MEMBRANE TECHNIQUES IN THE REMOVAL OF INORGANIC ANIONIC MICROPOLLUTANTS FROM WATER ENVIRONMENT – STATE OF THE ART

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Abstract: A number of inorganic compounds, including anions such as nitrate(V), chlorate(VII), bromate (V), arsenate(III) and (V), borate and fluoride as well as metals forming anions under certain conditions, have been found in potentially harmful concentrations in numerous water sources. The maximum allowed levels of these compounds in drinking water set by the WHO and a number of countries are very low (in the range of μg/l to a few mg/l), thus the majority of them can be referred to as charged micropollutants. Several common treatment technologies which are nowadays used for removal of inorganic contaminants from natural water supplies, represent serious exploitation problems. Membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) in hybrid systems, Donnan dialysis (DD) and electrodialysis (ED) as well as membrane bioreactors (MBR), if properly selected, offer the advantage of producing high quality drinking water without inorganic anions.

INTRODUCTION

A number of inorganic compounds, including anions such as nitrate(V), chlorate(VII), bromate(V), arsenate(III) and (V), borate and fluoride as well as metals forming anions under certain conditions, have been found in potentially harmful concentrations in numerous water sources [4, 5, 8, 37, 38]. Some of these compounds are highly soluble in water and dissociate completely, resulting in ions that are chemically stable under normal water conditions. The maximum allowed levels of these compounds in drinking water set by the WHO and a number of countries are very low (in the range of μg/l to a few mg/l), thus the majority of them can be considered to be as charged micropollutants.

Several common treatment technologies, nowadays used for the removal of inorganic contaminants from water supplies, which include physical, chemical and biological processes, represent serious exploitation problems [4, 5, 8, 37, 38]. Membrane processes such as reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) enhanced with polymers or surfactants, Donnan dialysis (DD), electrodialysis (ED) as well as membrane bioreactors (MBR), if properly selected, offer the advantage

of producing high quality drinking water [4, 5, 8, 37, 38]. In many cases, one membrane process can be integrated with another (integrated/hybrid systems) to produce water of even higher quality. In these processes, the membrane can be viewed as a barrier between contaminated and purified water streams. The separation of the two streams often allows for operation with no or minimal chemical water pre-treatment, which otherwise can form deleterious by-products. However, in physical membrane processes, inorganic anions are not destroyed but concentrated and the concentrate disposal can be costly and difficult to permit in many cases. Therefore, post-treatment of the concentrate stream or hybrid membrane-assisted technologies capable of converting anionic contaminants to harmless products are highly desirable. Among them, membrane bioreactors (MBR) are especially appropriate for some anions removal, since they offer 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, 37, 38].

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 [22]. Almost 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 and membrane surface charge. The repulsion forces are greater for polyvalent ions than for monovalent anions [38]. The charge of the surface of NF membranes is caused not only by the presence of functional groups possessing electrical charge, but also by the adsorption of anions from water. Hence, the charge of membrane surface depends on the concentration of anions in the solution [38] and varies from negative values to zero in isoelectric point of a membrane, up to positive values in acidic environment (usually pH < 4), according to the adsorption of cations. Such a pH dependence influences anions separations, hence the selection of proper process conditions is crucial for the application of NF. The 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 have been performed and in significant part of them promising results were obtained (Table 1) [38].

The pollution of natural waters with **nitrates(V)** is a result of application of nitrogen fertilizers and disposal of municipal and industrial solid and liquid wastes to the environment [5]. The permissible content of nitrates in drinking water is established at the level of 50 mg/l (10 mg N/l). Nitrates can have several adverse effects upon human health, most notably, such as ethemoglobinemia, gastric cancer and non-Hoadgkin's lymphoma

Table 1. RO and NF for removal of inorganic anions in the production of drinking water

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)
RO, NF, UF	Different membranes and manufacturer	As	Pilot studies at various sites in USA
RO	Different membranes and manufacturer	As	Pilot studies at various sites in USA
NF	NF ES-10 (Nitto-Denko)	As	Ground water – 0.6 mg As/l (Japan)
NF	Different membranes (Nitto-Denko)	As	Model water
NF	Filmtec NF-45 (Dow Chemical)	As	Model water
NF	Nanomax 50 (Millipore)	NO_3^-	Model water
NF	Different membranes (Nitto-Denko)	NO_3^-	Surface water after MF (Japan)
NF	Filmtec NF-70 (Dow Chemical)	NO_3^-	Ground water (Belgium)
NF	NF-300 (Osmonics)	NO_3^-, F^-	Ground water (California, USA)
NF	Filmtec NF-45 (Dow Chemical)	F^-	Model water
NF	Filmtec NF-70 (Dow Chemical)	F^-	Model water
NF	TFCS (Fluid Systems)	CrO_4^{2-}	Model water

[29].The reverse osmosis process allows to decrease the amount of NO_3^- in drinking water to the level established in regulations. The relative purification costs are comparable with the costs of ion exchange and electrodialysis including costs of disposal of the concentrate. The allowable RO membranes are characterised by high values of the retention coefficient relating to inorganic salts, thus the required decrease of NO_3^- concentration in drinking water can be achieved by mixing the permeate and raw water [5, 22]. Nitrates as monovalent ions are not totally retained by nanofiltration membranes (NF) e.g. the retention coefficient of NO_3^- for NF-70 membrane (by Dow/FilmTec) is equal to ca. 76%, that is under as for RO membranes [35]. NF can be also used as a first step in the NO_3^- removal process integrated with RO or ion exchange [5, 22]. However, the presence of sulphates decreases the retention coefficient of NO_3^- ions during NF. Under such conditions, NF membranes practically do not eliminate NO_3^-, nevertheless they retain multivalent ions (Ca and Mg) what has a positive effect on RO and ion exchange performance.

Contamination of drinking water with **bromate(V)** (BrO_3^-) is usually associated with the formation of the so-called disinfection by-products (DBP) during ozonation of waters used for the production of drinking water containing bromides (Br⁻). The concentration of BrO_3^- in freshwaters varies between 15–200 µg/l [12], while the larger content appears in the groundwater [18]. To the removal of bromates(V), reverse osmosis and nanofiltration can be applied. Removal of BrO_3^- in NF process amounts to 75−100% with the initial contents of the ion at 285 µg/l and pressure of 739.5 kPa, while in the RO process the average retention coefficient of 97% at pressures of 276 and 517.5 kPa is reached [7]. These results were also confirmed by the Prados-Ramirez *et al.* [28], who observed for river water the 77% removal of BrO_3^- and 63% of Br⁻ using NF membrane at the initial concentration of BrO_3^- amounted to 300 µg/l. It was found that the NF is more

economical in terms of cost, mainly as a result of lower applied pressure. The disadvantages of the aforementioned techniques include deep deionization of the permeate, which requires remineralisation and the formation of waste stream retentate (concentrate), requiring treatment before discharge into the environment.

Due to the widespread use, their high mobility in the natural waters for drinking water production and low tendency to degradation, **chlorates(VII)** (ClO_4^-) constitute now a serious environmental problem [21]. Numerous studies have demonstrated toxicity of chlorates(VII) and their negative impact on the development and functioning of the human organism. Studies have shown that reverse osmosis and nanofiltration can be applied to the removal of this ion [17, 21, 23]. For NF retention coefficient of ClO_4^- amounts to 75–90%, and for RO ca. 96%, in the case when raw water has 100 mg ClO_4^-/l [21]. High-pressure RO membranes allow for the removal even of approximately 99.9% of ClO_4^- ions [24]. In the case of low pressure RO membranes, retention coefficient of ClO_4^- is lower (approximately 95%) [24]. Then, before the introduction of water to water network (customers), additional treatment of the permeate may be required by means of ion exchange, adsorption on activated carbon or in bioreactors [1, 24]. In principle the RO can be used as a stand-alone technology to the removal of chlorates(VII) in the production of drinking water only at low ClO_4^- concentrations. Because RO and NF are not destructive processes, retentate contains chlorate(VII) and other pollutants, which must be removed before discharge into the environment. In general, biological treatment, discharge to surface water, sewer or to the ground, and evaporation are taken into consideration [1].

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 [22, 38]. The application of reverse osmosis in fluorides removal is connected with partial demineralization of water, what is the main disadvantage of the process [22]. 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) [31]. During treatment of water which is characterised by 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 [33]. 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) [16]. The analysis of retention of monovalent ions for NF membranes indicates that smaller ions (fluorides) are retained more efficiently than other halogen ions (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) [16]. It explains the possibility of selective desalination of brackish water containing F^- using NF and allows to produce drinking water cheaper than when RO is applied.

Boron appears in the environment mainly in the form of boric acid (H_3BO_3) and its salts [3, 22]. Under lower pH the hydration of boric acid does not occur what causes the smaller retention during membrane separation. The dissociated form is totally hydrated and characterised by greater diameter and negative ion charge what results in higher retention [3]. 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 [3]. The removal of boron compounds from natural waters are of special importance for its desalination by reverse osmosis. 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 (the content of F$^-$ below 5 mg/l) or water disposed to the environment. In addition, high pH process conditions lead 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. 1) [3, 22]. The cost of removal of boron in the two-step process is very high [22] 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 [22].
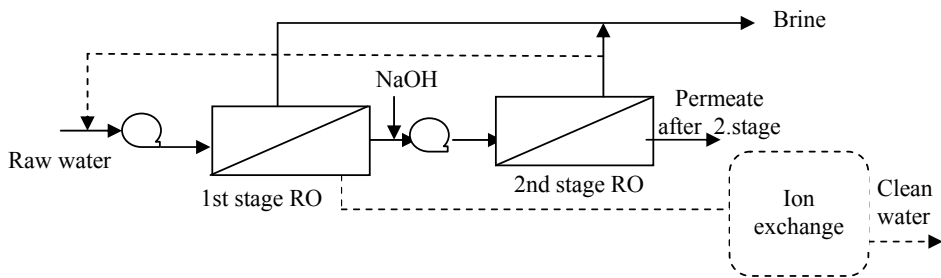

Fig. 1. Two stage RO system for boron removal

Also ultrafiltration and microfiltration can be used in boron removal from water. The interesting solution is **sorption-membrane hybrid process** used in boron removal from seawater or from permeate after seawater desalination with RO. Boron is removed by ion exchange resins (e.g. Dowex XUS 43594 – Dow Chemicals, Diaion CRB01 – Mitsubishi or others) of very small grain size (20 μm) and after sorption ion exchange is separated by means of microfiltration. The small size of grains of the resin allows to effectively decrease the 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) [9]. Also studies have been focused on the removal of boron from water solutions using ultrafiltration enhanced with polymers (PEUF), which generally are poly(vinyl alcohol) (PVA) 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 coefficient of boron decrease during the process (starting from values close to 1) as amount of active centers of the chelating polymer decrease. The retention depends also on pH, boron and polymer concentration in the feed.

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 and

As(V) as ions $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}, whose concentration depends on pH. The form of As(V) ions has a direct impact on the choice and effectiveness of the removal methods. In order to decrease arsenic content in drinking water, reverse osmosis and nanofiltration membranes as well as hybrid process of coagulation-MF/UF are applied [5, 32]. RO is an effective technique for removing arsenic, which demonstrated the tests carried out at the laboratory on pilot scale [5, 25, 32]. RO membranes TFC-ULP (by Koch) allowed to remove 99% of arsenic from groundwater (the decrease from 60 µg/l to 0.9 µg/l), whereas DK2540F membranes (by Desal) retained 88−96% of the pollutant [32]. The removal of As(III) is always lower than that of As(V), e.g. ES-10 polyamide and NTR-729HF polyvinyl alcohol membranes, both by Nitto-Japan, proved the lower removal of As (III) than As (V) in the pH range of 3−10. pH and the content of dissolved organic matter have a great influence on arsenic removal [27]. The removal of As(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 As(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% [27]. The higher removal of arsenic(V) (90%) was observed for waters of lower organic matter content, while in comparison to higher organics content it was equal to 80%. One can draw a conclusion that oxidizing conditions for carrying out the removal of arsenic are recommended. **Nanofiltration** membranes are also applied to As removal [5, 25]. 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 [8]. In the 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. The degree of removal of As(V) with use of NF-45 membrane significantly increases with the increase of pH [5], according to the difference in As ion hydration 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. 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. Microfiltration and ultrafiltration can be also used for arsenic removal from water [5, 14, 32]. 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 [5, 32]. Other MF and UF membranes can be used mainly by means of integrated systems with coagulation and flocculation [14]. In the article [32] 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. As a result, from the water of As content equal 40 µg/l, the water containing less than 2 µg/l of As was obtained. In integrated process, the As removal was caused thanks to the adsorption of As on coagulation flocks and separation of those flock by MF membrane. In such a case the removal of As(III) is also less effective than that of As(V) and often preliminary oxidation of As(III) to As(V) is required.

Chromium(VI) compounds are soluble in water and at pH 1−6 they occur in the form of $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions and at pH > 6 as CrO_4^{2-} ions. These compounds are highly toxic to living organisms occurring in the environment, so its permissible concentration in drinking water is regulated, and in Poland amounted to 0.05 mg/l, including 3 µg/l for

Cr(VI) [22, 26]. Studies were carried out for Cr(VI) removal from water by reverse osmosis using Osmonics membranes Sepa-S type and membranes made of cellulose acetate (CA) [22, 26]. It was found that the CA membranes retain 96% of Cr(VI) ions, while Osmonics membranes 80–96%, depending on the membrane compactness. It was also found that permeate flux obtained for CA membranes was much smaller than that for Osmonics ones. It seems that a better solution in the removal of Cr(VI) from water is nanofiltration. In this case, retention coefficient increases with pH for higher values of this parameter, but the effect is more pronounced for membranes with less separation capacity (from 47 to 94.5% for Osmonics membranes) compared to more compact membranes (from 84 to 99.7% for Osmonics membranes). There was also observed the retention coefficient dependence on the concentration of Cr in feed for NF membranes, but the range of effect depends on pH. In an acidic solution at higher concentrations of Cr in feed, higher retention was found, while at pH 6.5–11 the nature of this relationship was the opposite, i.e. lower retention was obtained for higher concentrations of Cr. This particular phenomenon, with general importance, is due to the fact that the Cr(VI) changes the ion forms with a change in pH. In an highly acidic environment, Cr(VI) occurs in the form of no dissociated chromic acid (H_2CrO_4), and forms $HCrO_4^-$ ions when pH is changed to 6.5, and with the increase of pH the concentration of these ions is also increased. Further increasing pH above 7 causes formation of CrO_4^{2-} ions, the concentration of which also depends on pH. In solution the $Cr_2O_7^{2-}$ ions are also present, with concentration depending on the feed concentration and pH. Usually this ion is dominant at high concentrations of Cr and in strong acid environment (pH 1–7) but its concentration decreases with further pH increase [5, 13, 34].

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, 38, 40]. For anion removal, anion exchange membrane separates two solutions, which differ in 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 to that of the anion target ion in order to maintain electroneutrality (Fig. 2) [40]. The ions, which are permeable to the membrane, will equilibrate between the two solutions until the Donnan equilibrium is obtained. Since concentration ratios determine the Donnan equilibrium, not concentration differences, Donnan dialysis
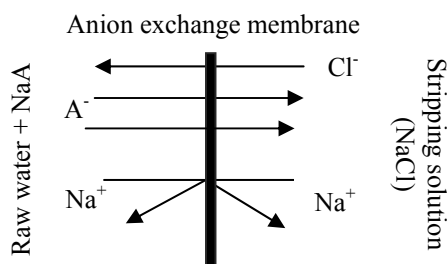

Fig. 2. Scheme of Donnan dialysis process (A⁻ target anion)

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(V) and fluoride, by Donnan dialysis has received attention (Table 2) [38].

Table 2. Donnan dialysis and electrodialysis in the removal of inorganic anions in drinking water production

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 [38]. In ED membrane fouling and scaling are frequently observed, therefore, the ED systems are usually operated 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 in particular nitrate(V) (Table 2). [38, 40].

So ED can provide an efficient removal of inorganic anions from drinking water. Since most known toxic anions are monovalent, the use of monovalent anion permselective exchange membranes is especially attractive [38]. ED appears to be less applicable for waters of very low salinity (conductivity of less than 0.5 mS), for which Donnan dialysis can be a better solution, and in cases when besides ions, removal of low-molecular weight non-charged compounds (to which ED is obviously ineffective) from the water is desired. In the latter case, pressure-driven membrane processes such 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 the removal of **nitrate(V)** from groundwater in Austria [38, 40]. 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 [40].

Electrodialysis process, and especially the reversal electrodialysis (EDR), is also proposed to the removal of **bromates** (BrO_3^-) from water [36, 41]. Studies of ED with anion exchange membrane (Neosepta AMX) showed the BrO_3^- removal with the efficiencies of 86−87%, while for the monoanionselective membranes (Neosepta ACS) even 99%, at a current density of 20 A/m². The efficiency of the removal of other anions changed from 80% (HCO_3^-) to 93% (NO_3^-) [41]. This means that the ED of water with initial concentration of BrO_3^- of 100 µg/l causes the final concentration of these ions of approximately 1 µg/l, thus significantly below the limit value in the drinking water (10 µg/l BrO_3^-). The increase in power density for ED with standard anion exchange membrane results in an increase in the anions transport rate by 36%.

ED and EDR were also tested as an autonomous technology for the **chlorate(VII)** ions (ClO_4^-) removal, especially at high concentrations of silica (approximately 80 mg/l), because in the EDR installations silica and its concentration does not affect the water recovery degree. During removal of chlorate(VII) ions using EDR method, retention coefficients of other anions with similar valence (e.g. nitrate) are also important. Pilot tests have shown the removal of chlorate(VII) ions in the range from 70% to 97%, depending on the initial concentration of chlorate(VII) and the number of steps in the configuration of EDR system [1, 30].

The carried out studies of **arsenic** removal from water by means of electrodialysis has shown that it is possible to remove As with efficiency exceeding 80% for As(V) and 50% for As(III) [2, 20], using the water recovery of 85%. In other studies with EDR, a concentration of arsenic in eluate of 0.003 mg/l at initial level of 0.021 mg/l was obtained, which corresponds to the retention coefficient of 86% [20].

The application of electrodialysis (ED) to **fluorides** (F⁻) removal from water that contains significant amount of F⁻ ions is beneficial as the process characterises with insensitivity to seasonal changes of fluorine concentration, satisfying selectivity, low demand of other substances and low energy consumption [38]. The degree of removal of fluorides and soluble substances is very often higher than that obtained for RO and it increases with the increase of electrical potential difference, temperature and flow rate [38, 40]. When fluorides concentration is below the permissible level, ED devices can be shut down for a longer time period. In order to minimize the precipitation of salts of bivalent ions (sulphates and carbonates) in the concentrate chambers two configurations of ED process are proposed [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 to obtain water of municipal quality.

Electrodialytic removal of **boron** from water and wastewater, similarly to RO, also requires high pH value, as boric ions are transported through anion exchange membrane. The main advantage of ED in comparison to 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 a similar extent as boron [3, 19]. 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 [19]. In order to omit high demineralization of the diluate, monopolar membrane under alkali process conditions (pH = 9–10) should be applied [3].

MEMBRANE BIOREACTORS

The main disadvantage of pressure-driven membrane processes and electrodialysis is production of the concentrate with high load of anions That is why for the removal of anionic micropollutants from RO and NF as well as ED concentrates and natural water, membrane bioreactors (MBR) is proposed, which allows to decrease concentration of pollutants to a value which corresponds to drinking water quality [4, 8, 38].

The biological **denitrification** is based on the reduction of nitrate(V) to molecular nitrogen under anaerobic conditions at the presence of microorganism and proper donor of electrons [5, 8, 38]. The kinetic of the reaction depends on a kind of microorganisms and biodegradation process conditions (pH, nitrates concentration) [8]. Heterotrophic bacteria which naturally occur in soil and water as well as autotrophic bacteria are used in biological nitrates removal processes. The addition of organic substrates (ethanol, methanol and acetates) is required for heterotrophic microorganisms, whereas autotrophic denitrification needs inorganic compounds (e.g. sulphur compounds and hydrogen) as electron donors [4, 5]. The second advantage of autotrophic denitrification is lower production of activated sludge, however the process runs slowly [22]. When heterotrophic denitrification is applied the removal of dissolved organic carbon and biomass from treated water is required [38]. Disadvantages of conventional biological denitrification can be eliminated by application of a membrane bioreactor (MBR), which assures the total retention of biomass. For nitrate(V) removal, the configuration of MBR can be arranged as the system with pressure driven membrane modules (Fig. 3 and Table 3) [4, 5] or as extractive membrane bioreactors (membrane contactors) (Fig. 4) [8, 11].
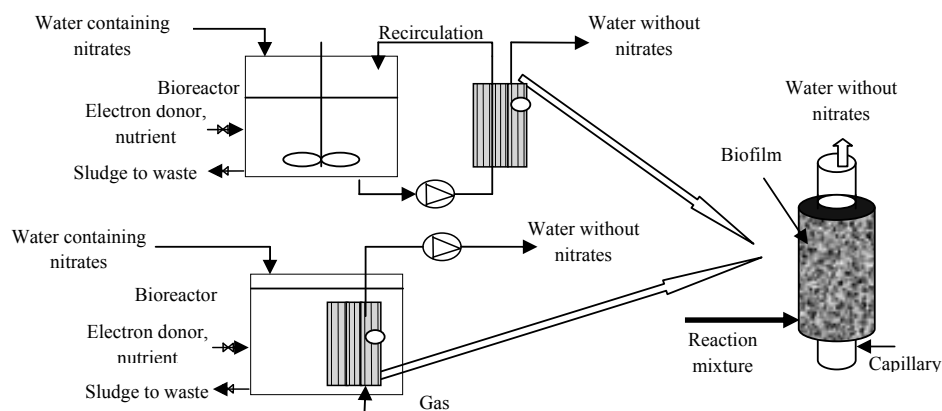

Fig 3. Membrane bioreactors with pressure driven membrane module

Table 3. Membrane bioreactors with pressure-driven modules for the removal of inorganic anions in drinking water production

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)

In the case of MBR with pressure-driven membrane process, MF or UF membrane may be placed inside or outside bioreactor. 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. 4) water with nitrates(V) 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 [4, 5]. In these conditions, both electron donor and denitrification biomass are separated from the water by membrane.
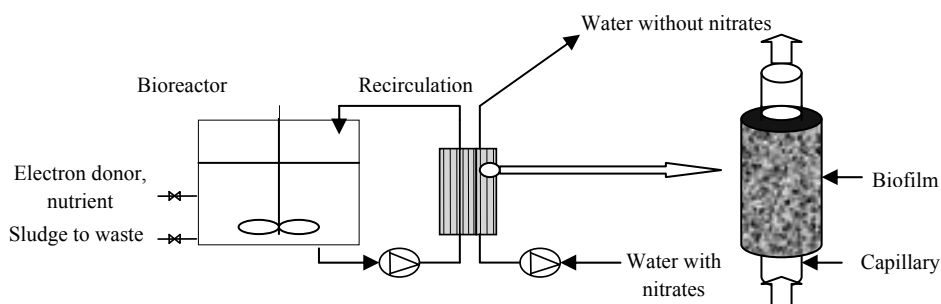

Fig. 4. Extractive membrane bioreactor

Biological degradation of oxyanions may also be used to the removal of not only nitrates(V) but also of **bromates**(V) and **chlorates**(VII). Studies have shown their full reduction to bromides and chlorides by bacterial cultures used for nitrates(V) reduction [10, 15, 39]. Most commonly ethanol is used as an electron donor and a source of carbon. Reduction of bromates(V) and chlorates(VII) is thermodynamically less favorable (less energy is released) in relation to the reduction of nitrate(V). The studies reported [15] in-

dicate that the removal of ClO_4^- and BrO_3^- from the water by biological methods requires long hydraulic retention times, owing to the low rate of oxyanions reduction and the need of completely prior removal of nitrates(V). Similarly as in the case of nitrate, the treated water requires a post-treatment because of the possibility of secondary contamination of water by the microorganism cells, residual carbon source and/or metabolic transformation by-products.

A new membrane bio/process for the removal and bioconversion of ionic micropollutants from water streams is the ion-exchange membrane bioreactor (IEMB) [8, 38]. In this process, the ionic micropollutant is transported from the water stream through a non-porous ion-exchange membrane into a biological compartment where it is simultaneously converted by a suitable microbial culture into harmless products. The driving force for pollutant transport through the membrane is the anion electrochemical potential difference. Therefore, as for Donnan dialysis, pollutant transport against its concentration gradient is possible due to the presence of driving counter-ions in a higher concentration (Fig.5). 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 nonionizable carbon source and other required nutrients in a continuous mode. In addition, the bioconversion of the pollutant in the IEMB keeps its concentration at low levels and guarantees an adequate driving force for transport.
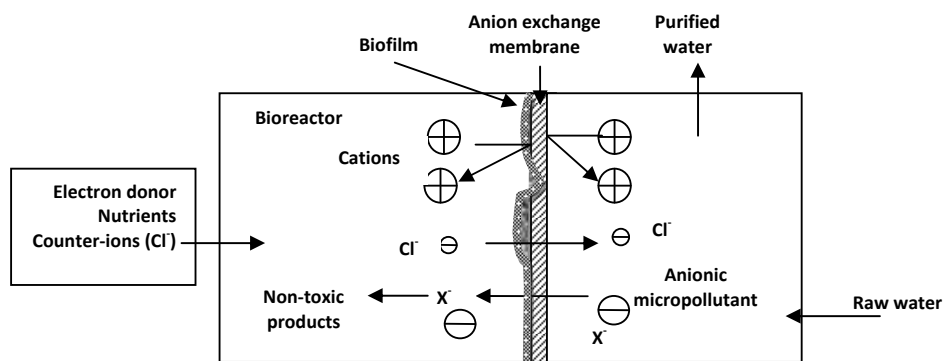

Fig. 5. A schematic diagram of the ion transport mechanism in the ion exchange membrane bioreactor (IEMB)

This concept was first demonstrated in synthetic waters for the removal and bioconversion of nitrate to harmless nitrogen gas using Neosepta ACS mono-anion permselective membrane and ethanol as the carbon source [38]. 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. As the major counter-ion in IEMB for oxyanions removal, chloride ions are used. Within the concentration relevant to nitrate polluted water (50–350 mg NO_3^-/l), a complete denitrification was achieved without accumulation of NO_3^- and NO_2^- ions in the biocompartment. A maximum water production rate of 33 l/m²h and a nitrate removal rate of 3.5 g/m²h were obtained [38].

CONCLUDING REMARKS

The use of membranes in the treatment of water sources containing anionic micropollutants for drinking purpose is a developing technology. NF (RO) and ED can provide more or less selective removal of the target pollutants, especially when separations between mono- and multi-valent anions are desired. In NF, this is a consequence of both, ion size according to molecule size and charge exclusion effects, while in ED it is due to the use of ion exchange membranes with mono-anion permselectivity. However, the concentrate brine discharge and/or treatment can be problematic in many cases.

Combining the advantages of membrane separation with biological reactions for the treatment of polluted water supplies has resulted in the development of three major membrane bio/processes: pressure-driven membrane bioreactors, biological membrane contactors, and ion exchange membrane bioreactors. In the first case, membranes are essentially regarded as micro/ultra porous barriers to promote high biomass for the process intensification and avoid contamination of the treated water with microbial cells. However, secondary water pollution by an incompletely degraded organic carbon source and other low-molecular mass compounds is possible. Membrane bioreactors in the contactor form work in the conditions of separation of treated water from both biomass and electron donors, while ion exchange membrane bioreactors can provide a highly selective target ion removal and avoid secondary pollution of the treated water.

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TECHNIKI MEMBRANOWE W USUWANIU NIEORGANICZNYCH MIKROZANIECZYSZCZEŃ
ANIONOWYCH ZE ŚRODOWISKA WODNEGO – STAN WIEDZY

Szereg związków nieorganicznych, w tym aniony (głównie: azotany, nadchlorany, bromiany, arseniany, borany i fluorki), jak również metale tworzące w określonych warunkach aniony (np. chrom), występuje w potencjalnie szkodliwych stężeniach w licznych źródłach wody do picia. Maksymalne dopuszczalne wartości ich stężeń w wodzie do picia, ustalone przez WHO i szereg krajów, są bardzo niskie (w zakresie od µg/l do kilku mg/l) i w związku z tym większość z nich może być zaliczona do mikrozanieczyszczeń. Kilka tradycyjnych technologii, które stosuje się obecnie do usuwania zanieczyszczeń nieorganicznych ze źródeł wody naturalnej, stwarza poważne problemy eksploatacyjne. Procesy membranowe, odwrócona osmoza (RO), nanofiltracja (NF), ultrafiltracja (UF) i mikrofiltracja (MF) w systemach zintegrowanych, dializa Donnana (DD) i elektrodializa (ED) oraz bioreaktory membranowe (MBR), właściwie dobrane, umożliwiają produkcję wody do picia o wysokiej jakości, pozbawioną anionów nieorganicznych.