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Application of membrane techniques for the removal of micropollutants from water and wastewater

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Abstract

A number of inorganic anions and heavy metals, microorganisms, natural organic matter, and organic micro-pollutants, among them disinfection by-products, pharmaceutical active compounds and endocrine disrupting compounds, 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 µg/L to a few mg/L).

Several common treatment technologies, which are nowadays used for removal of inorganic and organic contaminants from natural water supplies, represent serious exploitation problems. Membrane processes such as RO and NF, UF and MF in integrated systems, Donnan dialysis and electrodialysis as well as MBR and liquid membranes, if properly selected, offer the advantage of producing high quality drinking water as well as purified wastewater which can be drained off to natural water sources.

High-pressure membrane techniques, i.e. RO and NF can be used for direct removal of inorganic and organic micropollutants, while low-pressure (MF and UF) in integrated systems, first of all with coagulation and adsorption and in MBR as well as after complexion with polymers or surfactants.

Processes with ion-exchange membranes are suitable for micropollutants having electrical charge. Because of that property they are used in many large scale applications including the separation of ions, desalination, removal of ionic species etc.

Keywords: membrane techniques, removal of inorganic micropollutants, removal of organic micropollutants

1. Introduction

In the treatment of natural water for drinking and household needs and industrial wastewaters, pressure-driven membrane techniques are principally applied. But also other processes are taken into consideration, such as electrodialysis and electrodeionisation, Donnan and diffusion dialysis, membrane contactors and bioreactors. The choice of an appropriate membrane process depends on the scope of removed effluents and admixtures present in water. They can be used for the removal of effluents as independent processes or combined with unit complementary processes, forming a treatment process line.

More and more often numerous micro-pollutants occur in the degenerated water environment, mainly in surface waters, but in underground waters as well. Micropollutants in surface waters come from rainfall, sewage, industrial wastewaters and landfill leachate as well as earth flow from the drainage area. Concentration of the micropollutants in surface waters depends on their source and the pollution grade of the drainage area and sewage. Pollutants and organic additives present in natural waters are mainly dispersed substances and micro-organisms, organic compounds, including natural organic matter (NOM), endocrine active compounds (EAC, EDC) and pharmaceuticals residues and personal care products as well as inorganic substances, first of all heavy metals and toxic anions [1,2].

2. Inorganic micropollutants removal

A number of inorganic compounds, including anions (nitrate(V), chlorate(VII), (V) and (III), bromate (V), arsenate (III) and (V), borate and fluoride) and heavy metals, have been found at potentially harmful concentrations in natural water sources and wastewaters [1-4]. 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 World Health Organisation (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 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 – sedimentation - filtration, chemical precipitation, adsorption, 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]. 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 [1,2,4].

2.1.Anions

The RO 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 [5]. As a result, processes suitable for selective removal of toxic anions at moderate desalination are desired. NF fulfils such requirements as it enables 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 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 [4]. 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 [4] 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 anions, mentioned above, 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 [1-4].

The use of MF and UF in removal of inorganic micropollutants is possible in four integrated systems with: coagulation, adsorption, complexing with polymers or surfactants and biological reactions [1,2].

Donnan dialysis is a process that uses an ion exchange membrane without applying an external electric potential difference across the membrane [4,6]. For anions removal anion exchange membranes are used. Membrane separates two solutions i.e. raw solution and stripping solution (concentrate) which differ in both, composition and concentration. The type of operation as DD requires an addition of so-called driving counter-ion to the stripping solution (usually NaCl), which is transported in an opposite direction than the target anion in order to maintain electroneutrality [1,2,5]. Since not the concentration differences but their ratios determine the Donnan equilibrium, DD 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, DD has received attention in the removal of inorganic ions from drinking water, especially nitrates (V) and fluorides [4]. In DD the achieved ion fluxes may be low for certain applications, so ED is proposed. In ED, 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) [1,2,4]. The ED systems are usually operated in the so-called electrodialysis reversal (EDR) mode to prevent membrane fouling and scaling. Since most known toxic anions are monovalent, the use of monovalent anion permselective exchange membranes is especially attractive [4]. 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/cm), 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, e.g. nitrates (V), bromates (V), chlorates (VII), arsenic (V), boron and fluorides as well as various heavy metals [4,6]. The brine discharge or treatment remains important for all of these separation processes.

The main disadvantage of RO, NF and ED processes is the production of the concentrate which is highly loaded with anions. 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 [1,2,4,7]. The biological degradation of oxyanions (NO_3^-,ClO_4^-, BrO_3^-) is based on their reduction to harmless substances (N_2, Cl^-, Br^-) at anaerobic condition and the presence of microorganism (heterotrophic or autotrophic bacteria) and proper electron donors (ethanol, methanol and acetates for heterotrophic conditions and sulphur compounds and hydrogen for autotrophic ones) [4,7]. The kinetic of the reaction depends on a kind of microorganisms and biodegradation process conditions (pH, anion concentration) [7]. The advantage of autotrophic degradation is the lower production of the excess sludge; however the process runs slowly [5]. When heterotrophic process is applied the removal of dissolved organic carbon and biomass from treated water is required [4]. For this purpose, MBR processes is arranged as the system with pressure driven membrane modules (MF, UF) [1,2] or as extractive MBR (membrane contactors) [1,2,4]. In the case of MBR with pressure-driven membrane process, MF or UF membrane may be placed inside or outside bioreactor. When the retention of ions and low molecular mass compounds (electron donors, some metabolic by-products) is required, water post-treatment are necessary or extractive membrane bioreactor is proposed, where water with anions is supplied to the inside (lumen side) of hollow-fibre membranes and anions diffuse to the outside (shell side) [1,2]. In these solution, both electron donor and biomass are separated from the water by membrane.

2.2. 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. The permissible concentration only for part of them is established in country's regulations on tap water at very low level. 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. Membrane techniques like RO, NF, UF and ED are more often applied to remove of heavy metals from water solutions in the industrial scale [1-3,8]. A series of investigations were conducted on the removal of heavy metals from aqueous solutions using RO technology [9-11]. Bakalár et al. [9] presented the results of the removal of Cu, Ni and Zn 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 [11] tested removal of Cu^{2+} and Cd^{2+} ions by means of RO and NF. The results showed that the removal efficiency of individual heavy metals by RO was high and amounted to 98% for Cu and 99% for Cd, while for NF it was above 90%. 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 [12]. The obtained retention coefficients of Cu and Cd sulphates are close to 100% independently of pressure. In the case of chlorides and nitrates, the retention rates increase with pressure to values which depend 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 H^+ ions in solution causes gradually neutralization of the negative active centres 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.

ED is particularly useful and very often applied to treat washery effluents and wastewaters from electroplating plants [1,2]. 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. 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 [2]. The principal disadvantage of ED is the inability to remove simultaneously the non-ionic substances (e.g. organic compounds) from the dilute stream, what can be done with the use of RO.

An interesting solution of the removal of heavy metals from aqueous solutions is the polymer enhanced ultrafiltration (PEUF) process [12]. It 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. The process was applied for deactivation of radioactive liquid waste containing metal ions, i.e. Cs, Co, Sr, Sb and Te isotopes, the major components of the radioactive wastewater and for the separation of the lanthanides (^{140}La, ^{152}Eu and ^{169}Y) [13]. A significant reduction in permeate radioactivity was observed. Mavrov et al. [14] 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/L using the 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. Korus [12] conducted studies on the removal of heavy metals (Ni, Cu, Zn) from synthetic and galvanic wastewater with the application of the PEUF process. PVA (50,000 Da), PEI (30,000-40,000 Da), polyacrylic acid and sodium polyacrylate as complexing agents were used in connection with polysulphone and polyamide membranes. The efficiency reached 85-97% for polyamide membrane depending on the polymer to the metal ratio, the pH and the kind of metal.

2.3. Chromium

A separate discussion of the chromium is associated with the fact that in the natural environment Cr most commonly occurs at third oxidation state as cation (Cr^{+3}) and at Cr(VI) in the form of anions ($HCrO_4^-$ and $Cr_2O_7^{2-}$ ions, while at pH > 6 as CrO_4^{2-}). Cr(VI) is a strong oxidant, which is easily reduced to Cr(III). Chromium (III), who is naturally present in the environment, is an essential nutrient, while chromium (VI) is formed in industrial processes and gets into the environment as anthropogenic pollution. Influence of Cr compounds for living organisms depends on the oxidation state of chromium, solubility, and the way of entry into the body. Cr(III) is trace element essential for the proper functioning of plant, animal and human [1,2,8], while Cr(VI) are highly toxic to living organisms, so their permissible concentration in drinking water amounts to 0.05 mg/L, including 3 μg/L for Cr(VI). The traditional way removing and recovering of chromium salts from contaminated water and wastewater is reduction of Cr (VI) to the Cr (III), and then precipitation of Cr(III) hydroxide and in the final stages the filtration of suspension [15]. For the chromium removal several other methods are also proposed, such as: adsorption and biosorption, ion exchange (used on an industrial scale), solvent extraction and electrochemical methods [1]. High importance in the recovery and disposal of Cr have high-pressure membrane processes and low pressure only enhanced with surfactants and polymers [1,2,5,15]. Application has also found: liquid membranes and processes based on the ion-exchange membranes, including ED, electrodeionization (EDI) and membrane electrolysis [1,5].

3. Organic micropollutants removal

The following organic groups of micropollutants can be found in the waters and wastewaters [2,16]:

1. Disinfection and oxidation by-products (DBPs),
2. Endocrine disrupting compounds (EDCs),
3. Pharmaceutical active compounds (PhACs).

It should be noted that part of both, secondary DBPs and residues of PhACs in the aquatic environment may exhibit properties of compounds with estrogenic biological activity. Organic micropollutants have strong carcinogenic and mutagenic properties. The presence of NOM in water may change the chemical properties of micropollutants and contributes to their migration on a significant distance. They can also increase the water solubility of non-polar compounds, cause hydrolysis of some pesticides, photo-degradation of organic substances and restrict the bioaccessibility by aquatic organisms [16]. These properties significantly depend on the form of occurrence of organic micropollutants i.e. whether they are the free state or they are adsorbed on the other substances. The removal of micropollutants during water treatment is usually performed using activated carbon sorption or advanced oxidation processes (AOPs). The first method becomes economically unattractive when the amount of NOM in water is high, whereas in case of AOPs there exists a possibility of formation of by-products of undefined biological activity [16]. It results in necessity of development of new separation processes among which pressure driven membrane processes seem to be a good solution. Additionally, they can be performed as independent processes as well as be a part of integrated/hybrid systems with coagulation, sorption on activated carbon or in membrane bioreactors [2,16].

Disinfection and oxidation by-products constitute a group of undesirable substances, which are formed as a result of the reaction of disinfectants and other strong oxidants with water pollutants and admixtures. RO and NF are most often applied to remove trihalomethanes (THMs), halogenated acetic acids (HAs) and other halogenated hydrocarbons from water. The study showed that retention of RO and NF Osmonic membranes were depended on the membrane permeability i.e. the higher permeate flux the lower retention coefficient [2,16]. It was found that the increase of THMs MW resulted in the increase of a retention coefficient according to the following series: $CHCl_3$ < $CHBrCl_2$ < $CHBr_3$ < $CHBr_2Cl$. The removal rate of chloroform varied from 67 to 87%, bromodichloromethane 65-96.5%, dibromo-chloromethane 57-90.5% and tribromomethane 61-92% depending on the applied membrane type [16]. In another study, investigating the effectiveness of removal of THMs by means of NF with the use of NF200 and DS5 Osmonics membranes [16,17], it was shown that operating pressure did not affect THM retention, whereas initial concentration of THM had noticeable influence on flux and retention. NF process is also suggested for the removal of HAs (chloro-, dichloro- and trichloroacetic acid; bromo- and dibromoacetic acid) from water [18]. There are also studies on the removal of HAAs from the water in bioreactor with immobilized enzymatic ultrafiltration membranes [19]. In the immobilization process enzymes isolated from strains of bacteria coming from activated sludge were used. 37% of the monochloroacetic acid, 35% of monobromoacetic acid and 48.4% of dichloroacetic acid degradation were obtained [19].

Recent investigations focus especially on **Endocrine Active Compounds** as groups of micropollutants which appear more often in natural waters and wastewaters, even ones biologically purified [2]. According to the definition those are chemicals that may interfere directly or indirectly with the endocrine system and cause effect in target organs or tissues. EDCs group includes endogenic hormones, natural organic compounds produced by fungi (including toxins i.e. mycoestrogenes) and plants (phytoestrogenes), and a wide range of anthropogenic micropollutants among which the most important are [2,16]:

- polycyclic aromatic hydrocarbons (PAHs),
- surfactants,
- plant protection products (pesticides, herbicides and insecticides),
- phthalates,
- haloorganic compounds, including dioxins, furans, polychlorinated biphenyls,
- phenols compounds (alkylphenols, bisphenols)

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

Phytoestrogens and **mycoestrogenes** can be removed by RO and NF processes with effectiveness amounting to 70-93%, depending on the type of the tested compound and membranes. **PAH** and **surfactants** are removed using RO and NF processes with effectiveness ranging from 85.9% to 99% and 92 to 99%, respectively. In case when the concentration of the pollutant in water is greater than critical micelle concentration, UF process can be used, for the surfactants removal. **Plant protection products (**pesticides, herbicides and insecticides) which belong to xenoestrogenes appear in surface and ground waters. These are substances with low molecular weight, thus they can be effectively removed from water during NF or by integrated systems of MF or NF and activated carbon adsorption (powdered or granulated) [2,14]. NF membranes eliminate pesticides of molecular weight above 190 Da to the amount below the limit of detection, and, generally, the retention coefficient varies from 50 to 100%, depending on molecular weight and concentration of pesticides in water as well as on the presence of organic and inorganic compounds [2,14]. According to their negative effects on living organisms, the concentration of **phthalates** in different parts of the environment, especially in water, should be controlled. The surprisingly high retention of phthalates was observed during both, RO and NF processes (initial concentration 40 μg/L) [20]. Retention rates achieved for diethyl phthalate, di-n-butyl and di-2-ethylhexyl were very high and amounted from 89.7% (UF) to 99.9% (RO and NF). Results obtained during removal of phthalates of molecular weight 222-391 Da revealed that the molecular weight of a compound did not influence on the effectiveness of removal. **Phenolic xenoestrogenes** (octylphenol, nonylphenol, bisphenol A and bisphenol F) can be removed from water by means of NF. Both, the retention coefficient and the rate of adsorption of xenoestrogenes strongly depend on a type of removed compound as well as on a membrane type [2,16]. The high retention of octylphenol and nonylphenol in the range from 61 to 73% was observed for SF-10 and DS-5-DK membranes, while in case of bisphenol A DS-5-DK (69%) and MQ-16 (75%) membranes were more efficient [21]. Recently, an increase in concentrations of the **synthetic hormone** (α -ethinylestradiol, mestranol and diethylstibelstrol) resulting of discharges of large amounts of expired pharmaceuticals, both from households and from wastewater and hospital wastes as well as pharmaceutical plants, has been observed. It was shown that elimination of this type of pollutants from water could be performed by means of membrane processes [22]. Considering relatively low molecular weight of those pollutants RO or NF must be applied. It was found that RO membranes totally eliminate particular hormones while retention coefficients obtained for NF and UF membranes were lower [22]. Membrane bioreactors are also proposed to the removal of hormones from wastewaters. The effectiveness of the operation of the MBR pilot installation (polyvinylidene difluoride membrane - PVDF) was studied, comparing the obtained results with the conventional installation working in a full-scale [23].

One of the most important and quite specific and anthropogenic groups of substances affecting the environment are compounds that expertly are called **Pharmaceutical and Personal Care Products** (PPCPs). This group includes both, compounds with pharmaceutical activity, as well as substances used by people to maintain personal hygiene [24]. PPCPs enter quite significantly to wastewaters and surface water and groundwater. Main sources of aqueous environment pollution with pharmaceuticals are households and hospitals, diagnostic units, pharmaceutical plants and livestock farms. Studies of comparative efficiency of removal of drugs in wastewater treatment plants have shown that biological methods are not always sufficient [1]. The methods of medicines removal from water and wastewater are advanced oxidation, activated carbon adsorption on granulated beds and membrane processes – NF and RO [25], and, in case of wastewater treatment, membrane bioreactors [24,26].

It was found that MBR installations used the in wastewater treatment improved the efficiency of removal of organic PPCPs in refer to conventional wastewater treatment plant. It was caused not only by the extension of retention time and increasing age of biomass, but also by increase of its concentration and adsorption ability of micropollutants on the much larger flocks of activated sludge. Radjenović et al. [27] observed significant improvement in the efficiency of removal of regulators of lipids and cholesterol, statin drugs (gemfibrozil, bezafibrat, clofibric acid and pravastatin), β-blockers (atenolol and metoprolol), antibiotics (ofloxacin and erythromycin) and some painkillers and anti-inflammatory drugs in MBRs. Other studies indicate on a very high and stable rate of removal of clofibric acid and diclofenac in plants equipped with the MBR. The efficiency of removal of clofibric acid usually amounted to 50-70% and diclofenac to 51% [57] during conventional wastewater treatment.

NF and RO processes, used for the purification of wastewater and natural waters, can also be used for removal of residues of PPCPs [2,24]. It was found that the NF membranes exhibited relatively low retention (40%) for polar PhACs, low volatile and low hydrophobicity. In the case of polar organic compounds retention significantly depended on the dipole moment and pH [28]. Test results showed that the negatively charged and ionic compounds such as the analgesic diclofenac could be removed in more than 90- 95%, regardless of the other physico-chemical properties, mainly according to electrostatic repulsion [2]. In case of neutral compounds, retention takes place according to molecular exclusion and adsorption. For example, the neutrally charged antipyretic drug phenacetin or anti-inflammatory and antirheumatic drug ibuprofen show a lower retention (phenacetin only > 20%), because they are significantly adsorbed on membranes with relatively high hydrophobicity [2]. On the other hand, another neutral antipyretic medicament, piramidon, is always retained in more than 70%, suggesting that its retention is affected also by other phenomena. In addition, the retention of pharmaceuticals in the RO and NF is affected by membrane material [24]. For example, it was found that polyamide membranes had higher efficiency (57-91%) than cellulose acetate membranes. It was found that in the case of polyamide membranes, molecular weight of the compound could be used as a retention trend indicator (separation based on molecular sieving), while the polarity allowed to predict retention of individual compounds in the case of cellulose acetate membranes. Retention of pharmaceuticals depends also on the concentration [27]. Experiments conducted at a concentration of 100 ng/L gave significantly lower retention (14-72% for NF and for 50-80% RO) compared to tests taken at a higher concentration amounted to 100 μg/L (19 - 93% for NF and 71 - 95% for RO). It was evaluated the conventional drinking water treatment processes at typical Water Treatment Plants conditions for the removal of antibiotics (carbadox, sulfachloropyridazine**,** sulfamethoxazole, sulfamerazine, sulfametazine, sulfathiazole and trimethoprim) [2]. They showed a very high efficiency of RO in the removal of all antibiotics.

LITERATURE

[1]. Bodzek M., Konieczny K., *Usuwanie zanieczyszczeń nieorganicznych ze środowiska wodnego metodami membranowymi,* Wydawnictwo Seidel-Przywecki, Warszawa 2011, ISBN 978-83-60956-18-2.

[2]. Bodzek M., Membrane technologies for the removal of micropollutants in water treatment, in: Basile A., Cassano A., Navin K. Rastogi (Eds.), *Advances* in *Membrane Technologies for Water Treatment: Materials, Processes and Application*s, Elsevier Science,Woodhead Publishing Ltd., Cambridge 2015, pp.465-515, ISBN 13: 9781782421214.

[3]. Bodzek M., Konieczny, K., Membrane techniques in the removal of inorganic micropollutants from water environment – state of the art, Archives of Environmental Protection, 37(2) (2011) 15-29.

[4]. Velizarov S., Crespo J.G., Reis M.A., Removal of inorganic anions from drinking water supplies by membrane bio/processes, Reviews in Environmental Science & Bio/Technology, 3 (2004) 361–380.

[5]. Kołtuniewicz A.B., Drioli E., *Membranes in clean technologies*, Wiley-VchVerlag GmbH, Weinheim 2008, ISBN-13: 978-3-527-32007-3

[6]. Wisniewski J., Electromembrane processes, in: Noworyta A., Trusek-Hołownia A. (Eds.), *Membrane Separations*, Argi, Wrocław 2001, pp.147–179.

[7]. Crespo J.G., Velizarov S.,Reis M.A., Membrane bioreactors for the removal of anionic micropollutants from drinking water, Current Opinion in Biotechnology, 15 (2004) 463–468.

[8]. Bodzek M., Usuwanie metali ze środowiska wodnego za pomocą metod membranowych – stan wiedzy, Monografie Komitetu Inżynierii Środowiska Polskiej Akademii Nauk, 66 (2012) 305–313.

[9]. Bakalár T., Búgel M., Gajdošová, L., Heavy metal removal using reverse osmosis, Acta Montanistica Slovaca, 14 (2009) 250-253.

[10]. Qdais H.A., Moussa H., Removal of heavy metals from wastewater by membrane processes: A comparative study, Desalination, 164 (2004) 105-110.

[11]. Mehiguene K., Garba Y., Taha S., Gondrexon N., Dorange, G., Influence of operating conditions on the retention of copper and cadmium in aqueous solutions by nanofiltration: experimental results and modeling, Sep. Pur. Techn., 15 (1999)181-187.

[12]. Korus I., *Wykorzystanie ultrafiltracji wspomaganej polimerami do separacji jonów metali ciężkich,* Wydawnictwo Politechniki Śląskiej, Gliwice 2012, ISBN: 978-83-7335-927-7.

[13]. Zakrzewska-Trznadel G., Radioactive solution treatment by hybrid complexation-UF/NF process, J.Membr.Sci., 225 2003 25-39.

[14]. Mavrov V., Nikolov N.D., Islam M.A. Nikolova J.D., An investigation on the configuration of inserts in tubular ultrafiltration module to control concentration polarization, J.Membr.Sci., 75 (1992)197-201.

[15]. Owlad M., Aroua M.K., Daud W.A., Baroutian, S., Removal of hexavalent chromium - contaminated water and wastewater: A review, Water Air Soil Pollution, 200 (2009) 59–77.

[16]. Bodzek M., Przegląd możliwości wykorzystania technik membranowych w usuwaniu mikroorganizmów i zanieczyszczeń organicznych ze środowiska, Inżynieria i Ochrona Środ*owiska*,16(1) (2013) 5-37.

[17]. Uyak V., Koyuncu I., Oktem I., Cakmakci M., Toroz I., Removal of trihalomethanes from drinking water by nanofiltration membranes, J. Hazard. Mater., 152 (2008) 789–794

[18]. Chalatip R., Chawalit R., Nopawan R., Removal of haloacetic acids by nanofiltration, *J. Environ. Sci.*, 21 (2009) 96–100.

[19]. Kowalska M., Dudziak M., Bohdziewicz J., Biodegradacja kwasów halogenooctowych w bioreaktorze z poliamidową, enzymatyczną membraną ultrafiltracyjną, Inżynieria i Ochrona Środowisk*a*, 14 (2011) 257-266.

[20]. Bodzek M., Dudziak M., Luks–Betlej K., Application of membrane techniques to water purification. Removal of phthalates, Desalination, 162 (2004) 121 – 128.

[21]. Dudziak M., Bodzek M., Removal of xenoestrogens from water during reverse osmosis and nanofiltration – effect of selected phenomena on separation of organic micropollutants, Architecture Civil Engineering Environment, 1(3) (2008) 95 – 101.

[22]. Bodzek M., Dudziak M., Elimination of steroidal sex hormones by conventional water treatment and membrane processes, Desalination, 198, (2006) 24–32.

[23]. Zuehlke S., Duennbier U., Lesjean B., Gnirss R., Buisson H., Long-term comparison of trace organics removal performances between conventional and membrane activated sludge processes, Water Environ. Res., 78 (2006) 2480–2486.

[24]. Heberer T., Feldmann D., Removal of pharmaceutical residues from contaminated raw water sources by membrane filtration, in *Pharmaceutical in the Environment*, Berlin-Heidelberg, Springer 2008, pp.427-453, ISBN 978-3-540-74664-5.

[25]. Snyder S., Adham S., Redding A., Cannon F., DeCarolis J., Oppenheimer J., Wert E., Yoon Y., Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals, Desalination, 202 (2007) 156–181.

[26]. Clara M., Strenn B., Gans O., Martinez, E., Kreuzinger N., Kroiss H., Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants, Water Research, 39 (2005) 4797–4807.

[27]. Radjenovic J., Petrovoc M., Barcelo D., Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment, Water Research, 43 (2009) 831-841.

[28]. Kimura K., Toshima S., Amy G., Watanabe Y., Rejection of neutral endocrine disrupting compounds (EDCs) and pharmaceutical active compounds (PhACs) by RO membranes, J. Mem. Sci., 245 (2004 71–78.