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MICHAŁ BODZEK^{*}, KRYSTYNA KONIECZNY^{*}

MEMBRANE TECHNIQUES IN WATER TREATMENT AND WATER RENOVATION

Due to the changes in the approach to water treatment for consumption purposes and the growing requirements imposed on the quality of potable water, membrane technologies are currently viewed as alternative processes in water treatment operations. Membrane techniques can be used as independent processes for the removal of impurities from water or can be combined with complementary processes applied in water treatment systems (physical, chemical or biological).

The paper describes the possibility of applying membrane techniques in water treatment processes. Desalination of sea, brackish and mine water, softening of natural waters and treatment for drinking water purpose as well as the removal of nitrates and volatile organics by membrane techniques have been discussed.

1. INTRODUCTION

Due to the changes in the approach to the concept of water treatment for consumption purposes currently under way and following the growing requirements imposed on the quality of potable water, membrane technologies are presently viewed as alternative processes in water treatment operations. It is particularly viable for pressure-driven membrane techniques. Membranes' techniques can be used as independent processes for the removal of impurities from water or combined with complementary processes applied in water treatment systems (physical, chemical or biological), forming a technological line for water treatment.

The application of membrane techniques in the treatment of natural waters may solve the following problems [1]:

• microfiltration may be used as a method for water clarification,

• ultrafiltration membrane forms an impermeable barrier to suspended substances and all microorganisms; therefore, it can be used for the clarification and disinfection of water,

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^{*}Silesian Technical University, Faculty of Environmental and Energy Engineering, Institute of Water and Wastewater Engineering, Konarskiego 18, 44-100 Gliwice, Poland.

• nanofiltration can be used to remove colloidal suspension, many low-molecular organic compounds and divalent ions; it can, therefore, be used for water softening and removal of microimpurities,

• reverse osmosis allows us to retain monovalent ions and the majority of lowmolecular organic compounds; it is used for the desalination of brackish and saline waters as well as for the removal of microcoimpurities (e.g. pesticides),

• pervaporation may be applied in the removal of volatile organic substances from water.

2. DESALINATION OF NATURAL WATER

The process of water desalination is one of the major production methods of potable water and industrial water. About 86% of the world-wide population – over two billion – have limited access to clean water sources [2]. Since the world's population is predicted to double over the next 50 years, many experts express opinions that we are facing a world-wide water crisis.

Natural waters can be classified as: fresh waters, brackish waters, sea waters and brines [2]. Fresh waters contain up to 1000 mg/dm³ of dissolved substances, brackish waters 1000–35000 mg/dm³ and sea waters over 35000 mg/dm³. According to other classifications, waters are regarded brackish when they contain below 10000 mg/dm³ of dissolved substances (moderately saline waters), and the range of 10000–35000 mg/dm³ is considered as 'difficult brackish waters'. Run-off waters from arable areas constitute another source of waters subject to desalination.

Taking into consideration the separation mechanism, the desalination processes can be divided into three categories [3, 4]:

• separation is obtained through the process of phase inversion: thermal methods, freezing,

• separation is obtained through the application of a membrane: reverse osmosis, electrodialysis and electrodialysis reversal,

• ion exchange.

Typical concentration ranges of substances dissolved in water subject to desalination, using the distillation method, reverse osmosis, electrodialysis and electrodialysis reversal as well as the ion-exchange method, are respectively: 100, 45, 10 and 0.8 g/dm^3 [5].

Tables 1 and 2 present the capacity of desalination facilities in particular parts of the world and with respect to the applied desalination process [6].

The domination of reverse osmosis as the desalination process is caused by the lowest consumption of energy when applying this method. Table 3 provides comparative data of energy consumption in various desalination processes [2, 4]. It should be emphasized that there is a possibility of lowering the energy consumption costs by another 30%, especially when desalinating waters of high salinity rate by the application of energy recovery systems.

Table 1

Capacity-based distribution of desalination facilities world-wide depending on the applied process

Desalination	Capacity (%)		
process	USA	World	
Thermal processes	21	70	
Electrodialysis	6	5	
Reverse osmosis	73	25	

Table 2

Capacity-based distribution of desalination facilities in different parts of the world

Region	Capacity (%)		
West Asia and Middle East	63		
North America	11		
North Africa	7		
Europe	7		
Pacific	4		
Caribbean Islands	2		
Former USSR countries	2		
Other countries	4		

Table 3

Energy consumption when desalinating brackish waters (10 kg/m³)

Technological process	Energy consumption (kWh/m ³)	Concentration of salt in the product (kg/m ³)	Water recovery (%)
Reverse osmosis	5.26	150	50
Electrodialysis	10.5	500	33
Distillation	23.7	5	57
with vapours' compression			
MSF distillation	36.8	5	25

2.1. DESALINATION SYSTEMS

The diagram of a typical membrane desalination system is presented in Fig. 1 [5]. Each system consists of pre-treatment and post-treatment, and of the actual desalina-

tion process. The scope of pre-treatment and post-treatment is requirement-specific and depends on the receiver of desalinated water. Furthermore, in many cases, the desalination system may be designed in the split-treatment system. In this case, some volume of water is by-passing the desalination facility and is mixed with the desalination product. Such a concept may result in lowering the required capacity of the desalination facility, which, with the same production volume maintained, lowers total costs of the process.

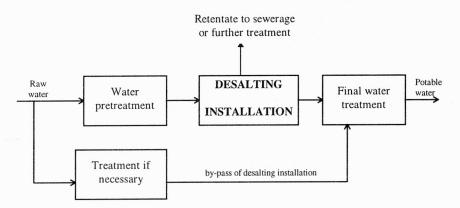


Fig. 1. Diagram of a typical desalination system with by-pass of the desalination facility

A desalination facility comprises membrane modules for the processes of reverse osmosis, electrodialysis or electrodialysis reversal. The high-capacity installations usually consist of a number of identical modules combined parallelly, which are fed with water following the pre-treatment. Due to modular structure of the system, the installation can be developed with minimum costs.

In the designing phase of desalination systems with reverse osmosis, a single or two-stage system can be applied (Fig. 2). The selection of a particular operational system of the membrane process is requirement-specific and depends principally on the quality of desalinated water and fresh water. For the desalination of brackish waters with the application of reverse osmosis, single-stage installations are used in most cases, and in the case of sea waters or high-salinity waters – single or two-stage installations [2, 4, 5]. Sometimes there is a necessity to apply a three-stage desalination system, especially when minimum final concentration level of retentate should be obtained [4].

Another important factor in water desalination process is the selection of appropriate membrane material. Modern material for the production of desalination membranes should be characterized by high permeability to water and should satisfy the requirements involving uncomplicated operation and low consumption of energy. Membranes made of cellulose acetate turned out to be useful in the desalination of brackish waters, in spite of a number of flaws, although their capacity is too low in terms of contemporary requirements. Latest generations of composite membranes have many advantages and are therefore favoured in the desalination of sea waters or high salinity brackish waters. Although the cost of cellulose acetate membranes is lower compared to composite membranes, the price of the latter is becoming lower as new production technologies are being introduced and production potentials are enhanced. The application of cellulose acetate membranes necessitates water chlorination and the use of higher pressure compared to composite membranes. Furthermore, composite membranes work in higher range of pH and temperature. It contributes to the reduction of energy consumption and chemicals used in the process.

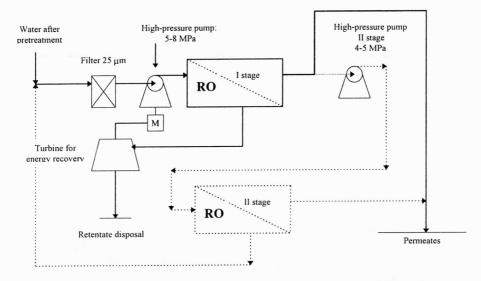


Fig. 2. Diagram of a single- and two-stage reverse osmosis desalination installation

In the reverse osmosis desalination technologies, principally the spiral modules and the ones made of hollow fibres are applied [5], however, over last years, new installations have been furnished with spiral modules. Such an approach results from the fact that flat membranes are easier to accommodate to industrial conditions compared with membranes made of hollow fibres. Spiral configuration of a module does not require intensive pre-treatment of raw water, offers relatively easy cleaning conditions, is characterized by high compactness and is cost-effective [2].

2.2. WATER INTAKE AND ITS PRE-TREATMENT

In the designing process of conventional water-treatment systems, the composition of raw water should be taken into account. It applies also to the designing process of desalination systems, where the selection of process parameters and economic ones should to much greater extent allow for the composition of raw water and the composition of desalinated water than in the case of conventional treatment. Water pretreatment is required principally to protect the membrane system against fouling in order to ensure longer running time of the system. The selection of a pre-treatment method depends on the characteristic of raw water, kind of membrane and present process parameters. The requirements concerning the pre-treatment may be quite minimal, e.g. filters for underground waters or more developed involving coagulation sedimentation and filtration as, for instance, for surface waters [2, 5].

For reverse-osmosis systems, the pre-treatment usually consists in adding chemicals, protecting against the formation of membrane scale (CaCO₃, CaSO₄, BaSO₄, SrSO₄, CaF₂, SiO₂), and filtration through a cartridge filter (usually with the mesh size of 1, 5, 10 or 20 μ m) to protect the membranes against the deposition of mechanical impurities [2, 5, 7]. Raw water is often acidified to reduce pH; this stage is practically always applied to cellulose membranes. Also, such membrane-scale inhibitors are applied as sodium hexamethaphosphate or other chemicals reducing the formation of carbonate or sulphate sediments [5, 7]. The deposition of silica on the membrane surface is dependent not only on its concentration in raw water, but also on the temperature and pH (water pH over 8 and below 7 stops the precipitation of silica). Raising the temperature and lowering the volumetric capacity of permeate also contribute to the reduction of SiO₂ deposition.

The formation of biological sediments depends on the kind and extent of microbiological fouling of raw water, presence of biogenic substances, temperature and intensity of water flux in the system [7]. Water chlorination is used as a method to prevent the formation of biological deposits. In most cases, the dosage allowing us to obtain the 5 mg/dm³ concentration level of chlorine is used. However, the majority of polymeric membranes undergo degradation under its influence. Therefore, in such cases, formaldehyde or sodium hydrosulfate (IV) can be applied, which reduce the development of micro-organisms.

Suspended substances (suspensions) present in the feed water settle on the membrane surface and form amorphous sediments. This problem can be solved by the application of pre-treatment, using multi-layer filters and cartridge filters of 5 μ m mesh size or even bigger [7]. Colloidal substances, including metal oxides, pass through standard filters and do not undergo simple gravimetric sedimentation. Principally alsifers and simple salts of iron, manganese and aluminium [5, 7] cause the fouling of membranes. Iron (III) compounds come both from natural impurities present in water and from corrosion affecting metal parts of the equipment. Colloidal substances form jelly-like sediments on the membrane surface. The method for their removal from water consists in coagulation with iron (III) compounds or aluminium compounds, polymer and/or polyelectrolite flocculation, sedimentation and final filtration.

Also organic substances may cause membrane fouling, and therefore they must be removed during either the pre-treatment of feed water or the periodic cleaning of the membranes. Oils, lubricating agents, hydrocarbons and organic solvents may destroy the membranes used for reverse osmosis or electrodialysis.

The diagram of water pre-treatment prior to its introduction to reverse-osmosis membrane modules for brackish waters is presented in Fig. 3.

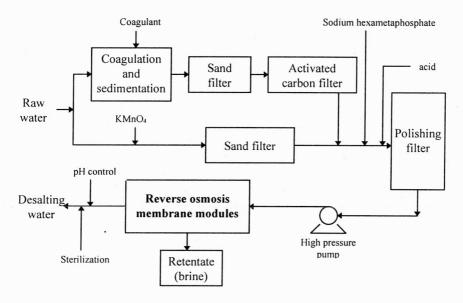


Fig. 3. Simplified flow chart of brackish water desalination process using reverse osmosis

Standard pre-treatment of feed water for the electrodialysis system involves the filtration through cartridge filters (usually with mesh size of 10 or 20 μ m) and admixture of chemicals to the retentate recirculation stream [4]. The systems for electrodialysis and electrodialysis reversal tolerate higher concentration of colloidal substances than the membranes for reverse osmosis in spiral module, which are again less sensitive than the membranes made of hollow fibres [5].

2.3. FINAL TREATMENT OF DESALINATED WATER AND DISPOSAL OF RETENTATE

Final cleaning (treatment) of desalinated water must be carried out in the cases when the water is to be used for municipal purposes, and it usually consists in removal of dissolved gases (carbon dioxide and hydrogen sulfide), pH correction to prevent corrosion, and disinfection [2, 5].

The removal of gases is usually carried out through expelling in columns with filling [5]. In most cases, carbon dioxide must be removed to stabilize water coming from the reverse osmosis installation. If hydrogen sulphide is present, deacidification of desalinated water is usually carried out for the water from reverse osmosis installation, but also for electrodialysis and electrodialysis reversal, to remove odour and to reduce the amount of added disinfection substances (e.g. chlorine). In the process of reverse osmosis, the adjustment of water pH is usually carried out by means of caustic soda, calcined soda or burnt lime. By the application of these alkaline substances we may obtain water which does not generate corrosion, but in some cases the same result can be obtained by means of other chemicals or by mixing the desalinated water with raw water or other waters. Disinfection of desalinated water is usually carried

out through chlorination, but if the desalination process makes it possible for trihalomethanes (THMs) to penetrate the permeate, the application of chlorine dioxide or chloroamines is required to meet the requirements imposed on potable water [5].

One of the main desalination problems, whose solution is very often associated with considerable costs, is the neutralization of waste concentrate (retentate). Liquid waste from the membrane installation is usually discharged directly to the sea, surface waters or indirectly through storm-water piping system to the idle areas left after the exploitation of ground waters, evaporated in ponds, concentrated to salts using evaporation methods or, if it is acceptable, introduced to the sewage system running to the treatment plant [5]. Waste concentrates can sometimes be used as irrigation water, in particular when the desalination process involves waters of low content of dissolved substances [2, 5]. The method for their disposal and the necessity to clean them are considered in the designing phase of the process, and a respective solution must comply with legal requirements and regulations.

2.4. ECONOMIC ANALYSIS OF THE DESALINATION PROCESS

The costs of membrane desalination may vary considerably since they are limited by many factors, and the most crucial of them are as follows [5]:

• kind, size and localization of the installation,

• source, quality and temperature of raw water and the required level of pretreatment,

• planned quality of desalinated water and the possible rate of mixing the product with raw water,

- storage and treatment of desalinated water,
- depreciation rate,
- material and operational costs including chemicals,
- labour costs involving the operation,
- costs of energy and replacement of membranes,
- costs of waste-concentrate disposal.

When analysing the economic profitability of the desalination process, investment costs and yearly operational costs are taken into consideration [2, 5, 9, 10]. The distribution of various components of operational costs, involving the desalination of sea water and brackish water using the reverse osmosis and electrodialysis, is given in Fig. 4 (data for the USA) [2].

In the United States, the investment costs of the electrodialysis or electrodialysis reversal membrane unit for the desalination of brackish waters of the capacity of 4-40 thousand m³/day usually range between 0.16 and 0.33 US dollar/m³ of the permeate/day [5]. For the reverse osmosis desalination systems, the operational costs

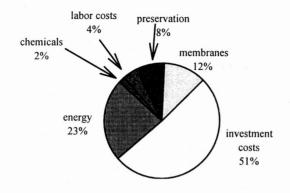


Fig. 4. Cost distribution of sea water desalination using the reverse osmosis and electrodialysis (data for calculations: capacity – 360 m³/day, concentration: of water – 42000 mg/dm³; of permeate – 500 mg/dm³)

may be design-specific and hence may vary depending on the project. In the United States, such costs for the installation of the capacity of 4–40 thousand m^3/day amount usually to 0.13–0.4 US dollar/m³ of the permeate [5], whereas the operational costs amount to 0.26–0.66 US dollar/m³ of the permeate, assuming that the permeate is not mixed with raw water, and depreciation is 90%. By mixing permeate with raw water, the costs can considerably be reduced. The cost of sea water membrane desalination is a few times lower than the desalination of brackish waters. The costs of potable water production from sea water with the application of the reverse osmosis method of the capacity of 4–20 thousand m³/day usually range between 1 and 2 US dollars/m³.

According to currently available data, the cost of potable water production using the reverse osmosis method is as follows [11]:

- for low-salinity waters (up to 4 g/dm^3) 0.4 US dollar/m³,
- for sea waters $(35-42 \text{ g/dm}^3)$ 1.1. US dollars/m³.

3. DESALINATION IN WATER RENOVATION PROCESS

Water renovation provides the possibility of reusing wastewater following their final treatment with the application of physicochemical methods, and is therefore a crucial factor involving the management of water in areas devoid of sufficient water supply. Water renovation is to be understood as a set of unit processes aimed to bring wastewater to such purity standards that it can be reused as industrial water or as a protection agent against eutrophication in reservoirs. Technological processes for the removal of biogenic compounds from biologically treated wastewaters are referred to as three-stage treatment processes. Biologically cleaned wastewaters (after the twostage treatment) are fouled up with various substances, the most important of which are: organic microimpurities, inorganic toxic compounds, dissolved mineral substances and biogenic compounds [12].

Recent advances in technological and economic development concerning the process of reverse osmosis offer vast possibilities to apply this separation technique in the treatment of industrial wastewaters, municipal sewage and run-off waters from arable areas to obtain usable water. It particularly involves wastewaters, which have been subjected to two- or three-stage treatment and are to be utilized for municipal purposes [13, 14]. Raw wastewaters or wastewaters subjected to mechanical treatment (single-stage treatment) are here not taken into consideration. The results of pilot testing and testing of selected industrial installations [13] have shown that the reverse osmosis applied to the water renewal process is very effective in the removal of many organic substances, microorganisms and biogenic compounds.

A very important factor in the application of reverse osmosis to the renewal of water is the pre-treatment of wastewater prior to its introduction onto membrane modules. The scope of these operations is dependent on the quality of wastewaters after the two-stage treatment, kind and efficiency of membranes and frequency of their regeneration, present level of permeate recovery and also the present quality of permeate.

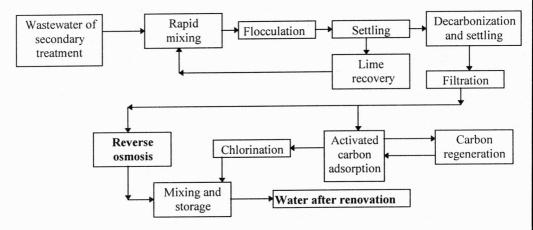


Fig. 5. Diagram of water renovation process in Water Factory 21, USA

One of the first large reverse osmosis installations for the treatment of municipal and industrial wastewaters of the capacity of 8000 m³/day was built in San Juan in New Mexico (USA) [13, 14], but the most distinguished installation of that type is the plant in Orange County, California (USA) – Water Factory 21 – of the capacity of 19000 m³/day, where wastewaters after the second-stage treatment are treated.

The main purpose of water renovation in Water Factory 21 (Orange County, California, USA) is the production of low-salinity water to be introduced to the ground in order to prevent sea water infiltration into fresh waters. The system is based on reverse osmosis (19000 m^3 /day) (Fig. 5) [14]. After the two-stage treatment, wastewa-

ters pass through the pre-treatment system which consists of lime clarification, decarbonization, chlorination and filtration through multi-layer filters. Then 1/3 of the flux volume is directed to the reverse osmosis system and the remaining volume to filters with granulated active carbon. The permeate from reverse osmosis and the water from active carbon filtration are mixed and discharged to the ground. The reverse osmosis system is equipped with spiral modules with membranes made of cellulose acetate. The removal ratio of dissolved substances was maintained at the level of 92–96% over the time period 04.89–02.91 [14].

4. DESALINATION AND PROCESSING OF MINE WATERS

The process of coal mining is accompanied by natural water outflow to mine headings. The waters are driven to the surface, and, since they carry a considerable charge of salt and are introduced to rivers, they contribute to their salinity. In consequence, this process results, among others, in [15]:

• destruction of water flora and fauna whereby rivers cannot be used for municipal or agricultural purposes,

- costs involving additional demineralization of river waters in production plants,
- the necessity to provide water from distant areas, which is very expensive.

According to the classification used in Polish mining industry [15, 16], mine waters (underground waters) can be divided into four categories, taking into account the possibility of their direct application or potential utilization. The total content of chloride and sulfate ions is a distinguishing factor that influences this categorization:

• group I: potable waters wherein the content of $Cl^{-} + SO_4^{2-} \le 0.6 \text{ kg/m}^3$,

- group II: industrial waters wherein the content of $Cl^{-} + SO_4^{2-} \le 0.6-1.8 \text{ kg/m}^3$,
- group III: low-salinity waters wherein the content of $Cl^{-} + SO_4^{2-} \le 1.8-42 \text{ kg/m}^3$,
- group IV: brines wherein the content of $Cl^{-} + SO_4^{2-} \ge 42 \text{ kg/m}^3$.

The discharge of high-salinity waters into rivers can be eliminated by:

• the application of technologies allowing removal of salts present in river waters with simultaneous economic utilization of these salts [16, 17],

• mining operations, i.e. water recirculation, deep pumping, stopping the mining process at the seams from which high-salinity waters flow out to the surface [18, 19].

Physicochemical methods for the removal of salts from water should result in the acquisition of potable water, salt and concentrated lye from which many useful products can be obtained. The most effective utilization processes of saline waters are as follows:

• reverse osmosis method – enables us to acquire high-quality potable water and is characterized by low consumption of energy,

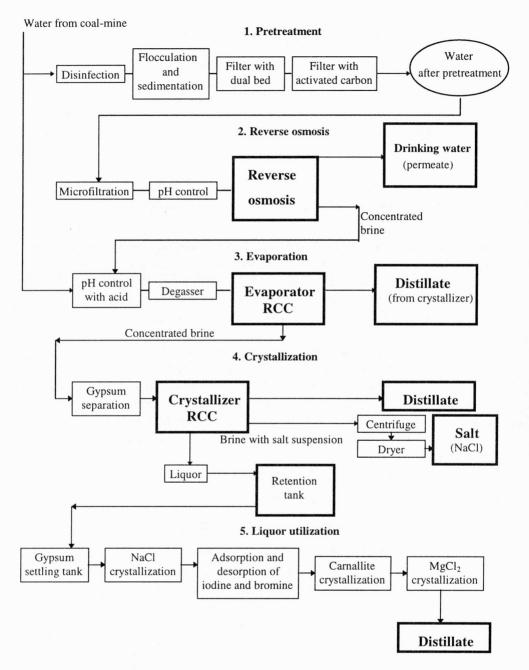


Fig. 6. Diagram of mine water utilization from coal mines 'Debiensko' and 'Budryk' with the application of reverse osmosis and thermal methods

• evaporation methods, by means of which the utilization of mine waters can be 'successful', i.e. separation of dissolved salts is achieved.

In practice, both of these desalination techniques are applied together.

In 1995, a desalination installation [20] eliminating saline waters from coal mines 'Debiensko' and 'Budryk' (Poland) was brought into operation. The installation is based on reverse osmosis due to the possibility of obtaining high-quality potable water and on evaporation methods, by the application of which the utilization process of saline water may bring about the elimination of all salts from the water. With full operational capacity, the plant will be processing 24 thousand m³/day of mine waters of the salinity level ranging from 8000 to 115000 mg/dm³. The day production of potable water is to amount to 9000 m³, 4000 m³ of condensate from distillation, almost 300 ton of salt (99.8% NaCl) and a number of other chemicals [20]. The installation consists of the following steps (Fig. 6):

- pretreatment of mine waters,
- reverse osmosis together with the station for potable water preparation,
- thermal evaporation and crystallization,
- recovery, drying and cooling of the salt,
- recovery, cooling and utilization of postcrystallization lyes.

5. MEMBRANE SOFTENING OF WATER

Nanofiltration has successfully been applied on technical scale in the processes of underground and surface water treatment [21–26], principally for softening purposes. Separation properties of nanofiltration membranes involve the possibility of separating divalent ions from monovalent ions and retention of organic substances of molar mass over 300 Da.

Conventional processes of the elimination of water hardness involve softening on ionites (synthetic zeonites or ionites) and chemical softening with lime or with lime and soda. They have some drawbacks as, for example, expensive methods pertaining to the removal of post-regeneration solutions and neutralization of calcium sediments [21, 22, 26]. Very often, using the classical methods for water softening, we cannot obtain a respective reduction in the content of accompanying impurities like colour or trihalomethanes [25].

Membrane softening of water by means of nanofiltration is competitive with respect to conventional softening. The most important advantages of this process are as follows [21, 22, 24, 26]:

• smaller size of the equipment (10:1),

• no problems with the removal of sediments generated during the softening by chemical methods,

• lower demand for chlorine since the concentration of organic compounds in water after the softening is very low,

- higher flexibility to seasonal changes of raw water quality and to its demand,
- generally better quality of produced water, because of better removal of impurities,

• retention of bacteria and viruses,

• better possibilities to satisfy more stringent regulations involving water quality without the introduction of additional treatment operations.

The diagram of membrane process of water softening is in principal quite similar to a typical one used for the desalination of brackish waters (Fig. 7) [22], except for such a few aspects relating to designing process of the installation as: a number of stages for membrane separation, type of applied pump, water pretreatment and the way of retentate disposal [21]. In most cases, a three-stage system is applied, by which the obtained volumetric capacity of permeate may amount to 90%.

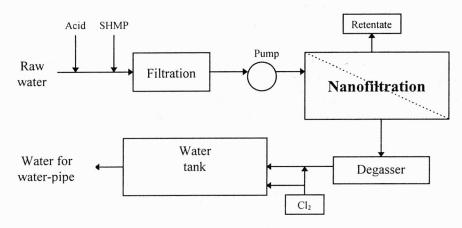


Fig. 7. Diagram of the process for membrane softening of water

The retentate stream from the membrane softening installation is not as difficult to neutralize as the retentate from brackish water desalination [21, 22] due to the fact that the concentration of salt in this flux is much lower, usually below 2000 mg/dm³. It results from the lower retention coefficient of monovalent ions and lower content of dissolved substances in raw water (usually <2000 mg/dm³).

Table 4 presents comparative characteristics of typical raw water (Florida, USA) subject to softening, water which was softened with conventional methods (lime and soda) and with membrane method, as well as the requirements for potable water specified by WHO and EPA (USA) [21].

It is evident from the data that the quality of softened water is higher than the quality specified in the standards in as much that it can be mixed with raw water prior to its introduction into the distribution network, which reduces the costs of treatment and size of the installation.

Water softening nanofiltration membranes for the production of potable water made by the firm Filmtec have the capacity from 160 m³/day to 10 thousand m³/day and are used in the USA and Europe [26]. The cost of the installation is about 350 US dollars/m³ of the capacity [26]. Taking into consideration the running time of the installation (20 years), it corresponds to real costs amounting to 0.16–0.19 US dol-

lars/m³. Taking into account the fact that water produced with the use of this method is of better quality than the water obtained by classical methods, the said cost is not too high [34]. According to data published in the USA [22], the investment costs of the installation for membrane softening are conditioned by the capacity of the installation and are as follows:

- for the installation of the capacity $<4000 \text{ m}^3/\text{day} 0.25 \text{ US dollars/m}^3$,
- for the installation of the capacity $4000-20000 \text{ m}^3/\text{day} 0.20 \text{ US dollars/m}^3$,
- for the installation of the capacity >20000 $m^3/day 0.17$ US dollars/m³.

Table 4

Parameter	Raw water	Water after conventional softening	Water after membrane softening	Requirements according to WHO	Requirements according to EPA
Ca, mg/dm ³	91	18	23		
Mg, mg/dm ³	5	4	2		
Na, mg/dm ³	16	16	7	200	160
Fe, mg/dm ³	0.3	0.02	0.02	0.3	0.3
HCO ₃ , mg/dm ³	264	33	23		
CO ₃ , mg/dm ³	0	4	0		
Cl, mg/dm ³	35	35	15	250	250
SO ₄ , mg/dm ³	17	17	40	400	250
NO ₃ , mg/dm ³	-	-	· · · · ·	10	10
pH	7.2	9.3	7.4		6.5-8.5
SiO ₂ , mg/dm ³	12	12	2.4	15	
Colour, PCU	50	15	<1	1	15
Turbidity, NTU	1.1	<1	< 0.1		1
TOC, mg/dm ³	7	-	<1		
THMPF, $\mu g/dm^3$	350		<20		
THM, $\mu g/dm^3$		30		30	100
TDS, mg/dm ³	429	127	110	1000	500

Characteristics of waters obtained using classical method and membrane softening method

TOC - total organic carbon, TDS - total dissolved solids, THM - trihalomethanes, THMPF - trihalomethanes formation potential.

The costs provided above are similar to the costs of brackish water desalination and may vary depending on the site of the installation, quality of raw water, costs of the allotment and others. Operating costs include labour, chemicals, energy, membrane replacement and regular operation, and oscillate between 0.10 and 0.17 US dollars/m³ [4].

To satisfy new and more stringent requirements for the content of by-products of the disinfection process in potable water, particularly trihalomethanes, membrane technologies offer vast potentials to meet these requirements, which should be considered by engineers designing water supply systems and by water distribution plants.

6. ULTRAFILTRATION AND MICROFILTRATION AS AN ALTERNATIVE TO CLASSICAL WATER TREATMENT METHODS

The necessity to improve the existing water treatment techniques and to implement new ones resulted from three basic factors [2, 3, 27, 28]: gradual degradation of the quality of existing water resources, growing demand for good-quality potable water, more stringent legal regulations and requirements concerning the quality of potable water and wastewaters discharged to the natural environment. Primary benefits arising from the application of membrane processes compared with conventional treatment are as follows [1, 27]: production of water of invariable quality, much lower quantity of added chemicals, low consumption of energy, compactness of the installation and short time needed to start its operation.

In the installation for potable water treatment, a number of interrelated, detached processes are applied. Depending on the quality of raw water, they encompass disinfection, disinfection and filtration and, additionally, coagulation and sedimentation, adsorption on active carbon and chemical oxidation. Water clarification with the application of coagulation/flocculation, sedimentation and/or filtration requires that respective chemicals be added (coagulants and flocculants) to ensure stabilization and aggregation of colloidal particles. Aluminium or iron salts as well as natural and synthetic polymers are applied most frequently. The basic drawbacks of chemicals addition to water are of two types [1, 27–29]:

• if the coagulation phase is not carried out in a proper way, treated water may contain coagulant residues which deteriorate the final quality of water directed to distribution,

• apart from natural substances occurring in water subject to treatment, the formed deposits contain man-made substances.

To obtain the good quality of drinking water, the treatment conditions should be constantly adjusted, depending on the quality of raw water. It is particularly critical with respect to proportioning of coagulants and determining pH of the flocculation [28]. Another problem to be solved is the utilization of generated sediments [2, 27, 28]. The quantity of formed sediments depends on the type of water and treatment methods, and amounts on average to about 0.5–2.0% of the quantity of treated water. It translates into about 1000 m³/day of sediments per 100 thousand inhabitants. The sediments contain about 2000 kg of chemicals which should not be discharged to waters [1]. Apart from this, the current legal regulations involving the efficiency of clarification process and filtration are becoming more restrictive, and water turbidity according to American or West-European standards should not surpass the value of 0.2 NTU [28].

Before the introduction into water distribution networks, the water is undergoing disinfection to ensure its respective microbiological quality. Water chlorination is applied in most cases, but recently the attention has been focused on such by-products of the disinfection method as trihalomethanes, which are ranked as heavily toxic chemical compounds. Therefore, alternative disinfection methods are gaining recognition, as for example ozonization. Ultrafiltration membranes constitute an effective barrier against viruses, bacteria and other microorganisms and therefore, the ultrafiltration process may be taken into account as a disinfection phase in water treatment processes [1, 30].

All inconveniences related to the traditional treatment of natural waters have triggered the demand for the application of new separation techniques, of which the membrane methods are the most advantageous and are endowed with vast potentials. Membrane techniques can help to solve the problems involving conventional techniques of water treatment [1], since:

• membrane is an absolute filter; assuming that the size of its pores or cut-off is appropriately selected, it will effectively be separating the impurities without the necessity to add reagents,

• quality of treated water will not depend on the quality of raw water,

• waste stream from membrane separation (retentate) will only be containing natural impurities removed from water; so it will be devoid of by-products of chemical reactions or other substances introduced during the treatment process.

Special efforts should be made to introduce ultrafiltration and microfiltration as well as nanofiltration into the treatment of natural waters. They should be focused on [1, 27]:

• selection of a respective membrane material which would comply with water treatment conditions,

• control to restrain the occurrence of fouling and development of methods which might be applied to minimize its influence on investment or operational costs.

The type of ultra- or microfiltration modules is of essential importance to the optimization of the process of membrane water filtration. Tubular modules, both multichannel and capillary, are most suitable for the water treatment compared to other configurations [1–3, 27]. They are characterized by lower consumption of energy, are more compact (especially capillary modules), can easily be regenerated by backflushing and have the highest packing density. Multi-channel tubular modules are made principally of non-organic materials, whereas capillary ones are made of synthetic polymers.

For the treatment of ground water, direct ultrafiltration is the best solution [1, 27, 29]. A unitary ultrafiltration system equipped with capillary modules Aquasource (France) has been designed [1], which is producing water of constant capacity (permeate flux: $100 \text{ dm}^3/\text{m}^2\text{h}$ under the pressure below 0.05 MPa and at temperature of 10 °C). After passing through a coarse-filter, raw water is supplied continuously to modules at constant flow rate. Backflushing of the module will take place as soon as the transmem-

brane pressure reaches a high, preset value. The first two installations of the capacity of 190 m³/h (Amoncourt-France) and of the capacity of 1200 m³/h (Douchy-France) were put into service in the years 1988 and 1989 for the treatment of underground waters [1]. The quality of the treated water obtained from these installations was constant and independent of the quality of raw water. The water also satisfied the standards with respect to turbidity and microbiological parameters (Table 5).

Table 5

Parameters	Units	Raw water I	Treated water	Raw water II	Treated water
Turbidity	NTU	0.28	0.06	3	0.06
Fe	$\mu g/dm^3$	40	<20	40	<20
Mn	$\mu g/dm^3$	<5	<5	<5	<5
Al	$\mu g/dm^3$	<10	<10	195	<10
Total coli bacteria	$1/cm^3$	44	0	10	0
Faecal type bacteria	$1/cm^3$	0	0	364	0
Total bacteria	$1/cm^3$	6	<1	>300	<1

Quality of raw water and treated water using ultrafiltration method at Douchy (France)

Also organic capillary membranes (Romicon) and multi-channel ceramic membranes were applied and compared for this purpose [2]. The treatment results obtained with the application of microfiltration through ceramic membranes are presented in Table 6 (cross-flow velocity over the membrane surface -3 m/s and pressure -0.3 MPa) [2]. The concentrations of all water load factors were reduced below the standards required for potable water.

Table 6

Parameters	Units	Raw water	Treated water
Turbidity	NTU	100	0.1
Organics	mg O ₂ /dm ³	6.5–7.3	0.5
Al	$\mu g/dm^3$	2700	15
Fe	$\mu g dm^3$	3000	40
Mn	$\mu g/dm^3$	45	?4

Results of microfiltration of underground waters using ceramic membranes

The authors of this paper [31, 32] also investigate the treatment and disinfection of ground and surface water. Table 7 presents the results of the application of ultrafiltration (UF) and microfiltration (MF) using polymeric membranes made of polyacrylo-

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nitrile (PAN), polysulfone (PSF) and ceramic membranes as well as modules of various configuration (flat, tubular multi-channel, capillary) for the removal of impurities from well and surface water.

Table 7

Modul	e type	Fe (%)	Turbidity (%)	TOC (%)	E. coli bacteria (%)	Mesophilic bacteria (%)
Capillary		95-100	94–99	12-32	100	100
Tubular	MF	83-100	92–99	17-48	100	89-100
Ceramic	UF	76-100	99.5	31-34	100	83.3-89
	PAN	98-100	91-99	20-52	94-100	86-99.5
Plate	PSF	98-100	91.5-99.5	36.5-53	100	95.5-100
	mixed	98-100	86–93	11–46	80-99.8	90–98

Effectiveness of well and surface water treatment and disinfection using UF and MF

Surface waters, in contrast with ground waters, very often contain a considerable amount of bacteria, viruses and microorganisms and are characterized by high turbidity, high concentration of organic substances and frequent occurrence of such microimpurities as pesticides, odoriferous or flavour substances. In such a situation, membrane processes applied as a single unit process are inappropriate due to hydraulic reasons (reduced production caused by membrane fouling) and inappropriate quality of produced water [1, 27]. Therefore, in such cases the ultrafiltration process is combined with oxidation and/or adsorption on powdered active carbon or nanofiltration is used [1, 2, 29]. Such systems are applied either directly to raw water treatment or after the clarification using a classical method.

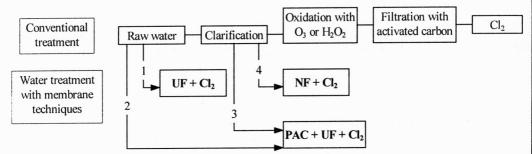
The presented potentials based on treatment systems of potable water from surface water sources are presented in Fig. 8 [37].

Ultrafiltration through open membranes (LED-UF) may be applied to the treatment of raw water, directly or in combination with other stages of treatment, e.g., preoxidation or adsorption on powdered active carbon, depending on the character of water (underground, surface, pollution degree with mineral organic or biological compounds). Moreover, with respect to more polluted waters, ultrafiltration can be used as the final phase after the conventional clarification. Compact ultrafiltration membranes (ZENON) may be used directly for the treatment of raw water, immediately after filtration through the 200 μ m filter, whereas the nanofiltration membranes Filmtec – after the clarification stage.

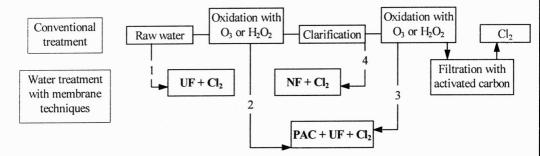
Table 8 presents selected parameters of water quality for the said treatment systems [37]. The membranes remove the particles of most substances (permeate turbidity was principally 0.1 NTU) and microorganisms (parasites, bacteria and viruses). With the application of direct ultrafiltration, only 10–20% of organic carbon

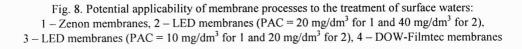
is removed, and when combined with adsorption on active carbon -40-80%. By pre-oxidation in the system of active carbon-ultrafiltration over 60-80% of UV adsorption can be removed, and along with it the problem of taste and odour of water is solved as well. The quality of permeates after nanofiltration is higher than the quality of treated water from all combinations specified above. We can therefore ascertain that due to filtration through compact ZENON membranes or the combination: oxidation-active carbon-ultrafiltration applied to raw water after clarification, as well as nanofiltration through Filmtec membranes, the quality of obtained water satisfies most of the quality parameters required by European health organizations.

1. Surface water with low concentartion of organics



2. Surface water with high concentartion of organics





Ultrafiltration is an economically attractive method for most of ground water treatment installations where there is no need to subject the membranes to chemical regeneration processes. It has been found that for polluted waters, especially for surface ones, ultrafiltration is less expensive than nanofiltration (Table 9) [1].

Table 8

Feed	Treatment	Turbidity (NTU)	<i>Coli</i> bacteria removal	20 nm particle removal	DOC removal	UV substances removal	Pesticides (antrazyne, simazyne)	(thre	nd smell shold nber)
		والمراجب والمست	S. S. C.					av.	max.
	UF	< 0.1	100%	100%	10-20%	10-20%	0	4	5
Raw	PAC+UF	< 0.1	100%	100%	40-70%	40-70%	<dl< td=""><td>2</td><td>3</td></dl<>	2	3
water	O ₃ +PAC+UF	< 0.1	100%	100%	60-80%		<dl< td=""><td>0.9</td><td>2</td></dl<>	0.9	2
	ZENON UF	< 0.1	100%	100%	50-60%	60-80%	-	5	: ⁻ -
	UF	< 0.1	100%	100%	10–15%	10–15%	0	8	10
Water	PAC+UF	< 0.1	100%	100%	20-30%	30-35%	<dl< td=""><td>4</td><td>8</td></dl<>	4	8
after	O ₃ +PAC+UF	< 0.1	100%	100%	20-30%	30-50%	<dl< td=""><td>0</td><td>1</td></dl<>	0	1
clarifi-	NF Filmtec	< 0.1	100%	100%	90%	90%	<dl< td=""><td>-</td><td>-</td></dl<>	-	-
cation									

Quality of permeates for various surface water treatment systems using ultrafiltration

UF – ultrafiltration through membranes of 0.01 μ m pore size, O₃ – ozonization, PAC – powdered active carbon, ZENON UF – ultrafiltration through membranes of cut-off of 4000–500 daltons, NF Filmtec – nanofiltration through membranes from Filmtec, DOC – dissolved organic carbon, DL – detection limit.

Table 9

Installation	Oxidation + a	active carbon	Nanofiltration		
capacity (m ³ /day)	Investment costs (US dollars/m ³ d)	Operation costs (US dollars/m ³)	Investment costs (US dollars/m ³ d)	Operation costs (US dollars/m ³)	
6000	370	0.14	740	0.26	
20000	310	0.13	420	0.22	

Cost evaluation of the treatment of clarified surface water

Wide experience concerning the operation and application of ultrafiltration to the treatment of usable water has been gathered within the last 5 years. Yet, it has been proved and cannot be now questioned that the application of ultrafiltration will enable:

• the reduction of turbidity to the level accepted by all standard setting organizations in Europe and other countries in the world,

• the application of this process as a disinfection phase.

The above means that the conventional physicochemical clarification process and disinfection will be replaced by a single unit process. The costs are already competitive for smaller installations. Together with the development of ultrafiltration technology, the costs of larger installations will also be reduced. A similar process of cost reduction has been observed over the last three decades with respect to reverse osmosis installations in the desalination process. In order to accelerate the pace of this evolution, many various aspects of the problem in question will have to be subjected to research investigation, principally the problems involving the reduction of membrane production costs and membrane modules production costs.

7. REMOVAL OF VOLATILE ORGANIC COMPOUNDS USING THE PERVAPORATION METHOD

Ground waters and surface waters are often polluted with volatile organic compounds which are very toxic, e.g. hydrocarbon halogen derivatives (trichloroethylenes, trihalomethanes, tetrahalomethanes) and aromatic ones (benzene, toluene, xylene) as well as by alcohols and ester solvents [3, 33–36]. They can be removed from water using a number of separation techniques [3, 35], depending on the concentration and whether the solvent is to be recovered or not. Some of these methods as, for example, air stripping only transfer the pollution from water media to gaseous media (air). With the application of burning, ozonization and UV radiation, new toxic organic compounds may be formed. On the other hand, during the adsorption on active carbon, the pollutant is transformed into solid phase, and the used active carbon must be burnt (possible emission of toxic substances to the air) or regenerated, which is still burdensome due to additional separation problems. In view of environment protection, the separation techniques of volatile organic compounds should be integrated into hybrid processes since the optimal concentration range of the pollutants being removed involves both of these methods.

The costs of the removal of volatile organic compounds by means of pervaporation are considerably diverse, depending on the goal to be achieved (water treatment or recovery of compounds). Figure 9 presents the diagram illustrating the application of pervaporation in the treatment of polluted underground water [36]. Water flux of the capacity of 76 m³/day is polluted with 1,1,2-trichloroethane of the concentration of 1000 mg/dm³ (0.01%). Assuming that the separation coefficient in this case is 200 (which is possible to obtain with the application of available membranes), the 99% removal of organic compound can be obtained, and the permeate will contain 4.1% of trichloroethane. After the condensation, the permeate is separated into two liquid phases: pure organic liquid, which can be separated by decantation, to be reused or burnt, and water flux containing 0.4% of the solvent, which is directed to the feedwater flux for further treatment. The investment cost of the installation is 115 thousand US dollars (about 2 US dollars/m³·d), and the operational cost about 4.1 US dollars/m³ of the feed [36]. The specified costs are comparable with the costs of other wastewater treatment methods.

Basing on the cost analysis, it has been found that pervaporation should be used as one of the pretreatment stages of water or wastewater. Therefore, hybrid systems utilizing this process are favoured. The whole treatment system may then be optimized, resulting in:

• COD reduction of the flux subjected to biological treatment,

• reduction of loading imposed upon active carbon deposit or aeration facility, which contributes to lower investments costs and lower operational costs of these facilities,

• precondensation of waste solvents prior to their burning.

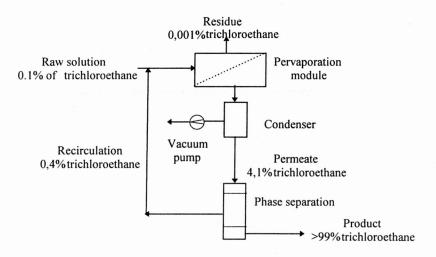


Fig. 9. Diagram of pervaporation system (PerVap[™]) of the capacity of 76 m³/day for the removal of 1,1,2-trichloroethane from water

With the application of a hybrid system, consisting of pervaporation and adsorption on active carbon, even the traces of volatile organic compounds can be separated from water [3] (Fig. 10).

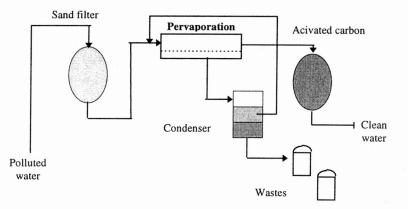


Fig. 10. Diagram of the pervaporation-active carbon hybrid process for the recovery of volatile traces of organic compounds from surface or ground water Pervaporation could find wider application in the recovery of organic compounds if more selective membranes for hydrophilic polar compounds were available. The existing membrane materials (e.g. silicone rubber) have the selectivity of 5–10. If materials of the selectivity of 40–50 are available for such compounds as acetic or formic acid, ethanol and methanol, pervaporation will become competitive compared with distillation or solvent extraction. Membranes characterized by such properties are being tested in laboratories, but, as yet, they have not been applied on technical scale.

8. DENITRIFICATION OF POTABLE WATER

In many cases, the concentration of nitrates(V) in potable water is higher than the permissible standards of 10–25 mg N/dm³ accepted by the World Health Organization or European Commissions. Potable water which surpasses such standards may pose hazards to human. Therefore, the polluted water should be subjected to an additional denitrification process. There are several methods for lowering the concentration of nitrates in potable water, which vary in terms of efficiency and simplicity level of their realization. The reduction of nitrate concentration to the level specified by the standards is currently obtained by mixing the waters highly polluted with nitrates with the waters having low content of nitrates or by the application of expensive methods which are not always effective, e.g. the ion-exchange method or biological processes [37–39]. In contrast to physicochemical processes, where the waste product is made up from a concentrated solution of nitrates, biological processes enable their reduction to gaseous nitrogen. Although the process of ion exchange is effective, it is expensive as well, and the removal of lyes after the regeneration of ionites creates considerable technical problem [4].

Membrane processes (reverse osmosis, electrodialysis) and ultrafiltration combined with biodegradation of nitrates, and ultrafiltration combined with ion exchange or reverse osmosis seem to be attractive taking into account technical and economic factors [4, 37–39].

As a result of the application of microorganisms in the denitrification process of potable water, they are often present in the final product, therefore the water, following such an operation, has to be subjected to filtration and bactericidal treatment. By using porous microfiltration and ultrafiltration membranes, the clarification of this water can be carried out, and the quality of the water entirely satisfies the standards with respect to turbidity and microbiological parameters. Therefore, combining the biological process with the process of membrane filtration has been proposed as an alternative technology in the discussed process [40–44]. Such a membrane bioreactor is much more advantageous than the traditional solution, mainly with respect to potable water, and one of its basic benefits is the lack of microorganisms in the treated water (water disinfection), as well as its almost complete denitrification.

The process of potable water denitrification, both pilot testing and industrial one, in the system with a membrane bioreactor was carried out over 6 months at Loiret in France [4]. The diagram of the installation is presented in Fig. 11. The tests were carried out on ultrafiltration membranes made by the firm Aquasource (France), and the operation conditions of the process are provided in Table 10.

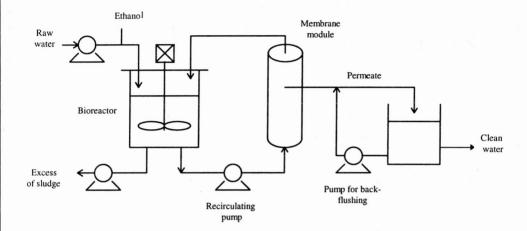


Fig. 11. Diagram of the installation used for the removal of nitrates from potable water using the membrane bioreactor

Table 10

Conditions of the water denitrification pilot-process using the membrane bioreactor

Bioreactor		Ultrafiltration	
Time of hydraulic retention, h	2.5	Surface of membranes, m ²	7.2
Age of sediment, days	5	Cross-flow velocity, m/s	0.9
Charge of nitrates in bioreactor,	0.6	Volumetric permeate flux, dm3/m2h	50
$kg NO_3/m^3 d$			all the second
Source of carbon	ethanol	Concentration of active carbon, g/m ³	10

The following results of the denitrification process were obtained:

- concentration of nitrates in raw wate: $62-90 \text{ mg NO}_3^-/\text{m}^3\text{d}$,
- concentration of nitrates in treated water: $mg NO_3^{-}/m^3 d$,
- removed charge of nitrates: $0.3-0.8 \text{ mg NO}_3^-/\text{m}^3\text{d}$.

By the application of reverse osmosis, the content of nitrates in raw waters can almost entirely be reduced, i.e. to the permissible level specified by legal regulations. Relative costs of treatment are in this case comparable with the costs of the ion exchange and elec-

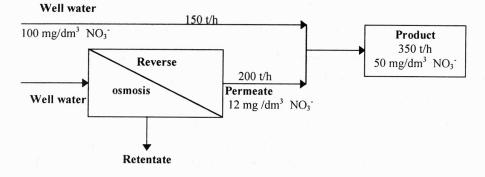
M. BODZEK, K. KONIECZNY

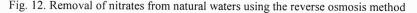
trodialysis processes, allowing also for the costs of concentrate disposal, which are comparatively low. Commercially available membranes for reverse osmosis are characterized by high retention coefficient with respect to inorganic salts, and therefore the required reduction of nitrate concentration in the treated water can be obtained due to passing only a part of this water through the membrane installation (Fig. 12) [38]. But since the osmotic membranes are not selective solely with respect to NO_3^- ions, all ions present in raw water are retained in the retentate, which is beneficial since their presence in potable water is very desirable (e.g. ions of magnesium, calcium, potassium) (Table 11) [38].

Table 11

Ion	Raw water I	Permeate	Raw water II	Permeate	
Ca^{2+} [mg/dm ³]	96	4	96.4	8	
Mg^{2+} [mg/dm ³]	18.8	0	23.1	1.2	
Na ⁺ [mg/dm ³]	26	7	24	6.4	
K^+ [mg/dm ³]	2	1	2.1	0.8	
SO_4^{2-} [mg/dm ³]	14.5	1.5	188	<10	
HCO ₃ ⁻ [mg/dm ³]	24.4	12.2	30	9	
$NO_3^{-}[mg/dm^3]$	95	12	94	14	
Cl ⁻ [mg/dm ³]	85	5	78	9	
$SiO_2 [mg/dm^3]$	13.6	1	-	-	
Fe [mg/dm ³]	-	-	< 0.005	0	
Mn [mg/dm ³]	- ² - ²	-	< 0.005	0	
	Exploitation	time: 2028 h,	Exploitation time: 24	400 h,	
	Pressure: 1.1	MPa,	Pressure: 1.23 MPa,		
120	Temperature:	16 °C,	Temperature: 12 °C,	- 16 - 11 - 11 - 11 - 11 - 11 - 11 - 11	
	Water recove	ry: 85%,	Water recovery: 70%,		
	Flux: 23 dm ³	/min	Flux: 14 dm ³ /min		

Comparison of ion composition in raw water and in permeate





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The removal of nitrates from water by means of electrodialysis, in particular the electrodialysis reversal, is applied when a high level of its recovery is required [37–39]. The process is more economic than in the case of reverse osmosis since the available water reduction coefficient is as high as 99%. Figure 13 presents the method for nitrites removal from saline water by means of electrodialysis [37]. Saline water containing among others nitrate ions is introduced into all chambers of the electrodialyser. The system of ion-selective membranes is set up in such a way that the ions migrating from dilution chambers (R) towards respective electrodes may penetrate the neighbouring chambers (condensation chambers Z), and the outflow of ions through the same membranes is not possible. Due to the above, the concentration of ions in dilution chambers decreases, and in condensation chambers – increases. Hence, two fluxes are obtained: the condensed flux containing ion components present in raw water and the diluted one almost totally devoid of them. Such a system might be regarded as ideal if the anion-exchange membranes were selective with respect to nitrate ions, since the removal of all ions from potable water is pointless.

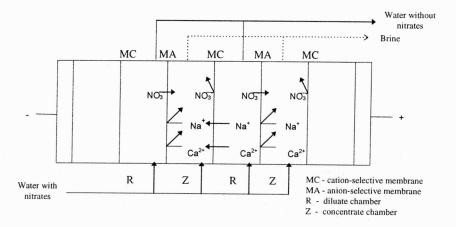


Fig. 13. Method for nitrates' removal from water using electrodialysis

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