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INORGANIC MICROPOLLUTANTS REMOVAL
BY MEANS OF MEMBRANE PROCESSES - STATE OF THE ART

USUWANIE MIKROZANIECZYSZCZEŃ NIEORGANICZNYCH
ZA POMOCĄ PROCESÓW MEMBRANOWYCH - STAN WIEDZY

Abstract: A number of inorganic anions and metals, especially heavy metals, at certain conditions, have been found in potentially harmful concentrations in numerous water sources. The maximum permissible levels of these compounds, in drinking water and wastewaters discharged to environment, set by the WHO and a number of countries are very low (from $\mu g/dm^3$ to a few mg/dm^3). 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 and nanofiltration, ultrafiltration and microfiltration in integrated systems, Donnan dialysis and electrodialysis as well as membrane bioreactors, if properly selected, offer the advantage of producing high quality drinking water without inorganic substances as well as purified wastewater which can be drained off to natural water sources.

Keywords: inorganic micropollutants, pressure-driven membrane processes, membrane bioreactors, electrodialysis and Donnan dialysis

Introduction

A number of inorganic compounds, including anions (nitrate(V), chlorate(VII), (V) and (III), bromate(V), arsenates(III) and (V), borate and fluoride) and heavy metals, have been found at potentially harmful concentrations in natural water sources and wastewaters [1-6]. Some of these compounds are highly soluble in water and dissociate completely what results in formation of ions that are chemically stable at normal water conditions. The maximum permissible levels of these compounds, in drinking water and wastewaters discharged to environment, set by the WHO and a number of countries are very low (in the range of $\mu g/dm^3$ to a few mg/dm^3). Thus, the majority of them can be referred to as charged micro-pollutants.

The pollution of the aquatic environment with metals and anions may be either natural or anthropogenic origin. Several common treatment technologies, including coagulation -

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sedimentation - filtration, adsorption, chemical precipitation, ion exchange, classical solvent extraction, evaporation and biological methods, which are nowadays used for removal of inorganic contaminants from natural waters or wastewaters, represent serious exploitation problems [1, 2, 4-6]. Increasingly, membrane processes are applied to remove inorganic micropollutants from aquatic environment. Primarily reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF) and microfiltration (MF) in hybrid systems, Donnan dialysis (DD) and electrodialysis (ED) as well as in combination with extraction (liquid membranes) and bioreactors are used [1-6].

Pressure driven membrane processes

Removal of anionic micropollutants

The **reverse osmosis** process is highly efficient in direct removal of inorganic anions during drinking water production. Additionally it guarantees safe detoxification. However, the complete desalination is undesired according to possible corrosion problems and remineralization requirements [7]. The water of hardness below 50 mg/dm^3 is corrosive for copper, iron, zinc and other metals [1-3]. As a result, other processes suitable for selective removal of toxic anions and moderate desalination are desired. **Nanofiltration (NF)** fulfills such requirements as it enables the selective desalination *ie* 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 consists not only of the difference in the rate of transport through a membrane, but also in the electrostatic repulsion between anions and membrane surface charge, which is greater for polyvalent ions than for monovalent anions [5]. The charge of the surface of NF membranes results not only of the presence of functional groups possessing electrical charge, but also of the adsorption of anions from water. Hence, the charge of membrane surface depends on the concentration of anions in the solution [5] and varies from negative values to zero in isoelectric point of a membrane, up to positive values in acidic environment (usually pH < 4), when the adsorption of cations takes place. The NF process is much more sensitive to ionic strength and pH of raw water than RO, hence the selection of proper process conditions is crucial for its application. Many studies considering the removal of toxic anions from natural waters and purified wastewaters by means of RO and NF have been performed and in significant part of them promising results were obtained [5].

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 [1, 2]. Ion exchange, reverse osmosis, electrodialysis and biological denitrification are the most often used methods for the removal of the excessive amount of nitrates [1, 2, 7]. Nitrates can have several adverse effects upon human health among which most notably are ethemoglobinemia, gastric cancer and non-Hoadgkin's lymphoma [8].

The **reverse osmosis** process allows decreasing the amount of NO_3^- in drinking water to the level established in regulations (10 mg N/dm^3). RO membranes characterised with high values of the retention coefficient of inorganic salts. Thus, the required decrease of NO_3^- concentration in drinking water can be achieved by mixing the permeate and raw water [1, 7].

Nitrates as monovalent ions are not totally retained by **nanofiltration**, *eg* the retention coefficient of NO_3^- for NF-70 membrane (Dow/FilmTec) is equal to 76%, which is lower than one of RO membranes [9]. Nanofiltration can be also used as a first step in the NO_3^- removal process in combination with RO or ion exchange [1, 7]. However, the presence of sulphates decreases the retention coefficient of NO_3^- ions during NF. At 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.

The relative purification costs of both processes are comparable with the costs of ion exchange and electrodialysis, including costs of disposal of the concentrate.

Reverse osmosis and nanofiltration membranes used for the removal of nitrates from water are twice as expensive as membranes applied in the **low-pressure membrane processes**. Moreover, their application is much more energy-consuming as they require much higher pressure. Hence, alternative methods consisted of ultrafiltration membranes (UF) and surfactants or polymers complexing nitrate ions are applied [7]. Complexes or micelles containing nitrate ions can be next retained by ultrafiltration membranes. In case of application of UF membranes and at surfactant concentration below the critical concentration of micelles formation the rate of removal of nitrate ions exceeds 79% depending on type and dose of surfactant used [7].

Contamination of drinking water with **bromates(V)** (BrO_3^-) is usually associated with the formation of disinfection by-products during ozonation of waters containing bromides (Br^-). The concentration of BrO_3^- in natural waters varies between 15-200 µg/dm^3, while the larger content appears in the groundwater. Removal of BrO_3^- in NF process reaches up to 75-100% with the initial content of 285 µg/dm^3, while for RO process the average retention coefficient of 97% is obtained [10]. Prados-Ramirez et al [11] observed the 77% removal of BrO_3^- and 63% of Br^- using NF membrane for the treatment of river water at the initial concentration of BrO_3^- amounted to 300 µg/dm^3. It was found that the NF was more economical in terms of cost, mainly as a result of lower pressure applied. The disadvantages of the discussed techniques include deep deionization of the permeate, which requires remineralization and the formation of waste stream *ie* retentate (concentrate), which need to be treated before discharge into the environment.
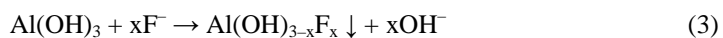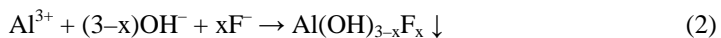
Due to the widespread use, high mobility in the natural waters and low tendency to degradation, **chlorates(VII)** constitute now a serious environmental problem. It is mainly because of their toxicity and negative impact on the development and functioning of the human organism. Studies have shown that RO and NF can be applied to remove ClO_4^- from aqueous solutions [2, 12]. For NF, ClO_4^- retention amounts to 75-90%, while for RO it is 96% at the initial concentration of 100 mg ClO_4/dm^3 [1, 2]. High-pressure RO membranes allow to remove even 99.9% of ClO_4^- ions and for low pressure RO membranes retention coefficient of ClO_4^- is lower (95%) [13]. Hence, in some cases additional treatment of the permeate before its introduction to the water network may be required e.g. by means of ion exchange, adsorption on activated carbon or in bioreactors [13]. In principle the RO can be used as a stand-alone technology to remove chlorates(VII) during the production of drinking water only at low ClO_4^- concentrations. As RO and NF are not destructive processes, retentate contains chlorate(VII) and other pollutants, which must be removed before its discharge into the environment. In general, biological treatment and evaporation are taken into consideration [13].

The appearance of **fluorides (F⁻)** in natural waters results of their presence in lithosphere and anthropogenic industrial activity. According to WHO, the maximum fluoride concentration in drinking water is established at 1.5 mg/dm^3 [5, 7]. Adsorption, coagulation with sedimentation, ion exchange and membrane processes *ie* RO, NF and electrodialysis are the main methods proposed for fluorides removal from water [1, 2].

The application of **reverse osmosis** to fluorides removal is connected with partial demineralization of water, what is the main disadvantage of the process [7]. RO membranes for water desalination allow to remove 98-99% of salts, what practically results in almost total retention of fluorides, *eg* below 0.03 mg/dm^3 for the initial content ranging of 1.3 to 1.8 mg/dm^3 [14].

During the treatment of water which characterises with high fluoride content, the application of **nanofiltration** is beneficial as the remineralization of permeate is not always required. The final concentration of F⁻ ions in permeate obtained for commercially available NF membranes, *ie* NF90 and NF270 (FilmTec) and TR60 (Toray) was in the range of 0.05 to 4.0 mg/dm^3, depending on the initial concentration and membrane type [15]. 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, *ie* NTR-7250, NTR-7450, F-70 (FilmTec), Desal-5-DL and Desal 51-HL (Osmonics), MT-08 (PCI) and SR-1 (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 (*eg* chlorides). The difference in selectivity results of 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.

Besides RO and NF, a **membrane coagulation reactor** (MCR) *ie* a combination of coagulation and microfiltration (MF) can be used for the removal of fluorides during drinking water production [17]. In the reactor aluminum salt is used as the coagulant and its hydroxide is the adsorbent. Sodium hydroxide can be added to provide hydroxide ions and adjust the pH during coagulation and adsorption. Hydrolysis [Eq. (1)], co-precipitation [Eq. (2)] and adsorption [Eq. (3)] may occur when Al$_2$(SO$_4$)$_3$ and NaOH are simultaneously added into raw water. The primary fluorides removal mechanism results of the low solubility of Al(OH)$_3$ and hard dissolution of the aluminum-fluoride complex. Thus, they are precipitated out of the solution or can be separated by the MF membrane.

$$Al^{3+} + 3OH^- \rightarrow Al(OH)_3 \downarrow \qquad (1)$$

$$Al^{3+} + (3-x)OH^- + xF^- \rightarrow Al(OH)_{3-x}F_x \downarrow \qquad (2)$$

$$Al(OH)_3 + xF^- \rightarrow Al(OH)_{3-x}F_x \downarrow + xOH^- \qquad (3)$$

Boron appears in the environment mainly in the form of boric acid (H$_3$BO$_3$) and its salts [7, 18]. At lower pH the hydration of boric acid does not occur what causes its low retention during membrane separation. The dissociated form of the contaminant is totally hydrated and characterises with greater diameter and negative ion charge what results in higher retention [18]. In the EU countries the permissible concentration of boron in drinking water is established at 1.0 mg/dm^3, while for industrial wastewater disposed to sewage it is 10 mg/dm^3 [18]. Boron is removed from the environment mainly by means of coagulation and electro-coagulation, adsorption and ion exchange as well as membrane processes *ie*

reverse osmosis, nanofiltration, electrodialysis and polymer enhanced ultrafiltration [1-3, 18]. However, only two of those methods are used in the industry *ie* reverse osmosis at high pH conditions and ion exchange [18].

The removal of boron compounds from natural waters by means of **reverse osmosis** is of special importance as any of the conventional desalination methods (distillation, electrodialysis) are capable to reduce boron content to the permissible level. The retention of boron at low or neutral pH varies from 40 to 60%, what is insufficient to obtain not only the permissible level for drinking water, but also for seawater desalination or water disposed to the environment. On the other hand, high pH process conditions lead to fouling and scaling, which are mainly caused by the precipitation of calcium and magnesium compounds. Thus, the RO permeate is alkalized to pH *ca*. 9.5 and once more treated by RO or ion exchange (Fig. 1) [7, 18]. The cost of boron removal via the two-step process is high and usually multistep (3-4 steps) RO processes are applied [7]. Hence, 2nd and 3rd stage RO membranes are operated at lower concentrations and pressure. Nowadays, studies focused on the development and testing of novel RO membranes that can be applied in one-step process are carried out.
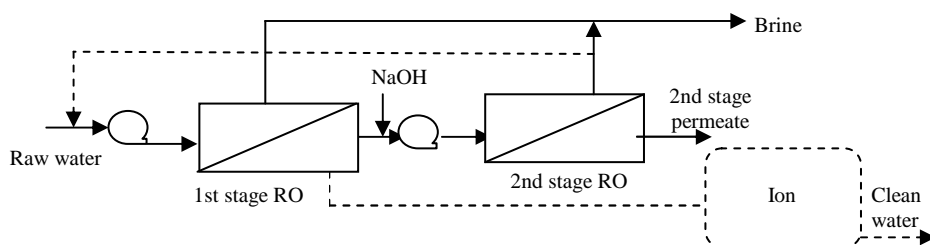

Fig. 1. Two stage RO system for boron removal

Ultrafiltration and microfiltration can also be used for boron removal from water. The interesting solution is the hybrid process of sorption-membrane separation used in boron removal from seawater or the permeate after seawater desalination with RO. Boron is removed by ion exchange resins (*eg* Dowex XUS 43594 - Dow Chemicals, Diaion CRB01 - Mitsubishi or others) of very small grain size (20 µm) and after the sorption the resin is separated by means of microfiltration. The small size of grains of the resin allows to effectively decreasing the boron content after 2 minutes from 2 to 0.243-0.124 mg/dm^3, depending on ion exchanger dose (0.25 to 1.0 g/dm^3) [19].

Other studies have been focused on the removal of boron from water solutions using ultrafiltration enhanced with polymers (PEUF), usually with poly(vinyl alcohol) (PVA) or other specially synthesized polymers [19]. The process consists of two stages: the complexation of boron with a polymer and the separation of complexes by capillary ultrafiltration membrane [19]. However, the decrease of boron retention coefficient is observed during the process (starting from values close to 1) as the number of active centers of the chelating polymer decreases. The retention depends also on pH, boron and polymer concentration in the feed.

Inorganic **arsenic** occurs in water in anionic forms as As(III) and As(V), and lower oxidation stage dominates in groundwater and higher in surface waters. At pH close to

neutral, As(III) occurs in the form of inert molecules H_3AsO_3 and As(V) as $H_2AsO_4^-$, $HAsO_4^{2-}$ and AsO_4^{3-}. The form of As(V) ions has a direct impact on the choice and effectiveness of the treatment method. In order to decrease arsenic content in drinking water, reverse osmosis and nanofiltration membranes as well as hybrid process of coagulation-MF/UF are applied [1, 2, 20].

Reverse osmosis membranes, *eg* TFC-ULP (Koch) allow to remove 99% of arsenic from groundwater (the decrease from 60 to 0.9 µg/dm³), whereas DK2540F membranes (Desal) retain 88-96% of the pollutant [21]. The removal of As(III) is always lower than As(V), and the oxidizing conditions during the process are recommended [20]. pH and the content of dissolved organic matter have a great influence on arsenic removal. The rate of As(V) removal at pH = 3 reaches 80%, while it can be up to 95% at pH range 5-10 (NTR-729HF membrane). The higher removal of arsenic(V) (90%) is observed for waters with lower organic matter content, while in comparison to higher organics concentration it is equal to 80% [19]. Number of other laboratory and pilot research on arsenic removal using reverse osmosis membranes have also been performed [1, 2].

Nanofiltration membranes can be also applied to As removal. For NF-70 FilmTec membrane, 97% removal of As(V) is obtained, and for NF-45 membrane, it varies from 45 to 90%, depending on initial concentration of the pollutant in water [22]. 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 rate of removal of As(V) with the use of NF-45 membrane significantly increases with the increase of pH [22], according to the difference in As ion hydration. The influence of pH in the range of 4 to 8 on the retention coefficient of As(III) is 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 surface.

Microfiltration and ultrafiltration can be also used for arsenic removal from water, but mainly by means of integrated systems with coagulation [19, 23]. For example from the water of As content equal 40 µg/dm³ the water containing less than 2 µg/dm³ of As can be obtained using ferric coagulants and membranes of pore size 0.22 and 1.22 µm [19]. In the integrated process, the As removal is caused by the adsorption of As on coagulation flocks and separation of those flocks 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 appear as $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions, while at pH > 6 - CrO_4^{2-} ions are formed. These compounds are highly toxic to living organisms, so their permissible concentration in drinking water amounts to 0.05 mg/dm³, including 3 µg/dm³ for Cr(VI). Studies carried out on Cr(VI) removal from water involved reverse osmosis using Osmonics membranes Sepa-S type and membranes made of cellulose acetate (CA) [2, 7, 24]. It was found that the CA membranes retained 96% of Cr(VI) ions, while Osmonics membranes 80-96%, depending on the membrane compactness.

It seems that **nanofiltration** is a better solution for the removal of Cr(VI) from water. In this case, retention coefficient increases with pH increase, but the effect is more pronounced for membranes with lower separation capacity (from 47 to 94.5% for Osmonics membranes) compared to more compact membranes (from 84 to 99.7% for Osmonics membranes) [25]. The dependence of the retention coefficient on the concentration of Cr in

feed was also observed for NF membranes [25], but the range of the effect also depended 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 its ionic form with the change of pH. In the highly acidic environment, Cr(VI) occurs in the form of no dissociated chromic acid (H_2CrO_4) and when pH is changed to 6.5, $HCrO_4^-$ ions are formed, the concentration of which increases with the parameter increase. Further increasing of pH above 7 causes the formation of CrO_4^{2-} ions, the concentration of which also depends on pH. $Cr_2O_7^{2-}$ ions are also present in the solution and their concentration depends on the initial concentration of the contaminant in the feed and pH. This ion is usually dominant at high concentrations of Cr and in strongly acidic environment (pH 1-7) but its concentration decreases with pH increase [1, 2, 25].

Removal of heavy metals

Heavy metals are one of the most dangerous impurities present in natural waters and wastewaters. As natural waters are the main source of drinking water it is also possible that they will appear in it. If the daily, monthly or annual consumption of water is considered, the danger resulted of the presence of heavy metals in water is quite significant. Metals like lead, mercury, selenium, iron, nickel, manganese, copper, cobalt, cadmium, zinc, chromium and other are present in drinking water. The permissible concentration only for part of them is established in Polish regulations on tap water. Except of iron, manganese and aluminum the permissible concentrations of following metals are specified: antimony - 0.005 mg/dm^3, arsenic - 0.010 mg/dm^3, chromium - 0.050 mg/dm^3, cadmium - 0.05 mg/dm^3, nickel - 0.020 mg/dm^3, copper - 2.0 mg/dm^3, lead - 0.025 mg/dm^3, mercury - 0.001 mg/dm^3, selenium - 0.010 mg/dm^3 and silver - 0.010 mg/dm^3 [2]. Conventional methods such as precipitation, extraction or ion exchange have many shortcomings, especially with respect to processing of large volumes of water containing low concentration metal ions. Nowadays, these contaminants are most frequently precipitated as hydrated metal oxides, hydroxides or sulphides with the use of flocculation or coagulation. One of major problems pertaining to the precipitation process involves the formation of substantial quantities of sludge containing metals [26]. Very often the concentration of metal ions in the filtrate after the final filtration process is still above the level of several mg/dm^3. Membrane techniques like reverse osmosis, nanofiltration, ultrafiltration and electrodialysis are more often applied to remove of heavy metals from water solutions in the industrial scale.

Metal ions can be successfully removed from water solutions by means of **reverse osmosis** or **nanofiltration** as membranes applied in those processes are able to retain dissolved salts of particle sizes not even greater then few nanometers what have been shown in number of studies [27-29].

A series of investigations were conducted on the removal of heavy metals from aqueous solutions using reverse osmosis technology. For example, Bakalar et al [27] presented the results of the removal of copper, nickel and zinc using composite polyamide membrane TW30-1812-50 (Dow Filmtec). They determined effect of the accompanying anions (co-ions), the concentration of cations and transmembrane pressure on the separation efficiency. In turn Qdais and Moussa [28] in their work tested removal of Cu^{2+} and Cd^{2+} ions by means of reverse osmosis and nanofiltration. The results showed that the removal

efficiency of individual heavy metals by RO was high and amounted to 98% for copper and 99% for cadmium, while for NF it was above 90%. In the case of a solution containing simultaneously both metals, RO membranes reduced concentration of ions from 500 mg/dm^3 to about 3 mg/dm^3 (removal rate 99.4%), while the rejection efficiency of NF amounted to average 97%. Nanofiltration (NF) is a promising technology for the rejection of heavy metal ions such as nickel, chromium(III), and copper from wastewater [30]. NF process benefits from ease of operation, reliability and comparatively low energy consumption as well as high efficiency of pollutant removal [30]. In recent years, Murthy and Chaudhari [31, 32] devoted a lot in the removal of heavy metal ions using NF membrane. They reported the application of a thin-film composite polyamide NF membrane for the rejection of nickel ions from aqueous wastewater [31, 32]. The maximum observed rejection of nickel is found to be 98% and 92% for an initial feed concentration of 5 and 250 mg/dm^3, respectively. And they investigated the binary heavy metals (cadmium and nickel) separation capability of a commercial NF membrane from aqueous solutions [31, 32]. The maximum observed solute rejection of nickel and cadmium ions is 98.94% and 82.69%, respectively, for an initial feed concentration of 5 mg/dm^3.

These studies showed that NF is also an appropriate technique to remove heavy metals from wastewater to a level acceptable by environmental regulations. In addition, as in RO, it was possible to reuse permeate for rinsing purpose and recycle the retentate containing heavy metals. Retention of the cations in the process strongly depends on the energy of hydration, type and valence of co-ions passing through NF membrane as well as the applied pressure and pH. For example, the retention of Cu^{2+} and Cd^{2+} ions is greater for the higher co-ions valence and higher cation hydration energy [29]. The obtained retention coefficients of copper and cadmium sulphates are close to 100% independently of pressure. In the case of chlorides and nitrates, the retention rates increase with pressure to specific values which depends on the nature of the co-ions. Heavy metals retention during NF also strongly depends on the pH. In a highly acidic environment high concentration of hydrogen ion in solution causes gradually neutralization of the negative active centers on the membrane surface, so the impact of membrane charge on the cations and anions retention is significantly reduced. At such conditions, nitrate and chloride ions easily pass through a membrane and in order to maintain an electrostatic balance of the solution through the membrane protons also penetrate it. Therefore, copper and cadmium ions are retained in retentate. Cu^{2+} and Ni^{2+} ions were successfully removed by the RO process and the rejection efficiency of the two ions increased up to 99.5% by using Na_2EDTA [30].

The application of reverse osmosis to the removal of heavy metals from solutions can be presented on the example of wastewaters treatment from the electroplating industry. The wastewater consists mainly of effluent from products washing processes after the electroplating coating and used electroplating baths. The concentration of metal ions in such the wastewater ranges of 0.025 to 1 mg/dm^3 [26]. Most frequently the electroplating effluents contains Cr, Cu, Cd, Zn, Ni, Pb and Ag ions, and since the metal coating technologies are based to a great extent on cyanide solutions, the presence of toxic cyanide anion is also important. The reverse osmosis process allows to recover water of very high purity level which in many cases can be directly returned to the technological process without additional treatment, The concentrated solution (retentate) may be reused to fill up the electroplating bath [26]. In Figure 2 a typical diagram of the installation operating in the closed cycle applied to such a process is presented [26].
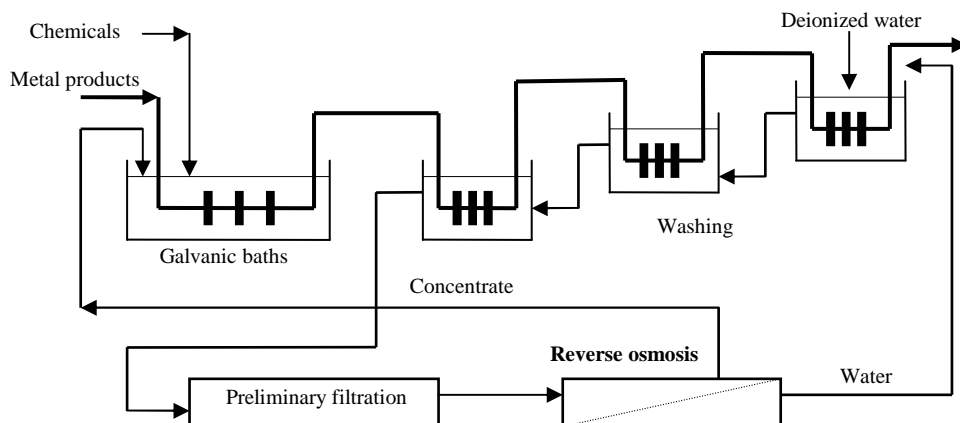
Fig. 2. The diagram of the electroplating process line integrated with reverse osmosis

Since the pore sizes of UF membranes are larger than dissolved metal ions in the form of hydrated ions or as low molecular weight complexes, these ions would pass easily through UF membranes. To obtain high removal efficiency of metal ions, the **polymer enhanced ultrafiltration** (PEUF) and **micellar enhanced ultrafiltration** (MEUF) was proposed [2, 30].

The ultrafiltration enhanced with polymer (PEUF) combines UF with metal complexation using water-soluble polymers. The formed complexes have sufficiently large size to be retained by UF membrane. The permeate is deprived of metal ions and retentate can be undergone regeneration in order to recover both, the metal and polymer [33, 34]. After that, retentate can be treated in order to recover metallic ions and to reuse polymeric agent. The main concern of the previous PEUF studies was to find suitable polymers to achieve complexation with metal ions. Complexing agents such as polyacrylic acid (PAA), polyethyleneimine (PEI), diethylaminoethyl cellulose and humic acid, etc., have been proven to achieve selective separation and recovery of heavy metals with low energy requirements [30]. The main parameters affecting PEUF are metal and polymer type, the ratio of metal to polymer, pH and existence of other metal ions in the solution.

The process was applied for deactivation of radioactive liquid waste containing metal ions, *ie* cesium, cobalt, strontium, antimony and technetium isotopes, the major components of the radioactive wastewater and for the separation of the lanthanides (^{140}La, ^{152}Eu and ^{169}Y) [35]. A significant reduction in permeate radioactivity was observed.

Mavrov et al [36] carried out investigations of the removal of Cu(II), Ni(II) and Co(II) ions from synthetic aqueous solutions with initial metals concentration of 10^{-4} mol/dm^3 using the hybrid PEUF method with polyacrylonitrile membranes (UF-25-PAN) (cut-off of 25 kDa). Polyvinyl alcohol (PVA) (50,000 Da) and polyethyleneimine (PEI) (30,000-40,000 Da) were used as complexing agents. It was shown that the optimal concentration of PEI was 2-6 times higher in comparison with stoichiometric concentration and retention rates of formed complexes ranged within 85-99%. The highest retention rate was obtained for PVA complexes (97-99%), at the ratio of metals concentration to the polymer concentration ranged of 1: 4 to 1: 8 [36].

Molinari et al [37] used PEI as a polymer to study the complexation-ultrafiltration process in the selective removal of Cu(II) from Ni(II) contained in aqueous media. Preliminary tests showed that optimal chemical conditions for Cu(II) and Ni(II) complexation by the PEI were pH > 6.0 and 8.0, respectively, and polymer/metal weight ratio of 3.0 and 6.0, respectively. Aroua et al [38] investigated the removal of chromium species from aqueous dilute solutions using PEUF process by three water-soluble polymers, namely chitosan, PEI and pectin. High rejections approaching 100% for Cr(III) were obtained at pH higher than 7 for the three tested polymers.

Korus et al [33, 39] conducted studies on the removal of heavy metals (Ni, Cu, Zn) from synthetic and galvanic wastewater with the application of the hybrid complexation-ultrafiltration process. Polyvinyl alcohol (50,000 Da), polyethylimine (30,000-40,000 Da), polyacrylic acid and sodium polyacrylate as complexing agents and polysulphone and polyamide membranes were used. The efficiency reached 85-97% for polyamide membrane depending on the polymer to the metal ratio, the pH and the kind of metal. The high removal efficiency of zinc and nickel ions (97-99%) was obtained for polysulphone membrane. The decomplexing process enabled the recovery of metal from the concentrated solution to the extent suitable for its reuse. Sodium poly(styrene sulphonate), a water-soluble anionic polymer with strong cation-exchange groups was used as a complexing agent for lead ions complexing [39]. The high rate of metal removal (85-99%) depended on ratio of metals to polymer, pH of the solution and operating ultrafiltration conditions were obtained for polysulphone membrane. It was possible to obtain the retentate with a concentration of Pb 20-times higher than the concentration of the feed solution which contained 50 mg Pb/dm^3. 5-fold the excess of polymer in relation to metal as well as at pH = 6 and at pressure of 0.1 MPa were the main process parameters. Decomplexation-ultrafiltration process involved breaking of polymer-metal bond and allowed to recover 85% of metal, while the diafiltration conducted with sufficient volume of water enabled 5-15 fold reduction of the concentration of metal-remaining in retentate, so the recovery and the reuse the polymer were possible.

The advantages of PEUF include high removal efficiency, high binding selectivity and highly concentrated metal concentrates for reuse, *etc*. [30]. There are a lot of publications in this topic, but it has not spread wide in the industry yet.

MEUF has been proven to be an effective separation technique to remove metal ions from wastewater. This separation technique is based on the addition of surfactants to wastewater. When the concentration of surfactants in aqueous solutions is beyond the critical micelle concentration (CMC), the surfactant molecules will aggregate into micelles that can bind metal ions to form large metal-surfactant structures. The micelles containing metal ions can be retained by a UF membrane with pore sizes smaller than micelle sizes, whereas the untrapped species readily pass through the UF membrane. To obtain the highest retentions, surfactants of electric charge opposite to that of the ions to be removed have to be used. Sodium dodecyl sulphate (SDS), an anionic surfactant, is often selected for the effective removal of heavy metal ions in MEUF. Metal removal efficiency by MEUF depends on the characteristics and concentrations of the metals and surfactants, solution pH, ionic strength, and parameters related to membrane operation [30]. The retentate is the concentrated solution of surfactants and heavy metals retained by membrane. Since the surfactant may account for a large portion of operating costs, it is essential to recover and

reuse the surfactant as economically as feasible. And if the surfactant and heavy metals are not disposed, they will cause secondary pollution [30].

Landaburu-Aguirre et al [40] investigated the removal of zinc from synthetic wastewater by MEUF using SDS. They found that rejection coefficients up to 99% were achieved when the surfactant to metal molar ratio (S/M) was above 5. Sampera et al [41] used MEUF to remove Cd^{2+}, Cu^{2+}, Ni^{2+}, Pb^{2+} and Zn^{2+} from synthetic water using two anionic surfactants: SDS and linear alkylbenzene sulphonate (LAS) in a lab-scale membrane system. The molar concentration ratio of the surfactant to metal is higher than 5 in all the experiments. When the initial SDS concentration was below the CMC, metal retention higher than 90% was unexpectedly obtained, except for Ni^{2+}. Moreover, it was shown that complete removal of metal ions, except for Ni^{2+}, could be achieved at an SDS concentration below CMC. Li et al [42] tested chelation followed by UF and acidification followed by UF for the separation of Cd^{2+} or Zn^{2+} from SDS micelles in simulated retentate solution of MEUF and the reuse of SDS. In the method using chelating agents, EDTA at pH 4.4 was the best for separating heavy metal ions (90.1% for Cd^{2+}, 87.1% for Zn^{2+}) and recovering SDS (65.5% for Cd^{2+}, 68.5% for Zn^{2+}). With the reclaimed SDS in MEUF, the removal efficiencies of heavy metal ions were 90.3% for Cd^{2+}, 89.6% for Zn^{2+}. In the method using acid agents, H_2SO_4 at pH 1.0 was the best for separating heavy metal ions (98.0% for Cd^{2+}, 96.1% for Zn^{2+}) and recovering SDS (58.1% for Cd^{2+}, 54.3% for Zn^{2+}). The efficiencies of reclaimed SDS were 88.1% for removing Cd^{2+} and 87.8% for removing Zn^{2+} in MEUF.

The performance of a membrane system based on microfiltration (MF) and reverse osmosis/nanofiltration (RO/NF) has been examined with reference to the removal of trace metals from classically-treated municipal wastewater, and associated costs determined [43]. Metals fate was assessed both at full and pilot scale. Metals rejection was found to be 94.5-99% on average; permeate metal concentrations were between 0.01 and 0.7 μg/dm^3 for Cu and Ni and 0.7-5.7 μg/dm^3 for Zn, and largely unaffected both by feed concentration and membrane type [43]. The operational expenditure (OPEX) was calculated from information from the full-scale plant, primarily comprised energy demand (47%) and membrane replacement (37%) and was largely independent of plant size for flow rates from 1 to 100 megalitres per day (MLD). Results confirmed the membrane-based process to reliably remove metals down to levels below 6 μg/dm^3, but only at a cost (~0.18 euro/m^3 OPEX) which makes the process untenable for this duty exclusively. Moreover, a further cost would be incurred from the management of the concentrate stream. However, the reliably high levels of removal permit possibility of employing RO or NF technology for treating only a fraction of the wastewater and blending with the untreated stream, depending on the required discharged wastewater quality.

This work investigated the removal of metals from wastewater using a combined Membrane Bioreactor-Reverse Osmosis (MBR-RO) system [44]. The concentrate produced by the RO system was treated by a fixed bed column packed with zeolite. The average metal removal accomplished by the MBR treating municipal wastewater was Cu (90%), Fe (85%), Mn (82%), Cr (80%), Zn (75%), Pb (73%), Ni (67%), Mg (61%), Ca (57%), Na (30%) and K (21%), with trivalent and divalent metals being more effectively removed than monovalent ones [44]. The metal removal achieved by the MBR system treating wastewater spiked with Cu, Pb, Ni and Zn (4-12 mg/dm^3 of each metal) was Pb (96%) > Cu (85%) > Zn (78%) > Ni (48%). The combined MBR-RO system enhanced metal removal from municipal wastewater to the levels of >90.9 - >99.8%, while for wastewater spiked with

heavy metals the removal efficiencies were > 98.4%. Fixed bed column packed with zeolite was effective for the removal of Cu, Pb and Zn from the RO concentrate, while Ni removal was satisfactory only at the initial stages of column operation. The presence of heavy metals increased inorganic fouling.

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 [5, 45]. For anions removal anion exchange while for cations removal cation exchange membranes are used (Fig. 3). Membrane separates two solutions *ie* raw solution and stripping solution (concentrate) which differ in both, composition and concentration. The type of operation as Donnan dialysis requires an addition of so-called driving counter-ion to the stripping solution (usually NaCl solution of concentration of 0.1 to 1 M is used), which is transported in an opposite direction than the target anion or cation in order to maintain electroneutrality (Fig. 3) [45]. The ions, which are permeable to the membrane, equilibrate between the two solutions until the Donnan equilibrium is obtained. Since not the concentration differences but its ratios determine the Donnan equilibrium, Donnan dialysis allows to transport the charged micropollutants against their concentration gradients, what is important for drinking water supplies, as they usually contain only trace amounts of polluting ions. Due to its properties, Donnan dialysis has received attention in the removal of inorganic ions from drinking water, especially nitrates(V) and fluorides, and some cations [5].
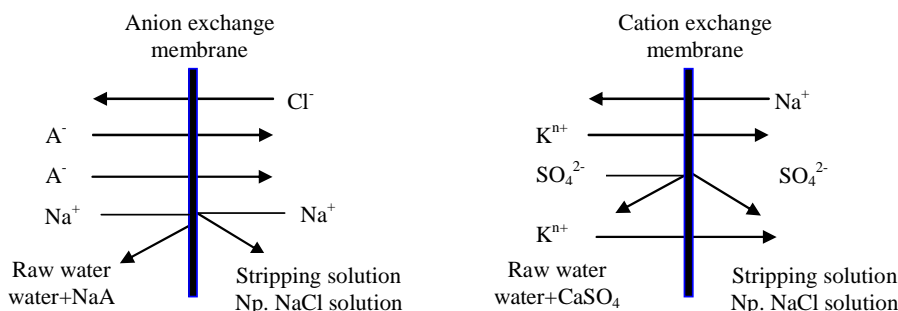
Fig. 3. The scheme of Donnan dialysis process (A^- - target anion, K^{n+} - target cation)

Since in Donnan dialysis the mechanism of ion transport is governed solely by the Donnan equilibrium principle, the achieved ion fluxes may be low for certain applications.

Electrodialysis (ED) is another membrane process for the separation of ions across charged membranes from one solution to another using an electric field as the driving force ED has also proven a promising method in heavy metal and toxic anions removal from wastewater treatment. In electrodialysis, the transport of ions is accelerated due to an externally applied electric potential difference, what allows obtaining higher anion fluxes than those in DD. In this process, anion exchange and cation exchange membranes are applied alternately, what allows to obtain the solutions of varying concentration (diluate and concentrate) [2, 5]. The ED systems are usually operated in the so-called electrodialysis

reversal mode (EDR) to prevent membrane fouling and scaling. The suitability of ED depends strongly on the ionic composition of contaminated water. Thus, the process appears to be less applicable to waters of very low salinity (conductivity less than 0.5 mS), for which DD can be a better solution. In cases when low-molecular weight non-charged compounds besides ions removal is necessary, pressure-driven membrane processes may be preferable. Successful applications of ED and EDR include removal of various anions, *eg* nitrates(V), bromates(V), chlorates(VII), arsenic(V), boron and fluorides as well as various heavy metals [2, 5]. The brine discharge or treatment remains important for all of these separation processes. Since most known toxic anions are monovalent, the use of monovalent anion permselective exchange membranes is especially attractive [5].

The use of a monovalent anion permselective membrane in ED process was proved successful in a full-scale ED plant located in Austria, which was designed to remove **nitrates(V)** from groundwater [2, 5]. The NO_3^- concentration in the raw water was 120 mg NO_3/dm^3 and the removal efficiency (66%) was adjusted to obtain a product concentration of 40 mg NO_3/dm^3 at the desalination rate ca. 25%.

ED and EDR are also proposed to remove **bromates** from water [2, 3, 46]. Studies on ED with anion exchange membrane (Neosepta AMX) resulted in BrO_3^- removal efficiencies of 86-87% and with the use of monoanionselective membranes (Neosepta ACS) even up to 99%, at a current density of 20 A/m^2. The removal rates of other anions were from 80% (HCO_3^-) to 93% (NO_3^-) [46]. This means that the ED of water with initial concentration of BrO_3^- of 100 µg/dm^3 allow to decrease their final concentration to approximately 1 µg/dm^3, which is significantly below the limit value of the drinking water (for BrO_3^- 10 µg/dm^3). The increase in power density for ED with standard anion exchange membrane results in an increase in the anions transport rate by 36%.

Investigations were also carried out on **chlorate(VII)** ions removal by ED and EDR, also at high concentrations of silica (approximately 80 mg/dm^3). Regardless of the presence SiO_2 and its concentration, the water recovery in the EDR installations was not affected. Pilot studies have shown that the removal of ClO_4^- varied in the range of 70% to 97% depending on the initial concentration of the anion and the number of steps in the configuration of EDR system [13]. During removal of chlorate(VII) ions using EDR method, retention coefficients of other anions with similar valence (*eg* nitrate) are also important.

ED can be applied to **fluorides** removal from water that contains significant amount of this contaminant. The removal rate of F$^-$ is very often higher than that obtained for RO and it increases with the increase of electrical potential difference, temperature and flow rate [2, 5]. In order to minimize the precipitation of salts of bivalent ions (sulphates and carbonates) in the concentrate chambers, preliminary removal of bivalent ions is proposed using two-step ED with the application of various ED membranes in each step or by chemical methods followed by conventional ED [2]. The content of fluorides is generally decreased from 3.0 to 0.63 mg/dm^3 for the first configuration and to 0.81 mg/dm^3 for the second one, what allows obtaining water of municipal quality. The first method is preferably used according to its simplicity and elimination of other chemicals addition step.

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 [13, 47]. The main advantage of ED in comparison to RO is the smaller sensitivity of ion

exchange membranes to pH and fouling. High pH values also prevent 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 [13, 47]. 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 [47]. In order to omit high demineralization of the diluate, monopolar membrane at alkali process conditions (pH = 9-10) should be applied [13].

The studies on **arsenic** removal from water by ED have shown that it is possible to remove As with the efficiency exceeding 80% for As(V) and 50% for As(III) [48], with the water recovery of 85%. In other studies with EDR, a concentration of arsenic in eluate was decreased to 0.003 mg/dm^3 while its initial level was 0.021 mg/dm^3, what corresponded to the retention coefficient of 86% [3].

Nataraj et al [49] performed a new working system to investigate the removal of hexavalent **chromium** ions using a built ED pilot plant comprising a set of ion-exchange membranes. Exploration of a new working system to investigate the removal of chromium ions in its hexavalent oxidation state singly in connection with different parameters and associated moieties in feed mixtures was performed using an indigenously built electrodialysis (ED) pilot plant comprising a set of ion-exchange membranes. In order to check the efficacy of ED unit, parameters like applied potential, pH, initial chromium concentration of diluate and flow rates were varied. Significant results were obtained with lower initial concentrations of less than 10 mg/dm^3. Results were satisfactory in meeting the maximum contaminate level (MCL) of 0.1 mg/dm^3 for chromium. Effect of working parameters on energy consumption was investigated using ion-exchange membranes. Results of this study are useful for designing and operating different capacities of ED plants for recovering different ions. The ED plant used in this research was found to be satisfactory to produce good quality drinking water from the simulated mixture by removing the unwanted ions.

Lambert et al [50] studied the separation of Cr(III) from sodium ion by ED using modified cation-exchange membranes. Trivalent chromium Cr(III) in wastewaters produced by leather tanning processes must be treated before discharge in the environment. The membrane modification consists of a polyethylenimine layer electrodeposited on the membrane surface. This layer is positively charged in acidic media and repels multivalent ions while monovalent ions cross the membrane. The modified membrane in this study was a Nafion® 324 membrane. The transfer of chromium, sodium, calcium, magnesium, chloride and sulphate ions from a mixture was investigated. The pH must be regulated in order to avoid chromium hydroxide precipitation in the dilute chamber. The behaviour of sulphate chloride system is unusual for the AMX membrane. Adsorption of PEI on the membrane surface is assumed to explain this behaviour. The overall current efficiency was close to 96-98% for cations and anions.

Mohammadi et al [51] investigated the effect of operating parameters on Pb^{2+} separation from wastewater using ED. Lead removal from wastewater is an important problem in battery industries. The separation process by means of electrodialysis (ED) shows several advantages such as highly selective desalination, high water recovery, only a partial addition of chemicals and the possibility of a stop-and-go operation. The performance of an ED plant is determined by a set of fixed and variable process parameters such as stack construction, feed and product concentrations, membrane permselectivity,

flow velocities, current density, recovery rates, etc. For an efficient operation of ED, the process has to be optimized in terms of overall costs considering component design and properties as well as all operating parameters. The results showed that increasing voltage and temperature improved cell performance; however, the separation percentage decreased with an increasing flow rate using two types of commercial membranes on lead removal were studied. Experiments were carried out on three levels of concentration: 100, 500 and 1000 mg/dm^3; temperature: 25, 40 and 60°C; voltage: 10, 20 and 30 V; flow rate: 0.07, 0.7 and 1.2 cm^3/s using laboratory ED cell. The results show that increasing voltage and temperature improved cell performance; however, the separation percentage decreased with an increasing flow rate. At concentrations of more than 500 mg/dm^3, dependence of separation percentage on concentration diminished. Using membranes with higher ion-exchange capacity resulted in better cell performance

ED is particularly useful and very often applied to treat washery effluents and **wastewaters** from electroplating plants [26]. The diagram of installation is similar to Figure 2, but instead of RO, ED is applied. The retentate, which is a concentrated solution of metal ions, is used for filling up the electroplating bath, whereas the dialysate is returned to the washing installation. Hence, practically the whole quantity of water and salts present in washery effluents can be utilized [26]. Recently, the application of ED for the recovery of metals for electroplating with such metals as Au, Pt, Ni, Ag, Pd, Cd, Zn and Sn/Pb from diluted electroplating wastewaters has been gaining attention [26]. The solution of metal salt can be concentrated to the level that corresponds to the components content in the electroplating bath, *eg* for Ni from 1 to 60 g/dm^3 [26], which is much greater than with the application of RO. The principal disadvantage of ED is the inability to remove simultaneously the non-ionic substances (*eg* organic compounds) from the dilute stream, what can be done with the use of reverse osmosis. The effectiveness of electrodialysis (ED) for (a) the separation of Cu and Fe and (b) water recovery from solutions analogous to those found in copper electrowinning operations, has been studied by Cifuentes et al [52]. A five-compartment ED cell with recirculation of the electrolytes and a synthetic solution, similar to a copper electrowinning electrolyte, were used. The experimental variables were: applied current density, recirculation flow rate and time of operation. Ion removal rates from the working solution increased with cell current density and solution flowrate. They found that ED proved very effective in the removal of Cu and Fe from the working solution, which means that water, can be recovered from these electrolytes.

Electrochemical separation techniques are becoming an alternative method of **chromium** removal from water environment. This toxic metal is present in various streams produced by number of industrial processes, which also contain other substances (mainly metals), that should be separated from the chromium. Therefore, electrochemical technology is more flexible than other membrane techniques and is applied to recovery chromic acid(VI) from the bath coating metal parts (large concentration of chromium) or as a method of disposal and recovery of chromium from wastewater coming from washing of these elements. In most cases, among others in plating industry, so-called three-compartment electro-electrodialysis (EED) is applied. It is based on the electrolysis reactions running on electrodes and the electrodialysis process [53] (Fig. 4).
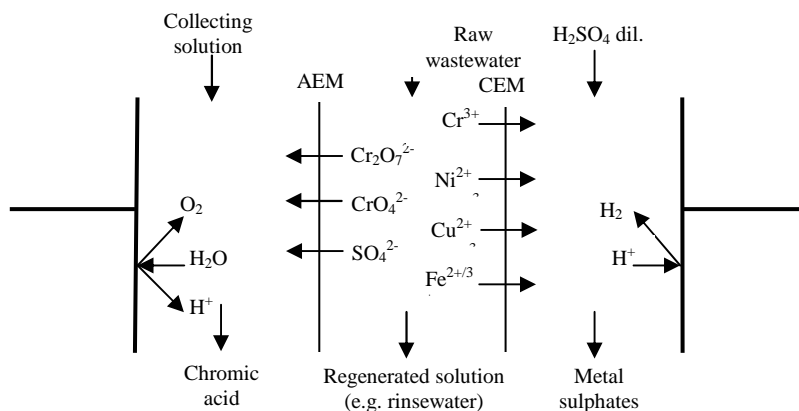
Fig. 4. Principles of three-compartment electro-electrodialysis (EED) for chromic acid recovery (AEM - anion exchange membrane, CEM - cation exchange membrane)

It can simultaneously manage three different tasks: removal of impurities, chromic acid recovery and purification of rinse water. Treated solution feeds center chamber of the device, which is separated from the anolite chamber by the anion exchange membrane and from the catolite chamber by the cation exchange membrane [53]. The anolite chamber is supplied with water, while the catolite chamber with sulphuric acid. Cr(VI) ions migrate to the anolite, where they form the chromic acid(VI) with protons formed on the anode. In turn, metal cations permeate to catolite chamber, where sulphuric acid neutralizes the hydroxide ions formed on the cathode, so in this part of the device the soluble metal sulphates(VI) are formed. Both the electrodialysis (ED) and electrodeionization (EDI) processes can be applied for the removal and separation of metal ions and their mixtures, including **chromium**. In the ED, the electrical resistance in dialysate chambers increases in time, as the ions are removed from the diluted solution to the concentrate chamber, what causes higher energy consumption and decreases the efficiency of the process. One of the solution to this problem is EDI process, in which the dilute solution chamber is filled with an ion exchange resin [2]. The applied voltage improves the migration of ions to the respective electrodes and thus to concentrated stream and causes water dissociation into H^+ and OH^- ions, which regenerate the ion exchange resin. Alvarado et al [54] in his work assessed the feasibility of EDI and ED continuous processes for the removal of chromium(VI) from synthetic solutions at pH = 5. ED/EDI installation consisted of electrodes and two acrylic separation plates between which anion-exchange membrane by Neosepta was placed (Fig. 5) [54]. Two cation-exchange membranes, by the same producer, separated the electrodes from the separation plates. In this way two chambers with diluate and concentrated solution were formed. Synthetic wastewater containing 100 mg/dm^3 of Cr(VI) was treated. During the EDI process, chamber with diluted solution was filled with mixed ion exchange resin. In the ED process the removal of Cr amounted to 98% during 6.25 h at energy consumption amounted to approximately 1.2 kWh/m^3 and at the maximum limited current (I_{lim}) of 85%. In the EDI process with the use of mixed bed at the same I_{lim}, 99.8% removal of Cr(VI) was reached within 1.3 h (energy consumption 0.167 kWh/m^3).
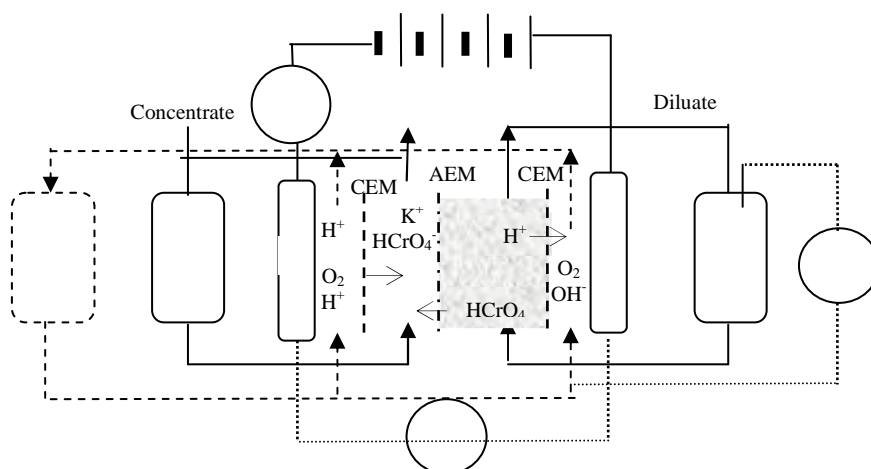
Fig. 5. The diagram of the apparatus for electrodialysis/electrodeionization processes (AEM - anion exchange membrane, CEM - cation exchange membrane)

Membrane bioreactors

The main disadvantage of pressure-driven membrane processes and electrodialysis is the production of the concentrate which is highly loaded with anions and/or metal ions. Thus, the use of membrane bioreactors (MBR) for the removal of micropollutants from RO, NF and ED concentrates as well as natural water and wastewaters, is proposed. It allows to decrease concentration of pollutants to a value which corresponds to drinking water quality [1-6].

The biological degradation of oxyanions is based on their reduction to harmless substances (N_2, Cl^-, Br^-) at anaerobic conditions, the presence of microorganism (heterotrophic and autotrophic bacteria) and proper electron donors (ethanol, methanol and acetates for heterotrophic conditions and sulphur compounds and hydrogen for autotrophic ones) [1-6]. The kinetic of the reaction depends on a kind of microorganisms and biodegradation process conditions (pH, anion concentration) [3]. The advantage of autotrophic degradation is the lower production of the excess sludge, however the process runs slowly [7]. When heterotrophic degradation is applied the removal of dissolved organic carbon and biomass from treated water is required [5]. Disadvantages of conventional biological anions biodegradation can be eliminated by application of a membrane bioreactor (MBR), which assures the total retention of biomass. The configuration of MBR processes can be arranged as the system with pressure driven membrane modules (microfiltration, ultrafiltration) (Fig. 6) [1, 2] or as extractive membrane bioreactors (membrane contactors) (Fig. 7) [3].

In the case of MBR with pressure-driven membrane process, MF or UF membrane may be placed inside or outside bioreactor, as the retention of ions and low molecular mass compounds (electron donors, some metabolic by-products) by porous membranes is generally insufficient; therefore either process modifications or water post-treatment are necessary. The solution is extractive membrane bioreactor (Fig. 7), where water with anions

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is supplied to the inside (lumen side) of hollow-fiber membranes and anions diffuse to the outside (shell side). Here, anionic micropollutants are used by existing microorganisms as an electron donor for the reduction process [1, 2]. In these conditions, both electron donor and biomass are separated from the water by membrane.

Biological degradation of oxyanions may also be used to the removal of not only nitrates(V) but also bromates(V) and chlorates(VII). Studies have shown their full reduction to bromides and chlorides by the same bacterial cultures which are used for nitrates(V) reduction [55].
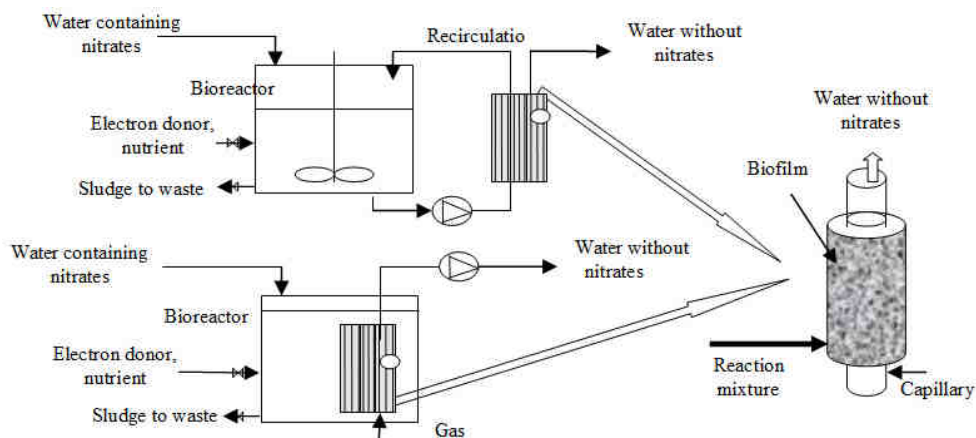

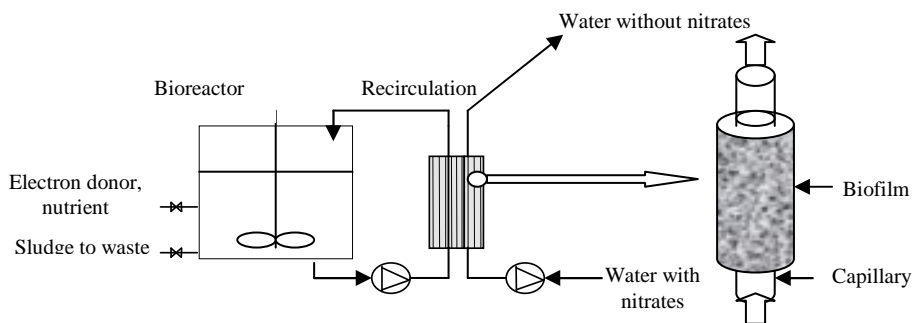Fig. 6. Membrane bioreactors with pressure driven membrane module

Fig. 7. Extractive membrane bioreactor

A new membrane bioprocess for the removal and bioconversion of ionic micropollutants from water streams is the ion-exchange membrane bioreactor (IEMB) [3, 4]. In this process, the ionic micropollutant is transported from the water stream through a non-porous ion-exchange membrane into a biological compartment. There it is simultaneously converted into the harmless product by a suitable microbial culture at the presence of adequate carbon source and other required nutrients. The mechanism of anion pollutants transport through the membrane is the same as in Donnan dialysis (Fig. 8). The

co-ions (cations) are excluded from the positively charged membrane and the target anion(s) transport is combined with its bioconversion. In addition, the bioconversion of the pollutant in the IEMB keeps its concentration at low levels, what guarantees an adequate driving force for transport.
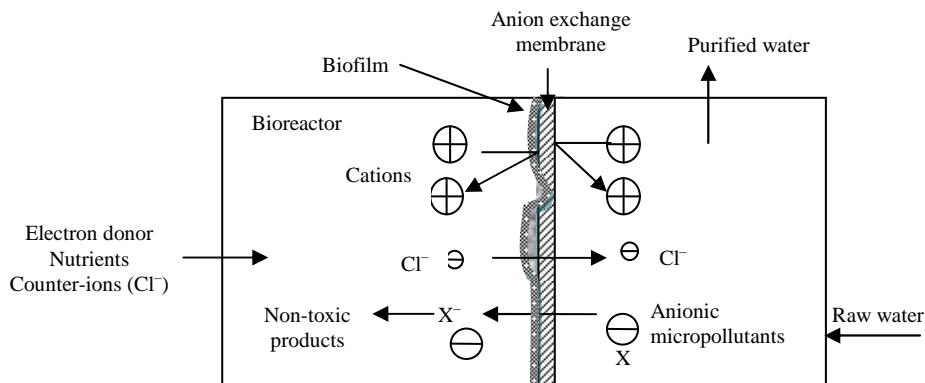

Fig. 8. The schematic diagram of the ion transport mechanism in the ion exchange membrane bioreactor (IEMB)

    This concept was first demonstrated on the example of synthetic waters prepared for the removal and bioconversion of nitrate to harmless nitrogen gas using Neosepta ACS mono-anion permselective membrane and ethanol as the carbon source [4]. 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. Chloride ions were used as the major counter-ion in IEMB for oxyanions removal. Within the concentration relevant to nitrate polluted water (50-350 mg NO_3^-/dm^3), a complete denitrification was achieved without accumulation of NO_3^- and NO_2^- ions in the biocompartment [4].

    The use of membrane separation in combination with biological removal of metals from a solution (membrane bioreactors) is of a great interest. Wastewaters with high load of metals usually contain compounds which may be toxic for microorganisms or inhibits their growth, often have high salinity or show a high pH. Conventional biological removal of metals from wastewater is often impossible to carry out due to inactivation of microorganisms. The solution can be the extractive membrane bioreactors with sulphate-reducing bacteria (EMBR-SRB), which eliminate these restrictions according to physical separation of biomass from effluents (Fig. 9) [56]. Sulphate-reducing bacteria (SRB) oxidize simple organic compounds under anaerobic conditions and the SRB transform the sulphates into hydrogen sulphide

$$3SO_4^{2-} + 2CH_3CH(OH)COOH \rightarrow 3H_2S + 6HCO_3^- \tag{4}$$

where $CH_3CH(OH)COOH$ stands for simple organic compounds.

    Hydrogen sulphide permeates membrane and reacts with divalent soluble metals to form insoluble metal sulphides [30]. In EMBR-SRB membrane, usually made of silicone polymers, performs simultaneously two functions: separates two water phases and enables

H₂S transport from the phase containing biomass to wastewater, where the precipitation of metal sulphide(s) takes place. The study on zinc removal from synthetic wastewater using EMBR-SRB membrane bioreactors showed that the reaction rate between H₂S and Zn ions was high due to large concentration gradient of H₂S on both sides of the membrane. When the pH of biological mixture decreased, the quantity of non-dissociated H₂S grew, increasing its concentration gradient. More than 90% removal of Zn ions from solutions containing 250 mg/dm^3 of this metal was obtained [56]. The transport rate of H₂S is also depended on the membrane thickness. It was found that on the side of wastewater, thin layer of zinc sulphide was formed on the membrane surface, which constituted a significant resistance to H₂S transport. This problem can be solved by changing the hydrodynamic conditions of the water stream or using the pulse flow.
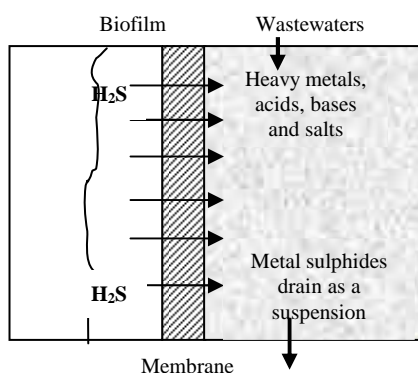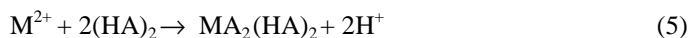

Fig. 9. The scheme of bioreactor with sulphate-reducing bacteria - EMBR SRB

Liquid membranes

Liquid membrane processes have been suggested as a clean technology due to their characteristic of high specificity, high intensity and productivity as well as low emissions and low energy requirements. Thus, the use of liquid membranes has gained a general interest in the treatment of effluents where solute concentrations are low and large volume solutions must be processed, and if possible, without generating any secondary waste [57-59]. There are two types of liquid membranes, unsupported and supported liquid membranes. Nonsupported liquid membranes, *ie* bulk liquid membranes and emulsion liquid membranes, are considered not very attractive for practical use due to various problems that they present under operation [59]. Supported liquid membranes (SLMs) are very effective for the removal and recovery of metals from wastewaters and process streams since they combine extraction and stripping, into one step. Extraction and stripping in conventional processes are carried out in two separate steps [57]. A one-step liquid membrane process provides the maximum driving force for the separation of a targeted species, leading to its best possible clean-up and recovery [57].

In the transport of metal ions in a SLM, the ion in the aqueous feed solution forms a complex with the extractant HA in the organic membrane phase at the interface between these two bulk phases as follows [2]:

$$M^{2+} + 2(HA)_2 \rightarrow \ MA_2(HA)_2 + 2H^+ \tag{5}$$

Then, the metal-extractant complex diffuses from this interface across the SLM to the interface between the organic phase and the aqueous strip solution, where the metal ion is stripped. The aqueous strip solution contains a strong acid, *eg*, sulphuric acid. The stripping reaction is as follows:

$$MA_2(HA)_2 + 2H^+ \rightarrow \ M^{2+} + 2(HA)_2 \tag{6}$$

This stripping reaction also regenerates the extractant at this interface, which diffuses across the SLM back to the feed-membrane interface to complete the facilitated transport cycle. In other words, the metal ions are "carried" by the extractant molecules to facilitate transport across the SLM [2, 58]. The transportation of the metal ion from the feed phase to the strip phase where both the phases are separated by liquid membrane supported with the relevant carrier acting as the barrier, is shown in the Figure 10 [2, 58].
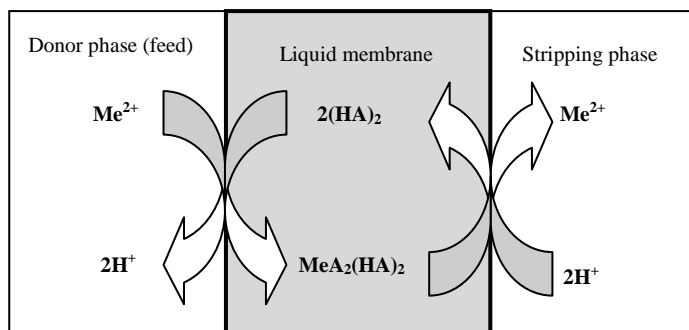

Fig. 10. Transport mechanism of the metal ions across the supported liquid membrane (SLM)

Supported liquid membranes are based on the use of a porous solid membrane (polymeric or ceramic), which supports or hold the organic phase and separates the feed and the stripping aqueous solutions. The pores of the solid membrane are completely filled with the organic and/or carrier phase and this impregnation process makes relatively stable and heterogeneous solid-liquid membranes. [59]. Often, the solid supports are hydrophobic in nature, which facilitates wetting by the organic solution and the reject of the aqueous phases. At present, there are few, if any, large scale operations of supported liquid membranes basically due to their apparent lack of stability under long term operation. Normally, this decreasing in stability is due to the loss of the organic phase filling the membrane pores as well as the loss of membrane stability by a decreasing in the membrane permeation coefficient or the membrane flux [59].

To overcome this drawback the supported liquid membranes (SLMs) with strip dispersion have been developed for the removal and recovery of heavy metals from waste waters and process streams [57]. As shown in Figure 11, an aqueous strip solution is dispersed in an organic membrane solution containing an extractant. The water-in-oil dispersion formed is then pumped to contact with one side of a microporous support, which is passed through the shell side of a microporous polypropylene hollow-fiber module. The aqueous feed solution, containing a targeted species to be extracted, is on the other side of

the support, which is passed through the tube side of the fibers. The continuous organic phase of the dispersion readily wets the pores of a hydrophobic microporous support (*eg* microporous polypropylene hollow fibers in the module), and a stable liquid membrane (the organic phase), supported in the pores of the micro porous support, is formed.
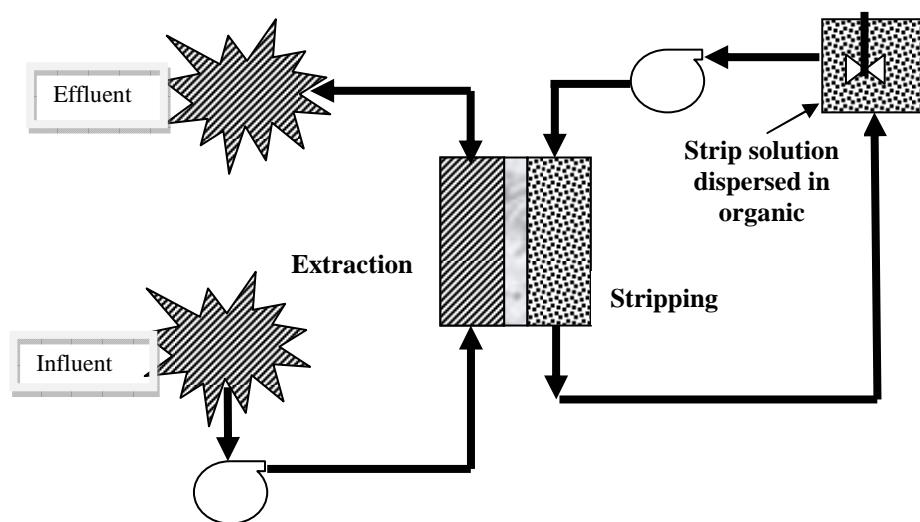

Fig. 11. A schematic diagram of supported liquid membrane with strip dispersion

Supported liquid membrane process is being applied for the extraction/separation/removal of valuable metal ions from various resources. It is one of the promising technologies for possessing the attractive features such as high selectivity and combine extraction and stripping into one single stage. It is also acts on nonequilibrium mass-transfer characteristics where the separation is not limited by the conditions of equilibrium. The limitations like aqueous/organic phase ratio, emulsification, flooding and loading limits, phase disengagement, large solvent inventory, and so forth, can be avoided [58]. The supported liquid membranes (SLM) have applications in both industrial and analytical fields for separation, preconcentration, and treatment of wastewater [57-59]. Thus SLM technology has been considered as an attractive alternative over conventional unit operations for separation and concentration of metal ions in the hydrometallurgical process [57-59].

The use of supported liquid membranes for the separation and concentration of metal ions has received considerable attention since last three decades due to characteristics such as easy operation, high selectivity, low operating cost, and so on [57-59]. SLM is being used for recovery of metals from industrial process streams, not only because the metals are valuable, but also to meet increasingly stringent regulatory requirements. Separation and recovery of copper, zinc, nickel, cadmium and mercury, precious metals, rare earth metals, alkali metals, and anions like Cr(VI), from aqueous solutions and contaminated wastewaters using SLM have been extensively studied [1, 2, 57-59].

The supported liquid membrane process has been tested on pilot scale for recovery of copper and uranium from sulphate solutions, for the recovery of uranium from wet

phosphoric acids, and recently for the recovery of zinc from the waste liquors [58, 60]. The cost of uranium extraction has been compared on the basis of minimum plant capacities for the profitable operations. The recovery of uranium from the acidic sulphate leach liquor has been examined using a supported liquid membrane process. The performance of a supported liquid membrane process in long term field trials has been examined [58]. Copper has been recovered from the acidic sulphate solution on bench scale in a brief field trial [58].

However the supported liquid membrane process could prove more attractive for the small scale plant for the recovery of valuable metals from the dilute leach liquors. The SLM process can contribute for reduction of environmental pollution by metal finishing industry [61]. Application of SLM is dependent on the availability of lower cost support materials, preferably tubular form (hollow fiber liquid membranes), and the demonstration of the long effective membrane life. Hollow fiber modules are usually more expensive but they offer much higher surface area per unit of module volume up to 500 m^{-1}.

Selective permeation of plutonium is clearly demonstrated from real waste solutions containing other fission products such as Cs-137, Ru-106, and Eu-154 and it was possible to achieve an efficient separation of Pu in presence of fission products. This is advantageous in SLM system to treat real waste streams for recovery of Pu(IV) from the acidic wastes [58].

The SLM system with strip dispersion at the low feed pH of 1.9 was effective used for copper removal and recovery from waste waters and process streams. The SLM removed the copper to less than 0.1 mg/dm^3 in the treated feed solution containing about 150 mg/dm^3 copper in less than about 90 min [57]. Winston et al [57] have also developed SLM system with strip dispersion at the low feed pH of 1.9 for zinc removal and recovery from waste waters and process streams. The organic membrane solution in the strip dispersion consisted of 8 wt. % Cyanex 301, 2 wt. % dodecanol and 90 wt. % n-dodecane. The aqueous strip solution was 3 M sulphuric acid. A relatively high volume ratio of about 5.7 between the organic and strip solutions was used for concentrating the zinc from about $4,600 \text{ mg/dm}^3$ to about $18,000 \text{ mg/dm}^3$. SLM system with strip dispersion was also identified as an effective at the low feed pH of 3 for nickel removal. The organic membrane solution in the strip dispersion consisted of 24 wt. % of the new extractant di(2-butyloctyl) monothiophosphoric acid (C12 MTPA), 4 wt. % dodecanol, and 72 wt. % n-dodecane. The aqueous strip solution was 2.5 M sulphuric acid. The results show almost completely removal of zinc after 60-70 min of operation.

Concluding remarks

The use of membranes in the treatment of water sources containing anionic and metal micropollutants for drinking and industrial purposes is a developing technology. NF (RO) and ED can provide more or less selective removal of the target pollutants, especially when the separation of mono- and multi-valent ions is desired. In NF, it can be obtained by both, ion size and charge exclusion effects, while in ED it is due to the use of ion exchange membranes with mono-anion permselectivity. However, the concentrated brine discharge and/or treatment can be problematic in many cases.

The use of microfiltration and ultrafiltration in removal of micro-pollutants is possible in four integrated systems with: coagulation, adsorption, complexing with polymers or surfactants and biological reactions. In the last case three major membrane bioprocesses

have been developed: pressure-driven membrane bioreactors, biological membrane contactors and ion exchange membrane bioreactors.

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USUWANIE MIKROZANIECZYSZCZEŃ NIEORGANICZNYCH ZA POMOCĄ PROCESÓW MEMBRANOWYCH - STAN WIEDZY

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Abstrakt: Szereg anionów nieorganicznych i metali, w tym metale ciężkie, 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 $\mu g/dm^3$ do kilku mg/dm^3). 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 i pozbawioną mikrozanieczyszczeń nieorganicznych, jak również oczyszczone ścieki, które mogą być odprowadzone do źródeł wód naturalnych.

Słowa kluczowe: elektrodializa i dializa Donnana, mikrozanieczyszczenia nieorganiczne, bioreaktory membranowe, ciśnieniowe procesy membranowe