Michał Bodzek, Krystyna Konieczny

APPLICATION OF MEMBRANE TECHNIQUES IN THE REMOVAL OF INORGANIC IMPURITIES FROM WATER ENVIRONMENT– STATE OF ART

Abstract. 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 as well as electrodialysis. 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. 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 micro-pollutants, also inorganic. To remove nitrate ions and fluoride, boron and metals (Fe, Mn and heavy metals) is successfully applied reverse osmosis, nanofiltration and electrodialysis, as well as bioreactors and ultrafiltration integrated with coagulation and oxidation.

Keywords: Membrane processes, removal of inorganic compounds, water desalination and softening, removal of anions and metals.

INTRODUCTION

The contamination of drinking water sources with inorganic compounds is a matter of concern, because of their harmful effect on human health. Some of these compounds are highly soluble in water and dissociate completely, resulting in ions that are chemically stable under normal water conditions. Examples of polluting substances, besides salinity and hardness, include anions (first of all nitrate, perchlorate, bromate, arsenate and fluoride) and metals (Fe, Mn, Cr and other heavy metals), for which the proposed guideline values for drinking water quality are quite low (μg/l - mg/l) owing to their carcinogenic effects or other risk factors to public health [3,4,8,26,27], and therefore, the part of them can be referred as micro-pollutants.

Technologies available for the treatment of water contaminated with inorganic ionic compounds include physical, chemical and biological processes [3,4,8,26,27]. In the first type of process, ions are concentrated rather than destroyed. A brine stre-

Michał BODZEK, Krystyna KONIECZNY – Silesian University of Technology, Institute of Water and Wastewater Engineering

am containing a high concentration of ions is generated, which must then undergo additional treatment and disposal. Large-scale plants usually apply coagulation with aluminum or iron salts followed by filtration but a number of anions (e.g. nitrate) have very little tendency to coordinate with metal ions and low potential for co-precipitation [8,26,27]. Also small scale treatment facilities often use ion exchange and/or adsorption; however, regeneration and additional costs, associated with the disposal of the regenerants used, represent serious problems. Membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF), Donnan dialysis (DD), electrodialysis (ED) and liquid membranes (LM), if properly selected, offer the advantage of producing high quality drinking water [3,4,8,26,27]. In many cases, one membrane process can be integrated with another to produce water of even higher quality (hybrid systems). Among them, membrane bioreactors (MBR) are especially appropriate for some anions removal, since it offers selective removal of the target anion from water due to anoxic bacteria, which under appropriate conditions (pH, oxidation–reduction potential, temperature, etc.) can use anions as electron acceptors and organic (heterotrophic microorganisms) or inorganic (autotrophic microorganisms) compounds as electron donors for their growth [8,26,27]. For cations removal ultrafiltration enhanced with polymers or surfactants are frequently used [4].
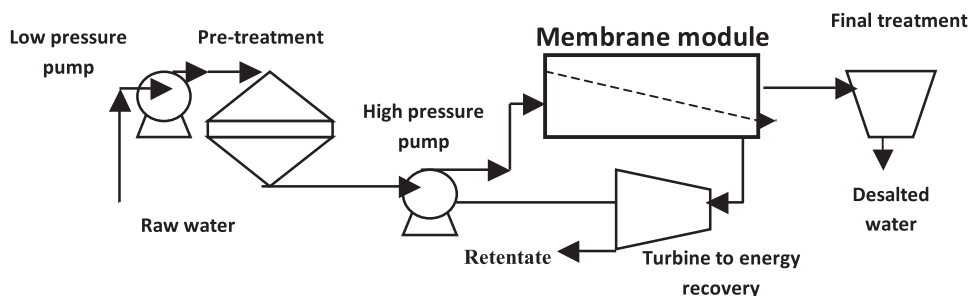
DESALINATION

Desalination of water is one of the ways of obtaining drinking water from seawater (35,000 mg/l) and underground brackish waters (2,000-5,000 mg/l). Most significant in view of drinking water production are desalination processes based on thermal and membrane separation methods [3]. For membrane desalination, reverse osmosis and electrodialysis are principally applied [3]. The most frequently used thermal method is the multi-stage flash process (MSF) [3,29].

Brackish water desalination was the first successful application of reverse osmosis [29], and the first large-scale plants appeared already in the late 1960s. In the 1980s RO became competitive with the classical distillation techniques. At present, over 90% of RO installations produce drinking water and ultra-pure water for the needs of power industry, semiconductors etc. [29]. 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) [3,4,12,29].

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 [3,12,29]. It can be very simple, comprising only filtration processes without any chemicals added if the de-

salination involves clean ground waters, and in the case of surface waters, the treatment procedure can include filtration with coagulation and adsorption on activated carbon. Also UF and MF are applied as the suitable methods for pretreatment before desalination, removing suspended substances, some organic compounds and microbiological pollution [12,29]. In the membrane system for desalination, hollow-fiber or spiral-wound modules of cellulose acetate, aromatic polyamide and composite membranes are used [29]. 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 [3,12,29]. The preparation of water after its desalination depends on its destination. Desalted water for drinking and domestic purposes should be degassed (decarbonisation), subjected to pH and alkalinity correction, chlorination and remineralization [3,12,29].

Fig. 1. Diagram of water desalination system using RO method with energy recovery from retentate
Rys. 1. Schemat systemu odsalania metodą RO z odzyskiem energii z retentatu

The advantage of reverse osmosis is a relatively low cost of the desalted water [3]. 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 depends on the water quality, the size and installation location, qualification of workforce, price and the nature of applied energy and the type of the technology used [3,12,29]. Roughly estimated that the costs of desalination of seawater were 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 21st age [12,29] 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 [12,29]. 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 [3,12,29].

Water desalination requires large of energy, which constitutes 25-40% of all desalination cost [3,4,8]. 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 [12,29]. For example: energy consumption for MSF process amounted to ≈10 kWh/m^3, whereas for desalination of sea water with RO 7.7 kWh/m^3 and for brackish water only 0.8 kWh/m^3 [3].

Integrated/hybrid systems in desalination are made through combing reverse osmosis with thermal processes and nanofiltration with RO or distillation, as well as various energy sources [3,4,29]. Cost of such a solutions is frequently lower than every process alone [3]. In the case of integration MSF with RO, takes place only mixing MSF distillate with RO permeate. 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 [12]. 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 and RO-wind-PV [12,29].

WATER SOFTENING

In 80s, nanofiltration had become established and known method of water softening, as an alternative to chemical softening and ion-exchange method [3,6,25,28]. 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 1) [3]. In such a way treated water should have hardness not higher than 60-500 mg $CaCO_3$/l, what is in accordance with drinking water regulations. Ion selectivity of NF membrane is due to the presence of groups with negative charge (-COOH or -SO$_3$H), 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 NF the solution components of the diameters about 1-3 nm are retained and pressure difference is in the range 1-3 MPa [3], that means below the values that would be necessary for RO to obtain the same fluxes.

Table 1. Comparison of the characteristics of NF and RO membranes (FilmTec)
Tabela1. Porównanie charakterystyk membran do NF i RO (FilmTec)

Membrane	Pressure MPa	Retention coefficient, %			
		NaCl	MgCl$_2$	NaNO$_3$	MgSO$_4$
RO - 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

The diagram of the NF installation is similar to that which is applied in the RO desalination process [3,6] 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 (generally aeration and disinfection). Costs of membrane softening not deviate much from the chemical softening, but are less than the cost of water desalination by RO method.

The performed investigation confirmed the possibility to obtain soft and low-hardness waters (total hardness <200 mgCaCO$_3$/l) from very hard and hard waters (total hardness >300 mgCaCO$_3$/l) (table 2) [28]. High retention level of total (>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 [6,28]. Total hardness removal during NF softening depends also on type of membrane used (table 2) [25], and it is possible to choice the proper membrane for a given type of water salinity and hardness.

Table 2. Water softening results using NF membranes with different compactness
Tabela 2. Wyniki zmiękczania wody za pomocą membran do NF o różnej zwartości

Membrane	NF-70 Filmtec	NF-45 Filmtec	UTC-20 Toray	UTC-60 Toray	NF Osmonics	
					Well water I	Well water II
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	590[*)]	560[*)]
Retention coefficient, %	95	59	95	79	69	68

[*)] in mg/l

REMOVAL OF ANIONS

Pressure driven membrane processes

The reverse osmosis process is highly efficient in removal of inorganic anions from drinking water and additionally, it guarantees safe detoxification [16]. The complete desalination, however, is undesired according to possible corrosion problems and remineralization requirements. 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 NF have negative electrical charge in neutral and alkaline solutions. Thus, the separation of anions not only consists in the difference in the rate of convection 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 [26]. The charge of surface of NF membranes is caused not only by the pre-

sence 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 [26] and varies from negative values to zero in iso-electric point of a membrane, up to positive values in acidic environment (usually pH<4), according to the adsorption of cations. Such a pH dependence influences on anions separations, hence the selection of proper process conditions is crucial for the application of NF. NF process is much more sensitive to ionic strength and pH of raw water than RO. 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 3) [26].

Table 3. Pressure-driven membrane processes for removal of inorganic anions in the production of drinking water
Tabela 3. Ciśnieniowe procesy membranowe w usuwaniu anionów nieorganicznych w produkcji wody do picia

Process	Membrane and manufacturer	Anion	Water origin
RO	RO 4040-LHA-CPA2 (Hydranautics)	NO_3^-	Natural with $188 mgNO_3^-/l$ (South Africa)
RO, NF	Different membranes (Osmonics)	NO_3^-	Tap water (Poland)
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^-	Ground water (Belgium)
NF	NF300 (Osmonics)	NO_3^-, F^-	Ground water (California, USA)
NF	Filmtec NF45 (Dow Chemical)	F^-	Model water
NF	Filmtec NF70 (Dow Chemical)	F^-	Model water

The pollution of natural waters with nitrates is a result of application of nitrogen fertilizers and of solid and liquid wastes to the environment [3]. The permissible content of nitrates in drinking water is established at the level of 50 mg/l (10 mg N/l). The reverse osmosis process allows decreasing 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 RO membranes characterise with high values of the retention coefficient of NO_3^- (ca.91-96%) and inorganic salts, thus the required decrease of nitrates concentration in drinking water can be achieved by mixing the permeate and raw water [3,16]. 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 RO membranes [25]. Thus, NF can be used as a first step in nitrates removal process integrated with RO or ion exchange [3,16]. 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 exploitation of RO and ion exchange processes.

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 [16,26]. The application of reverse osmosis in fluorides removal is connected with partial demineralization of water, what is the main disadvantage of the process [16]. RO membranes for water desalination allow for the removal of 98-99% of salts, what practically results in almost total retention 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) [21]. During treatment of water which characterise with high fluoride content the application of nanofiltration is beneficial as the remineralisation of permeate is not always required. The final concentration of F$^-$ ions in permeates, obtained for commercially available NF membranes, i.e. NF-90 and NF-270 (by FilmTec) and TR-60 (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 [23]. The results obtained during similar studies confirmed the possibility of drinking water production from brackish water 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) [14]. 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 results from the differences in hydratation energy of particular ions, as the higher energy causes the better retention (hydratation energy of F$^-$ equals 515 kJ/mol while for Cl$^-$ – 381 kJ/mol) [14]. It explains the possibility of selective desalination of brackish water containing F$^-$ using NF and allows producing drinking water cheaper than in case when RO is applied.

Boron appears in the environment mainly in the form of boric acid (H$_3$BO$_3$) and borates [2,16]. 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 [2]. In the EU countries and in Poland the permissible concentration of boron in drinking water as well as in wastewater disposed to natural water and soil is established at 1.0 mg/l, while for industrial wastewater disposed to sewage 10 mg/l [2]. Investigation aimed at removal of boron compounds from aqueous solution is of especial importance for desalination by RO. The retention of boron for RO membranes under low or neutral pH varies from 40 to 60%, what is not sufficient to obtain the permissible level for drinking water, even for seawater desalination (content of F$^-$ below 5 mg/l) or water disposed to environment. In addition, high pH process conditions leads to fouling and scaling. Thus, the

RO permeate is alkalised to pH ca. 9.5 and once more treated by RO or ion exchange (Fig. 2) [2,16]. The cost of removal of boron in the two-step process is very high [16] and usually multistep (3-4 steps) RO processes are applied. Hence, 2nd and 3rd stage RO membranes are operated at lower concentrations and at lower pressure [16].
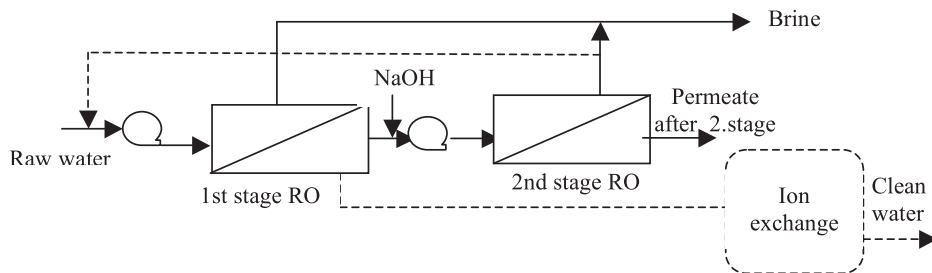
Fig. 2. Two stage RO system for boron removal
Rys. 2. Dwustopniowy system usuwania boru

Studies focused on the removal of boron from water solutions using ultrafiltration enhanced with polymers (PEUF), which generally are poly(vinyl alcohol) or specially synthesized polymers [9]. The process consists of two stages: the complexing of boron with a polymer and the separation of complexes by capillary ultrafiltration [9]. Retention coefficients of boron are decreasing during the process (starting from values close to 1) as amount of active centers of the chelating polymer are decreased. The retention depends also on pH, boron and polymer concentration in the feed.

The interesting solution in boron removal from seawater or from permeate after seawater desalination with RO is sorption-membrane hybrid process. 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 after sorption ion exchange is separated by means of microfiltration. The small size of grains of the resin allows to effectively decreasing boron content after 2 minutes from 2 mg/l to 0.243-0.124 mg/l, depending on ion exchanger dose (0.25 to 1.0 g/l) [7].

Ion exchange membrane processes

Donnan dialysis (DD) is a process that uses an ion exchange membrane without applying an external electric potential difference across the membrane [8,26,30]. Ion exchange membrane separates here two solutions, which differ both composition and concentration – raw solution and stripping solution (concentrate). The Donnan dialysis type of operation requires the addition of a so-called driving counter-ion to the stripping solution (usually NaCl with a concentration of 0.1 to 1 mol/l), which is transported in a direction opposite that of the target ion in order to maintain electro neutrality (Fig.3) [30]. The ions, which are permeable to the membrane, will equilibrate between the two solutions until the Donnan equilibrium is obtained. Since con-

centration ratios determine the Donnan equilibrium, 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. Due to these properties, the removal of inorganic anions from drinking water, especially nitrate and fluoride by Donnan dialysis has received attention (Table 4) [26].
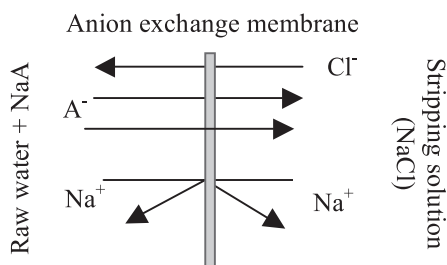
Fig. 3. Scheme of Donnan dialysis process
Rys. 3. Schemat procesu dializy Donnana

Table 4. Donnan dialysis (DD) and electrodialysis (ED) in the removal of inorganic anions in drinking water production
Tabela 4. Dializa Donnana (DD) and elektrodializa (ED) w usuwaniu anionów nieorganicznych w produkcji wody do picia

Process	Membrane type, producer	Anion	Type of water
DD	Neosepta AFN; 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; 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

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 [26]. In ED membrane fouling and scaling are a frequently observed, therefore, the ED systems are usually opera-

ted in the so-called electrodialysis reversal mode (EDR), 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 and hardness (cations are also removed from the water), depending on the voltage and type of the membranes used, is obtained. 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 and especially nitrate, have received attention (Table 4), especially for efficient removal of inorganic anions from drinking water [26,30].

Since most known toxic anions are monovalent the use of monovalent anion permselective exchange membranes is especially attractive [26]. 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 DD can be a better solution, and, in cases when besides ions, removal of low-molecular weight 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 use of a monovalent anion permselective membrane in ED process proved successful in a full-scale ED plant designed to remove nitrate from groundwater in Austria [26,30]. The NO_3^- concentration in the raw water was 120 mg NO_3/l and the removal efficiency (66%) was adjusted to obtain a product concentration of 40 mg NO_3/l. Under these conditions, the desalination degree was about 25%, therefore the nitrate selectivity was reasonably high [30].

The application of ED to fluorides removal from water is beneficial as the process characterises with seasonal changes of fluorine concentration, satisfying selectivity and low energy consumption [26]. The degree of removal of fluorides and soluble substances is very often higher than for RO and it increases with the increase of voltage, temperature and flow rate [26,30]. In case when F^- concentration is below the permissible level, ED devices can be shut down for longer time period. To omit the precipitation of bivalent ions sulphates and carbonates in the concentrate chambers, two configurations of ED process are proposed [4]:
- two-step ED with application of bivalent ions selective membranes in the 1st step and conventional membranes in the 2nd step,
- 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 obtaining water of municipal quality.

Electrodialytic removal of boron from water, similarly as RO, also requires high pH value, as boric 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 prevent also the 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 [2,15]. 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 [15]. In order to omit high demineralization of the diluate, monopolar membrane under alkali process conditions (pH=9-10) are applied [2].
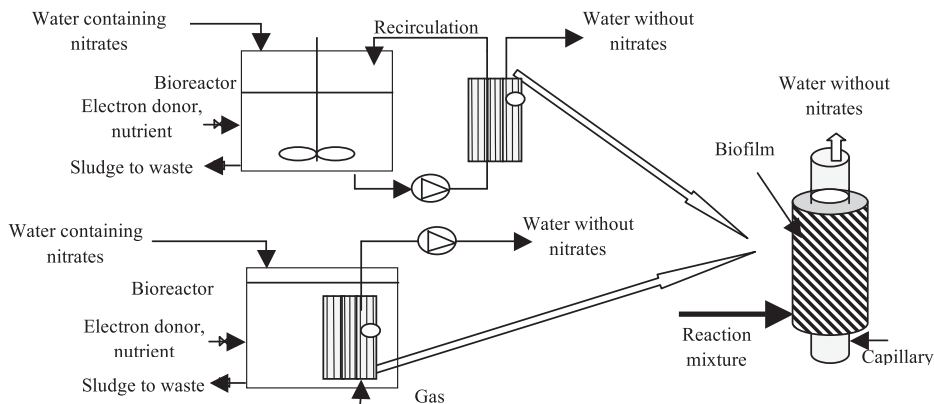
Membrane bioreactors

The main disadvantage of RO, NF and ED is production of the concentrate with high load of anions. The method proposes for the removal of anionic micropollutants, in which the reduction of oxyanions to harmless compounds takes place, is treatment in membrane bioreactors (MBR) [8,26,27]. The content of bioreactor during or/and after process can be treated in UF/MF process, what allows to separate the treated solution and biomass. MBR can be used for the removal not only nitrates but also bromates and perchlorates [8,26].

The biological denitrification is based on the reduction of NO_3^- to N_2 under anaerobic conditions at the presence of microorganism and proper donor of electrons [3,8,26]. The kinetic of the reaction depends on kind of microorganisms and biodegradation process conditions (pH, NO_3^- concentration) [8]. Heterotrophic bacteria which naturally occur in soil and water and 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 H_2) as electron donors [3,4]. The advantage of autotrophic denitrification is lower production of activated sludge; however the process runs slowly [16]. When heterotrophic denitrification is applied the removal of dissolved organic carbon and biomass from treated water is required [20]. 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 MF/UF) (Fig. 4 and Table 5) [3,4] or as extractive membrane bioreactors (membrane contactors) (Fig. 5) [8,11].

In the case of MBR with pressure-driven membrane process, MF or UF membrane may be placed inside or outside bioreactor (Fig.4). A general limitation of the pressure-driven membrane bioreactors is the treated water quality. While contamination of water with microbial 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 first solution (Fig.5) water with nitrates is supplied to the inside (lumen side) of hollow-fiber 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. In these conditions, both electron donor and gentrification biomass are separated from the water with membrane.

Fig. 4. Membrane bioreactors with pressure driven membrane module
**Rys. 4.** Bioreaktory membranowe z ciśnieniowymi modułami membranowymi

Table 5. Membrane bioreactors with pressure-driven modules for the removal of inorganic anions in drinking water production
Tabela 5. Bioreaktory membranowe z ciśnieniowymi modułami w usuwaniu anionów nieorganicznych w produkcji wody do picia

| 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)

A new membrane bio/process for the removal and bioconversion of ionic micropollutants from water is the ion-exchange membrane bioreactor (IEMB) [8,26]. The anion is transported from the water through ion-exchange membrane into a biological compartment, where it is simultaneously converted by a suitable microbial culture into harmless products. As discussed previously for Donnan dialysis, pollutant is transported against its concentration gradient due to the presence of driving counter-ions in a higher concentration (Fig.6). 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.
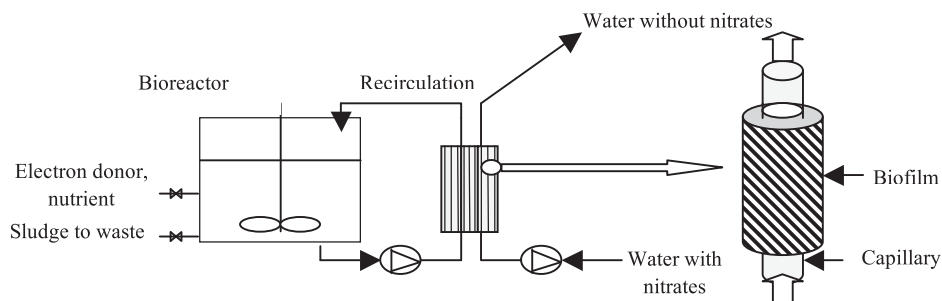
Fig. 5. Extractive membrane bioreactor
Rys. 5. Ekstrakcyjny bioreaktor membranowy
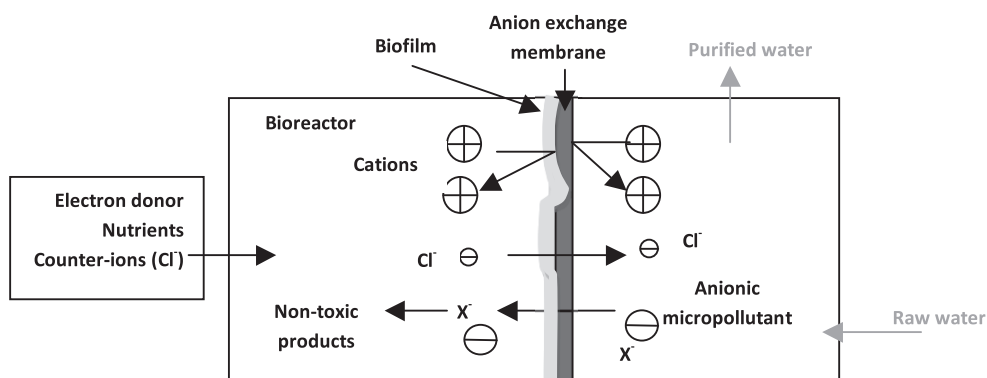
Fig .6. A schematic diagram of the ion transport mechanism in the ion exchange membrane bioreactor (IEMB)
Rys. 6. Schemat mechanizmu transportu jonów w bioreaktorze z membraną jonowymienną

This concept was first demonstrated for the removal and bioconversion of nitrate to nitrogen gas in synthetic waters using Neosepta ACS mono-anion permselective membrane and ethanol as the carbon source [26]. Due to its very low diffusion coefficient (three orders of magnitude 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.

METAL REMOVAL

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 [3,4,10]. 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 equipment. The technological flowchart of the installation used for the removal of iron and manganese comprises the stage of pre-oxidation (aeration and $KMnO_4$ dosing) followed by membrane filtration. 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) [3]. Reactor, in which membranes are immersed, is aerated, thereby maintaining the oxidizing environment and prevents membrane fouling.

Table 6. Results of the removal of Fe and Mn by ZeeWeed® method
Tabela 6. Wyniki usuwania Fe i Mn metodą ZeeWeed®

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

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 [16,24]. 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.

Arsenic

Inorganic arsenic occurs in two oxidation degrees, as As(III) and As (V), and lower oxidation dominates in groundwater and higher in surface waters. In the aquatic environment, at pH close to neutral, As(III) occurs in the form of inert molecules H_3AsO_3 (pK = 9.2), and As(V) as ions $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-} (pK = 2.2; 6.8; 11.6), which concentration depends on pH. The form of As(V) ions has a direct impact on the usefulness and effectiveness of removal methods. In order to decrease arsenic content in drinking water RO and NF membranes as well as hybrid process of coagulation-MF/UF are applied [3,22].

Reverse osmosis is an effective technique for removing arsenic, which demonstrated the tests carried out at the laboratory and pilot scale [3,17,22]. RO membranes TFC-ULP (by Koch) [22] 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. 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 also observed. pH and content of dissolved organic matter have a great influence on arsenic removal [19]. 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% [19]. The higher removal of arsenic(V) (90%) was observed for waters of lower organic matter content, while in comparison to higher NOM content it was equal to 80%. Also other laboratory and pilot research has been performed onto arsenic removal using RO membranes [3,19,22]. Presented results show a high retention of As(V) while low for As(III) at neutral reaction. This is confirmed by the fact that oxidizing conditions for carrying out of the process are recommended, and that the charge of the membrane surface and electrostatic repulsion play a significant role in the mechanism for removing arsenic.

Nanofiltration membranes are also applied to As removal [3,17]. For NF-70 FilmTec membrane, 97% removal of As (V) was obtained, and for NF-45 membrane it varied from 45 to 90% depending on initial concentration of the pollutant in water [3]. 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 NF membranes is based on both, the sieving separation, and electrostatic repulsion between ions and charged membrane. The degree of removal of As (V) with use of NF-45 membrane significantly increases with the increase of pH [3], according to the difference in As ion hydratation and, as a result, to the greater radius. 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 [3,13,22]. 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, in some cases, for As removal [3,22]. Other MF and UF membranes are used to remove only some forms of arsenic from water, mainly by means of integrated systems with coagulation and flocculation [13]. In the article [22] 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. The obtained results indicated that the effective-

ness of As removal was greater for hybrid systems than for MF alone, 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.

Heavy metals

Metals like: lead, mercury, selenium, iron, nickel. manganese, copper, cobalt, cadmium, zinc, chromium and other are present in drinking water. Membrane techniques like: reverse osmosis, nanofiltration, microfiltration and ultrafiltration enhanced with surface-active compounds and polymers, electrodialysis as well as liquid membranes 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 sizes not even greater then few nanometers [3]. In NF 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. If environmental protection is taken into account NF 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 [1,20].

Membrane processes are very important for recovery of chromium [16,18]. RO and NF allow to directly separate chromium compounds from treated solutions and are applied in that field [16,18]. Polymeric and inorganic membranes can be applied for removal of Cr(III) and Cr(VI). During RO and NF using Osmonics membranes the retention coefficient of chromium(VI) ions amounted to 96 - 98% [4]. The retention of chromium by means of NF 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, which also depends 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 [3,4,18].

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 by ultrafiltration are also carried out [5,31]. Polyvinyl alcohol (PVA MW = 50,000) and

polyethyleneimine (PEI MW=30,000 - 40,000) as well as polyacrylic acid and sodium polyacrylate are used as complexing agents. 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. This method was also successfully applied to remove Cr(VI) from groundwater using such complexing agents as: hexadecylpyridinium chloride or cationic polyelectrolyte (PEI).

CONCLUDING REMARKS

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 RO, 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 RO are the methods of water softening, as well as to remove disinfection by-products precursors and micro-pollutants. 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) in the treatment process based on conventional filtration.

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.

REFERENCES

1. Bakalár T., Búgel M., Gajdošová L., (2009), Heavy metal removal using reverse osmosis, Acta Montanistica Slovaca, 14, 250-253.
2. Bick A., Oron G., (2005), Post-treatment design of seawater reverse osmosis plants: boron removal technology selection for potable water production and environmental control, Desalination, 178, 233-246.
3. Bodzek M., Konieczny K., (2005), Application of membrane processes in water treatment, Oficyna Wydawnicza Projprzem-Eko, Bydgoszcz (In Polish).
4. Bodzek M., Konieczny K., (2010), Application of membrane processes in drinking water treatment.I Removal of inorganic compounds, Technologia Wody, no 1, 9-21,26. (In Polish).
5. Bodzek M., Korus I., Loska K., (1999), Application of the hybrid complexation – ultrafiltration process for removal of metal ions from galvanic wastewater, Desalination, 121, 117-121.
6. Bodzek M., Koter S., Wesołowska K, (2002), Application of Membrane Techniques in Water Softening Process, wyd. Elsevier, Desalination 145, 321-327.
7. Bryjak M., Wolska J., Kabay N., (2008), Removal of boron from seawater by adsorption–membrane hybrid process: implementation and challenges, Desalination, 223, 57–62.
8. Crespo J.G., Velizarov S., Reis M.A., (2004), Membrane bioreactors for the removal of anionic micropollutants from drinking water, Current Opinion in Biotechnology, 15, 463–468.
9. Dilek C., Ozbelge H.O., Bicak N., Yilmaz L., (2002), Removal of boron from aqueous solution by continuous polymer enhanced-ultrafiltration by polyvinyl alcohol, Sep. Sci. Technol., 37, 1257–1271.
10. Ellis D., Bouchard C., Lantagne G., (2000), Removal of iron and manganese from groundwater by oxidation and microfiltration, Desalination, 130, 255-264.
11. Ergas S.J., Rheinheimer D.E., (2004), Drinking water denitrification using a membrane bioreactor, Water Research, 38, 3225-3232.
12. Fritzmann C., Löwenberg J., Wintgens T., Melin T., (2007), State-of-the-art of reverse osmosis desalination, Desalination, 21, 6 1–76
13. Han B., Runnells T., Zimbron J., Wickramasinghe R., (2002), Arsenic removal from drinking water by flocculation and microfiltration, Desalination, 145, 293-298.
14. Hu K., Dickson J.M., (2006), Nanofiltration membrane performance on fluoride removal from water, Journal of Membrane Science, 279, 529–538.
15. Kabay N., Arar O., Acar F., Ghazal A., Yuksel U., Yuksel M., (2008), Removal of boron from water by electrodialysis: effect of feed characteristics and interfering ions, Desalination 223, 63–72.
16. Kołtuniewicz A.B., Drioli E., (2008), Membranes In Clean Technologies, Wiley-VchVerlag GmbH, Weinheim.
17. Nguyen C.M., Bang S., Cho J., g Kim K.-W., (2009), Performance and mechanism of arsenic removal from water by a nanofiltration membrane, Desalination, 245, 82–94.
18. Owlad M., Aroua M.K., Daud W.A.W., Baroutian S., (2009), Removal of hexavalent chromium-contaminated water and wastewater: A Review, Water Air Soil Pollution, 200, 59–77.
19. Pawlak Z., Żak S., Zabłocki L., (2006), Removal of hazardous metals from groundwater by reverse osmosis, Polish J. of Environ. Stud., 15, 579-583.
20. Qdais H.A., Moussa H., (2004), Removal of heavy metals from wastewater by membrane processes: A comparative study. Desalination, 164, 105-110.

21. Sehn P., (2008), Fluoride removal with extra low energy reverse osmosis membranes: three years of large scale field experience in Finland, Desalination, 223, 73–84.
22. Shih M.-C., (2005), An overview of arsenic removal by pressure-driven membrane processes, Desalination, 172, 85-97.
23. Tahaikt M., Haddou A., El Habbani R., Amor Z., Elhannouni F., Taky M., Kharif M., Boughriba A., Hafsi M., Elmidaoui A., (2008), Comparison of the performances of three commercial membranes in fluoride removal by nanofiltration. Continuous operations, Desalination, 225, 209–219.
24. Teng Z., Huang J.Y., Fujita K., Takizawa S., (2001), Manganese removal by hollow fiber micro-filter. Membrane separation for drinking water, Desalination, 139, 411-418.
25. Van der Bruggen B., Vandecasteele C., (2003), Removal of pollutants from surface water and ground water by nanofiltration: overview of possible applications in the drinking water, Environmental Pollution, 122, 435-445.
26. Velizarov S., Crespo J.G., Reis M.A., (2004), Removal of inorganic anions from drinking water supplies by membrane bio/processes, Reviews in Environmental Science & Bio/Technology, 3, 361–380.
27. Velizarov S., Matos C., Oehmen A., Serra S., Reis M., Crespo J., (2008), Removal of inorganic charged micropollutants from drinking water supplies by hybrid ion exchange membrane processes, Desalination, 223, 85–90.
28. Wesołowska K., Bodzek M., Koter S., (2002), NF- and RO- membranes in drinking water production, w: Proceedings of Membranes in Drinking and Industrial Water Production MDIW 2002, Mulheim an der Ruhr, Germany, B.37a, 357-363.
29. Wilf M., (2007), The Guidebook to Membrane Desalination Technology, Balaban Desalination Publications, L'Aquila.
30. Wiśniewski J., (2001), Electromembrane processses, in: Membrane Separations (A.Noworyta, A.Trusek-Hołownia, Eds), Argi, Wrocław 147-179.
31. Zakrzewska-Trznadel G., (2003), Radioactive solutions treatment by hybrid complexation-UF/NF process. J. Membr. Sci., 225, 25-39.

ZASTOSOWANIE TECHNIK MEMBRANOWYCH W USUWANIU ZANIECZYSZCZEŃ NIEORGANICZNYCH ZE ŚRODOWISKA WODNEGO – STAN WIEDZY

Streszczenie. Wprowadzenie i rozwój technik membranowych w produkcji wody do picia, w ostatnich 30. latach, jest uważane jako znaczący krok w dziedzinie skuteczności uzdatniania wody, porównywalny z wprowadzeniem filtrów piaskowych na początku 20. wieku. Szczególną rolę odegrały w tym zakresie wysoko- jak i niskociśnieniowe procesy membranowe oraz elektrodializa. Odsalanie wody morskiej i zasolonych wód podziemnych jest częstym sposobem otrzymywania wody do picia. Znaczne ulepszenia w technologii i projektowaniu procesu odwróconej osmozy, dostępność alternatywnych źródeł energii, możliwości wstępnego oczyszczania oraz stosowanych materiałów spowodowały, że proces stał się przyjaznym ekologicznie źródłem wody słodkiej w wielu regionach świata, szczególnie w tych, gdzie ich źródła są ograniczone. W latach 80. wzrosło zainteresowanie nanofiltracją i w pewnym zakresie odwróconą osmozą jako metodami zmiękczania wody, natomiast w latach 90. zaczęto je stosować do usuwania mikrozanieczyszczeń, w tym nieorganicznych. Do usuwania jonów azotanowych i fluorkowych, boru oraz metali (Fe, Mn i metale ciężkie) z powodzeniem stosuje się odwróconą osmozę, nanofiltrację i elektrodializę, jak również bioreaktory membranowe oraz ultrafiltrację wspomaganą koagulacją i utlenieniem.

Słowa kluczowe: Procesy membranowe, usuwanie związków nieorganicznych, odsalanie i zmiękczanie wody, usuwanie anionów i metali.