Membrane separation techniques – removal of inorganic and organic admixtures and impurities from water environment – review

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Abstract: Introduction and development of membrane techniques in the production of drinking water and purification of wastewaters, in the last 40 years, was important stage in the field of water treatment effectiveness. Desalination of sea and brackish water by RO is an established way for drinking water production. Significant improvements in design of RO, the application of alternative energy sources, modern pretreatment and new materials have caused the success of the process. NF is the method of water softening, because NF membranes can retain di- and multivalent ions, but to a limited extend monovalent. Drinking water containing viruses, bacteria and protozoa, as well as other microorganisms can be disinfected by means of UF. Viruses are retained by UF membranes, whereas bacteria and protozoa using both UF and MF membranes. For the removal of NOM it is possible to use direct NF or integrated systems combining UF or MF with coagulation, adsorption and oxidation. The use of NF, RO and ED, in the treatment of water containing micropollutants for drinking and industrial purposes, can provide more or less selective removal of the pollutants. The very important are disinfection byproducts, residue of pharmaceuticals and endocrine disrupting compounds. For endocrine disrupting compounds, special attention is paid onto polycyclic aromatic hydrocarbons and surface-active substances, chlorinated pesticides, phthalates, alkylphenols, polychlorinated biphenyls, hormones, synthetic pharmaceuticals and other substances disposed to the environment. The application of MF and UF in the removal of inorganic and organic micropollutants is possible in integrated systems with: coagulation, adsorption, complexion with polymers or surfactants and biological reactions.

Introduction

Above 70% of Earth is covered with water, but 97.5% of this is water with salt content above 1 g/L. Among the remaining 2.5% of water sources, 69% is glacier and permafrost ice, while less <1% of total fresh water sources, i.e. around 0.01% of total water sources, is available for humans (Bodzek and Konieczny 2017). The disproportional distribution of water sources is one of the most serious problems influencing the growth and development of the societies. Water is a very important raw material, its resources are renewable, but, on the other hand, limited. The limited access to fresh water is mainly caused by the pollution of the natural waters by industry and agriculture as well as municipal wastewaters, increase of human population accompanied with the growing life standard and climate changes (Bodzek and Konieczny 2011a).

The choice of the technology for water and wastewater treatment is depended on its type. Ground water may be simply purified before its distribution to the water system, while surface water and wastewater treatment are more complex due to the presence of dangerous contaminants. The partial solution to the problem of water contamination is the development and implementation of new technologies (Sozański et al. 2009), and membrane separation techniques are highly recommended (Bodzek and Konieczny 2010).

In the treatment of drinking water and wastewater, pressure-driven membrane techniques are frequently applied. The choice of an appropriate membrane process depends on the types of effluents and admixtures present in water (Bodzek and Konieczny 2017, 2006). Reverse osmosis (RO) retains monovalent ions and the majority of low-molecular compounds and principally is used for water desalination/demineralization and the removal of inorganic and organic micropollutants. Nanofiltration (NF) retains bivalent ions and low-molecular organic/inorganic compounds and is applied to water softening and removal of micropollutants. Ultrafiltration (UF) and microfiltration (MF) are able to direct the removal of colloids, suspended substances and microorganisms and can be used for water clarification and disinfection, but in integrated systems for the removal of organic and inorganic pollutants/micropollutants. In addition, other membrane techniques also are applied to

pressure-driven processes. For example, forward osmosis (FO) is recently proposed for desalination and the removal of some micropollutants and electrodialysis (ED) and liquid membranes for inorganic compound removal.

The above techniques can be used for the removal of effluents as independent process or combined with unit processes, e.g. bioreactors, forming hybrid processes.

Removal of inorganic pollutants

Water desalination/demineralization

Desalination of seawater and salty groundwater is a common method of potable and industrial water production in regions with dry climate. At the end of 2015, there were approximately 18,000 desalination plants worldwide, with a total production capacity of 86.55 million m³/day (Voutchkov 2016). The number of desalination installation constantly increases not only in the Middle East or Northern Africa (44%), but also in regions in which one would never suppose the possibility of application the method, e.g. Spain and Australia (i.e. dry and semi dry areas) (Ghaffour et al. 2013, Voutchkov 2016).

Despite the fact that the desalination installations are increasing fast, their price is still quite high for most of people, but desalination is still a cheaper solution than e.g. long distance water transport (Ghaffour et al. 2013, Subramani et al. 2011). Nowadays, investment costs of large water desalination plants are comparable with costs of conventional drinking water treatment plant (Bodzek and Konieczny 2011a).

Seawater is an unlimited source of the feed for desalination processes, and brackish water, most often collected from ground water, is also important in water desalination. The salt concentration in seawater varies from 24,000 to 42,000 mg/L, depending on the localization (Table 1) (World Bank 2004). The concentration of salts in brackish water is much lower and varies from 2,000 to 5,000 mg/L.
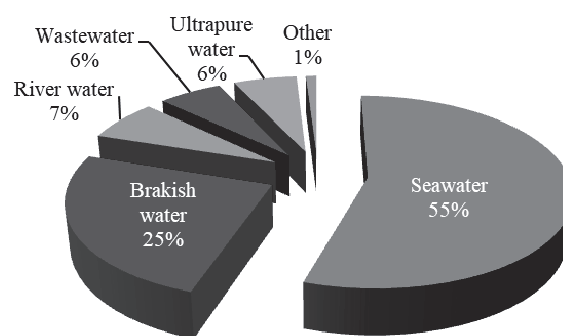
Desalination can be performed using different methods, first of all RO and ED as well as various types of distillation (Bodzek and Konieczny 2017, El-Ghonemy 2012, Subramani et al. 2011). The latest research shows that forward osmosis can be used for desalination (Chung et al. 2012, Gryta 2012, Linares et al. 2015, Subramani et al. 2011). Globally, 65% of water produced via desalination is obtained using membrane processes and 28% by means of thermal methods (Kaselain et al. 2019). In the last 10 years, seawater and brackish water reverse osmosis desalination have come to dominate desalination markets, at costs comparable to other fresh water production methods (Malaeb and Ayoub 2011). Nowadays, more than 90% of RO installations are involved in the production of drinking and potable water as well as to treatment of water for energy, semiconductors, etc. Figure 1 shows the percentage of RO installations capacities used for different types of water and wastewater treatment (Bodzek and Konieczny 2017). The main desalination feed is seawater (55%), next brackish ground water (25%), and the rest are surface and wastewater (Ghaffour et al. 2013). However, this data is very unstable due to the dynamics of desalination market. In Table 2 the most important operational parameters of thermal and membrane methods are compared (Fritzman et al. 2007).

The scheme of a typical installation for water desalination by RO is shown in Figure 2 (Al-Karaghouli and Kazmerski 2013, Bodzek and Konieczny 2017, 2011a, El-Ghonemy 2012, Wilf 2007). It is divided into: water intake, raw water pretreatment, high-pressure pump with membrane modules and energy recovery from retentate, and treatment of desalted water before distribution sections.

The present RO installations are equipped with polyamide composite membranes (TFC) which comprise of three layers: polyester support layer (thickness 120–150 µm), microporous transient layer i.e. polysulphone UF membrane (thickness about 40 µm) and a very thin active layer (skin thickness – 0.2 µm)

Table 1. Salinity of seawater and brackish water

Water	Total salinity, g/m³
Oceans	35,000
The Red Sea	41,000
Persian Gulf	45,000
The Mediterranean Sea	38,000
Aral Sea	29,000
The Baltic Sea	7,000
Low saline brackish water	1,000–5,000
Highly saline brackish water	5,000–15,000

Fig. 1. Performance of desalination installations according to the type of feed

Table 2. Comparison of the operating parameters of thermal and membrane desalination methods

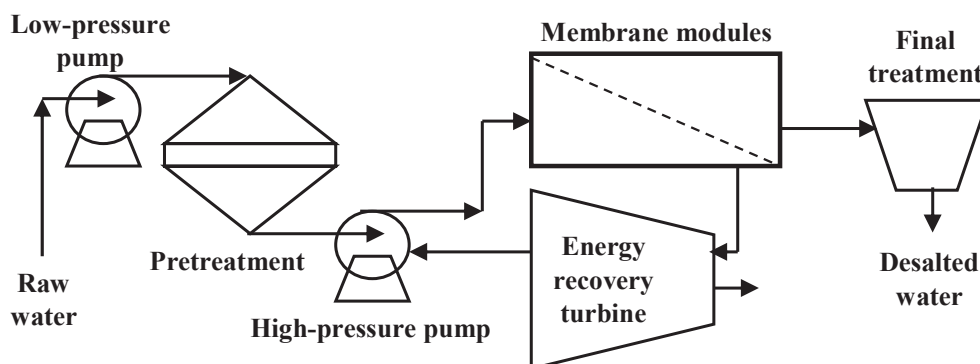| Parameter	MSF	RO	ED
Thermal energy demand, kWh/m³	12	–	–
Electrical energy demand, kWh/m³	35	0.4–0.7	1
Salinity of raw water, g/L	30–100	1–45	0.1–3
Desalted water, mg/L TDS	<10	<500	<500

Fig. 2. Performance of desalination installations according to the type of feed

(Lee et al. 2011). Active skin layer for membranes of new generation contain nanomaterials, first of all zeolites, nano-silica, carbon nanotubes, and graphene (Songa et al. 2018). Such membranes are characterized with higher permeability compared to osmotic membranes used nowadays (Subramani et al. 2011) at unchanged salt retention. In most RO desalination installations, spiral wound membrane modules are used (Al-Karaghouli and Kazmerski 2013, Bodzek and Konieczny 2011a). They characterize with better set of parameters like the ratio of permeability to packing density, fouling control and exploitation procedure, easy scaling up and others (Wilf 2007). There are four main companies which supply RO membrane modules to industrial seawater desalination plants, i.e. DOW, Toray, Hydranautics and Toyobo (Bodzek and Konieczny 2017, 2011a).

The main exploitation problem of RO installations is fouling, which is the deposition of substances present in the feed water on the membrane surface and/or inside membrane pores. Fouling may be caused by microorganisms (biofouling), precipitation of $CaCO_3$, $CaSO_4$ and $BaSO_4$ (scaling) and the formation of filtration cake by dissolved or suspended substances (Bodzek and Konieczny 2011a, Gryta 2012). Fouling may have reversible character, if the deposit formed on the membrane surface can be totally removed and the initial capacity of the membrane can be restored. The irreversible fouling is found when contamination of membrane takes place inside membrane pores and thus the mechanical, but also chemical cleaning is not sufficient enough to recover the initial efficiency (Bodzek and Konieczny 2017, 2011a). In order to limit the impact of fouling on the process efficiency, the pretreatment of feed is carried out. It may comprise all or chosen operation units used in water treatment, i.e. coagulation and filtration, adsorption, oxidation, final filtration and so on (Bodzek and Konieczny 2017, 2011b, 2005, El-Ghonemy 2014, Perez-Gonzalez et al. 2012). Recently, UF and MF are reliable methods for removal of suspended substances, some organic and microbiological contaminants, including pathogens (Bodzek and Konieczny 2017, 2011b, Halpern et al. 2005).

In modern installations for water desalination it is possible to recover 30–40% of the energy from high pressure retentate by means of special mechanical devices (Fritzmann et al. 2007, Subramani et al. 2011). Special mechanical systems dedicated to the transport of energy present in the retentate to the RO feed water are used. The energy recovery systems can decrease the overall energy demand to 2–4 kWh/m³ in the case of seawater desalination, and to <1 kWh/m³ for brackish water treatment systems (Fritzmann et al. 2007, Subramani et al. 2011).

The permeate obtained from RO does not meet the standards of drinking water, that is why it should be the treated. Water dedicated to human consumption and to municipal purposes is degassed (decarbonized), submitted to pH improvement and disinfected before distribution or storage (Fritzmann et al. 2007, Subramani et al. 2011). Another solution is water remineralization using lime stone and alkalinity increase.

One of the most crucial parameters of all desalination technology is concentrate utilization or neutralization (Kim 2011, Perez-Gonzalez et al. 2012, Subramani and Jacangelo 2014), especially for plants localized far away from oceans. Brine may be deposited to oceans, surface water, deep wells or special evaporation lagoons or may be introduced directly to soil. The separate option is their treatment with the use of RO, ED, thermal methods or their combination, membrane distillation and FO (Bodzek and Konieczny 2011a, Kim 2011, Perez-Gonzalez et al. 2012, Subramani and Jacangelo 2014).

Modern desalination systems operated nowadays are mostly configured into integrated (hybrid) units, among which one can distinguish: (i) integration of RO with thermal methods, (ii) use of NF for prevention of scaling, (iii) replacement of conventional pretreatment with UF or MF, and (iv) combination of RO with ion exchange or electro-deionization (EDI) to production of deionized water (Ang et al. 2015, Bodzek and Konieczny 2011b, Helal 2009).

Desalination of water with the use of renewable energy is already applied in some regions and may become more popular in the nearest future. There are many combinations between renewable energy sources and desalination processes (AbKadir et al. 2010, Eltawil et al. 2009). In Figure 3 the possible desalination systems with renewable energy are shown (Eltawil et al. 2009).

The technological progress within the last 30–40 years has decreased water desalination costs, due to the reduction of materials and energy costs and energy consumption. The detail comparison of different desalination plants is difficult to make as actual costs depend on many variables, which are specific for every investment. The costs of desalination mainly depend on raw water quality, configuration and capacity of the installation, localization of the investment, accessibility and price of electrical energy, concentrate utilization and others (Bodzek and Konieczny 2011a, El-Ghonemy 2012, Ghaffour et al. 2013). Table 3 presents costs of energy and water (average

values) in commercial large scale desalination processes (Bodzek and Konieczny 2017).

Summing up, over the past several years, desalting of seawater and brackish water became a method for the production of water at a cost comparable to the cost of fresh water production by other methods. The dominant techniques used on a large scale are RO and MSF. Recently, research on new desalination techniques has been carried out, especially on membrane distillation and forward osmosis. Significant improvements in technology and process design, the availability of alternative sources of energy, the possibility of pretreatment and new materials used meant that the desalination process has become ecologically-friendly source of fresh water in many regions of the world, especially in those where their sources are limited.

Water softening

Nanofiltration process is an established and known method for water softening, as an alternative to chemical and ion-exchange (Bodzek 2002, Bodzek and Konieczny 2011a, Ghizellaoui et al. 2005). The NF membranes are characterized with low retention of monovalent ions and high retention of di- and multi-valent ions, as well as organics with a molecular weight above 200–500 Da (Bodzek and Konieczny 2011a, 2006). Ion selectivity of NF membrane is based on the presence of functional groups (mainly –COOH or –SO$_3$H) with negative charge on the surface or inside the pores of the membrane. Electrostatic interactions retain multivalent ions in retentate. This phenomenon is not observed for RO membranes.

After softening using NF, the salt concentration in permeate is very low and, often, its remineralization is necessary. The performed experiments confirmed the applicability of NF membranes for the softening of water (Bodzek 2002, Ghizellaoui et al. 2005, Van der Bruggen et al. 2001, Wesolowska et al. 2002). They showed that it is possible 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 4) (Wesolowska et al. 2002). Also, high retention 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 raw water (Bodzek et al. 2002, Wesolowska et al. 2002). Total hardness removal during NF softening depends also on type of membrane used (Table 4), so it is possible to choose the proper membrane for a given type of water salinity and hardness (Anim-Mensah et al. 2008, Homayoonfal et al. 2010, Van der Bruggen et al. 2001).

Izadpanah and Javidnia (2012) performed the experiments with commercial spiral-wound NF membrane (pressure range of 4–10 bar) to remove hardness and ions from diluted seawater. The results show that this membrane is capable of retaining 96–98% of the total hardness, and 79–89% of the total dissolved solid (TDS).

At the present time, NF is rather seen as a combinatory process capable of removing hardness and a wide range of other components in one step. Gorenflo et al. (2002) examined the NF-200B membrane for the treatment of groundwater with high hardness and natural organic matter (NOM) content. The results showed almost complete rejection of NOM (>95%) and 74% and >86% rejection of Ca^{2+} and Mg^{2+} respectively. Also Orecki et al. (2004) studied surface water treatment by NF using AFC30 membrane with cross-flow mode operation and transmembrane pressure between 10–25 bars. They also
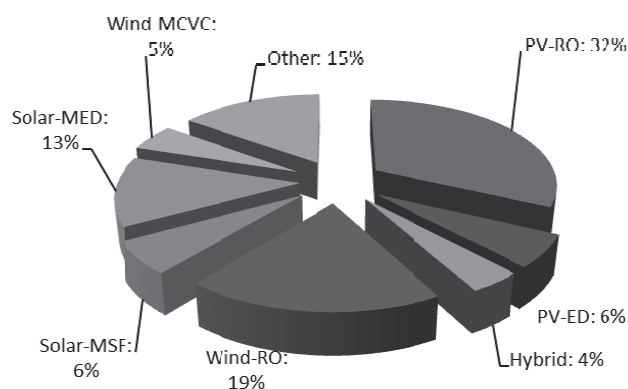
Fig. 3. Distribution of renewable energy in desalination process (PV – pervaporation, MSF – multi-stage flash distillation, MED – multi-effect distillation, MCVC – mechanical vapor compression)

Table 3. The cost of energy and water (average values) in commercial large scale desalination processes

Process	Heat kWh/m³	Electricity kWh/m³	Total energy kWh/m³	Investment costs USD/m³/d	Total cost of water USD/m³
MSF	7.5–12	2.5–4	10–16	1200–2500	(0.8–1.5)[a]
MED	4–7	1.5–2	5.5–9	900–2000	0.7–1.2
SWRO	–	(3–4)[b]	3–4	900–2500	0.5–1.2
BWRO	–	0.5–2.5	0.5–2.5	300–1200	0.2–0.4

[a] Including grants (fuel price); [b] Including energy recovery system.

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, mgCaCO$_3$/L	14	114	14	59
Raw water hardness, mgCaCO$_3$/L	280	280	280	280
Retention coefficient, %	95	59	95	79

obtained complete removal of total organic carbon (TOC) and reduced the SO_4^{2-} content by approximately 90–99%, carbonate by 82% and total hardness by 85.2%.

Costs of membrane softening do not differ much from those of the chemical softening, but membrane softening is more beneficial in view of the environment protection. Shahmansouri and Bellona (2015) compared the costs of different options for water softening and color removal. Unit water costs were calculated for three alternative processes, i.e. lime and soda ash softening, lime and soda ash softening + ozone injection + granular-activated carbon (GAC for color removal), and softening using NF membranes. Results showed that for smaller treatment plants (<150,000 m^3/day), NF is a more cost-effective method (water costs about 0.25 USD/m^3), compared to lime and soda ash softening system. For large softening facilities (i.e. systems with capacity>200,000 m^3/day) water costs are smaller (<0.25 USD/m^3) and similar to other softening methods. Other advantages of NF over lime softening include small footprint, reduced chemical requirements, reduced chemical storage, increased organic matter removal, and no sludge production. For highly colours water, NF membrane systems produce water at a cheaper price compared to installations with lime soda, ozonation, and GAC processes.

The softening of water by means of UF or MF enhanced with polymers consists in the complexing of metal ions and polymers dissolved in water. The obtained complexes are retained by UF membrane compared to unbounded metal ions. The process was applied in the removal of metals from diluted solutions. Natural and synthetic polyelectrolytes with high content of carboxylic and/or amino groups are used as complexing polymers, e.g. chitosan, poly(ethylamine) (PEI), poly(diallyldimethylammonium) chloride (PDADMAC), sodium salt of polyacrylic acid and others (Fatin-Rouge et al. 2006).

There is also the possibility of the application of ED and EDI methods to eliminate the hardness from water (Bodzek and Konieczny 2011a). A characteristic feature of the ED and EDI processes is the ability to obtain a high degree of water recovery. In addition, the EDI system is characterized by a lower energy consumption and higher economic efficiency compared to the ED system.

Inorganic micropollutants

A number of inorganic anions (nitrate(V), chlorate(VII), (V) and (III), bromate(V), arsenates(III) and (V), borate and fluoride) and heavy metals at harmful concentrations in natural water sources and wastewaters can have adverse influence on human health (Bodzek and Konieczny 2011a, b). The permissible levels of these compounds, in drinking water and wastewaters discharged to the environment, set by the WHO and a number of countries are very low (in the range of μg/L to a few mg/L). Thus, the majority of them can be considered as charged micropollutants.

Several treatment technologies, such as coagulation/chemical precipitation – sedimentation – filtration, adsorption, ion exchange, classical solvent extraction, evaporation and biological methods, which are normally used for the removal of inorganic micropollutants from natural waters or wastewaters, represent a lot of exploitation problems. Membrane processes, i.e. RO, NF, UF and MF in hybrid systems, and ED as well as in liquid membranes and bioreactors, are also used for the removal of micropollutamts (Bodzek 2015, Bodzek and Konieczny 2011a, b, Crespo et al. 2004, Velizarov et al. 2004). In many cases, one membrane process can be integrated with another system to produce high quality water. However, in physical membrane processes, inorganic compounds are not destroyed but concentrated. Therefore, post-treatment of the concentrate stream can be difficult and costly in many cases.

Removal of anions

The RO process is highly efficient in direct removal of inorganic anions during drinking water treatment. However, during the RO complete desalination is obtained, that is why remineralization process of permeate is required (Bodzek 2015, Bodzek and Konieczny 2011a, b). NF enables the partial desalination because it separates polyvalent from monovalent ions with higher capacity at lower transmembrane pressures (TMP) in comparison with RO process. Many studies considering the removal of anions from natural waters and purified wastewaters by means of RO and NF have been performed and promising results were obtained (Table 5) (Bodzek 2015, Bodzek and Konieczny 2011a, b, Velizarov et al. 2004).

Table 5. RO and NF for removal of inorganic anions in the production of drinking water

Process, membrane and manufacturer	Anion	Feed
RO 4040-LHA-CPA2 (Hydranautics)	NO_3^-	Natural water-188 mgNO_3^-/L (South Africa)
RO, NF – different membranes (Osmonics)	NO_3^-	Tap water (Poland)
RO, NF, UF – different membranes and manufacturer	As(V)	Pilot studies at various sites in USA
NF ES-10 (Nitto-Denko)	As(V)	Ground water – 0.6 mg As/L (Japan)
NF – different membranes (Dow Chemical and Nitto-Denko)	As(V)	Model water
NF Nanomax 50 (Millipore)	NO_3^-	Model water
NF – different membranes (Nitto-Denko)	NO_3^-	Surface water after MF (Japan)
NF Filmtec NF-70 (Dow Chemical)	NO_3^-	Ground water (Belgium)
NF NF-300 (Osmonics)	NO_3^-, F^-	Ground water (California, USA)
NF Filmtec NF-45 and NF-70 (Dow Chemical)	F^-	Model water
NF TFCS (Fluid Systems)	Cr(VI)	Model water

The use of MF and UF in the removal of inorganic micropollutants is possible in integrated systems with: coagulation, adsorption, complexing with polymers or surfactants and biological reactions (Bodzek 2015, Bodzek and Konieczny 2011a, b). The interesting solution is the hybrid process of sorption-membrane separation used for boron removal from seawater or water after seawater desalination with RO. Boron is removed by ion exchange resins (e.g. Dowex XUS 43594 – Dow Chemicals, Diaion CRB01 – Mitsubishi or others) of very small grain size (20 μm). Next resin is separated by means of MF. The small size of grains of the resin allows to effectively decrease the boron content from 2 to 0.243–0.124 mg/L, depending on ion exchanger dose (0.25 to 1.0 g/L) (Dilek et al. 2002). Studies have also been performed on the removal of boron from water solutions using UF enhanced with polymers (PEUF), usually with poly(vinyl alcohol) (PVA) or other polymers (Dilek et al. 2002). The process consists of the complexation of boron with a polymer and the separation of complexes by UF membrane. The retention depends also on pH, boron and polymer concentration in the feed. MF and UF can be used for arsenic removal from water by integrated systems with coagulation (Dilek et al. 2002). For example, from the water of As content equal to 40 μg/L, the water containing less than 2 μg/L can be obtained, using ferric coagulants and membranes of pore size 0.22 and 1.22 μm (Dilek et al. 2002). In the integrated process, As is adsorbed on coagulation flocks and next flocks are separated by MF membrane. In such a case the removal of As(III) is more effective than that of As(V) and preliminary oxidation of As(III) to As(V) is required.

Successful applications of ED and EDR include the removal of various anions, e.g. nitrates (V), bromates (V), chlorates (VII), arsenic (V), boron and fluorides as well as various heavy metals (Velizarov et al. 2004, Wisniewski 2001).

During the RO, NF and ED processes the concentrate with high concentration of anions is formed. Thus, the use of membrane bioreactors (MBR) for the removal of micropollutants from RO, NF and ED concentrates as well as natural water and wastewaters, is proposed (Bodzek 2015, Bodzek and Konieczny 2011a, b, Crepso et al. 2004, Velizarov et al. 2004, 2008). The biological degradation of oxyanions (NO_3^-, ClO_4^-, BrO_3^-) is based on their reduction to harmless substances (N_2, Cl^-, Br^-) at anaerobic condition and the presence of microorganism (heterotrophic or autotrophic bacteria) and proper electron donors (ethanol, methanol and acetates for heterotrophic conditions and sulphur compounds and hydrogen for autotrophic ones) (Crepso et al. 2004, Velizarov et al. 2004). Autotrophic degradation gives lower amount of the excess sludge, but the rate of process is low (Kołtuniewicz and Drioli 2008), compared to heterotrophic ones (Velizarov et al. 2004). Studies have shown full reduction of nitrates (V), bromates (V) and chlorates(VII) to nitrogen, bromides and chlorides by the same bacterial cultures which are used for nitrates (V) reduction (Wang et al. 2008).

Metal removal

Iron and manganese can be removed from underground waters by combining air oxidation with MF, particularly when the concentrations of these metals are high and changing (Bodzek and Konieczny 2011a). This hybrid method is similar to the classical one, but instead of depth filtration, MF is applied. The obtained water has high quality, e.g. the concentration of Fe and Mn in treated water is <0.1 and <0.05 mg/L, respectively (Bodzek and Konieczny 2011a). The removal of Mn by means of membrane filtration cannot be performed without oxidation of dissolved Mn(II) ions to Mn(IV). The oxidants used are $KMnO_4$, O_3, Cl_2, ClO_2, sodium hypochlorite or catalytic bed covered with manganese compounds (AWWA 2005, Koltuniewicz and Drioli 2008).

The permissible concentration of **heavy metals** is established in country's regulations at very low level. Conventional methods such as precipitation, extraction or ion exchange have many disadvantages, especially when large amount of water with low concentration of metal ions is treated. Membrane techniques (RO, NF, UF and ED) are often applied to remove heavy metals from water and wastewaters on industrial scale (Bodzek 2015, 2012, Bodzek and Konieczny 2011a, b).

Bakalár et al. (2009) presented the results of the removal of Cu, Ni and Zn using RO technology with composite polyamide membrane TW3-1812-50 (Dow Filmtec). They determined effect of the concentration of cations and TMP on the separation efficiency. In turn, Qdais and Moussa (2004) tested the removal of Cu^{2+} and Cd^{2+} ions by means of RO and NF. The RO removal efficiency was high and amounted to 98% for Cu and 99% for Cd, while for NF it was above 90%. NF is a better process for heavy metals removal, due to ease of operation, reliability and comparatively low energy consumption as well as high efficiency (Fu and Wang 2011). Murthy and Chaudhari (2008, 2009) reported the application of a thin-film composite polyamide NF membrane for the rejection of Ni ions from aqueous wastewater. The observed rejection was 98% and 92% for an initial feed concentration of 5 and 250 mg/L, respectively. For binary solution of Cd and Ni, separation efficiency for commercial NF membrane was 98.9% for Ni and 82.7%, for Cd ions. Retention of the cations in the NF process strongly depends on the energy of hydration, type and valence of co-ions passing through membrane as well as the TMP and pH.

The application of RO to the removal of heavy metals from wastewaters can be presented on the example of electroplating industry. Most frequently such effluents contain Cr, Cu, Cd, Zn, Ni, Pb and Ag ions, with concentration of 0.025 to 1 mg/L (Bodzek 1999). The RO process allows recovering of water of very high purity which can be returned to the technological process without additional treatment. The concentrated retentate may be reused in the electroplating bath (Bodzek 1999).

An interesting solution of the removal of heavy metals from aqueous solutions is the polymer enhanced ultrafiltration (PEUF) process (Korus 2012). It combines UF with metal complexation using water-soluble polymers, such as polyvinyl alcohol (PVA) and polyethyleneimine (PEI), and formed complexes is retained by UF membrane. The permeate is free of metal ions and retentate is subjected to regeneration in order to recover both, the metal and polymer. The process was applied for deactivation of radioactive liquid waste containing metal ions, i.e. Cs, Co, Sr, Sb and Te isotopes, as well as lanthanides ([140]La, [152]Eu and [169]Y) (Zakrzewska-Trznadel 2003). Korus (2012) conducted studies on the removal of Ni, Cu and Zn from synthetic and galvanic wastewater with the application

of the PEUF process. PVA, PEI, polyacrylic acid and sodium polyacrylate as complexing agents were used in connection with polysulphone and polyamide membranes. The obtained efficiency was 85–97% for polyamide membrane depending on the polymer to the metal ratio, the pH and the kind of metal. Sodium poly(styrene sulphonate), a water-soluble anionic polymer with strong cation-exchange groups was used as a complexing agent for lead ions complexing (Korus, 2010). The high rate of metal removal (85–99%) depended on ratio of metals to polymer, pH of the solution and operating UF conditions. It was possible to obtain the retentate with a concentration of Pb 20-times higher than the concentration of the feed solution which contained 50 mg Pb/L. Molinari et al. (2008) used PEI to study the PEUF process in the selective removal of Cu(II) from Ni(II) from solution. Preliminary tests showed that optimal chemical conditions for Cu(II) and Ni(II) complexation by the PEI were pH>6.0 and 8.0, respectively, and polymer/metal weight ratio of 3.0 and 6.0, respectively. Aroua et al. (2007) investigated the removal of chromium species from aqueous dilute solutions using PEUF process by three water-soluble polymers, namely chitosan, PEI and pectin. High rejections approaching 100% for Cr(III) were obtained at pH higher than 7 for the three tested polymers.

Recently, ED is frequently applied for the recovery of Au, Pt, Ni, Ag, Pd, Cd, Zn and Sn/Pb metals from wastewaters, first of all to treat washery effluents and wastewaters from electroplating plants (Bodzek and Konieczny 2011a, b). The solution of metal salt can be concentrated to the level that corresponds to the electroplating bath, e.g. for Ni from 1 g/L to 60 g/L (Bodzek 1999), which is much greater than with the application of RO. The obtained retentate is used for filling up the electroplating bath, whereas the dialysate is returned to the washing installation. Hence, practically the whole quantity of water and salts present in washery effluents can be utilized.

Liquid membrane processes, especially supported liquid membranes (SLMs), have been suggested for heavy metal removal due to their high specificity, high intensity, productivity and low energy requirements (Bodzek and Konieczny 2011a). SLMs are very effective for the removal and recovery of metals from wastewaters and process streams since they combine extraction and stripping, into one step. In the transport of metal ions in a SLM, the ion in the aqueous feed solution forms a complex with the extractant HA in the organic membrane phase at the interface between these two bulk phases as follows (Bodzek and Konieczny 2011a):

$$M^{2+} + 2(HA)_2 \rightarrow MA_2(HA)_2 + 2H^+$$
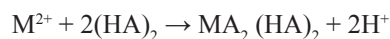
Then, the metal-extractant complex diffuses from this interface across the SLM to the interface between the organic phase and the aqueous strip solution, where the metal ion is stripped. The aqueous strip solution contains a strong acid, e.g. sulfuric acid. The stripping reaction is as follows:

$$MA_2(HA)_2 + 2H^+ \rightarrow M^{2+} + 2(HA)_2$$
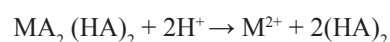
This stripping reaction also regenerates the extractant at this interface, which diffuses across the SLM back to the feed-membrane interface to complete the facilitated transport cycle.

Chromium

Chromium most commonly occurs as cation (Cr^{+3}) and Cr(VI) in the form of anions ($HCrO_4^-$ and $Cr_2O_7^{2-}$ ions, while at pH>6 as CrO_4^{2-}). Cr(VI) is a strong oxidant, which is easily reduced to Cr(III). Cr(III) is naturally present in the environment, as an essential nutrient, while Cr(VI) is formed in industrial processes. The traditional way of removing Cr from water and wastewater is reduction of Cr(VI) to the Cr(III), precipitation of $Cr(OH)_3$ and filtration of suspension (Owlad et al. 2009). Several other methods are also proposed, such as: adsorption and biosorption, ion exchange (used on an industrial scale), solvent extraction and electrochemical methods (Owlad et al. 2009).

The recovery and disposal of Cr can be made by high-pressure and low pressure membrane processes, liquid membranes, ED and EDI (Bodzek 2012, Bodzek and Konieczny 2011a, Koltuniewicz and Drioli 2008, Owlad et al. 2009). RO and NF can be used to directly separate Cr compounds from solutions. Studies carried out on Cr(VI) removal using RO Osmonics (Sepa-S) and cellulose acetate (CA) membranes show that retention coefficients amounted to 80–96% and 96%, respectively, depending on the membrane compactness (Bodzek et al. 2011a, Koltuniewicz and Drioli 2008, Owlad et al. 2009). The removal of Cr, using RO and NF, becomes cost-effective only if Cr concentration does not exceed 1–2 g/L (Bodzek 2012). The obtained filtrate is then devoid of Cr, but contains a significant amount of salt, which can be used for the preparation of etching baths. From the concentrated Cr solution hydroxide is precipitated, and then dehydrated sludge is dissolved in sulphuric acid and the resulting solution can be used directly, for example, in the process of tanning (Religa and Gawroński 2006). Retention coefficients of Cr in NF increase with the increase of pH for higher Cr(VI) concentrations. In strongly acidic pH Cr(VI) non-dissociated chromic acid (H_2CrO_4) is formed. The increase of pH to 6.5 causes the formation of hydrochromate ions ($HCrO_4^-$), the concentration of which increases with further pH increase. If pH is <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 pH is in the range of 1–7 and its concentration can be decreased by the increase of pH (Bodzek and Konieczny 2011a, b).

In the case of UF, the following possibilities of Cr removal can be used: the pretreatment by UF before further purification with conventional methods or high-pressure membrane processes, and application of PEUF or MEUF processes (Bodzek 2012, Koltuniewicz and Drioli 2008, Owlad et al. 2009).

Both the ED and EDI processes can also be applied for the removal and separation of Cr ions and their mixtures. Alvarado et al. (2009) studied the ability of EDI and ED for the removal of Cr(VI) from synthetic solutions containing 100 mg/L of Cr(VI), using anion-exchange membranes by Neosepta. In EDI process, a chamber with diluted solution was filled with mixed ion exchange resin. In the ED the removal of Cr amounted to 98% at energy consumption of 1.2 kWh/m³, whereas in the EDI process with the use of mixed bed 99.8% removal of Cr(VI) was reached at energy consumption of 0.167 kWh/m³.

Removal of organic pollutants

Dispersed substances and microorganisms

The turbidity of water is caused by the presence of suspended mineral and organic molecules of different sizes (colloids, coarse and fine suspensions). Usually, MF or UF are applied to decrease water turbidity to 1 NTU, which corresponds to drinking water level. There is little research in the literature on the turbidity removal with membrane processes, but it follows them clearly that the water of turbidity below 1 NTU can be obtained from water of the initial turbidity 100 NTU and greater (Taylor and Wiesner 2000). UF and MF are used for water clarification (Bodzek and Konieczny 2005). The study of application of UF "Aquasource" module (France) showed that drinking water of turbidity 0.03–0.04 NTU can be obtained from waters with turbidity from 0.1 to 11.5–24.8 NTU (Taylor and Wiesner 2000). Similar results were obtained for various membrane modules (Taylor and Wiesner 2000). When water contains colloidal fraction, membrane filtration is integrated with coagulation in order to obtain flocks of greater size (Bodzek and Konieczny 2005). Table 6 summarizes the percentage removal of turbidity and natural organic matter (NOM) by various membrane techniques (Bodzek and Konieczny 2006).

Water can become naturally biologically contaminated neededgustrial purposes, gically during its treatment or transport in pipelines (Bodzek et al. 2019). Water, which contains viruses, bacteria and protozoa as well as other microorganisms (fungi, algae, snails, worms and crustaceans), if dedicated to potable purposes, may seriously harm human health (Taylor and Wiesner 2000).There are several methods which can be used for water disinfection, but some of them have a number of advantages and disadvantages. It is also valid to treated and untreated wastewater discharge to natural water source and sewage systems. Low-pressure membrane filtration can be applied to water disinfection because it practically removes viruses, bacteria and protozoa. The size of viruses' cells is of a range of 20–80 nm, while pore size of UF membranes is below 10 nm, hence, theoretically, those cells should be completely rejected. The sizes of bacteria (0.5–10 μm), cysts and oocysts (3–15 μm) are larger, thus UF and MF can practically completely remove them (Bodzek and Konieczny 2005, Taylor and Wiesner 2000). The comparison of pore sizes of UF and MF membranes with sizes of microorganisms indicates that UF process can be successfully used for water disinfection (Bodzek and Konieczny 2005). In Figure 4, the reduction of viruses, bacteria and protozoa in water for different UF membranes is shown (Chen and Chen 2016, Kosiol et al. 2017, Taylor and Wiesner 2000). The obtained removal for all types of microorganisms was greater than 4 log, i.e. 99.99%.
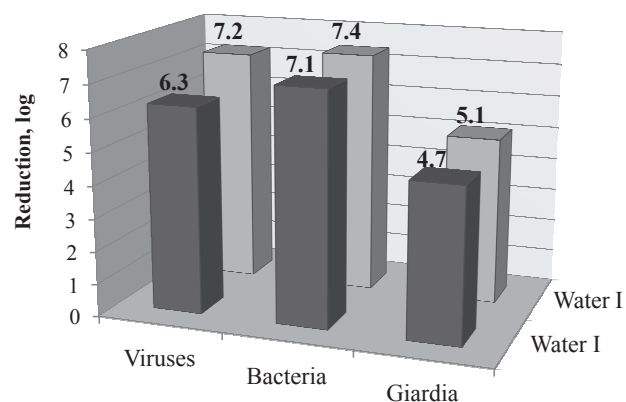
Fig. 4. Removal of microorganisms by means of UF

Practice has shown, however, that the UF membranes are not always able to completely eliminate bacteria and viruses from water. This is primarily connected with imperfections in the membranes and membrane modules and the secondary development of bacteria in water during its transport to the final recipient of water. In commercial membranes skin layer can have discontinuity through which micro-organisms can pass, as well as seals of the raw water from the permeate streams 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 modules (Bodzek and Konieczny 2005). Furthermore, it was found that cells of microorganisms can penetrate membrane pores with diameters much smaller than the dimensions of the cells (Sosnowski et al. 2004).

Natural organic matter

NOM in water ecosystems is the mixture of many compounds with various properties and chemical structure, first of all soluble in water fulvic acids (MW≤2000 Da), hydrophobic humic acids (MW≤2000–5000 Da) and insoluble humins (Bodzek 2015). Humic substances are usually dissolved in water, colloids and non-dissolved admixtures, and the presence of a given form depends on water pH. The dissolved NOM fraction in natural water is equal to ca. 80–90% of total NOM. Humic substances cause intensive color of water from brown to black. Additionally, complexation reactions of humic substances with heavy metals or adsorption onto toxic organics cause many health hazards. Humic substances are also precursors of disinfection by-product (DBP) (Bodzek et al. 2019).

The removal of NOM is an important processes in water treatment technology. The application of membrane techniques in water treatment can remove DBP precursors including part of NOM (Wilf 2010). Application of chloride to water disinfection results in the formation of DBPs, including trihalomethanes (THMs), halogenated acetic acids, and other halogenated compounds (Bodzek 2015, Bodzek and Konieczny 2005). Pressure-driven membrane processes allow for controlling the formation of DBP, because membranes retain NOM including DBP precursors (Van der Bruggen and Vandecasteele 2003). The removal of NOM also decreases the amount of chlorine required for disinfection, what is necessary in the distribution system (Bodzek 2015, Bodzek

Table 6. Turbidity and NOM removal using membrane techniques

Process	Pressure, kPa	Turbidity removal, %	NOM removal, %
Microfiltration	<100	>97	<2
Ultrafiltration	<100	>99	<10
Nanofiltration	<500	>99	>90

and Konieczny 2005). Effectiveness of NOM removal depends on properties of membranes, thanks to a very wide molecular size distribution of NOM (from 1 nm to 0.45 μm) (Bodzek 2015).

The application of NF or RO enables total removal of NOM, including DBP precursors from water, however it is very often limited by high concentration of colloids and suspensions in surface waters (Bodzek and Konieczny 2007). UF and MF alone can be directly used to remove greater fractions of NOM, including part of high molecular weight (MW) DBP precursors, whereas medium and low MW compounds can be eliminated in integrated systems (Urbanowska and Kabsch--Korbutowicz 2016). The removal of humic substances from water by direct UF is possible only with modules with dense membranes (MWCO 1000 Da) or hybrid systems of UF or MF with coagulation, activated carbon adsorption or oxidation (ozonation, photocatalysis) (Bodzek et al. 2011, Urbanowska and Kabsch-Korbutowicz 2016). Recently, ion exchange – UF/MF integrated process has been proposed for NOM removal, especially MIEX resins (Kabsch-Korbutowicz et al. 2006, Rajca 2012). Such solution is better than coagulation-UF system. In Table 7 the comparison of effectiveness of NF, UF and MF processes in NOM content control in natural waters is shown.

Organic micropollutants

In waters and wastewaters the following main groups of micropollutants are present (Bodzek 2015, Bodzek and Konieczny 2018): disinfection by-products (DBPs), endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs). Some DBPs and PhACs in the aquatic environment may also have estrogenic biological activity. Organic micropollutants (OM) have strong carcinogenic and mutagenic properties.

The presence of NOM in water may change the chemical properties of organic micropollutants, i.e. increase solubility of non-polar compounds, cause hydrolysis and photo-degradation, and restrict the bioaccessibility by aquatic organisms (Bodzek 2015). The removal of OM during water treatment is usually performed using adsorption on activated carbon or advanced oxidation processes (AOPs) (Bodzek and Konieczny 2018). The first method is unattractive when the amount of NOM in water is high, whereas during AOPs process there is a possibility of formation of DBPs with biological activity (Bodzek and Konieczny 2018). Application of membrane processes seems to be a good solution. They can be carried out as independent processes as well as a part of integrated/hybrid systems with coagulation, adsorption or in membrane bioreactors (Bodzek 2015, Bodzek and Konieczny 2018).

Disinfection by-products

DBPs is a group of substances, which are formed during the reaction of disinfectants with water pollutants. The most important of DBPs are trihalomethanes (THMs) and haloacetic acids (HAAs) (Bodzek 2015, Bodzek and Konieczny 2018).

RO and NF are most often applied to remove THMs, HAAs and other halogenated hydrocarbons from water. The study showed that retention of RO and NF with Osmonic membranes depended on the membrane permeability, i.e. the higher permeate flux the lower retention (Bodzek 2015, Bodzek and Konieczny 2018). It was found that the MW increase of THMs resulted in the retention increase according to the following series: $CHCl_3 < CHBrCl_2 < CHBr_3 < CHBr_2Cl$. The removal rate of chloroform varied from 67 to 87%, bromodichloromethane 65–96.5%, dibromo-chloromethane 57–90.5% and tribromomethane 61–92% depending on the applied membrane type (Bodzek 2015). In another study, Uyak et al. (2008) showed that for NF200 and DS5 Osmonics membranes operating pressure did not affect THM retention, whereas initial concentration of THM had noticeable influence on flux and retention.

NF process is also suggested for the removal of HAAs (chloro-, dichloro- and trichloroacetic acid; bromo- and dibromoacetic acid) from water. The high reduction of HAAs (90–100%), caused first of all by repulsion forces, can be obtained for dense negatively charged membranes, e.g. ES10 aromatic polyamide membrane (Nitto-Denko Co. Ltd.) (Chalatip et al. 2009). Wang et al. (2018) obtained retention of HAAs amounted to >75% with a five-stage RO process during production of drinking water. Environmental and operational variables like pH, operating pressure, water matrix, and membrane age also played important roles in HAAs removal. Increasing pH from 6.5 to 8.5 and membrane age apparently enhanced HAA rejections.

There are also studies on the removal of HAAs from water in bioreactor with immobilized enzymatic ultrafiltration membranes (Kowalska et al. 2011). Enzymes isolated from activated sludge strains of bacteria were used. 37% of the monochloroacetic acid, 35% of monobromoacetic acid and 48.4% of dichloroacetic acid degradation were obtained (Kowalska et al. 2011).

Endocrine Disrupting Compounds

Recent investigations showed that EDCs appear more often in natural waters and wastewaters, even biologically purified

Table 7. Comparative assessment of MF, UF and NF processes for NOM removal (Bodzek and Konieczny 2017)

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

(Bodzek 2015). EDCs includes endogenic hormones, natural organic compounds produced by fungi (mycoestrogenes) and plants (phytoestrogenes), and a wide range of anthropogenic MP among which the most important are (Bodzek and Konieczny 2018):

– polycyclic aromatic hydrocarbons (PAHs) and surfactants,
– plant protection products (pesticides, herbicides and insecticides),
– phthalates, and phenols compounds (alkylphenols, bisphenols),
– synthetic hormones.

Major sources of EDCs are food and drinking water, to which these MPs are introduced with the rain, landfill leachate and industrial wastewater. EDCs are present in natural waters in the concentration ranging from ng/L to µg/L.

Phytoestrogens and **mycoestrogenes** can be removed by RO and NF processes with effectiveness amounting to 70–93%, depending on the type of compounds and membranes (Dudziak and Bodzek 2010). Dudziak (2013) studied the efficiency of the removal of selected mycoestrogens from water in coagulation, sorption on activated carbon and NF processes. He found that the coagulation removed mycoestrogens in 34%, adsorption with PAC>80%, whereas the NF from 70 to 88%.

One of the main anthropogenic MPs in drinking water sources are **polycyclic aromatic hydrocarbons** (PAHs). PAHs are harmful to human health, and most of them are very carcinogenic, e.g. benzo(a)phyrene (permissible concentration in drinking water – 0.010 µg/L and the sum of benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, ideno(1,2,3-cd)pyrene – 0.1 mg/L). The retention coefficient of PAHs, by means of RO and NF, was in the range from 85.9% to 99%, independently of MW of a compound and concentration (Bodzek 2015, Bodzek and Konieczny 2019, Luks-Betlej et al. 2001). Also UF membranes removed PAHs to a high level, despite the fact that the MW of these compounds are smaller than the cut-off of the UF membrane (Bodzek 2015, Luks-Betlej et al. 2001). The cause of this phenomenon was the adsorption of PAHs on the surface of the UF membranes (Bodzek 2015). Studies on the removal of PAHs from municipal landfill leachates and industrial wastewaters were carried out by Smol et al. (2014a). The total concentration of PAHs in permeates after RO was in the range from 3.9 to 5.1 µg/L, at initial concentration of PAHs in the raw landfill leachates amounting to 17.5–30.4 µg/L. The rate of the removal of PAHs in RO was 71% (for individual hydrocarbons were in the range 19–100%), and after initial treatment on sand bed it was equal to 89%. The removal of PAHs by means of NF and RO for biologically pretreated wastewater generated at coke plant was also high (Smol et al. 2014b). It was found that in the wastewater after the coagulation, the concentrations of PAHs gradually lowered to the value 58.9 µg/L, at the initial concentration equal 94.7 µg/L. The total content of 16 PAHs after NF reached 18.7 µg/L, and after RO 5.94 µg/L. The results show that a more effective PAHs removal is achieved using the integrated system: coagulation – reverse osmosis (Smol et al. 2014b).

Pressure driven membrane techniques are alternative methods for the removal of **surfactants** (SAAs) from water, while the effectiveness and the type of process depends on the concentration of the SAA (Bodzek 2015). When the concentration is below critical micelle concentration (cmc) the application of NF, eventually RO membranes, are suggested. In the case when the concentration of SAAs in water is greater than cmc, UF process can be used (Kowalska 2012).

Plant protection products (pesticides, herbicides and insecticides) can be effectively removed from surface and ground waters by NF or integrated systems of MF- or NF-activated carbon adsorption. NF membranes eliminate pesticides of MW above 190 Da to the amount below the limit of detection, and, generally, the retention coefficient varies from 50 to 100%, depending on MW and concentration MPs in water (Bodzek 2015, Taylor and Weisner 2000). Research on the application of UF process to the separation of atrazine from water was carried out by several scientists (Majewska-Nowak et al. 2001, Sarkar et al. 2007). The efficiency of the process depends on the type of membrane material and membrane compactness. The best separation shows membranes with cut-off about 1–2 kDa (retention rate – 60%) (Majewska-Nowak et al. 2001). The increase of the efficiency up to 85–95% can be obtained during UF at the presence of NOM and/or cationic polyelectrolyte.

The presence of **phthalates** in the environment is caused by massive production of plastics, mainly PVC, in which they are used as plasticizers. 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. The surprisingly high retention of phthalates was observed during both, the RO and NF processes (initial concentration 40 µg/L) (Bodzek 2005, Bodzek et al. 2004). Retention rates achieved for diethyl phthalate, di-n-butyl and di-2-ethylhexyl were very high and amounted from 89.7% (UF) to 99.9% (RO and NF). The results obtained during the removal of phthalates of MW 222–391 Da revealed that the MW of a compound did not influence the removal effectiveness.

Phenolic xenoestrogenes (octylphenol, nonylphenol, bisphenol A and bisphenol F) can be effectively removed from water by means of NF. The retention coefficient of phenolic xenoestrogenes strongly depends on a type of removed compound and a membrane type (Bodzek 2015, Dudziak and Bodzek 2008). The high retention of octylphenol and nonylphenol in the range from 61 to 73% was observed for SF-10 and DS-5-DK membranes, while in the case of bisphenol A retention was higher (for membranes DS-5-DK – 69% and for MQ – 16–75%) (Dudziak and Bodzek 2008).

Pharmaceutical and Personal Care Products
One of the most important and quite specific and anthropogenic MPs affecting the environment are compounds called **Pharmaceutical and Personal Care Products** (PPCPs). This group includes compounds with pharmaceutical activity, and substances used by people to maintain personal hygiene (Heberer and Feldmann 2008). PPCPs enter quite significantly to surface water and groundwater as well as wastewaters. Main sources of aqueous environment pollution with pharmaceuticals are households and hospitals, diagnostic units, pharmaceutical plants and livestock farms. Studies on efficiency of the removal of PPCPs in wastewater

treatment plants have shown that biological methods are not always sufficient (Bodzek and Konieczny 2018). The other methods of PPCPs removal from water and wastewater are advanced oxidation, activated carbon adsorption and membrane processes (NF and RO) (Snyder et al. 2007), and, in the case of wastewater, membrane bioreactors (Clara et al. 2005, Heberer and Feldmann 2008).

Recently, an increase in concentrations of the **synthetic hormones** (α-ethinylestradiol, mestranol and diethylstibelstrol) resulting from discharges of these pharmaceuticals from households, hospitals and pharmaceutical plants has been observed. It was shown that this type of pollutants can be eliminated by means of RO or NF. RO membranes totally eliminate particular hormones while retention coefficients obtained for NF and UF membranes were lower (Dudziak and Bodzek 2008). A novel hybrid membrane configuration, consisting of UF/NF and polymer-based activated carbon, was developed and investigated for the removal of natural hormones with a particular focus on estradiol (E2) (Tagliavini and Schäfer 2018). Retention coefficients amounted to 60–80% depending on membrane type (UF or NF). Removal of hormones from wastewaters is also proposed by membrane bioreactors, equipped with polyvinylidene difluoride membrane. Comparing the obtained results with the conventional activated sludge installation working in a full-scale (Zuehlke et al. 2006) it was stated that in the case of MBR, estradiol and estrone were removed in 99%, and ethinyloestradiol in 95%, but in conventional treatment installation more than 90%.

NF and RO processes, used for the purification of wastewater and natural waters, can also be used for the removal of residues of PPCPs (Bodzek 2015, Heberer and Feldmann 2008). The retention coefficients of polar and low volatile PhACs and with low hydrophobicity amounted only to 40%. For polar organic compounds retention depends on the dipole moment and pH (Kimura et al. 2005). Negatively charged PhACs such as diclofenac is removed in more than 90–95%, thanks to electrostatic repulsion (Bodzek 2015). For neutral compounds, retention takes place according to molecular exclusion and adsorption. For example, the neutrally charged antipyretic phenacetin or anti-inflammatory and antirheumatic ibuprofen show retention >20%, because they are adsorbed on membranes with relatively high hydrophobicity (Bodzek 2015). On the other hand, another neutral antipyretic medicament, piramidon, is always retained in more than 70%, suggesting that its retention is affected also by other phenomena. The retention of pharmaceuticals in the RO and NF processes is also depended by membrane material (Heberer and Feldmann 2008). For example, polyamide membranes had higher efficiency (57–91%) than cellulose acetate membranes. The concentration of PhAC also influences the retention rate (Radjenović et al. 2009). For example, at a concentration of 100 ng/L retention was lower (14–72% for NF and for 50–80% RO) compared to higher concentration amounted to 100 μg/L (19–93% for NF and 71–95% for RO).

Pressure-driven membrane processes (MF, UF, NF and RO) were also studied for the removal of EDCs, pharmaceuticals and personal care products in a pilot scale and industrial installations (Heberrer et al. 2008, Snyder et al. 2007). Heberrer et al. (2008) performed investigation with three-stage installation of capacity equal to 10,000 L/h which included duplex bag filters with a particle separation <0.5 μm, ultrafiltration and reverse osmosis performed as one or two stage process. The substrate of the study was water from Teltow Channel (Berlin) and treated wastewater from Ruhleben municipal wastewater treatment plant (Berlin). The presence of PhAC in treated water from Teltow Channel was not observed, whereas in RO permeate obtained during wastewater treatment the amount of pharmaceutical was below 10 ng/L for both, one and two stage configurations (Table 8) (Heberrer et al. 2008).

It was found that MBR installations used in wastewater treatment improved the efficiency of the removal of PPCPs in reference to conventional wastewater treatment plant. It was caused not only by the extension of retention time and increasing age of biomass, but also by increase of concentration

Table 8. 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
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
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

and adsorption of MPs on the flocks of activated sludge. MBRs with immersed UF modules have been checked for removal of selected pharmaceuticals (clofibric acid, diclofenac, ibuprofen, ketoprofen, mefenamic acid and naproxsen) (Kimura et al. 2005). In the experiments higher removal rates of ketoprofen and naproxen for MBR than for conventional treatment system have been observed. Removal rates of phenazone, propyphenazone, and **formylamino-antipyrine** were also lower in conventional activated sludge installation (15%) than in the MBR (60–70%) (Zuehlke et al. 2006). The removal of pharmaceuticals using the MBR depended on the structure of the PhAC molecules, e.g. the number of aromatic rings and pH, i.e. higher removal of PhAC was observed at low pH conditions due to adsorption on activated sludge flocks. Radjenović et al. (2009) observed that in MBRs there is a significant improvement in the removal efficiency of regulators of lipids and cholesterol, statin drugs (gemfibrozil, bezafibrat, clofibric acid and pravastatin), β-blockers (atenolol and metoprolol), antibiotics (ofloxacin and erythromycin) and some painkillers and anti-inflammatory drugs. Other studies indicate a very high removal rate of clofibric acid and diclofenac in plants equipped with the MBR, compared to conventional wastewater treatment (Radjenović et al. 2009). Thus, the use of bioreactors allows to receive treated wastewater of a very high quality, so that the load of the MPs introduced into surface waters is lower than that in the case of wastewaters coming from conventional treatment plants. The results presented in table 9 (Barceló et al. 2009) show a distinct advantage of the membrane bioreactors over the processes in typical wastewater treatment plants.

Mamo et al. (2018) compared the removal of selected PhACs by means of MBR-RO and MBR-NF processes from wastewater. RO membranes showed almost complete removal of PhACs (>99%) at different process conditions, whereas for NF, retention was lower (>90%). The choice between using a RO versus NF membrane depends on the permeate reuse, the discharge limits and the membrane MW cut-off and surface morphology. Also process parameters (membrane recovery and average permeate flux) and membrane condition have a significant effect on the removal of PhACs.

Concluding remarks

Membrane processes, such as RO, NF, UF, MF, ED and MBR, can be used for inorganic and organic pollutants removal from natural waters and wastewaters.

Introduction and development of membrane techniques in the production of drinking water and purification of wastewaters, in the last 40 years, was important stage in the field of water treatment effectiveness. Desalination of sea and brackish water by means of RO is an established way for drinking water production. Significant improvements in design of RO, the application of alternative energy sources, modern pretreatment and new materials have contributed to the success of the process. At the moment investment costs for large desalting installations are similar to the modern conventional water treatment plants. NF is the method of water softening, because NF membranes can retain di- and multivalent ions, but not monovalent. Drinking water containing viruses, bacteria and protozoa, as well as other microorganisms, can be disinfected by means of UF. Viruses are retained by UF membranes, whereas bacteria and protozoa using both UF and MF membranes. For the removal of NOM it is possible to use direct NF or integrated systems combining UF or MF with coagulation, adsorption and oxidation. NOM is regarded as precursors of disinfection by-products, so its removal from water is very important.

Inorganic and organic micropollutants are found in dangerous concentrations in water sources. Various classical treatment technologies which are used for their removal from water environment represent serious exploitation problems. The use of NF, RO and ED, in the treatment of water containing micropollutants for drinking and industrial purposes can provide more or less selective removal of the pollutants. Very important are disinfection by-products, residue of pharmaceuticals and

Table 9. The efficiency of removal of pharmaceuticals in installations with MBR,
as well as in conventional wastewater treatment plants

Pharmaceutics	Efficiency of the removal with MBR [%]	Efficiency of the removal in conventional wastewater treatment plant [%]
Naproxen	99.3	85.1
Ketoprofen	91.9	51.5
Ibuprofen	99.8	82.5
Diclofenac	87.4	50.1
Acetaminophen	99.6	98.4
Propyfenazon	64.6	42.7
Sulfamethoxazole	60.5	55.6
Erythromycin	67.3	23.8
Hydrochlorothiazide	66.3	76.3
Glibenclamide	47.3	44.5
Gemfibrozil	89.6	38.8
Bezafibrat	95.8	48.4
Klofibric acid	71.8	27.7

endocrine disrupting compounds. For endocrine disrupting compounds, special attention is paid onto polycyclic aromatic hydrocarbons, surface-active substances, chlorinated pesticides, phthalates, alkylphenols, polychlorinated biphenyls, hormones, synthetic pharmaceuticals and other substances disposed to the environment. The application of MF and UF in inorganic and organic micropollutants removal is possible in integrated systems with coagulation, adsorption, complexion with polymers or surfactants and biological reactions.

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Membranowe techniki separacji – usuwanie domieszek i zanieczyszczeń nieorganicznych i organicznych ze środowiska wodnego

Streszczenie: Zanieczyszczenia występujące w ujmowanych wodach, powodują, że skuteczne oczyszczanie jest kłopotliwe, a układ (schemat technologiczny) oczyszczania powinien być opracowywany indywidualnie dla danej wody na podstawie badań technologicznych. Aby zapewnić wymaganą jakość wody do picia bezpiecznych dla zdrowia i życia konsumentów, często niezbędne jest stosowanie niekonwencjonalnych i wysokoefektywnych procesów, mimo podwyższenia kosztów i potrzeby bardzo starannej i profesjonalnej eksploatacji układu oczyszczania wody. Ponadto, niedogodności związane z tradycyjnym oczyszczaniem wód naturalnych oraz zmieniające się podejście, co do koncepcji uzdatniania wód dla celów konsumpcyjnych, przede wszystkim wzrastające wymagania odnośnie jakości wody do picia, stwarzają możliwości zastosowania nowych technik separacji, wśród których metody membranowe mają największe zalety i możliwości i są obecnie brane pod uwagę jako procesy alternatywne. W uzdatnianiu wody i oczyszczaniu ścieków stosuje się przede wszystkim techniki membranowe, których siłą napędową jest różnica ciśnień po obu stronach membrany, ale brane są pod uwagę też inne procesy jak elektrodializa, perwaporacja, destylacja membranowa i membrany ciekłe. Wybór odpowiedniego procesu membranowego zależy od zakresu wielkości występujących i usuwanych z wody zanieczyszczeń i domieszek. Techniki membranowe mogą być stosowane do usuwania zanieczyszczeń z wody jako procesy samodzielne, lub w połączeniu z uzupełniającymi procesami jednostkowymi, tworząc systemy hybrydowe. W pracy omówiono możliwości wykorzystania technik membranowych w uzdatnianiu wód naturalnych. Odwrócona osmoza zatrzymuje jony jednowartościowe i większość związków organicznych małocząsteczkowych i jest stosowana do odsalania wód oraz do usuwania jonów azotanowych i mikrozanieczyszczeń organicznych. Membrany nanofiltracyjne zatrzymują koloidy, szereg związków organicznych małocząsteczkowych oraz jony dwuwartościowe; można je zatem zastosować do zmiękczania wody i usuwania mikrozanieczyszczeń organicznych. Ultrafiltracja i mikrofiltracja stanowią barierę dla substancji rozproszonych i mikroorganizmów i dlatego można je stosować do klarowania i dezynfekcji wody oraz jako metoda usuwania mętności wody. Procesy hybrydowe obejmujące techniki membranowe stosuje się do uzdatniania wody do picia w połączeniu z ozonowaniem, koagulacją, adsorpcją na węglu aktywnym do usuwania niżej cząsteczkowych związków organicznych lub w bioreaktorach do usuwania azotanów.