MEMBRANE PROCESSES IN PREPARATION OF PURIFIED WATER FROM MUNICIPAL WATER[#]

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[#] This paper is dedicated to Professor Roman Modic at his 90th birthday

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Abstract

Ultrafiltration, nanofiltration and reverse osmosis in series were tested in pilot plants as the proper treatment for water to be used in pharmaceutical industry, the feed being the municipal water. Ultrafiltration ensured the removal of colloid particles (lower SDI value), nanofiltration the removal of water hardness and reverse osmosis the deionization of water. The experimental data obtained from the pilot plant tests could be used as the basis for the design and performance of the industrial plant.

Introduction

Membrane processes have a large range of application and their use has grown rapidly in the last 50 years. They play a key role in many industrial and high-purity water treatment systems – both for pretreatment and as an integral part of the deionization systems.[1] Membrane is a permeable or semipermeable phase made from polymer or anorganic material or metal, that divides the feed stream into permeate stream (with lower concentration) and retentate or concentrate stream (with higher concentration).

There are several different membrane processes for different purposes, the three widely used are ultrafiltration, nanofiltration and reverse osmosis. All three processes are pressure-driven.

Ultrafiltration (UF) removes contaminants with molecular weight cutoff (MWCO) of 20000dalton–100000dalton. It can be useful to remove silica, tannins, lignins, viruses and endotoxines from water. In water systems, UF may be found within the pretreatment prior to reverse osmosis or ion exchange, or even as a final water polishing filter before use.[1] It uses the pressure difference between 2bar and 10bar.[2]

Nanofiltration (NF) is sometimes compared to reverse osmosis. Nanofiltration elements will remove contaminants of MWCO 200dalton–20000dalton, examples would include endotoxins and pyrogens, viruses, colloidal silica, sugar, pesticides and herbicides. Typical applications for NF are water softening as well as food, beverage and potable water treatment.[1]

In reverse osmosis (RO), a semipermeable membrane is challenged with a pressurized feed containing a solute. The pressure exerted is greater than the osmotic pressure of the feed, causing solvent to flow through the membrane.[3] In the RO unit, the pressure difference is bigger than in UF and NF and it can be up to 100bar.[2] Reverse osmosis removes contaminants with MWCO under 200. Examples include salts, metal ions, sugar, pesticides and herbicides. Uses for RO include boiler feedwater, potable water, pharmaceutical water. It is one of the primary methods of water deionization with the other two being ion exchange and electrodeionization.[1]

There is no sharp distinction between these three processes, this is shown in Figure 1, where the size of the separation and further examples of their use are also presented.

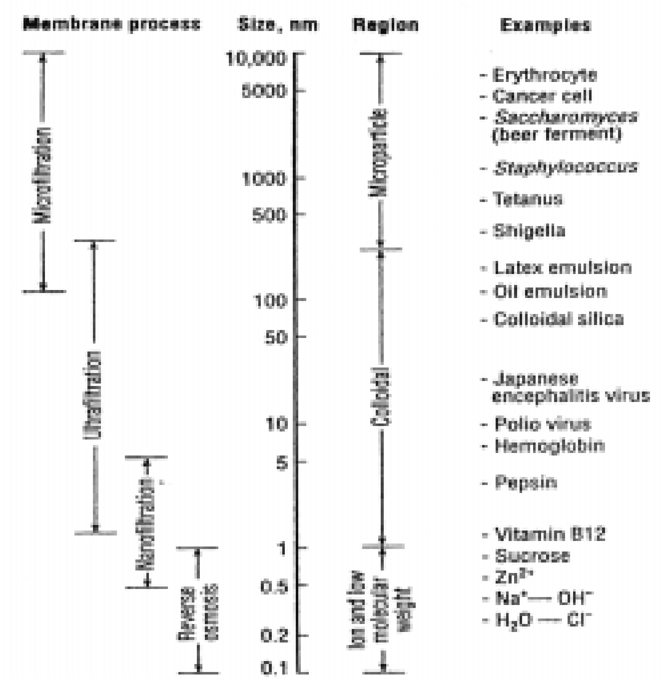

Figure 1: Pressure based membrane processes[4]

The common problem that occurs in membrane processes is membrane fouling, which may be defined as irreversible deposition of retained particles, colloids, macromolecules, etc., at the membrane surface or inside the membrane at the pore wall, which causes a continuous flux decline. Fouling occurs mainly in microfiltration and ultrafiltration where porous membranes are used.[3] Some authors reserve the term fouling for deposits of biofilms (organisms), metallic oxides, silica and various colloids. Scaling is seen in this definition as a deposition of materials that have their genesis in the RO process.[5] The most common scale formers are calcium salts, particularly $CaCO_3$ and $CaSO_4$. One of the possible prevention methods is water softening, that can be achieved with nanofiltration.

Municipal water often contains colloid particles that cause fouling on the reverse osmosis membranes when led to them directly. The permeate of the RO unit can be used in several ways in the pharmaceutical or other industries.

This work includes studies on the described three membrane processes, the experimental work was done in pilot plants. Thus the use of ultrafiltration (for the removal of the colloid particles) followed by nanofiltration (for removal of water hardness, which causes scaling on the reverse osmosis membranes) were tested as the proper pretreatment for the reverse osmosis unit. Such pretreatment can significanlty prolong the service life of the RO unit. Some experiments on the reverse osmosis unit were also made.

Experimental section

A pilot plant with a single tubular module with 5 membranes for ultrafiltration with the molecular weight cutoff 100000dalton was used. The content of the colloid particles was monitored by the SDI (silt density index) test.

The nanofiltration was carried out with a spiral wound module with molecular weight cutoff 150dalton–300dalton, using the permeate from the ultrafiltration experiments as the feed. For the reverse osmosis experiments a spiral wound module with a composite membrane was also used. For all three processes the recycle flow enabled higher fluxes and recovery (percentage of the feedwater that becomes product water) and the removal of material form the membrane surface which would otherwise cause fouling (cleaning of the membrane).

The pilot plants for NF and RO were similar to the one used for ultrafiltration (Fig. 2);

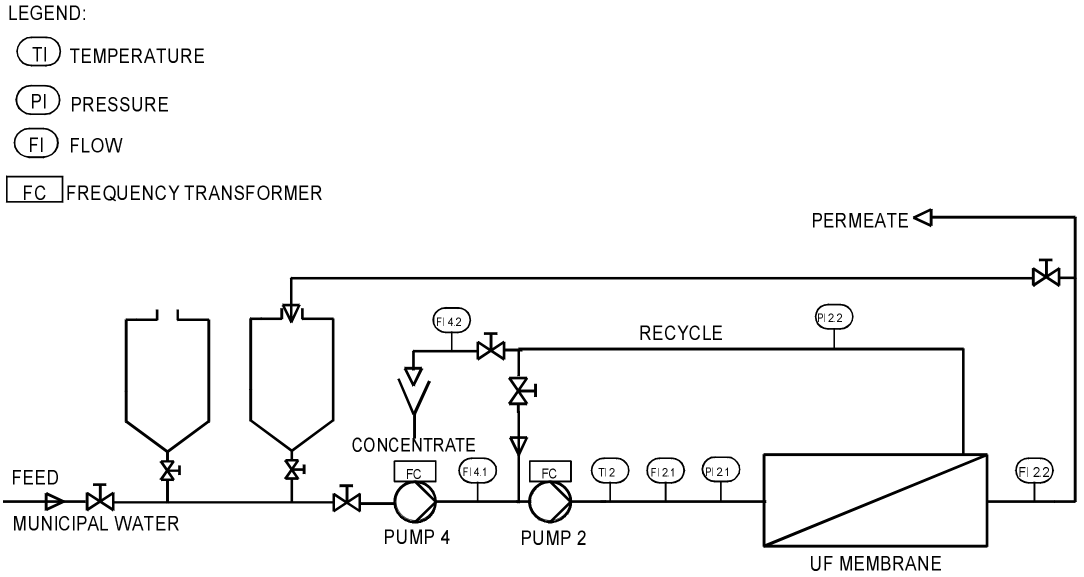

Figure 2: Ultrafiltration pilot plant

The experiments included:

- measurements of SDI and total hardness of municipal water
- dependence of permeate flux on transmembrane pressure (UF, NF, RO)
- dependence of permeate flux on axial velocity (UF)
- monitoring the permeate flux and SDI value as function of time (UF)
- dependence of total hardness on transmembrane pressure (NF)
- dependence of rejection on pressure (RO)

Results and discussion

Testing of municipal water:

- SDI value:

  The SDI value was measured during a four-month period and we noticed that its value did not change much. The average value was SDI_{water}=5.8, which is much higher than the required value ($SDI_{feed}<4$) for the most of the RO membranes, thus the pretreatment is obligatory.

- total hardness:

  Its value was monitored during a two-month period and it did not change much as well. The average value was 15.19°N, which indicates that the hardness should be removed before entering the RO plant.

Ultrafiltration

Dependence of permeate flux on the transmembrane pressure

The measurements show that the increase of transmembrane pressure increased the permeate flux up to some level, where the flux became almost constant. After the first experiment the membrane was cleaned using permeate as the feed, and the experiment was repeated at the same operating conditions. The rinsing enabled higher permeate fluxes. Such periodical cleaning should also be used in industrial plants.

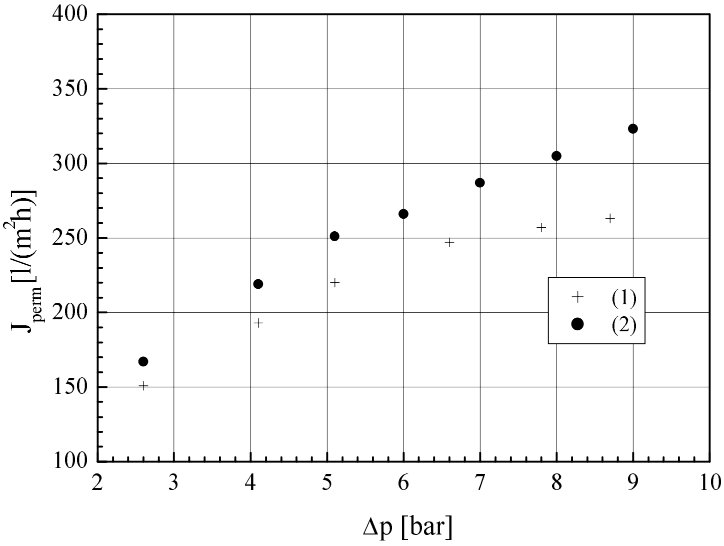

Figure 3: Dependence of permeate flux on transmembrane pressure

Dependence of permeate flux on axial velocity

The experiments were carried out at the constant transmembrane pressure Δp=5.3bar. The higher axial velocity gave higher permeate fluxes, because of the better rinsing of the membrane.

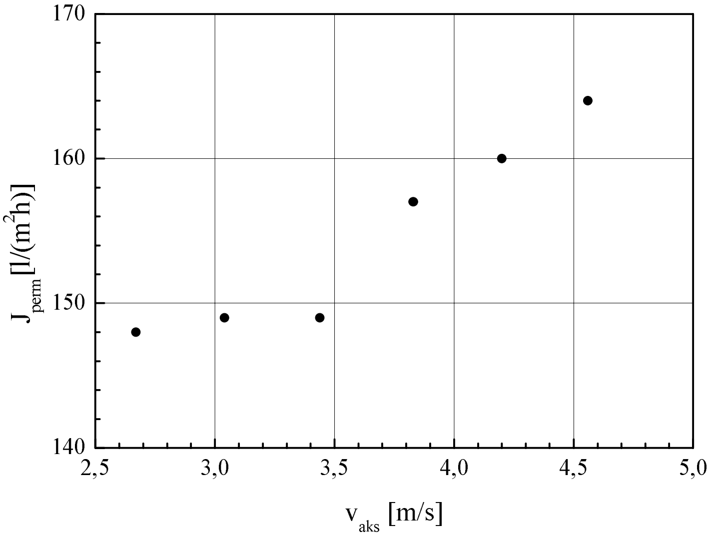

Figure 4: Increase of permeate flux with axial velocity

Permeate flux and SDI value change with time

The permeate flux did not decrease significantly with time. The SDI value did decrease with time, both changes could be attributed to the deposition of the material on the membrane surface (fouling). It worked as an additional resistance causing the SDI value and permeate flux decrease. The recycle and concentrate flow were constant during this measurement, and the pressure difference was also constant Δp=3.5bar.

The SDI value of the permeate was monitored also during several other experiments, in most cases its value was below SDI_{perm}=2 and always below the desired value SDI_{perm}=4.

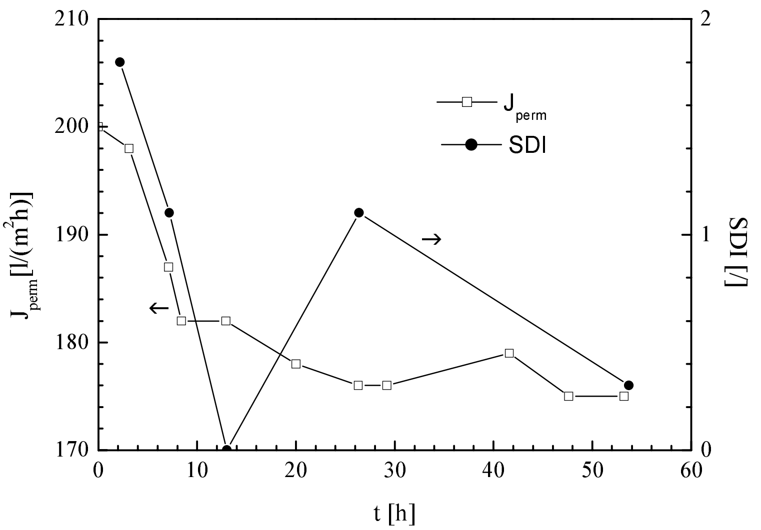

Figure 5: Decrease of permeate flux and SDI_{perm} value with time

Nanofiltration

Water hardness removal

The NF membrane had the molecular weight cut-off 150dalton–300dalton, which should partly remove water hardness in order to prevent scaling on the RO membranes. The permeate from the ultrafiltration was used as the feed for the nanofiltration, its total hardness was 8.2°N.

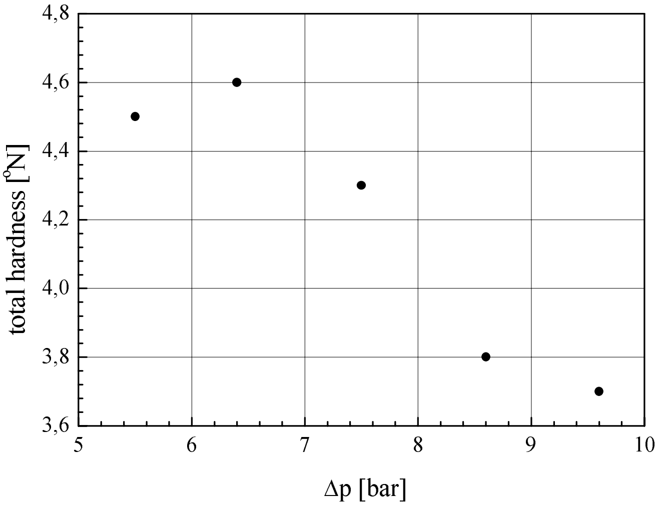

Figure 6: Water hardness removal

As seen from Fig. 6, the hardness removal decreased with increasing transmembrane pressure. It was, however, between 40% and 50%.

Dependence of permeate flux in transmembrane pressure

The permeate flux did increase with transmembrane pressure as noticed also with the UF experiments (Fig. 3). The NF membranes enabled higher transmembrane pressures, thus the level of constant flux was in this experiment not reached.

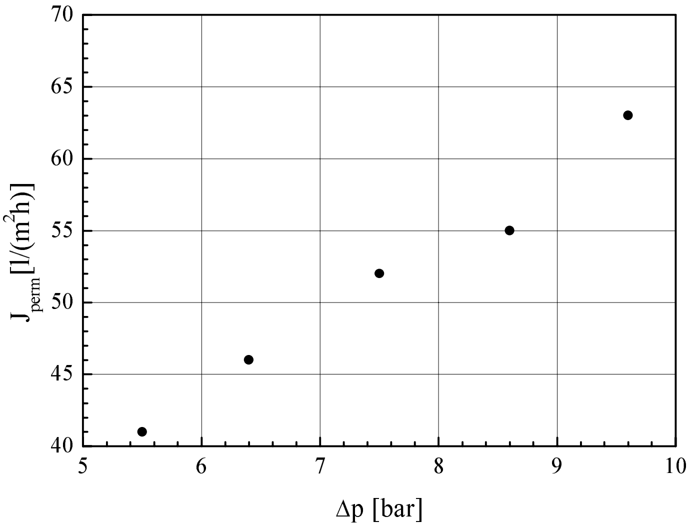

Figure 7: Increase of permeate flux with transmembrane pressure

Reverse osmosis

A spiral wound module was used. Besides the feed, recycle and concentrate flow, the conductivity of the permeate was also measured. It gave the data for the calculation of the rejection. The feed conductivity was 516μS/cm and the permeate conductivity was below 15μS/cm. We were unable to use nanofiltration permeate as the feed for the RO, thus an ion exchange unit had to ensure that the water hardness was below the desired value.

Dependence of permeate flow on transmembrane pressure

During the same experiment the rejection and permeate flow were measured, they increase with higher pressure. However the increase in rejection is only slight.

The concentrate and the recycle flow were kept constant during this experiment.

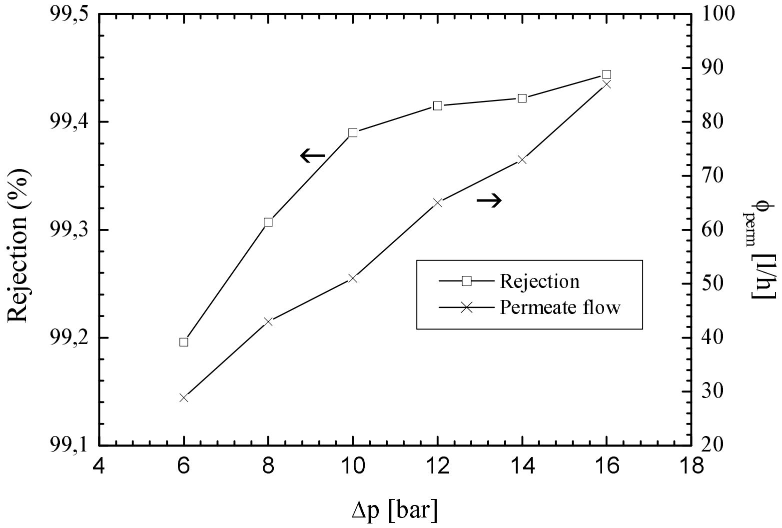

Figure 8: Increase of permeate flow and rejection with transmembrane pressure

Calculation of permeability

The permeability of the UF and RO membranes was calculated from the experimental data and compared with the literature reported range.

The permeability can be calculated from the equation:[6]

$$J_{perm} = K(\Delta p - \Delta\pi),\ K = \frac{P}{l} \tag{1}$$

Ultrafiltration

Experimental data:	Membrane data:
$J_{perm} = 180 l/(m^2 h)$	$d_{pore}=1.5*10^{-8}m$
$\Delta p = 3.5 bar$	$n_{pore}=3.0*10^{13}m^{-2}$
	$l=0.2*10^{-6}m$
	$\eta=10^{-3}Pas$

The osmotic pressure can be neglected and the permeability is

$$K_{UF,exp} = \frac{J_{perm}}{\Delta p} = 51.4 l/(m^2 hbar)$$

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The (theoretical) permeability could also be calculated form the membrane data and the viscosity of water;

$$K_{UF,theor} = \frac{\pi n_{pore} d_{pore}^4}{128 \eta l} = 1.86 * 10^{-10} \frac{m}{Pas} = 67.1 l/(m^2 hbar)$$

$$K_{UF,theor} = 67.1 l/(m^2 hbar)$$

Theoretical permeability was higher than the experimental one since in the calculation of the theoretical permeability the tortuosity and plugging of pores, etc., were disregarded. Both values ($K_{UF,exp}$ and $K_{UF,theor}$) are within the range reported by the literature (K=2 l/(m^2hbar) – 1130 l/(m^2hbar)).[7]

Reverse osmosis

The osmotic pressure can again be neglected. The average experimental data were used and the calculation then yields

$$K_{RO,exp} = 1.94 l/(m^2 hbar)$$

This value is in agreement with the literature data.[8]

Conclusions

A number of experiments in the UF, NF and RO pilot plants were done. The results gave the basic evaluation of applicability of these three processes and they show that they are useful for the desired purposes; the UF decreases the concentration of the colloid particles (SDI value), NF removes water hardness and RO removes the remaining ion species from water. The results gave also the basic operating data (Table 1) that may be of use for the design and performance of the industrial plant.

Table 1: Average operating data

	ultrafiltration	nanofiltration	reverse osmosis
J_{perm} [l/(m^{2}h]	180	52	ϕ_{perm}=65l/h
Δp [bar]	3.5	7.5	12
perm. quality	SDI<1	total hardness=4.3	rejection>99.3

The recovery (permeate flow / feed flow) should be sufficiently large (above 80%) for all three processes since the waste flow of water represents significant economic costs. Thus the use of recycle is necessary. The advantage of its use is also the possibility of achieving sufficiently high axial velocities on the membrane surface (for UF in our case above 4m/s), which prevents membrane fouling and scaling in large extent.

As the final criteria whether the product water can be used in the pharmaceutical industry a series of further analysis (TOC, concentration of chlorides, nitrates, etc., microbiological tests, etc.) should be made.

Nomenclature

d_{pore}	pore diameter, m
J_{perm}	permeate flux, l/(m^{2}h)
K	permeability, l/(m^{2}hbar)
l	membrane thickness, m
n_{pore}	pore density, m^{-2}
P	permeability coefficient, l/(mhbar), m^2/(hbar)
Δp	transmembrane pressure, bar
SDI	silt density index
t	time, h
v_{aks}	axial velocity, m/s
$\Delta\pi$	osmotic pressure, bar
η	viscosity, Pas
ϕ_{perm}	permeate flow, l/h

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Povzetek

S pilotnimi poskusi smo preverili ustreznost procesov ultrafiltracije, nanofiltracije in reverzne osmoze, vezanih zaporedno, za pripravo vode v farmacevtski industriji. Kot napajalno vodo smo uporabili pitno vodo iz vodovodnega omrežja. Z ultrafiltracijo smo zmanjšali vsebnost koloidnih delcev, z nanofiltracijo zmanjšali trdoto vode in z reverzno osmozo zagotovili deionizacijo vode. Podatki, dobljeni s poskusi na pilotnih napravah, bi lahko služili kot osnova za načrtovanje in vodenje industrijske naprave.