterococcus fecalis*	99.9-99.9999
Cellulose membrane	*E coli, Staphylococcus aureus*	100 %
Woven fabric membrane	*E coli*	99,9 %
Bacterial cellulose	E coli,	99.7-99.9 %
Polysulfone membrane	*Bacteriophage*	99.999%

Membrane performance. Degradation of separation and disinfection functions

Membrane material	Period	Performance
Polysulfone	120 days	93% biocidal activity after 4 month, 14% Ag loss in 2 weeks
Woven fabric membrane	90 days	Minimal Ag leakage 2-18 $\mu g\ l^{-1}$
Ceramic membrane	365 days	100% E. coli reduction, Qag leaching <20$\mu g\ l^{-1}$
POlyamide	28 days	Reduction of E. coli in 100 times, Stafilicoccus aureus in 1000 times

ANTIMICROBIAL ACTIVITY OF SILVER NANOPARTICLES, GRAPHENE OXIDE AND MXENES . MECHANISM

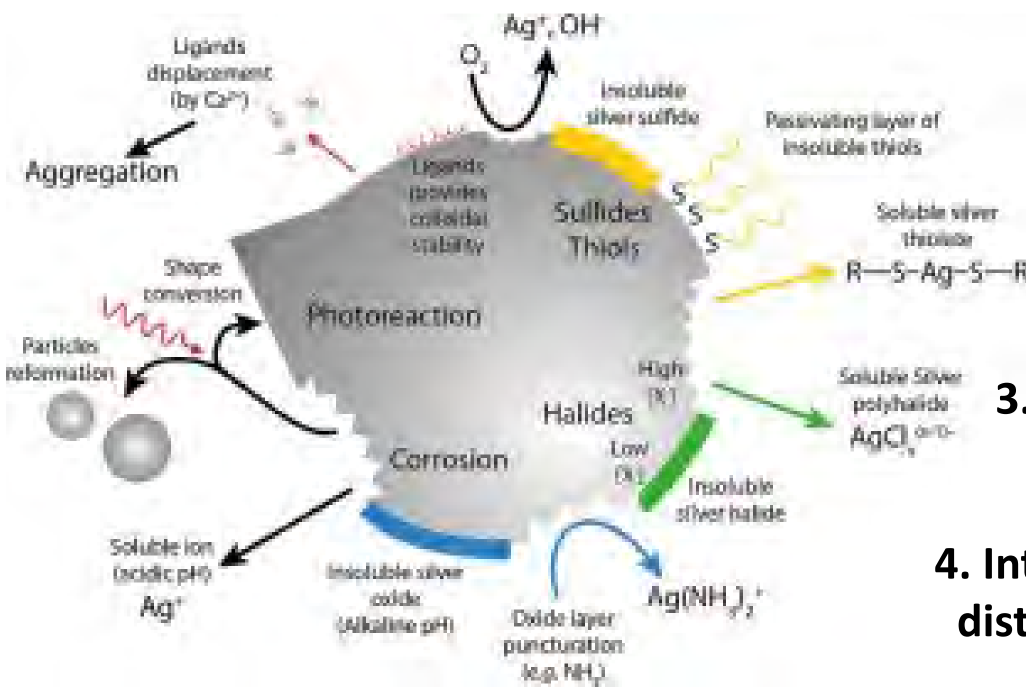
Ag nanoparticles

$$O_2 + H^+ \xrightarrow[slow]{Ag^0} Ag^+ + \text{peroxide intermediates} \xrightarrow[fast]{Ag^0} Ag^+ + H_2O$$

$$H_2O_2 \rightarrow O\bullet + H_2O$$

Two active agents are formed: Ag^+ ions and oxygen radicals.

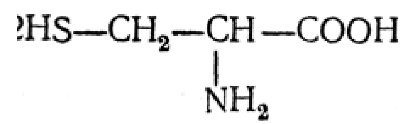
Action of Ag^+ ions and oxygen radicals.



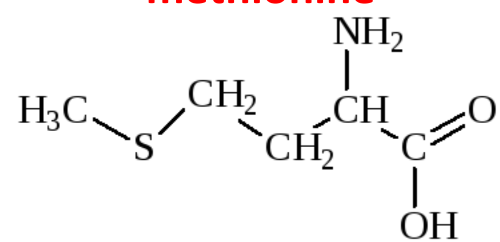
1. **Oxidation of the cell constituents with O• radicals.**

1. Bonding of Ag ions with –SH groups of aminoacids

cysteine



methionine

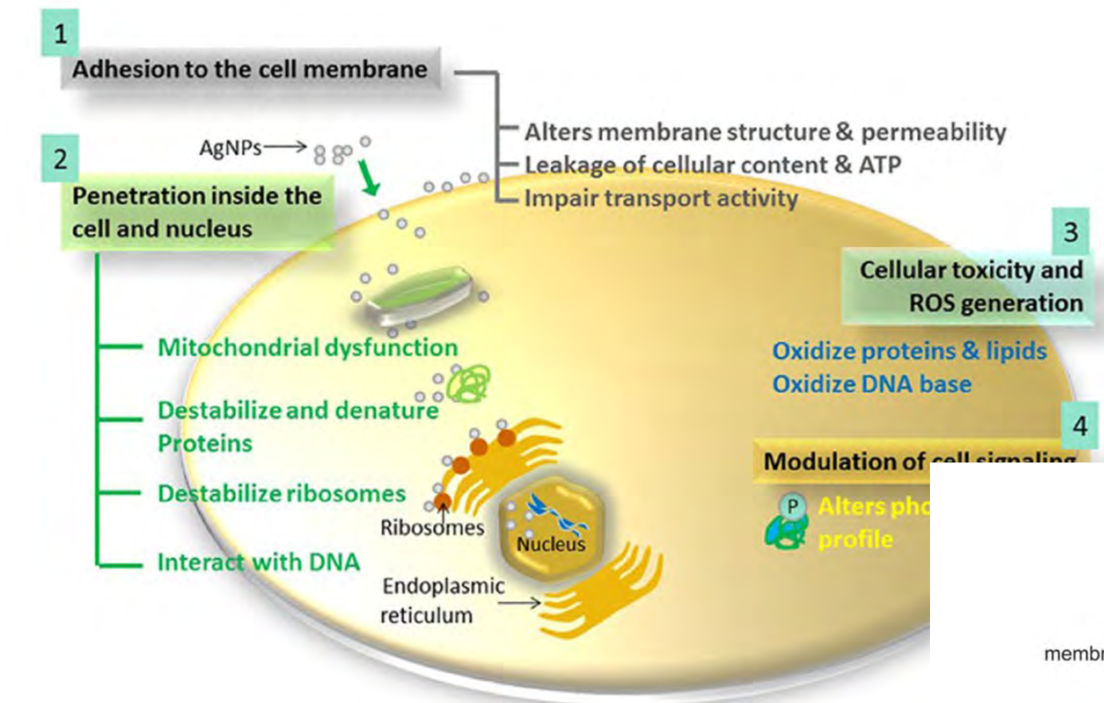


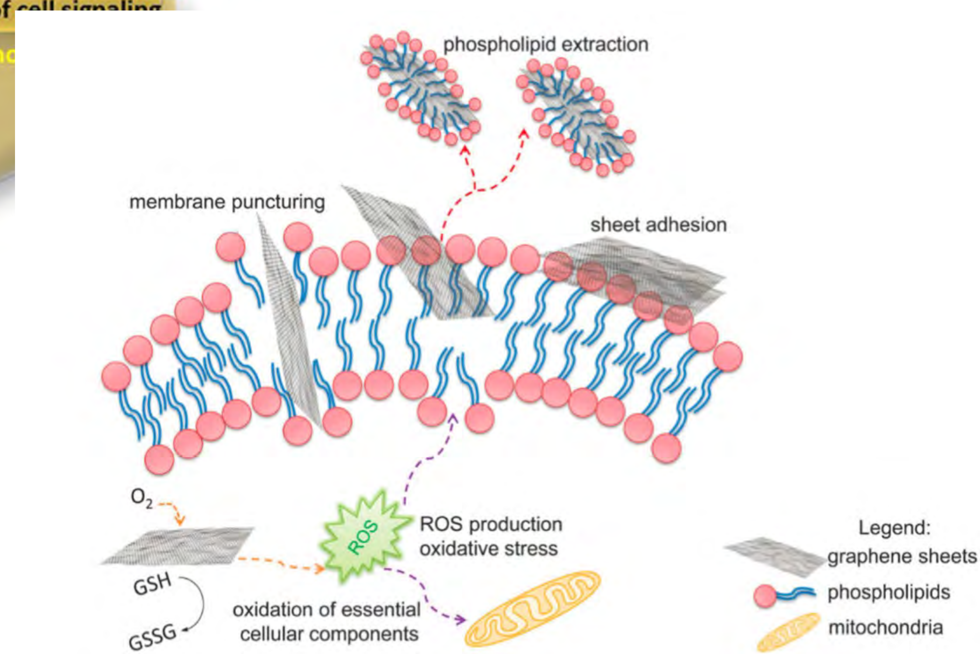
3. Bonding of Ag ions with aminogroups of aminoacids

4. Interaction of Ag^+ with Cl- anions, which disturbs water salt balance inside a cell.

5. Contribution of ions adsorbed on the nanoparticles during synthesis procedure.

DEGRADATION OF BACTERIUM CELLS AFFECTED BY SILVER NANOPARTICLES





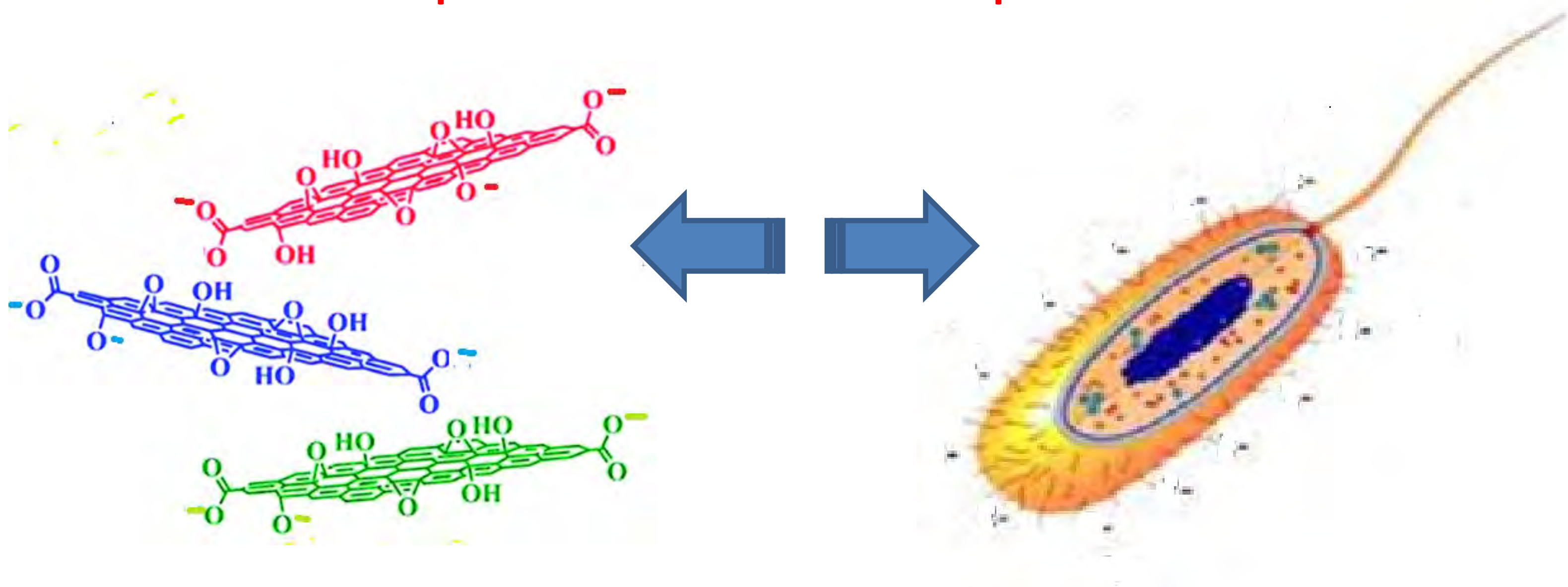
ANTIMICROBIAL ACTIVITY OF SILVER NANOPARTICLES, GRAPHENE OXIDE AND MXENES.

The antimicrobial activity of GO and Mxenes is mediated by physical and chemical interactions when sheets come in direct contact with bacterial cells. The cell membrane damage may be caused by the atomically sharp edges of graphene, which could penetrate the cell membrane and physically disrupt its integrity.

ly is possible omly in the case of ubcharfed steface, i.e. in acidic media .

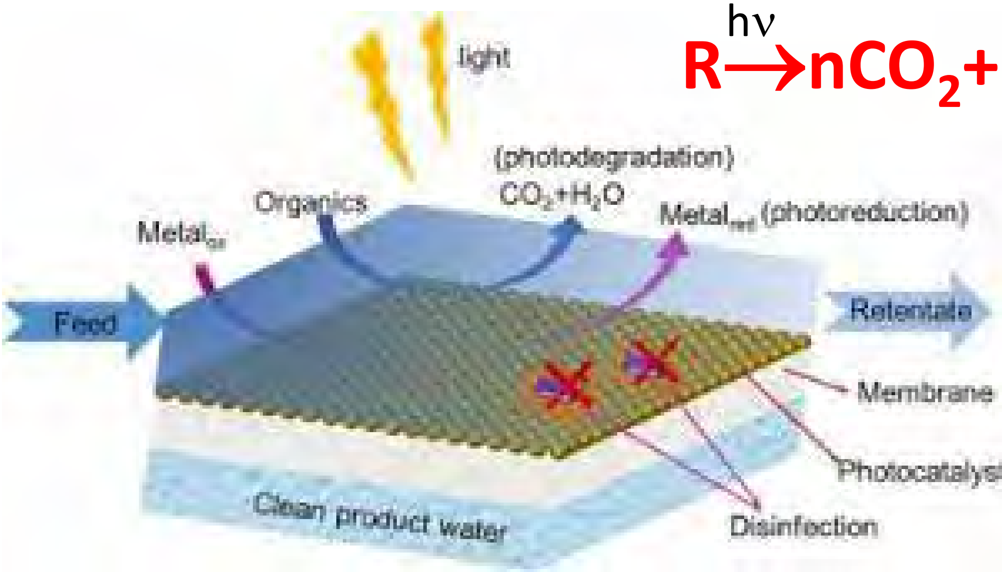
When GO or Mxene flakes are incorporated to the membrane, their negative charge provides repulsion of bacteria, the surface of which is charged negatively.

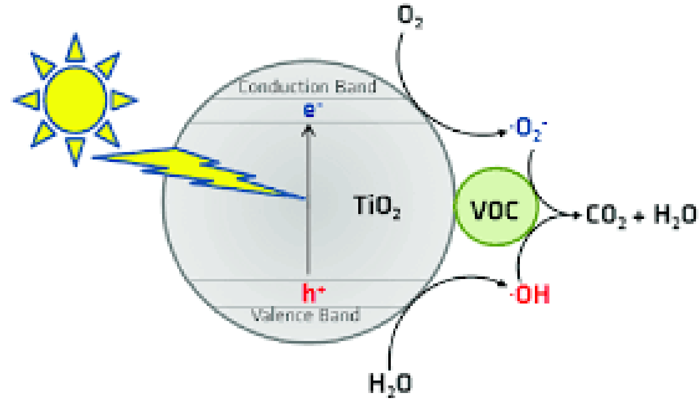
Repulsion of bacteria from GO particles



MEMBRANES MODIFIED WITH NANOPARTICLES WITH PHOTOCATALYTIC ACTIVITY

$$R \xrightarrow{h\nu} nCO_2 + mH_2O$$

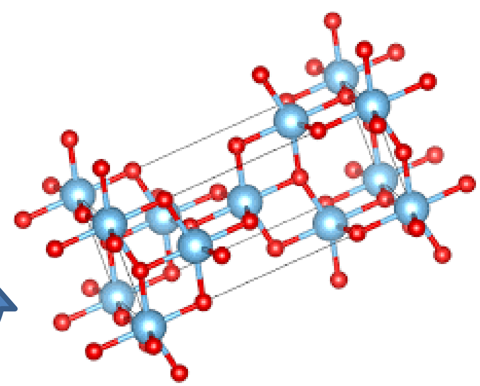




Materials possessing photocatalytic activity for membrane modifying

Graphene oxide,
Carbon nanodots.
Carbon nanoribes

Titanium dioxide (anatase)



Disadvantages of photocatalytic membranes

Photocatalysts works mainly under UV radiation,

Membrane module must be transparent to UV radiation,

Solution must ne transparent,

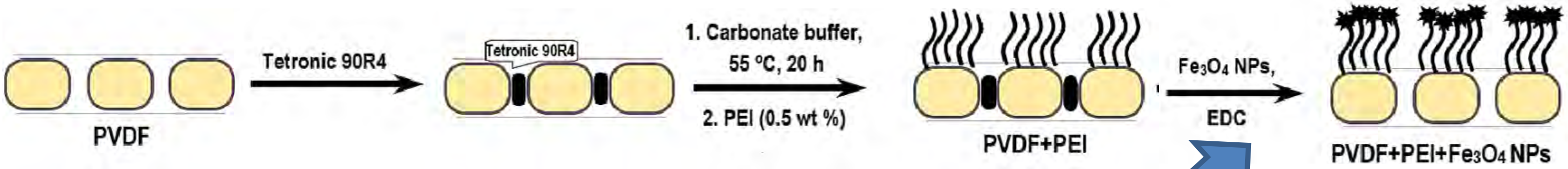
Incomplete oxidation,

TiO_2 degradation during membrane regeneration.

MEMBRANES MODIFIED WITH MAGNETIC NANOPARTICLES

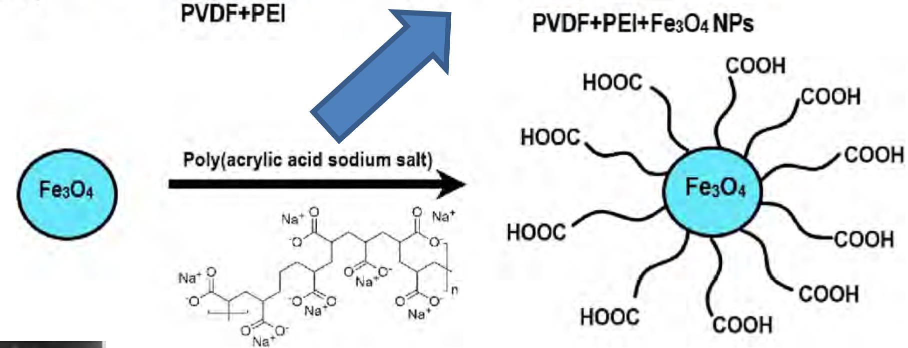
Stages of modifying

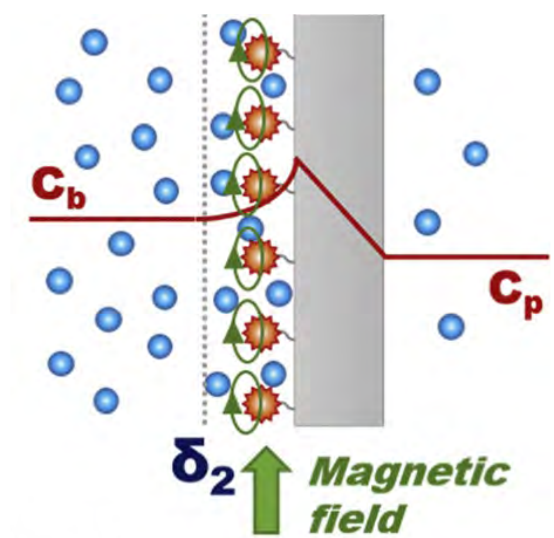
1. Grafting linear polymer spacers to the membrane surface,
2. Modifying of spacers with magnetic nanoparticles.

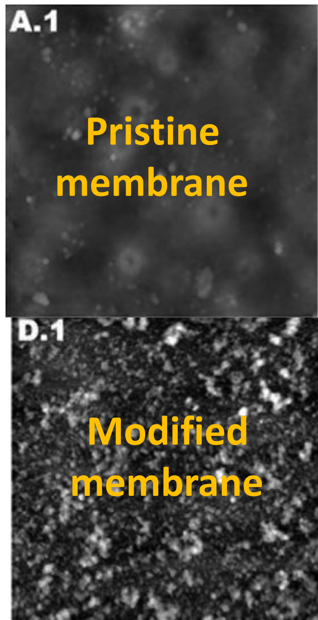


Operation principles

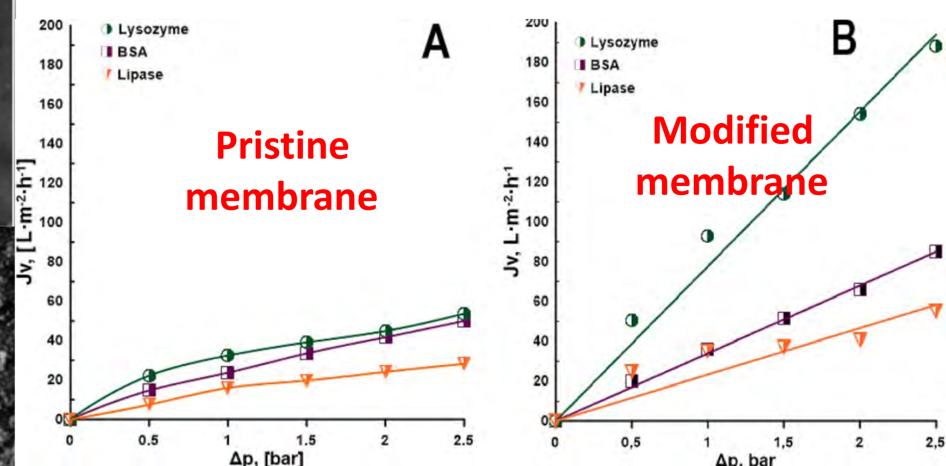
Movement of spacers in magnetic field→ Degradation of hydrodynamically immobile layer at the membrane surface
→minimization of concentration polarization
→ minimization of deposition.





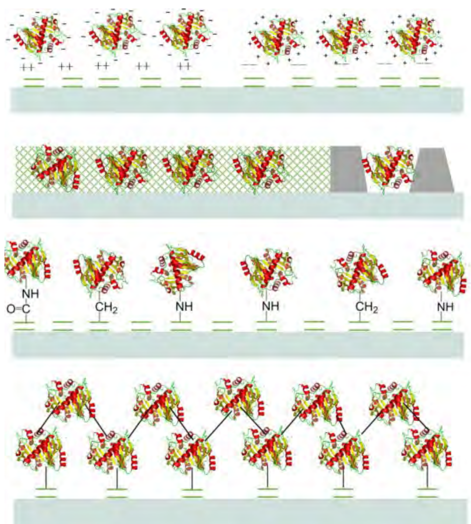


Permeate flux over filtration of protein solutions



MEMBRANES MODIFIED WITH ENZYMES

Immobilization methods



Adsorption
(cake formation)

Entrapment
(pore blockage)

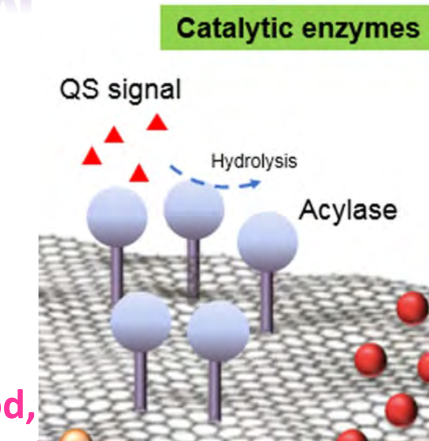
Covalent link

Cross-linking

Fouling-like immobilization

UV-induced method, the γ-irradiation method and the plasma method.

Cross-linking agents



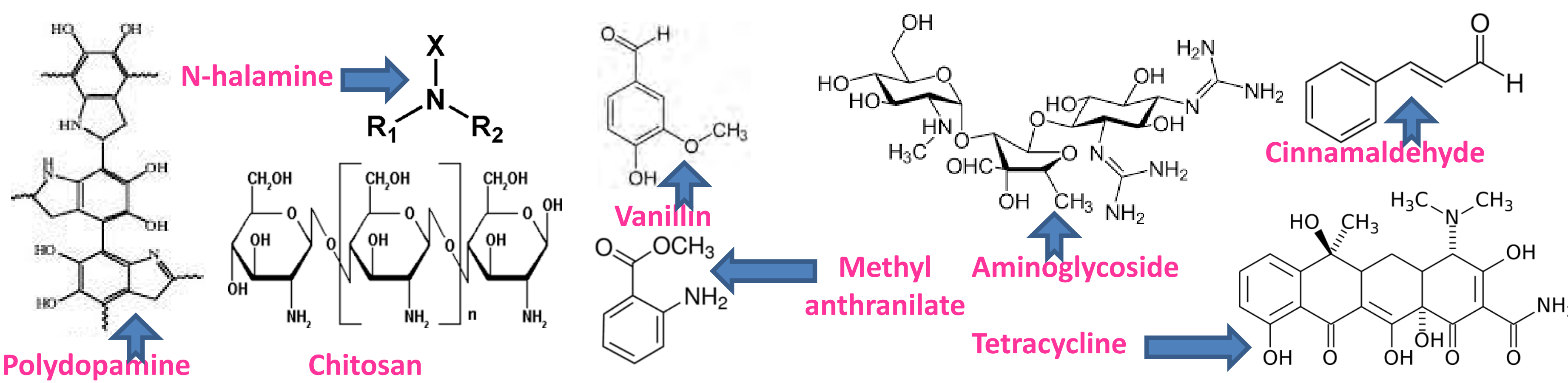
Membrane performance

Enzyme	Membrane	Immobilization	Treated liquid	Reaction duration	Activity after interaction
lipase	polypropylene	adsorption	olive oil	15 days	50%
lipase	polypropylene	covalent link	tributirin	10 runs	80%
lipase	polysulfone	adsorption	triolein	12 days	-
lipase	alginate	entrapment	lactic acid	6 runs	90%
cellulase	Fluorinated ethylene propylene	cross-linking	proteins	3 days	97%

MEMBRANES MODIFIED WITH BIOCIDAL COMPOUNDS

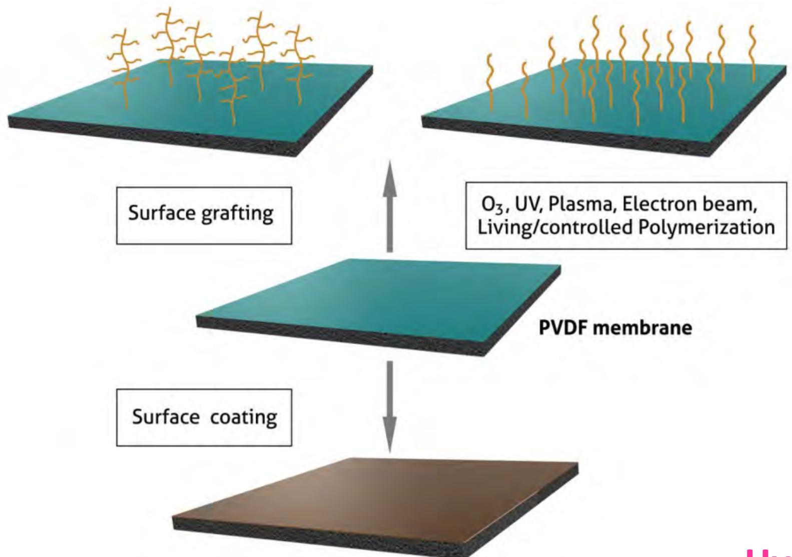
Biocidal compounds

Anti-biofouling materials	Examples	antimicrobial behaviour
Biomimetic material	Polydopamine, chitosan	• Anti-adhesion
Antibiotic	Aminoglycoside, tetracycline	• Disrupt cell outer membranes • Inhibit protein synthesis
Biocidal polymer	N-halamine, Polymer containing quaternary ammonium, guanidinylated polymers	• Transfer of biocidal element to the bacterial cell • Dissociate to free halogen in aqueous media
Quorum sensing inhibitor	Vanillin, cinnamaldehyde, methyl anthranilate	• interfere quorum sensing pathways • signal production blockage



MEMBRANES MODIFIED WITH HYDROPHILIC POLYMERS

The route of surface modification, including surface coating and surface grafting



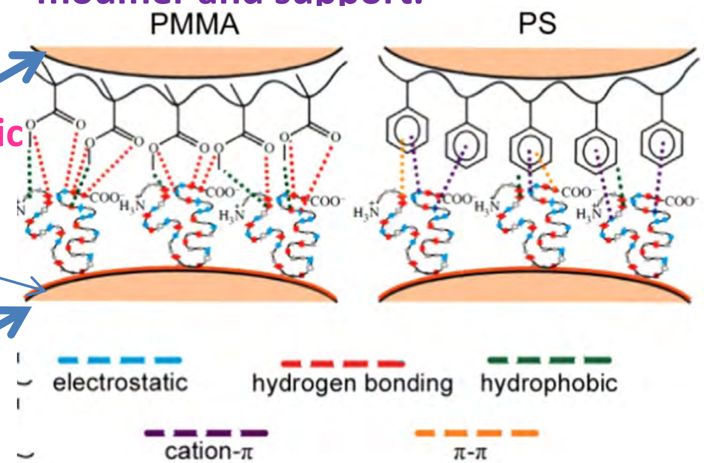
Surface coating. Mechanism

1. Adhesion/adsorption

The polymer modifier is fixed on the support due to the interaction between the functional groups and hydrophobic regions of the modifier and support.

Hydrophobic support

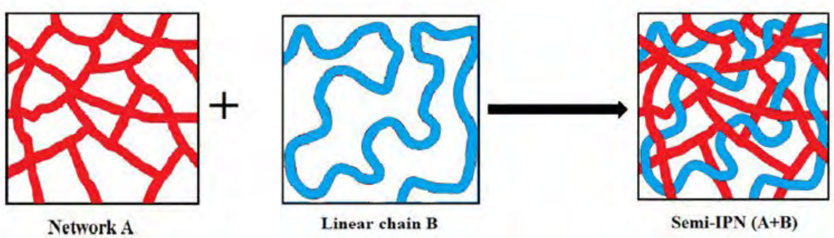
Hydrophilic modifier



2. Interpenetration of the polymers of hydrophobic support and hydrophilic modifier at their interface.

Interpenetraring network consists of two networks which are at least partially interlaced on a polymer scale but not covalently bonded to each other. The network cannot be separated unless chemical bonds are broken.

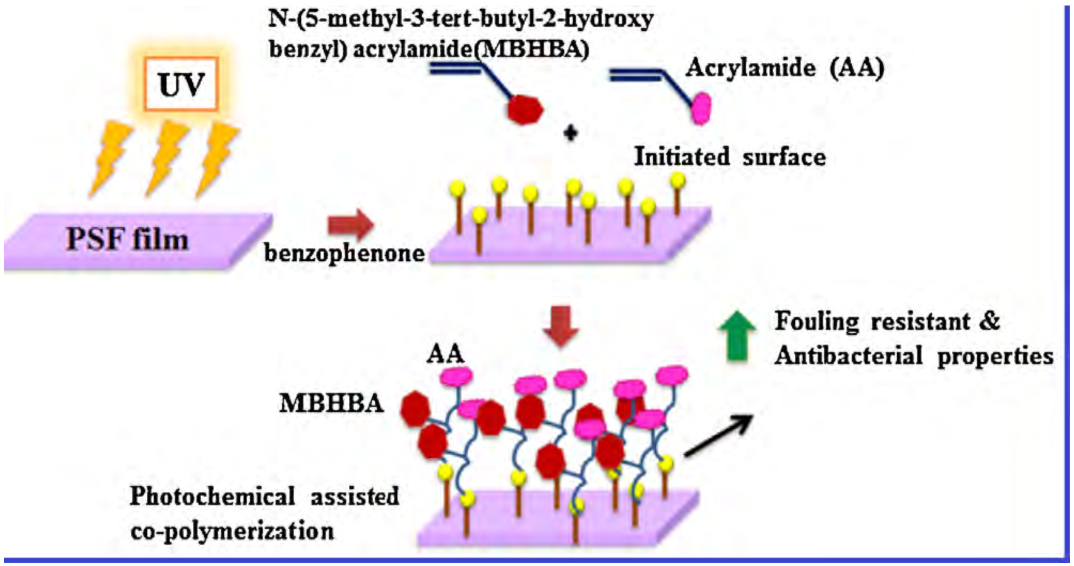
Hydrophobic support | Hydrophilic modifier | Support-modifier interface



MEMBRANES MODIFIED WITH HYDROPHILIC POLYMERS

3. Grafting technique

Initiators of grafting: O_3 UV radiation, electronic beams, plasma.



Advantage of grafting:

Strong fixing surface later.

Disadvantages of grafting

Deterioration of the mechanical durability of membranes,

Pore blocking

Blending technique

2. Mixing hydrophobic and hydrophilic polymers before the membrane preparation.

CONCLUSIONS

The papers devoted to modified membranes consider mainly synthesis procedure, composition, structure and physico-chemical properties of membranes. Filtration of calibrants or, at least, model substances is also studied.

However, real separation processes involving membranes with antifouling processes are not considered. Regeneration of the membrane systems, membrane stability against regenerating solutions are also outside the focus of attention.

Combining the development of antifouling membranes and REAL SEPARATION PROCESSES followed by membrane regeneration and concentrate treatment /utilization are the prospective direction of investigations.