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Application of membrane processes in drinking water treatment–state of art

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ABSTRACT

Membrane technology is widely accepted as a means of producing various qualities of water from surface water, well water, brackish water and seawater. In the treatment of water for drinking purposes first of all pressure-driven membrane techniques are used. The choice of the suitable membrane process depends on the size of the removed contaminants and admixtures from the water. Desalination of seawater and brackish groundwater is often the way to obtaining drinking water. Significant improvements in technology and design of reverse osmosis, the availability of alternative energy sources, the possibility of pretreatment and applied materials have caused the process to become environmentally-friendly source of fresh water in many regions of the world, particularly in those where their sources are limited. Nanofiltration and to some extent the reverse osmosis are the methods of water softening, as well as to remove disinfection by-products precursors and micropollutants. To remove inorganic micro-pollutants (nitrate, fluoride ions, boron, arsenic as well as chromium and heavy metals), nanofiltration, reverse osmosis, electrodialysis and Donnan dialysis, and ultrafiltration enhanced with polymers and surfactants as well as membrane bioreactors, have been successfully applied. Use microfiltration and ultrafiltration in the water purification processes, meet essentially the latest regulations, that dictate the need to more effectively remove turbidity and colloids (e.g., Fe and Mn) and micro-organisms in the treatment process based on conventional filtration. High pressure membrane processes (RO and NF) are an effective method for removal of soluble organic compounds (DOC) in the treatment of natural waters. Natural organic matter (NOM), anthropogenic organic pollutants and disinfection by-products, covering part of the NOM, and other micropollutants are typical examples of such compounds. To anthropogenic micropollutants found in waters count polycyclic aromatic hydrocarbons (PAHs) and surface-active substances as well as disinfection by-products and chemical oxidation used in the treatment of drinking water. In the processes volatile trihalomethanes (THM), and non-volatile compounds, mainly halogenacetic acids (HAA), are formed. In recent years special attention in natural waters is paid onto Pharmaceutical Active Compounds (PhACs) and Endocrine Disrupting Compounds (EDCs) which have biological activity. ECDs include a wide range of micropollutants, namely xenoestrogens, among which are the chlorinated pesticides, phthalates, alkylphenols, polychlorinated biphenyls, and the female sex hormone, synthetic pharmaceuticals (e.g., contraceptive components) and other chemicals and substances produced by man and put into the environment. Scarcity of water, environmental requirements and the simple logic of reusing water instead of discharging it are conditions, which call for increased use of membrane technology in a multitude of applications.

Keywords: Microorganisms removal; Removal of inorganic compounds; Water desalination and softening; Membrane processes; Removal of organic micropollutants; Natural waters

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1. Introduction

In the treatment of potable water and water for household needs, pressure-driven membrane techniques are principally applied. The choice of an appropriate membrane process depends on the scope of removed effluents and admixtures present in water [1]. They can be used for the removal of effluents as independent processes or combined with unit complementary processes, forming a treatment process line. The potentials involving the application of membrane techniques in the treatment of natural waters can be presented in the following way [1,2]:

- reverse osmosis (RO) retains monovalent ions and the majority of low-molecular organic compounds – principally desalination of waters and removal of inorganic and organic micropollutants,
- nanofiltration (NF) retains colloids, low-molecular organic compounds and bivalent ions – softening and removal of micropollutants from water,
- ultrafiltration (UF) – retention of suspended substances and microorganisms – clarification and disinfection,
- microfiltration (MF) – method for the removal of turbidity,
- hybrid processes covering membrane techniques, especially UF and MF, with coagulation, adsorption onto activated carbon and in bioreactors – treatment of drinking water.

2. Pressure-driven membrane processes in inorganic compounds removal

2.1. Desalination

Desalination of water is one of the way of obtaining drinking water from seawater (35,000 mg/l) and brackish waters, which are most often taken from underground sources (2000–5000 mg/l). Most significant in view of drinking water production are desalination processes based on thermal separation methods and membrane separation methods [1,2]. For membrane desalination, reverse osmosis and electrodialysis are principally applied [1]. The most frequently used thermal methods are the multi-stage flash process (MSF), multi-effect distillation (MED) process, and the vapor compression (VC) distillation process [1].

Brackish water desalination was the first successful application of reverse osmosis, and the first large-scale plants appeared already in the late 1960s [3]. In the 1980s RO became competitive with the classical distillation techniques. At present, over 90% of RO installations produce drinking water and domestic water as well as ultra-pure water for the needs of power industry, semiconductors etc. [4]. A typical installation for water desalination using RO method consists of water pretreatment system, membrane desalination RO system with a high-pressure pump, section of energy recovery from retentate and final finishing process to meet the requirements specified in the regulations on the quality of drinking water (Fig. 1) [1,3,5–8].

The purpose of the pretreatment of raw water is to prevent or limit membrane pollution, as fouling and scaling, and its extent depends principally on the quality of raw water and the type of the applied membrane module [1,4,5]. It can be very simple, comprising only filtration processes without any chemicals added if the desalination involves clean groundwaters, and in the case of surface waters, the treatment procedure is more complicated and can include filtration with coagulation and adsorption on activated carbon. Over the last 10 years UF and MF have turned out to be the most suitable methods, for pretreatment before desalination, removing suspended substances, some organic compounds and microbiological pollution [4,5]. In the membrane system for desalination, hollow-fiber or spiral-wound modules of cellulose acetate, aromatic polyamide and composite membranes are used [4]. What was important in the development of membrane methods applied for the desalination was the replacement of hollow fiber membranes widely applied in RO installations in the ‘70s and ‘80s by spiral-wound modules of a high efficiency [1,4,5]. The preparation of water after its desalination depends on its destination.

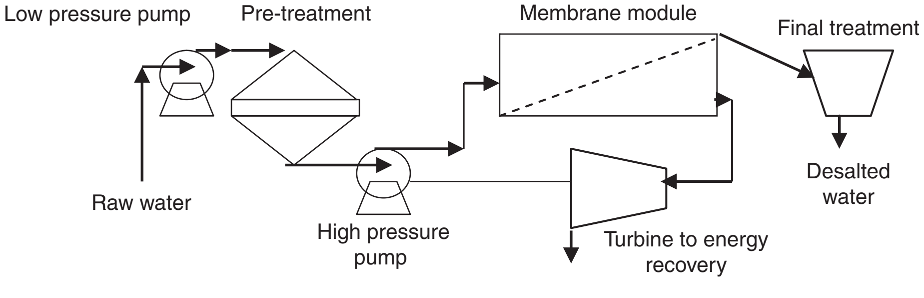


Fig. 1. Diagram of water desalination system using RO method with energy recovery from retentate.

Desalted water for drinking and domestic purposes should be degassed (decarbonisation), subjected to pH and alkalinity correction and chlorination [1,2,4]. The aim of chlorination is to prevent the development of microorganisms during the distribution and storing of desalted water.

The advantage of reverse osmosis is a relatively low cost of the desalted water [1]. Technological development in the last 30 years caused reduction of water desalination costs by lowering prices of material equipment, reducing power consumption and easier access (know-how) to the respective technology. The cost of water desalination affect the water quality, the size and installation location, qualification of workforce, price and the nature of applied energy and the nature of the technology (Table 1) [1,3–5,9,10]. Roughly estimated that the costs of desalination of seawater was reduced from approximately 1.7 USD/m^3 in 1988 to 0.55–0.80 USD/m^3 of desalted water at the beginning of the 21 age [3–5] for installations with a capacity of over 50,000 m^3/d. For installations with a capacity of 10,000–50,000 m^3/d this cost is 0.68–0.81 USD/m^3 of desalted water [3–5]. For brackish water desalination costs decreased from 0.50–0.80 USD/m^3 of desalted water in the 1980s even to 0.20–0.35 USD/m^3 at the moment [1,3–5].

Water desalination requires large of energy, which constitutes 25–40% of all desalination cost [1,4,5]. The energy requirements for the different processes and methods in each process are presented in Fig. 2, which shows that distillation methods are high energy consumers irrespective of salt content in the water, whereas RO has a lower energy demand depending on the salts concentration [1,2].

Integrated/hybrid systems in desalination are made through combing reverse osmosis with thermal processes and nanofiltration with reverse osmosis or distillation, as well as various energy sources [3–5,11]. Cost of such a solutions is frequently lower than every process alone [1]. In the case of integration MSF with RO, takes place not only mixing MSF distillate with RO permeate, but also combining water and power plants [12]. It is proposed also to use NF in seawater desalination and brackish underground water technologies (e.g., mining water) before a proper desalination process by RO or distillation. In such a solution NF significantly reduces scale-forming ions, allowing distillation process to be operated at high temperatures and RO with higher permeate recovery degree [5]. In the case of the use of alternative energy sources most often are combined solar energy with wind power, the dominant role in this case are photovoltaic (PV). In these cases is considered the following systems: RO-PV, RO-wind energy systems and RO-wind-PV [3–5,13–15].

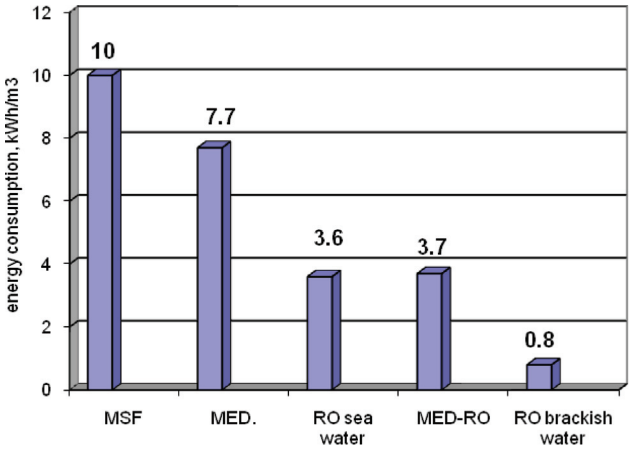


Fig. 2. Energy requirements according to process.

2.2. Water softening

By the second half of the eighties, nanofiltration had become established and known method of water softening, as an alternative solution to chemical softening and ion-exchange method [1,16–18]. For "low pressure" RO membranes and "compact" NF membranes, the salt concentration in permeate is very low, and often, after softening, its remineralization is necessary. The separation properties of NF membranes are based on capabilities of low retention of monovalent ions and high retention of divalent and multi-valent ions, as well as organic compounds with a molecular weight higher than 200–500 Da (Table 2) [1,2]. In such a way treated water should have a hardness complying with the regulations that means not higher than 60–500 mg $CaCO_3$/l. Ion selectivity of NF

Table 1
Costs of water desalination by reverse osmosis

Water type	Installation		Type of applied energy	
	Capacity m^3/d	Cost, euro/m^3		Cost, euro/m^3
Brackish	20–120	0.62–1.06	Photovoltaic	4.50–10.32
	40,000–46,000	0.21–0.43	Geothermal	2.00
Sea	1000–4800	0.56–1.38	Wind power	1.00–5.00
	15,000–60,000	0.38–1.30	Photovoltaic	3.14–9.00
	100,000–320,000	0.36–0.53	Solar	3.50–8.00

Table 2
Comparison of the characteristics of nanofiltration membranes NF-70 and NF-45 and reverse osmosis membrane FT-30 (FilmTec)

Membrane	Pressure MPa	Retention coefficient, %			
		NaCl	$MgCl_2$	$NaNO_3$	$MgSO_4$
FT-30	1.55	98	99.5	90	99.5
NF-70	0.5	75	70	50	97.5
NF-45	0.9	50	83	20	97.5

membrane is due to the presence of groups with negative charge (mainly –COOH or $–SO_3H$), located on the surface or inside the pores of the membrane, which thanks to electrostatic interactions disturbed permeation of multivalent ions. This phenomenon is not observed for RO membranes. In nanofiltration the solution components of the diameters about 1–3 nm are retained and pressure difference is in the range 1–3 MPa [1], that means below the values that would be necessary for reverse osmosis to obtain the same fluxes.

The diagram of the nanofiltration installation is similar to that which is applied in the reverse osmosis desalination process and include the pretreatment of water (addition of acid and agents preventing the formation of membrane scale, fine filtration –5 µm), membrane filtration and final treatment system (aeration, disinfection and corrosive stabilization) [1,17].

The performed investigation studies have confirmed the applicability of nanofiltration membranes for the softening of water [17–20]. The studies confirmed the possibility to obtain soft waters and low-hardness waters (total hardness ca.<200 $mgCaCO_3/l$) from very hard and hard waters (total hardness >300 mg $CaCO_3/l$) (Table 3) [19]. In view of the results of chemical analyses of permeates, high retention level of total hardness (>50%) and of carbonate hardness (>40%) as well as calcium and magnesium ions were obtained, depending on the type of membrane and source of raw water [17,19].

Total hardness removal during nanofiltration softening depends also on type of membrane used (Table 4), and it is possible to choice the proper membrane for a given type of water salinity and hardness [20–23].

Table 3
Results of well water softening using nanofiltration membranes (Osmonics)

Parameter	Water	Raw water	Retention coefficient (%)
Total hardness	Well water I	590 – very hard water	69
[$mgCaCO_3/l$]	Well water II	560 – very hard water	68

Table 4
Water softening results using NF membranes with different compactness

Membrane	NF-70 Filmtec	NF-45 Filmtec	UTC-20 Toray	UTC-60 Toray
Permeate hardness, mmol/l	0.14	1.14	0.14	0.59
Raw water hardness, mmol/l	2.8	2.8	2.8	2.8
Retention coefficient, %	95	59	95	79

Costs of membrane softening not deviate much from the chemical softening, but are less than the cost of water desalination by RO method. The following systems are develop [24]:

- for USA, the overall cost of treatment, including depreciation, exploitation and maintenance for installations with a capacity of 55,000 m^3/d is 0.15 USD/m^3,
- for European countries, costs are estimated at 0.23 $€/m^3$, for installations with a capacity of 20,000 m^3/d.

When mixing permeate with water obtained by other methods these costs can be reduced to 0.11 $€/m^3$.

The softening of water by means of ultrafiltration or microfiltration enhanced with polymers consists in the complexing of metals ions and polymers dissolved in water. Obtained complex compounds are retained by UF membrane as distinct from unbounded metal ions. The process was applied in the removal of metals from diluted solutions, hence the possibility of the use of UF in water softening [25,26]. Main advantages of the process are the low energy consumption (ultrafiltration process) and the high bounding activity of polymers dissolved in water [25]. Retention coefficients of cations responsible for water hardness are the function of pH [26]. Natural and synthetic polyelectrolites are used as complexing polymers. These polyelectrolites characterize with high content of carboxylic and/or amino groups of different order e.g., slightly basic cationic chitosan, poly(ethylamine) (PEI), poly(diallyldimethylammonium) chloride (PDADMAC), sodium salt of polyacrylic acid or natural polymer – algin, in structure of which amino and carboxylic groups are present, what significantly facilitates the complexing of bivalent metals ions [27,28].

2.3. Removal of anion micropollutants

The reverse osmosis process is highly efficient in removal of inorganic anions from water further used for drinking water production and, additionally, it guarantees safe detoxification [29]. The complete desalination, however, is undesired according to possible corrosion problems and remineralization requirements. The water of hardness below 50 mg/dm^3 is corrosive for copper, iron, zinc and other metals [2]. As a result, other processes suitable for selective removal of toxic anions and moderate desalination are desired. Nanofiltration (NF) fulfills such requirements according to the selective desalination i.e., the separation of polyvalent ions from monovalent ions with the higher capacity obtained for lower transmembrane pressures in comparison with RO process. Asymmetric membranes used in nanofiltration have negative electrical charge in neutral and alkaline solutions. Thus, the separation of anions not only consists in the difference in the rate of convention and diffusion through a membrane, but also in the electrostatic repulsion (Donnan exclusion) between anions in the solution and membrane surface charge. The repulsion forces are greater for polyvalent ions than for monovalent anions [30]. On the other hand, nanofiltration process is much more sensitive to ionic strength and pH of raw water than RO. The charge of surface of NF membranes is caused not only by the presence of functional groups possessing electrical charge, but also by the adsorption of anions from water. Hence, the charge of membrane surface depends on the concentration of anions in the solution and varies from negative values to zero in isoelectric point of a membrane, up to positive values in acidic environment (usually pH <4), according to the adsorption of cations [31]. Such a pH dependence influences on anions separations, hence the selection of proper process conditions is crucial for the application of nanofiltration. Many studies considering the removal of toxic anions from drinking water by means of RO and NF were performed and in significant part of them promising results were obtained (Table 5) [32].

Tabel 5
Pressure-driven membrane processes for removal of inorganic anions from drinking water

Process	Membrane and manufacturer	Anion	Water origin
RO	RO 4040-LHA-CPA2 (Hydranautics)	NO_3^-	Natural with 188mgNO_3^-/l (South Africa)
RO, NF	Different membranes (Osmonics)	NO_3^-	Tap water (Poland)
RO, NF, UF	Different membranes and manufacturer	As	Pilot studies at various sites in USA
RO	Different membranes and manufacturer	As	Pilot studies at various sites in USA
NF	NF ES-10 (Nitto-Denko)	As	Groundwater - 0.6 mg As/l (Japan)
NF	Different membranes (Nitto-Denko)	As	Model water
NF	Filmtec NF45 (Dow Chemical)	As	Model water
NF	Nanomax 50 (Millipore)	NO_3^-	Model water
NF	Different membranes (Nitto-Denko)	NO_3^-	Surface water after MF pretreatment (Japan)
NF	Filmtec NF70 (Dow Chemical)	NO_3^-	Groundwater (Belgium)
NF	NF300 (Osmonics)	NO_3^- and F^-	Groundwater (California, USA)
NF	Filmtec NF45 (Dow Chemical)	F^-	Model water
NF	Filmtec NF70 (Dow Chemical)	F^-	Model water
NF	TFCS (Fluid Systems)	CrO_4^{2-}	Model water

The pollution of natural waters with nitrates is a result of application of nitrogen fertilizers in agriculture as well as of disposal of solid and liquid wastes and industrial wastewaters to the environment [1,4]. The permissible content of nitrates in drinking water is established at the level of 50 mg/l (10 mgN/l). Ion exchange, reverse osmosis, electrodialysis and biological denitrification are the most often used methods for the removal of the excessive amount of nitrates [1,29].

The reverse osmosis process allows to decrease the amount of nitrates in drinking water to the level established in regulations. The relative purification costs are comparable with costs of ion exchange and electrodialysis including costs of disposal of the concentrate. The allowable reverse osmosis membranes characterise with high values of the retention coefficient relating to inorganic salts, thus the required decrease of nitrates concentration in drinking water can be achieved by mixing the permeate and raw water [1,2,29].

Nitrates as monovalent ions are not totally retained by nanofiltration membranes (NF) e.g., the retention coefficients of nitrates for NF-70 membrane (by Dow/FilmTec) are equal to ca.76%, that is under as for reverse osmosis membranes [20]. Thus, NF can be used as a first step in nitrates removal process integrated with RO or ion exchange [1,29]. However, the presence of sulphates decreases the retention coefficient of nitrate ions during NF. Under such conditions NF membranes practically does not eliminate nitrates, nevertheless it retain multivalent ions (Ca and Mg) what has a positive influence on reverse osmosis and ion exchange.

Reverse osmosis and nanofiltration membranes used for the removal of nitrates from water in comparison with membranes applied in the low-pressure membrane processes are twice as expensive, and their application in RO is much more energy-consuming as they require much more higher pressure. Hence, alternative methods consisted of ultrafiltration membranes (UF) and surfactants or polymers complexing nitrate ions are applied [29]. Complexes or micelles containing nitrate ions can be then retained by ultrafiltration membranes. In case of application of UF membranes and under surfactant concentration below the critical concentration of micelles formation the degree of removal of nitrate ions exceeds 79% depending on type and dose of surfactant used [29].

The appearance of fluorides (F^-) in natural waters results from their presence in lithosphere and anthropogenic industrial activity. According to WHO and polish regulations the maximum permissible fluoride concentration in drinking water is established at the level of 1.5 mg/l. Adsorption, coagulation with sedimentation, ion exchange and membrane processes i.e., reverse osmosis, nanofiltration and electrodialysis are main methods propose for fluorides removal from water [29,33–38].

The application of reverse osmosis in fluorides removal forces to consider the partial demineralization of permeates, what is the main disadvantage of the process [29]. RO membranes for water desalination (e.g., FilmTec XLE-440) are operated under relatively low pressure of 0.8 MPa and temperature equal to 8°C and under such condition 99% of salts is removed, what practically results in almost total removal of fluorides (the final concentration below 0.03 mg/l for the initial content in the range from 1.3 to 1.8 mg/l) [35].

During treatment of water which characterise with high fluoride content the application of nanofiltration is beneficial as the remineralisation of permeate is not required. The final concentration of F^- ions in permeates obtained for commercially available nanofiltration membranes, i.e.,, polyamides membranes NF90 and NF270 (by FilmTec) and TR60 (by Toray) of nominal molecular weight cut off equal 90, 270 and 400 Da respectively, was in the range from 0.05 to 4.0 mg/l depending on the initial concentration of fluorine (3.32, 6.32 and 22.32 mg/l) and membrane type [33]. The results obtained during similar studies confirmed the possibility of drinking water production from brackish waster of high fluorides content with the use of other commercial NF membranes i.e.,, NTR-7250, NTR-7450, F-70 (by FilmTec), Desal-5-DL and Desal 51-HL (by Osmonics), MT-08 (by PCI) and SR-1 (by Koch) [36]. The analysis of retention of monovalent ions for NF membranes indicates that smaller ions (fluorides) are retained more efficient than others (e.g., chlorides). The difference in selectivity stems from the differences in hydratation energy of particular ions, as the higher energy causes the better retention of an ion (hydratation energy of fluorides equals 515 kJ/mol while once of chlorides 381 kJ/mol) [36]. It explains the possibility of selective desalination of brackish water containing fluorides using nanofiltration and allows to produce drinking water cheaper than in case when reverse osmosis is applied.

Boron appears in the environment mainly in the form of boric acid (H_3BO_3) and borates [29,39]. Under lower pH the hydratation of boric acid does not occur what causes the smaller retention during membrane separation. On the other hand the dissociated form is totally hydrated and characterises with greater diameter and negative ion charge what results in higher retention [39]. In the European Union Countries and in Poland the permissible concentration of boron in drinking water as well as in wastewater disposed natural water and soil is established at 1.0 mg/l, while for industrial wastewater disposed to sewage system in must not exceed 10 mg/l [39]. Boron is removed from the environment mainly by means of coagulation and electro-coagulation, adsorption and ion exchange as well as membrane processes i.e., reverse osmosis, nanofiltration, electrodialysis and ultrafiltration with polymer complexing [39]. However, only two of those methods are used in industry i.e., reverse osmosis under high pH conditions and ion exchange [39].

Investigation aimed at removal of boron compounds from aqueous solution are of especial importance for desalination industry because none of the conventional desalination methods (distillation, reverse osmosis, electrodialysis) is capable to reduce boron content down to maximum permissible level even in seawater (where its content is below 5 mg/l). The retention of boron for reverse osmosis membranes under low or neutral pH varies from 40 to 60%, what is not sufficient to obtain the permissible level for drinking water or water disposed to environment. On the other hand, high pH process conditions leads to fouling and scaling which is mainly caused by precipitation of calcium and magnesium compounds. Thus, the RO permeate is alkalised to pH ca. 9.5 and once more treated via RO or ion exchange is applied (Fig. 3) [29,39]. The cost of removal of boron in the two-step process is very high [29] and usually multistep (3-4 steps) RO processes are applied. Hence, 2nd and 3rd stage RO membranes are operated at lower concentrations as well as at lower pressure [29]. Nowadays, studies focused on the development and testing of novel RO membranes that can be applied in one-step process are carried on.

The interesting modification of ion exchange is sorption-membrane hybrid process used in boron removal from seawater or from permeate from seawater desalination via reverse osmosis. Boron is removed by ion exchange resins e.g., Dowex XUS 43594 (By Dow Chemicals), Diaion CRB01 (by Mitsubishi) or others of very small grain size (20 μm) and the ion exchange is

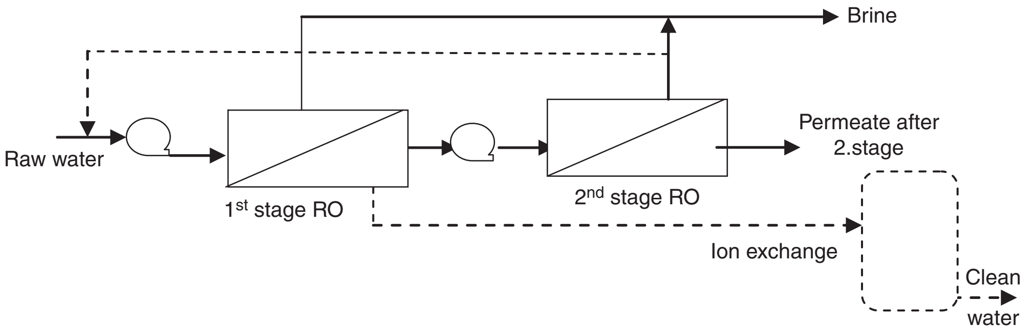


Fig. 3. Two stage RO system for boron removal or integrated system with ion exchange.

separated by means of microfiltration. The small size of grains of the resin allows to effectively decrease boron content after 2 min from 2 mg/l to 0.243–0.124 mg/l depending on ion exchanger dose (0.25 to 1.0 g/l) [40].

Studies focused on the removal of boron from water solutions by means of ultrafiltration enhanced by polymers (PEUF) were also performed [41,42]. Specially synthesized polymers are used in the process e.g., a compound obtained in the grafting reaction of N-methyl-D-glucamine (NMG) on poly(epichlorohydrin), derivatives of poly(amido-amines), and recently poly(vinyl alcohol) (PVA) was applied as a chelating polymer [41,42]. The process consists of two stages: the complexing of boron with a polymer and the separation of complexes during ultrafiltration. Capillary UF membranes working in the cross flow mode are used [41]. Retention coefficients of boron under such process conditions are decreasing during the process (starting from values close to 1) as active centers of the chelating polymer are occupied. The retention depends also on pH, boron concentration and polymer concentration in the feed.

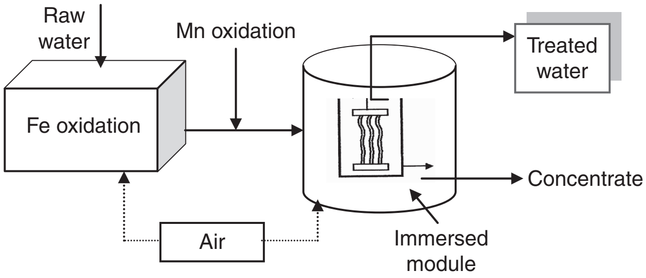


Fig. 4. Diagram of iron and manganese removal by means of hybrid system oxidation – MF.

Table 6
Results of the removal of Fe and Mn by ZeeWeed® method

Raw water	Raw water	Treated water
Fe, mg/l	>10	<0.1
Mn, mg/l	>5	<0.05
Turbidity, NTU	10–500	0.01

2.4. Metal removal

2.4.1. Iron and manganese in groundwater

Iron and manganese can be removed in a modern way from underground waters by combining oxidation with air and microfiltration, in particular when the concentrations of these metals are high and changing [1,43–46]. This method is similar to the classical one, but instead of deep filtration, MF is applied. The advantage of the system is the production of water with high quality regardless of raw water quality and compact nature of the equipment. The technological flowchart of the installation used for the removal of iron and manganese comprises the stage of pre-oxidation followed by filtration on the membranes (Fig. 4). GE Company (formerly Zenon) proposes the ZeeWeed® technology, because applied membranes are resistant to oxidants and can be used for the treatment of underground waters with a high turbidity and high content of iron and manganese (Table 6) [1]. Reactor, in which membranes are immersed, is aerated, thereby maintaining the oxidizing environment and prevents membrane fouling.

The removal of Mn by means of membrane filtration cannot be performed without oxidation of dissolved Mn(II) ions to Mn(IV). Except from potassium permanganate other strong oxidants are used, among which ozone, chlorine, chlorine dioxide, sodium hypochlorite or catalytic bed covered with manganese compounds are mentioned [29,44,46]. In the removal of manganese kinetics of oxidation of Mn(II) to MnO_2 is crucial. The possibility of formation of other impurities or toxins is a serious disadvantage caused by the application of mentioned oxidants in case of their improper dosing.

2.4.2. Arsenic

In order to decrease arsenic content in drinking water reverse osmosis and nanofiltration membranes as well as hybrid process of coagulation-MF/UF are applied [1,47].

Reverse osmosis membranes TFC-ULP (by Koch) allowed to remove 99% of arsenic from groundwater (the decrease from 60 µg/l to 0.9 µg/l), whereas DK2540F membranes (by Desal) retained 88–96% of the pollutant [47]. The content of dissolved organic matter as well as pH have a great influence on arsenic removal [24]. The higher removal of arsenic (V) was observed for waters of lower organic matter content (90%, while in comparison to higher NOM content it was equal to 80%). The removal of As (III) is always lower (e.g., for membrane DK2540F by Desal) than of As (V). During the study with ES-10 polyamide membrane and polyvinyl alcohol NTR-729HF membrane, both by Nitto-Japan, the lower removal of As (III) than As (V) in the pH range 3–10, was observed. The removal of arsenic (V) for ES-10 membrane was equal to 95% in the whole pH range, while for NTR-729HF the degree of removal was 80% for pH=3 and 95% for pH range 5–10. The retention coefficient of arsenic (III) was equal to 75% for ES-10 membrane in acidic solution and it increased to 90% for pH equal ca.10, whereas for NTR-729HF membrane the degree of removal was equal only to 20% [24]. Also other laboratory and pilot research has been performed onto arsenic removal using modules with reverse osmosis membranes [48–54].

Nanofiltration membranes are also applied to As removal [55–63]. 97% removal of As (V) was obtained for membrane NF-70 (by FilmTec), and for NF-45 membrane it varied from 45 to 90% depending on initial concentration of the pollutant in water [1,55]. In case of As (III), similarly as for RO, retention coefficients are much lower and decrease from 20% to 10% with the increase of the pollutant concentration in water. It indicates that the mechanism of arsenic removal using nanofiltration membranes is based on both, the sieving separation, and electrostatic repulsion between ions present in the treated solution and charged membrane. The degree of removal of As (V) with use of NF-45 membrane significantly increases with the increase of pH, according to the difference in As ion hydratation and, as a result, to the greater radius [55]. The influence of pH in the range from 4 to 8 on the retention coefficient of As (III) was not observed.

Microfiltration and ultrafiltration can be also used for arsenic removal from water [56,57,64–70]. However, the size of pores of MF and UF membranes is not sufficient for effective removal of dissolved and even colloidal chemical compounds. On the other hand, negatively charged UF membrane can be directly used for As removal [1,47]. Other MF and UF membranes are used to remove only part of arsenic forms from water, mainly by means of integrated systems with coagulation and flocculation [24,64]. In the article the removal of As from water with membranes of pore size 0.22 and 1.22 µm using ferric coagulants and polymeric cationic flocculants was described [47]. The obtained results indicated that the effectiveness of As removal was greater for hybrid systems than for single MF, according to the adsorption of As on coagulation flocks and separation of those flock by MF membrane. As a result, from the water of As content equal 40 µg/l, the water containing less than 2 µg/l of As can be obtained. The removal of As (III) is less effective than As (V) and often preliminary oxidation of As (III) to As (V) is required.

2.4.3. Heavy metals

Heavy metals are one of the most dangerous impurities present in drinking water. If the daily, monthly or annual consumption of water is considered, the danger resulted from the presence of heavy metals in water is quite significant. Metals like: lead, mercury, selenium, iron, nickel, manganese, copper, cobalt, cadmium, zinc, chromium and other are present in drinking water. The permissible concentration is established in polish regulations on tap water only for part of them. Except from iron, manganese and aluminum the permissible concentrations of following metals are specified: antimony – 0.005 mg/l, arsenic – 0.010 mg/l, chromium – 0.050 mg/l, cadmium – 0.05 mg/l, nickel – 0.020 mg/l, copper – 2.0 mg/l, lead – 0.025 mg/l, mercury – 0.001 mg/l, selenium – 0.010 mg/l and silver – 0.010 mg/l [71].

Membrane techniques like: reverse osmosis, nanofiltration, ultrafiltration and electrodialysis are more often applied for the removal of heavy metals in the industrial scale.

Metal ions can be successfully removed from water solutions by means of reverse osmosis or nanofiltration (NF) as membranes applied in those processes are able to retain dissolved salts of particle sizes not even greater then few nanometers [1]. In nanofiltration monovalent ions are more preferably transported than multivalent ones. In many cases RO and NF are an attractive alternative for traditional water and wastewater treatment methods considering aspects of environmental protection and the economy of the process. If environmental protection is taken into account nanofiltration can be considered as an effective process for removal of heavy metals from water under specified operating conditions, what is shown by the results of the studies [72–74].

Studies focused on the removal of Cu(II), Ni(II), Zn(II) and Pb(II) as well as radioisotopes (^{51}Cr, ^{124}Sb,

^{125}Sb, ^{141}Ce) and lanthanides (^{140}La, ^{152}Eu and ^{169}Y) from water by means of hybrid method of complexing with water-soluble polymers and concentration by ultrafiltration are also carried out [75–79]. Polyvinyl alcohol (PVA of molecular weight 50000) and polyethylamine (PEI of molecular weight 30000–40000) as well as polyacrylic acid and sodium polyacrylate are used as complexing agents. The polyelectrolyte used for lead ions complexing was sodium poly(styrene sulfonate) (PSSS), a water-soluble anionic polymer which contained groups of strong cation-exchange properties [80]. High degrees of removal of metal (85–99%) depended on ratio of metals ions content to polymer amount, pH of the solution necessary for formation of stable complexes and operating ultrafiltration conditions were obtained.

Membrane processes are very important for recovery of chromium [29,81]. High-pressure membrane techniques like reverse osmosis (RO) and nanofiltration (NF), low-pressure membrane processes i.e., microfiltration (MF) and ultrafiltration (UF) enhanced with surface-active compounds and polymers [82–94] are used.

Both high-pressure membrane techniques, reverse osmosis and nanofiltration, allow to directly separate chromium compounds from treated solutions and are applied in that field [29,81]. Polymeric and inorganic membranes can be applied for removal do Cr(II) and Cr(VI). Bohdziewicz et al. performed studies of the removal of chromium from groundwater of significant content of the element by means of RO and NF using Sepa-S RO membranes (by Osmonics) and following nanofiltration membranes: HG 19, SX 10, SV 10, SX 01, BQ 01, MX 07 (H-polysulphone, M-polyamide, S-cellulose acetate, B-unspecified polymer) which differ in retention coefficients of sodium chloride [85]. During reverse osmosis with SS membranes the decrease of chromium concentration from 0.05 mg/l to 0.002 mg/l was obtained, while for others membrane the final chromium concentration was at the level of 0.004 mg/l. In case of NF membranes, chromium (VI) ions were retained the most efficient by: SX 10–96%, SX 01–90% and SV 10–98% (the concentration of the xenobiotic in the permeate did not exceed 0.01 mgCr (VI)/dm^3). The retention of chromium by means of nanofiltration mainly depends on pH and Cr concentration. Retention coefficients of Cr increase with the increase of pH for higher chromium concentrations. It is caused by transformations of hexavalent chromium ions with the change of pH. In strongly acidic environment hexavalent chromium appears in the form of non-dissociated chromic acid (H_2CrO_4). The increase of pH to 6.5 causes the formation of hydrochromate ions ($HCrO_4^-$) concentration of which increases with the further pH increase. Under pH above 7 chromate ions (CrO_4^{2-}) are formed of concentration also dependent on pH. Dichromate ions are also present in the solution and their concentration depends on pH and chromium content in the feed. Usually, this ion is dominant when the concentration of chromium is high and the pH is in the range 1–7 and its concentration can be decreased by the increase of pH [82,84,95].

3. Other membrane processes in inorganic micropollutants removal

In water treatment technology, also other membrane processes are taken into consideration, especially such as Donnan dialysis and electrodialysis, membrane bioreactors and contactors [1,2].

Donnan dialysis (DD) is a process that uses an ion exchange membrane without applying an external electric potential difference across the membrane [32,96–98]. The ions, which are permeable to the membrane, will equilibrate between the two solutions until the Donnan equilibrium is obtained. The Donnan dialysis type of operation requires the addition of a so-called driving counter-ion to the stripping solution, which is transported in a direction opposite that of the target ion in order to maintain electroneutrality (Fig. 5) [98]. Since concentration ratios determine the Donnan equilibrium,

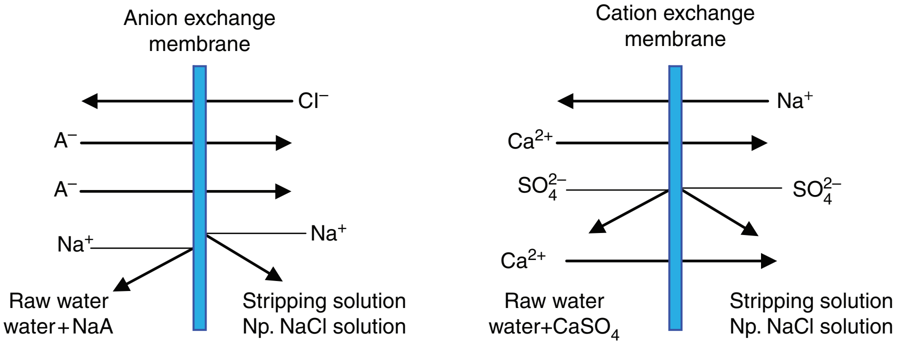


Fig. 5. Scheme of Donnan dialysis process.

not concentration differences, Donnan dialysis allows for transport of charged micropollutants against their concentration gradients, what is important for drinking water supplies, which usually contain only trace levels of polluting ions. Furthermore, the hydraulic residence time can be independently adjusted in the two compartments to optimize the degree of extraction of the target pollutant. Due to these characteristics, the removal of inorganic anions from drinking water, especially nitrate and fluoride, by Donnan dialysis has received attention (Table 4) [97].

Since in Donnan dialysis the mechanism of ion transport is governed solely by the Donnan equilibrium principle, the anion fluxes achieved may be low for certain applications. In electrodialysis (ED), the transport of ions present in contaminated water is accelerated due to an electric potential difference applied externally. In this process, besides anion exchange membranes, cation exchange membranes are also applied in order to transport cations to the cathode [32]. In ED membrane fouling and scaling are a frequently observed, therefore, the ED systems are usually operated in the so-called electrodialysis reversal mode, in which the polarity of the electrodes is reversed several times per hour to change the direction of ion movement. The external electric potential driving force allows to obtain higher anion fluxes than those in DD, but a different degree of demineralisation (cations are also removed from the water) depending on the voltage and type of the membranes used is obtained. When the purpose is the removal of inorganic toxic anion(s), reduction in water hardness could be a desired side effect in some cases but in others may cause a too deep softening (as in RO treatment); therefore the suitability of ED depends strongly on the polluted water ionic composition. Successful applications of ED include removal of various anions, e.g., fluoride, boron, perchlorate and especially nitrate as well as some metals (Table 7) [32,98].

So electrodialysis can provide an efficient removal of inorganic anions from drinking water. Since most known toxic anions are mono-valent the use of mono-valent anion perm-selective exchange membranes is especially attractive [32]. Situations, in which ED appears to be less applicable are for waters of very low salinity (conductivity of less than 0.5 mS), for which Donnan dialysis can be a better solution, and, in cases when besides ions, removal of low-molecular mass non-charged compounds (to which ED is obviously ineffective) from the water is desired. In the latter case, pressure-driven membrane processes as RO or NF may be preferable. The brine discharge/treatment issue, however, remains important for all these separation processes.

The use of a mono-valent anion perm-selective membrane proved successful in a full-scale ED plant designed to remove nitrate from groundwater in Austria [32,98]. The nitrate concentration in the raw water was 120 mg NO_3/l and the plant removal efficiency (66%) was adjusted to obtain a product concentration of 40 mg NO_3/l. Under these conditions, the total desalination degree was about 25%, therefore the nitrate selectivity was reasonably high [98].

Table 7
Donnan dialysis (DD) and electrodialysis (ED) in the removal of inorganic anions in drinking water production

Process	Membrane type, producer	Anion	Type of water
DD	Neosepta AFN; Neosepta AFX (Tokuyama Soda)	F^-	Model water
DD	Selemion DSV (Asahi Glass)	F^-	Model water
DD+ adsorption	Neosepta ACS (Tokuyama Soda)	F^-	Ground water (Morocco)
ED	Neosepta AFN; Neosepta ACS (Tokuyama Soda)	F^-	Brackish water
DD, ED	ADS (Morgan)	NO_3^-	Water from Montpellier (France)
ED	Selectivity for monovalent ions (No data)	NO_3^-	Ground water (Austria)
ED	Neosepta ACS (Tokuyama Soda)	NO_3^-	Ground water (Morocco)
ED	Neosepta ACS (Tokuyama Soda); Selemion AMV (Asahi Glass)	NO_3^-	Model water
ED	Ionics – no data	ClO_4^-	Ground water (Utah, USA)
DD	Neosepta ACM; AFN (Tokuyama Soda); SB-6407 (Gelman)	$Cr_2O_7^{2-}$	Model water

The application of electrodialysis (ED) to fluorides removal from water that contains significant amount of the impurity is beneficial as the process characterises with insensitivity to seasonal changes of fluorine concentration, satisfying selectivity, low demand of other substances and low energy consumption [34,99]. The degree of removal of fluorides and soluble substances is very often higher than once obtain for reverse osmosis and it increases with the increase of voltage, temperature and flow rate [99]. In case when fluorides concentration is below the permissible level ED devices can be shut down and unexploited for longer time period [100]. In order to minimize the precipitation of salts of bivalent ions (sulphates and carbonates) in the concentrate chambers two configurations of ED process are proposed:

- two-step ED with application of bivalent ions selective membranes in the 1st step and conventional membranes in the 2nd step,
- the preliminary removal of bivalent ions by chemical methods followed by conventional ED.

The first method is preferably used according to its simplicity and elimination of introduction of additional chemicals. The content of fluoride ions is generally decreased from 3.0 mg/l to 0.63 mg/l for the first configuration and to 0.81 mg/l for the second one, what allows to obtain water of municipal quality.

Electrodialytic removal of boron from water and wastewater, similarly as RO, also requires high pH value, as boronic ions are transported through anion exchange membrane. The main advantage of ED in comparison with RO is the smaller sensitivity of ion exchange membranes to pH and fouling. High pH values may also result in precipitation of Mg $(OH)_2$ and $CaCO_3$. However, even for such a high pH (9–10) chlorides are preferably transported and sulphates are removed in similar extent as boron [39,100]. The low mobility of boric ions, in comparison with others, is the main disadvantage of ED as boron can be transported only after significant decrease of other salt contents in diluate [100]. In order to omit high demineralization of the diluate, monopolar membrane under alkali process conditions (pH = 9–10) are applied [39].

The main disadvantage of pressure-driven membrane processes and electrodialysis is production of the concentrate with high load of anions [101]. The method propose for the removal of anionic micropollutants of that stream is treatment in membrane bioreactors (MBR), which allows to decrease concentration of pollutants to low value [96,100]. The content of bioreactor during or/and after process can be treated in ultrafiltration/microfiltration process what allows to separate the treated solution and biomass. MBR can be used for the removal not only nitrates but also bromides and perchlorates [32,96].

The biological denitrification is based on the reduction of nitrate to molecular nitrogen under anaerobic conditions at the presence of microorganism and proper donor of electrons [1,96,97]. The kinetic of the reaction depends on kind of microorganisms and biodegradation process conditions (pH, nitrates concentration) [1]. Heterotrophic bacteria which naturally occur in soil and water as well as autotrophic bacteria are used in biological nitrates removal processes. The addition of organic substrates (ethanol, methanol and acetates) is required for heterotrophic microorganisms, whereas autotrophic denitrification needs of inorganic compounds (e.g., sulphur compounds and hydrogen) as electron donors [1,2,102]. The second advantage of autotrophic denitrification is lower production of activated sludge, however the process runs slowly [29]. When heterotrophic denitrification is applied the removal of dissolved organic carbon and biomass from treated water is required [102]. Disadvantages of conventional biological denitrification can be eliminated by application of a membrane bioreactor (MBR), which assures the total retention of biomass. The configuration of MBR processes may be as the system of selective nitrates removal with pressure driven membrane techniques (microfiltration, ultrafiltration) (Fig. 6 and Table 8) [1,2] or as extractive membrane bioreactors (membrane contactors) (Fig. 7) [1,29].

A general limitation of the pressure-driven membrane bioreactors in the first version is the treated water quality. While contamination of water with microbial

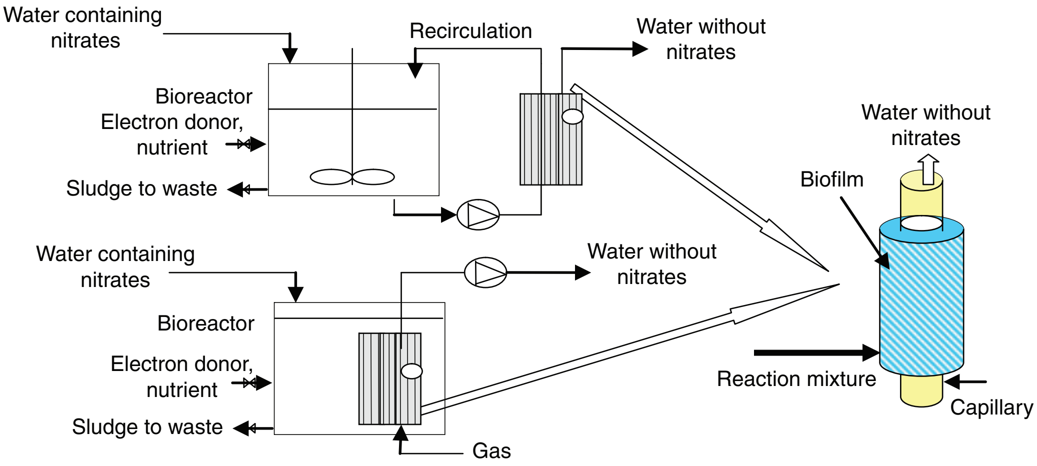


Fig. 6. Membrane bioreactors with pressure driven membrane module.

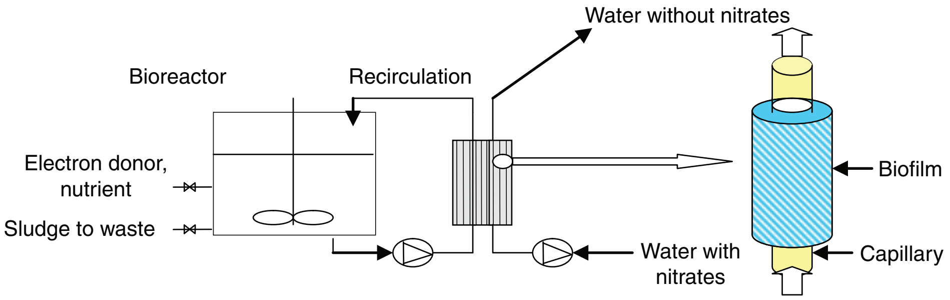


Fig. 7. Extractive membrane bioreactor.

Tabel 8
Pressure-driven membrane processes for removal of inorganic anions from drinking water

Process description	Membrane type and manufacturer	Electron donor	Water origin
Denitrification + UF	Cellulose derivates (Aquasource) 0.01 µm	Ethanol	Tap water with NO_3^- addition (France)
Denitrification + UF	UFP2 (Tech-Sep); cut-off 200 kDa	Ethanol	Tap water with NO_3^- addition (Japan)
Denitrification + UF	Polysulfone; cut-off 500 kDa	Acetate	Ground water (Portugal)
Denitrification + UF	Polysulfone, submerged module cut-off 750 kDa	Sulfur	Model solutions
ED brine denitrification + UF	Ceramic membranes; 0.05 µm	Ethanol	Ground water (France)

cells and biopolymers can be avoided, the retention of ions and low molecular mass compounds (electron donors, some metabolic by-products) by porous membranes is generally insufficient to meet the stringent drinking water criteria; therefore either process modifications (or water post-treatment are necessary). In the second solution water with nitrates is supplied to the inside (lumen side) of hollow-fibre membranes and NO_3^- ions diffuse to the outside (shell side), where it is used by existing microorganisms as an electron donor for the reduction of anionic micropollutants.

A new membrane bio/process for the removal and bioconversion of ionic micropollutants from water streams is the ion-exchange membrane bioreactor (IEMB) [32,97]. In this process, the ionic micropollutant is transported from the water stream through a non-porous ion-exchange membrane into a biological compartment where it is simultaneously converted by a suitable microbial culture into harmless products. The driving force for pollutant transport through the membrane is the anion electrochemical potential difference. Therefore, as discussed previously for Donnan dialysis, pollutant transport against its concentration gradient is possible due to the presence of driving counter-ions in a higher concentration (Fig. 8). The co-ions (cations) are excluded from the positively charged membrane and the target anion(s) transport is combined with its bioconversion by anoxic mixed microbial culture fed with an adequate carbon source and other required nutrients in a continuous mode. The selection of a nonionizable carbon source is preferable in order to minimize its transfer through the membrane. In addition, the bioconversion of the pollutant in the IEMB keeps its concentration at low levels and guarantees an adequate driving force for transport.

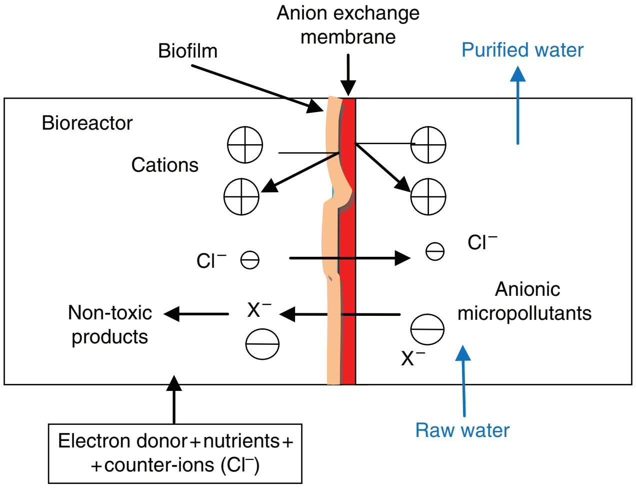


Fig. 8. A schematic diagram of the ion transport mechanism in the ion exchange membrane bioreactor (IEMB).

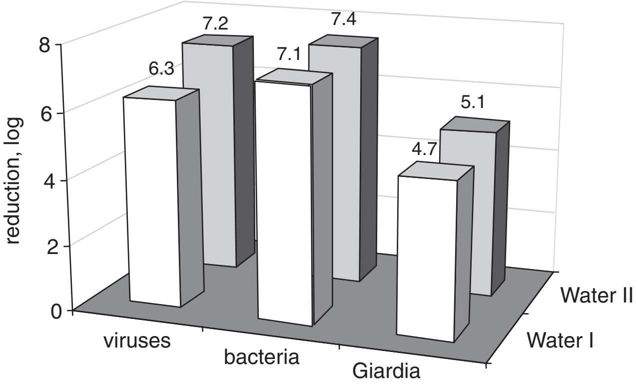
This concept was first demonstrated in synthetic waters for the removal and bioconversion of nitrate to harmless nitrogen gas using Neosepta ACS mono-anion permselective membrane and ethanol as the carbon source [32]. Due to its very low diffusion coefficient (three orders of magnitue lower than that in water) through this non-porous type of membrane, and the development of an ethanol-consuming biofilm on the membrane surface contacting the biocompartment, carbon source penetration into the treated water was avoided.

4. Removal of dispersed substances and microorganisms using low pressure membrane processes

The turbidity of water is caused by the presence of suspended mineral and organic molecules of different sizes (colloids, coarse and fine suspensions). Usually, microfiltration or ultrafiltration are applied to decrease water turbidity to the level below 1 NTU. Such a level of turbidity corresponds to once demanded for drinking water, as according to polish regulations it is established as 1 NTU. Only several studies described in the literature focused on the turbidity removal by means of membrane processes, whereas it is proved that the water of turbidity below 1 NTU can be obtained from water of the initial turbidity 100 NTU and greater [103]. It is accepted that UF and MF are used for water clarification [1]. The study of application of UF "Aquasource" membrane (France) revealed that from waters differ in turbidity from 0.1 to 11.5–24.8 NTU drinking water of turbidity 0.03–0.04 NTU could be obtained [103]. Similar results were obtained for various membrane modules during studies in USA, France and other countries [103]. Sometimes, when the turbidity is caused by colloidal fraction, membrane filtration is preceded by coagulation in order to obtain flocks of greater size [1]. Reverse osmosis and nanofiltration also eliminate this type of impurities and organic admixtures, however those process are not applied because of fouling phenomena.

Water which contains microorganisms i.e., viruses, bacteria, protozoa and others (fungi, algae, snails, worms and crustacea) may cause many negative health effects [103]. Polish regulations defining quality of drinking water establish the maximum permissible content of *Escherichia coli* and *Enteroccocus*, and, as additional requirements, the amount of *Coli* bacteria group, total number of microorganisms and *Clostridium Perfringens* [71]. Membrane filtration may significantly improve the disinfection process, as it practically totally eliminates viruses, bacteria and protozoa. The size of viruses varies from 20 to 80 nm, whereas pores size of UF membranes is less than 10 nm, thus theoretically the elimination of microorganisms is possible. On the other hand, bacteria (0.5–10 μm), cysts and oocytes (3–15 μm) are larger and thus they can be totally eliminated during MF [1,103]. The comparison of pores sizes of UF and MF membranes with sizes of microorganisms indicates that UF process can be successfully use for water disinfection [1]. In Fig. 9 degrees of removal of viruses, bacteria and protozoa for different UF membranes is shown [103]. The obtained removal for all types of microorganisms was greater than 4 log i.e., 99.99%.

Practice has shown, however, that the UF membranes are not always able to completely eliminate the bacteria and viruses from water. This is primarily connected with imperfections in the membranes and membrane modules and the secondary development of bacteria in the water after passage through a membrane. In commercial membranes discontinuous skin layer take place, through which micro-organism can pass, as well as the design of the modules require seals of the raw stream from the permeate stream which is not always appropriate. The most efficient in the disinfection are the capillary modules in which isolation of raw water from the permeate is easier than in the spiral wound and hollow-fibers modules [1]. Furthermore, it was found that cells of microorganisms can penetrate membrane pores with diameters of much smaller than the dimensions of the cells themselves, thanks to the pressure deformation with filtration of intracellular fluid, but tonus cellular membrane remains unchanged [1].



Level of disinfection expressed as reduction in logarithmic scale:
1 log = 90% of inactivation
2 log = 99% of inactivation
3 log = 99,9% of inactivation
4 log = 99,99% of inactivation

Fig. 9. Removal of microorganisms using UF method.

5. Removal of organic substances by means of pressure-driven membrane processes

Pressure-driven membrane processes effectively remove dissolved organic substances (usually expressed as dissolved organic carbon, DOC) from water [104]. Natural organic matter (NOM), anthropogenic impurities, disinfection by-products (DBP) and other micropollutants are typical examples of this type of compounds.

5.1. Natural organic matter (NOM)

Natural organic matter presence in aqueous ecosystems is the mixture of many compounds which characterise with various chemical structure and properties. It is found that soluble in water fulvic acids (MW ≤2000 Da), more hydrophobic humic acids (MW ≤2000–5000 Da) and insoluble humic fraction (humins) of bituminous character are part of NOM [1,105]. Humic substances usually appear in water as dissolved compounds, colloids and non-dissolved admixtures and usually the appearance of a given form strongly depends on water pH. The dissolved NOM fraction share in total NOM amount in natural water is equal to ca. 80–90%. Humic substances cause intensive colouration of water from brown to black colour. Additionally, complexing reactions of humic substances with heavy metals or adsorption of toxic organic substances creates many health hazards. Humic substances are also DBP precursors [105].

The removal of NOM is one of the most important processes in water treatment technology. The main advantage of application of membrane techniques in water treatment is the removal of DBP precursors including part of NOM [6,103]. Chlorination, as one of the most popular disinfection method results in formation of adsorbable organic halides (AOX) including trihalomethanes (THM), halogenated acetic acids, halogenated aldehydes and ketones, halogenated acetonitryles, amines and other DBP [1,2]. According to very wide molecular size distribution of NOM (from ca. 1 nm to ca. 0.45 μm) the effectiveness of removal depends on properties of applied membranes [1]. Introduction of nanofiltration and reverse osmosis to water treatment allows to control the formation of DBP as semi-permeable membranes retain NOM including DBP precursors. The removal of NOM also decreases the amount of chlorine required for disinfection what results in reduction of biological activity of water in the distribution system [6,104]. The application of NF or RO enables to totally remove NOM from water, however it is very often limited by high content of colloids and suspensions in surface waters [104].

Except from NF and RO processes, low pressure driven membrane filtration is also widely used in water treatment [106]. UF and MF membranes effectively remove colloids and ionic and non-ionic organic compound of sizes which correspond to nominal molecular weight cut off of UF or MF membranes. Thus, UF/MF alone can be directly used for removal of greater fractions of NOM from water, including part of high molecular weight DBP precursors, whereas medium and low molecular weight compounds can be eliminated in integrated systems [107]. In order to remove humic substances from water direct UF with modules equipped with dense membranes (e.g., ca. 1000 Da) or hybrid systems of UF or MF with coagulation, activated carbon adsorption or oxidation (ozonation, photocatalysis) can be applied [106,107].

In Table 9 the comparison of effectiveness of NF, UF and MF processes in NOM content control in natural waters is shown.

5.2. Organic micropollutants

Polycyclic aromatic hydrocarbons (PAHs) and surface active agents are main anthropogenic micropollutants present in water. Disinfection and chemical oxidation by-products (DBP), which are form during drinking water production are mainly volatile trihalomethanes (THM) and non volatile halogenated acetic acids (HAA) [1,2]. Recent investigations focus especially on Pharmaceutical Active Compounds (PhACs) and Endocrine Disrupting Compounds (EDCs) as groups of anthropogenic micropollutants which appear more often in natural waters. EDCs group includes xenoestrogenes among which chlorinated pesticides and herbicides are distinguished, alkylphenols, polychlorinated biphenyls, phthalates, natural organic compounds produced by fungi (including toxins i.e., mycoestrogenes)

Table 9
Comparative assessment of MF, UF and NF processes for NOM removal

Parameters	MF	UF	NF
NOM removal	<10%	0±30%	>80%
Removal of suspensions and colloids	20±40%	70±90%	>95%
DBP removal	No	50% THM; 32% HAA	>80%
Requirements for cleaning	Required backwashing	Cyclical cleaning required	Cyclical cleaning required
Performance problems	Moderate fouling	Fouling	Fouling, clogging
Pretreatment	In-line coagulation or other process	In-line coagulation or other process	No

and plants (phytoestrogenes), female hormones, synthetic pharmaceuticals (e.g., contraceptives) and other chemical compounds produced by men and disposed to the environment.

The removal of micropollutants during water treatment is usually performed using activated carbon sorption or advanced oxidation processes (AOPs). The first method becomes less attractive economically as the amount of NOM in water increases, whereas in case of AOPs there exists a possibility of formation of by-products of undefined biological activity [1]. It results in necessity of development of new separation processes among which pressure driven membrane processes seem to be a good solution.

5.2.1. Disinfection and NOM oxidation by-products and other anthropogenic compounds

In Table 10 results obtained during studies focused on removal of polycyclic aromatic hydrocarbons (PAHs) by means of reverse osmosis and nanofiltration are presented [108]. The most effective membrane used during studies was MQ16 (the retention coefficient of NOM in the range from 85.9% to 99%, independently of molecular weight of a compound). For other membranes the retention coefficient increased with the increase of molecular weight of the removed compound. The total amount of PAH i.e., benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, ideno(1,2,3-cd)pyrene in drinking water should not exceed 0.1 mg/l, while only for benzo(a)pyrene it must be below 0.01 mg/l [71].

Surface active agents (SAAs) are a very specific group of anthropogenic water pollutants. They affect wastewater treatment plants performance mainly because of toxic action on activated sludge, foam formation, simulation of solubility of many hazardous substances, etc. Pressure driven membrane techniques are alternative methods for removal of SAAs from water. In case when the concentration of pollutant in water is greater than critical micelle concentration (cmc) ultrafiltration process can be used, despite the molecular cut off of applied membranes is greater than molecular weight of eliminated compounds. Membranes of cut-off from 5000 to 30,000 Da are able to remove sodium dodecyl sulphate (SDS) (100 mg/l) in the range from 12.5 to 78%, depending on membrane density and type of membrane material [109]. However, when the concentration is below cmc the application of nanofiltration membranes are suggested, eventually, reverse osmosis is proposed. It was shown that NF membrane Desal 5K eliminated SAAs in 90–96% when the concentration was below cmc, while for the concentration higher that cmc the degree of removal varied from 92 to 99% [109].

Table 10
Comparison of retention coefficients of PAHs removed during RO and NF processes (membranes from Osmonics Company, USA)

Nazwa	Concentration in raw water, ng/l	Retention coefficient [%]		
		RO-SS10	NF-SF10	NF-MQ16
Fluorantene	50	39.6	45.9	89.9
Benzo(b) fluorantene	60	64.4	97.8	85.9
Benzo(a) pirene	50	62.8	96.4	99.2
Benzo(g,h,i) perylene	70	96.8	91.1	93.3

Reverse osmosis and nanofiltration are most often applied to remove trihalomethanes (THM), halogenated acetic acids (HAAs) and other halogenated hydrocarbons from water. In Poland, the permissible concentrations of THMs in water are established as follows: the total THM <100 μg/l, chloroform-30 μg/l, bromodichloromethane-15 μg/l [71].

The study, during which RO and NF Osmonic membranes (SS10 and MQ16) were applied, revealed that the degree of removal depended on the membrane capacity i.e., the higher permeate flux the lower retention coefficient [1,110]. It was found that the increase of molecular weight of halogenated compound resulted in the increase of retention coefficient according to the following series: $CHCl_3 < CHBrCl_2 < CHBr_3 < CHBr_2Cl$. The degree of removal of chloroform varied from 67 to 87%, bromodichloromethane 65–96.5%, dibromochloromethane 57–95% and tribromomethane 48.3–95% depending on the applied membrane type [110]. In another study, investigating the effectiveness of removal of THMs by means of nanofiltration with the use of NF200 and DS5 Osmonics membranes [111], it was shown that operating pressure did not influence on THM retention, whereas initial concentration of THM had noticeable influence on capacity and retention. NF200 membrane turned out to remove THM more effectively than DS5 membrane. The most effectively removed compound was dibromochloromethane what results from higher molecular weight of bromine and the same in greater size of the molecule.

Nanofiltration is a membrane process also suggested to removal of halogenated acetic acids (HAAs) (chloro-, dichloro- and trichloroacetic acid; bromo- and dibromoacetic acid) from water [112]. The high reduction of HAA content was found for dense negatively charged ES10 membrane formed from aromatic polyamide in comparison with open negatively charged NTR7410 from sulphonated polysulphone and neutral NTR729HF membrane from polyvinyl alcohol (all membranes by Nitto Denco Corp., Japan). The effective separation was caused by repulsion forces (Donnan effect) and sieving effect. ES10 membrane removes HAAs in 90–100% even at low operating pressure of 0.1 MPa and the change of linear velocity, which does not influence on membrane performance [112]. The increase of concentration of acids results in decrease of the degree of removal in case of all investigated membranes according to the greater concentration polarisation effect, which is the driving force for HAA anions diffusion through the membrane.

Results of studies suggest that nanofiltration is the best available technology for removal of THM and HAA from water.

5.2.2. Endocrine disrupting compounds

EDCs are present in natural waters in the concentration range from ng/l to µg/l.

Pesticides, herbicides and insecticides which belong to xenoestrogenes appear in natural surface water mainly as a result of runoff of falls. These are substances with low molecular weight thus they can be effectively removed from water (above 90%) during nanofiltration or by integrated systems of low pressure driven membrane processes (MF or NF) and activated carbon adsorption (powdered or granulated) [103]. Regulations defining quality of drinking water establish the permissible concentration of particular compounds or their sum at levels of 0.1 and 0.5 µg/l [71].

NF membranes eliminate pesticides of molecular weight >190 Da to the amount below the limit of detection, and, generally, the retention coefficient varies from 50 to 100% depending on molecular weight and concentration of pesticides in water as well as on the presence of organic and inorganic compounds [1,103]. The formation of complexes of organic matter, especially of humic acids, with pesticides molecules causes the increase of the retention of those compounds [1,113]. However, the presence of inorganic substances decreases the negative zeta potential of a membrane as well as causes the destruction of complexes of pesticides with humic acids and release of micropollutants, what finally leads to the decrease of the retention [103].

The presence of phthalates in the environment is caused by massive production of plastics, mainly PVC, in which they are used as plasticisers. According to their negative effects on living organisms the concentration of phthalates in different parts of the environment, especially in water, should be controlled. Polish regulations establish the permissible concentration of di-*n*-butyl phthalate at the level of 20 µg/l [71]. The surprisingly high retention of phthalates was observed during both, RO and NF processes (initial concentration 40 µg/l) (Table 11) [114]. Results obtained during removal of phthalates of molecular weight 222–391 Da revealed that the molecular weight of a compound did not influence on the effectiveness of removal.

The appearance of compounds that affect hormones production processes in living organisms is more often observed in surface waters. Among these compounds natural and synthetic hormones are specified. It was shown that elimination of this type of pollutants from water can be performed by means of membrane processes [115]. Considering relatively low molecular weight of those pollutants dense membranes (RO or NF) must be applied. It was found that RO membranes totally eliminate particular hormones while retention coefficients obtained for NF and UF membranes were lower than 100% [115]. In case of natural estrogens the concentration of micropollutants (10–1000 ng/l) does not influence on the separation effectiveness, whereas in case of synthetic estrogens the increase of the concentration causes the increase of the retention [115]. The separation of hormones by means of NF and UF strongly depends on hydrophobicity and molecular weight of a compound. Natural hormones i.e., estrone, estriol and estradiole are removed less efficient in comparison with their synthetic equivalents – ethinylestradiol and mestranol (greater hydrophobicity) (Table 12). It was also found that instead of single process elimination of hormones from water hybrid system of coagulation and nanofiltration can be performed [115].

Phenolic xenoestrogenes (octylphenol, nonylphenol, bisphenol A and bisphenol F) can be removed from

Table 11
Removal of phthalates with RO, NF and UF processes (membranes from Osmonics company, USA)

Phthalates	Molecular weight, Da	Concentration in raw water, µg/l	Process (membrane)	
			RO (DS-3-SE)	NF (DS-5-DK)
			Retention coefficient, %	
diethyl phthalate	222.2	40	95.1	99.9
di–*n*–butyl phthalate	278.3		95.1	99.9
2-ethylhexyl phthalate	390.6		99.9	99.9

Table 12
Retention of synthetic and natural hormones in pressure driving membrane processes (concentration in water 1 μg/l) (membranes from Osmonics company, USA)

Process (membrane)	Hormones(estrogens)					
	Natural			Syntetic		
	Estrone	17β-estradiol	Estriol	Mestranol	17α-ethynyl estradiol	Diethyl stilbestrol
	Retention coefficient, %					
UF (DSGM)	36.8	35.3	28.1	68.5	55.3	70.1
NF (DS-5-DK)	63.0	76.7	71.1	100	90.4	86.1
RO (DS-3-SE)	100	100	100	100	100	100

Table 13
Retention coefficients and adsorption degrees of phenol xenoestrogens in nanofiltration process (membranes from Osmonics company, USA)

Compounds	Nanofiltration membrane			
	SF-10	DS-5-DK	MQ-16	DS-51-HL
	Retention/adsorption coefficient [%]			
4-*tert*-oktylphenol (4tOP)	71.8/52.2	72.7/51.4	47.0/17.9	48.0/19.5
4-nonylphenol (4NP)	60.5/68.0	70.3/68.0	50.0/52.5	43.5/57.3
biphenyl A (BPA)	45.8/52.5	68.8/69.3	75.0/75.0	60.7/33.4

water by means of nanofiltration. Both, the retention coefficient and the degree of adsorption of xenoestrogenes strongly depend on type of removed compound (Table 13) as well as on membrane type. The high retention of octylphenol and nonylphenol in the range from 61 to 73% is observed for SF-10 and DS-%-DK membranes, while in case of bisphenol A DS-5-DK (69%) and MQ-16 (75%) membranes are more sufficient [116].

5.2.3. Pharmaceutical active compounds

Main sources of aqueous environment pollution with pharmaceuticals are households and hospitals, and, additionally diagnostic units, pharmaceutical plants and livestock farms. Medicines used by ill people are not totally metabolise in their organisms and are removed from it with urea and faeces finally reaching wastewater treatment plants. These compounds are detected in wastewaters, surface waters, groundwaters and drinking water. In Poland the concentration of pharmaceutical in waters are determined at the level of few μg/l [71]. The methods of removal of medicines from water and wastewater are advanced oxidation, activated carbon adsorption on granulated carbon and membrane processes – nanofiltration and reverse osmosis, and, in case of wastewater treatment, membrane bioreactors (MBRs) [117–119].

First results of studies performed at municipal wastewater treatment plants, during which MBRs equipped with MF or UF modules were used, revealed that the removal of trace amounts of pollutants is comparable with conventional treatment methods [119]. The higher age of activated sludge and elongated contact time achieved in MBR improve biological degradation and removal of PhAC and EDC.

Nanofiltration and reverse osmosis to natural water and wastewater treatment can also be applied to PhAC removal [117,118]. Snyder et al. carried out the study during which membrane filtration techniques (MF, UF, NF and RO) were applied to remove EDCs, pharmaceuticals and personal hygiene products from crude municipal wastewater, leachates after first, second and third treatment stage and saline groundwater, into which specified micropollutants were introduced [118]. Pilot and industrial scale tests were performed. The study revealed that only several compounds were removed during MF and UF while in case of NF and RO significant retention of all investigated compounds was observed.

Heberrer et al. [117] performed wide pilot study of PhAC removal using mobile installation for water treatment equipped with RO modules, which was used during natural disasters or military operations. The substrate of the study were water from Teltow channel

Table 14
The average concentrations of pharmaceuticals in biological treated wastewater and permeate after treatment with two-stage RO system

Compounds	Concentration, ng/l		Retention coefficient, %		
	Raw water	Permeate	After preliminary filtration and UF	After 1st RO stage	After 2nd RO stage
AMDOPH	811	<1	32	>99.9	>99.9
Benzafibrate	257	<5	7	96.0	>99.9
Carbamazepine	2282	<1	13	>99.9	>99.9
Clofibric acid	178	<1	20	>99.4	>99.4
Diclofenac	869	<1	44	>99.9	>99.9
Fenofibric acid	705	<1	22	97.0	>99.9
Gemfibrozil	16	<1	38	>93.3	>99.3
Ibuprofen	87	<1	12	98.5	>98.9
Indometacyn	46	<1	0	92.0	>97.8
Ketoprofen	99	<1	20	>99.0	>99.0
Naproxen	224	<1	0	98.2	>99.5
Oxazepam	153	<5	0	>99.3	>99.3
Primidone	734	<1	0	>99.9	>99.9
Propyphenazone	309	<1	46	99.3	>99.7

AMDOPH – (1-acetyl-1-methyl-2-dimethyl-oxamoyl-2-phenylhydrazide).

(Berlin) and treated wastewater from Ruhleben municipal wastewater treatment plant (Berlin). Prototypic three-stage installation of capacity equal to 10,000 l/h included duplex bag filters with a particle separation <0.5 µm, ultrafiltration and reverse osmosis, and RO could be performed as one or two stage process. The presence of PhAC in treated water from Teltow Channel was not observed, whereas in RO permeate obtained during treated wastewater treatment the amount of pharmaceutical was below 10 ng/l for both, one and two stage configurations (Table 14).

6. Concluding remarks

In the treatment of water for drinking purposes first of all pressure-driven membrane techniques are used. The choice of the suitable membrane process depends on the size of the removed contaminants and admixtures from the water.

Introduction and development of membrane technology in the production of drinking water, in the last 30 years, is considered as a significant step in the field of water treatment effectiveness, comparable with the introduction of sand filters at the beginning of 20 age. The special role played the high- and low- pressure-driven membrane processes. Desalination of seawater and brackish groundwater is often the way to obtaining drinking water. Significant improvements in technology and design of reverse osmosis, the availability of alternative energy sources, the possibility of pretreatment and applied materials have caused the process to become environmentally-friendly source of fresh water in many regions of the world, particularly in those where their sources are limited. At the moment investment costs for large desalting installations are roughly comparable to the cost of investment of modern conventional water treatment plants. In the 1980s increased interest of nanofiltration and to some extent the reverse osmosis as the methods of water softening, while in the 1990s they start to be applied to remove disinfection by-products precursors and micro-pollutants. Use microfiltration and ultrafiltration in the water purification processes, meet essentially the latest regulations, that dictate the need to more effectively remove turbidity and micro-organisms in the treatment process based on conventional filtration. Technology has been recently optimized and become competitive in comparison to conventional processes for the installation of large capacities. Projects exceeding 100,000 m^3/d in capacities are currently implemented. Effectively removing of biologically active organic and inorganic micro-pollutants from waters, in its treatment, is today one of the most important tasks of the engineering and environmental protection. Apply pressure-driven membrane processes, and to some extent electrodialysis becomes attractive both in terms of efficiency and cost of application.

The problem in operation membrane techniques is membrane fouling, causing of continuous decrease of membrane capacities in time and permeate quality deterioration. Methods to fouling prevent include currently the pre-treatment processes of water before membrane filtration, such as coagulation, adsorption on activated carbon, biological filtration and oxidation.

Application of membrane technology in environmental engineering are only at the beginning of the development. These techniques are still developed mainly by process engineering and transferred to the engineering environment. It is considered that membrane technologies in applications related to the treatment of water and wastewater belong to the so-called Best Available Technology (BAT).

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