Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.1002281

57 (2016) 1107–1131
January

Taylor & Francis
Taylor & Francis Group

The removal of boron from the aquatic environment—state of the art

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Received 7 July 2014; Accepted 8 December 2014

ABSTRACT

Boron is emitted into the environment in a natural (weathering of rocks) and anthropogenic (wastewaters coming from industry, agriculture) way. It is a micronutrient for plants and animals, as well as a useful component in many branches of commercial activities. However, an excess of boron is toxic for both plants and animals. Extremely narrow is the range between permissible and harmful doses both to people and plants. It is often necessary to remove it from water and wastewater. The acceptable content of boron in drinking water and wastewater discharge into the environment is 1 mg/L. Removal of boron from the aquatic environment can be carried out in the following ways: ion exchange and adsorption onto boron-selective resins; reverse osmosis, in multistage configurations with RO and sorption; hybrid systems combining sorption onto fine resins with membrane filtration and polymer-enhanced ultrafiltration; processes with application of ion exchange membranes. The work presents a comprehensive review of the literature on boron removal with abovementioned methods. The fundamentals of each process and the effect of experimental parameters are discussed.

Keywords: Boron removal; Ion exchange and adsorption; Reverse osmosis; Polymer-enhanced ultrafiltration; Electrodialysis and Donnan dialysis

1. Introduction

Boron is an element widely spread in earth's hydrosphere and lithosphere [1–5]. In the nature, it does not appear in the free form, but always as a compound with oxygen or other elements. In the lithosphere, it can be found in rocks and soil, and its concentration in the earth crust varies from 1 to 500 mg/kg, depending on the type of a rock [6] (usually it is around 10 mg/kg, which corresponds to 0.001% of the total elementary composition of earth [3,6,7]). The amount of boron in soil can be from 2 to 100 mg/kg (usually 30 mg/kg) [6]. In the hydrosphere, boron appears in sea water in the amount of ca. 3.5 mg/L [6] (the concentration range is from 0.5 to 9.6 mg/L) [8], in surface water at the concentration from 0.3 to 100 mg/L [6,8] and in groundwater from below 0.01 mg/L up to 1.5 mg/L, depending on the localization. In recent years, a significant increase of boron concentration in surface waters due to both natural and anthropogenic factors has been observed [8]. Natural boron emission sources are rock weathering, while anthropogenic ones are related to industrial activities. Boric acid and boron salts are widely used

Presented at the 12th Scientific Conference on Microcontaminants in Human Environment
25–27 September 2014, Czestochowa, Poland

in many branches of the industry [3,7]. It is used mainly in ceramics to produce borosilicate glass, glass fibre isolations, glazes, enamels, and porcelain and in production of herbicides (at high concentrations) and fertilizers (at low doses). Boron compounds are also used as additives decreasing the flammability of plastics and cellulose isolations. They can also be found in washing powders and soaps as well as in preservatives [6,8]. Relatively new application of boron compounds has been found recently in production of high-energy fuels, coolants and catalysts [6]. As a result, an increased concentration of boron up to 0.5 mg/L can be met near some wastewater deposition points [6], which increases the element concentration in surface water flowing through urban and industrial areas. Due to high volatility of boron, it can be found in acid rains, which is also a result of industrial activities [4,8]. Moreover, geothermal water intensively exploited nowadays contains significant amounts of boron at the level of 30–40 mg/L [9–12].

In the environment, boron mainly appears in the form of orthoboric acid (H_3BO_3) and orthoborates depending on the pH. At significantly low concentrations (below 2 mg/L), only monomolecular compounds, that is $B(OH)_3$ and $B(OH)_4^-$, while at higher levels and at higher pH, especially above 10, polymolecular compounds $[B_3O_3(OH)_5]^{2-}$ and $[B_4O_5(OH)_4]^{2-}$ are met [5,8]. The formation of cyclic ion forms is a result of the interaction of boric acid and borate ion according to the following reaction:

$$B(OH)_3 + 2B(OH)_4^- \Leftrightarrow [B_3O_3(OH)_5]^{2-} + 3H_2O \tag{1}$$

In the neutral environment (pH 7–8), which is characteristic of most natural waters introduced to the desalination process, the dominant form of boron is molecular boric acid (99.3% at pH 7 and 93.2% at pH 8) [3]. At higher pH values, the acid undergoes the transformation to borate ions, while at pH 12, only the ionic form is met. Boron is an element with electron deficit; therefore, the radius of boron acid crystals is quite high (0.244–0.261 nm) [11]. Moreover, molecular boric acid does not form hydrates, which is quite significant considering its transport during membrane separation. On the other hand, the dissociated form of boron is fully hydrated. Thus, its radius is higher and the ion charge is negative. It results in a higher retention during reverse osmosis separation caused by both the sieving effect and the electrostatic repulsion interaction with negatively charged osmotic membrane surface [3–5].

Boron is an important microelement for plants and animals; however, the difference between the necessary dose and the overdose is very small [3]. The concentration of boron in the irrigating water or in soil plays an important role considering the quality and quantity of crops [6]. The most important function of boron is its role in forming the cellular wall, where it assures the structure integrity [6]. It also improves transport through the cellular membrane, enzyme interactions, nucleic acids synthesis, phenol and hydrocarbons metabolism as well as transportation of sugars and hydroxy acids [6]. It has also been proved that boron is very important during the growing phase of embryo and deficit of that element can cause serious malfunctions [6]. The main role of boron in living organisms is related to bone metabolism and immunological system functioning [6]. The sensitivity of plant to boron is much diversified. Exemplary permissible concentration of boron for water used to different plant irrigations ranges between: currant, <0.5 mg/L; strawberry, 0.5–1.0 mg/L; potato, 1.0–2.0 mg/L; cabbage, 2.0–4.0 mg/L; tomato, 4.0–6.0 mg/L; and asparagus, —6.0–15.0 mg/L [3,8]. A daily dose of boron absorbed by an adult person should not exceed 0.16 mg/kg of body mass [3].

The presence of boron in drinking water causes a teratogenic effect [3]. According to WHO recommendation from 1993, the concentration of boron in potable water should not exceed 0.3 mg/L [3], but in 1998 the level was increased to 0.5 mg/L and in 2011 to 0.45 mg/L [3]. In European Union countries, the permissible level of the element in drinking water is established at 1.0 mg/L [13], and it is valid also in Poland [13]. The concentration of boron in wastewater deposited to natural collector or soil should not exceed 1.0 mg/L, while to streams introduced to sewage systems, it is 10 mg/L [14]. The problem with the increased boron environmental concentration does no longer affect only those countries with its high natural resources, but also developed ones. The exceeded boron concentrations in natural waters have also been reported in Poland. Such cases have been reported in groundwater (3–6 mg/L) and wastewaters containing boron, including municipal landfills leachates (33.5–68 mg/L) [15]. The most known example are leachates from the municipal landfill localized at chemical plant in Poland, where the concentration of boron determined in well water intakes has been found to be 30 mg/L (max. 62 mg/L), while in groundwater resources below the landfill area, it has been 700 mg/L [15]. The high concentration of boron (8–180 mg/L) is also reported in wastewater from installations of wet desulphurization of flue-gases depending on the type of combusted coal [3].

2. Technologies for boron removal

Due to a very serious danger of contamination of ground and surface water with boron present in wastewater as well as to the necessity of treatment of water containing boron to potable purposes, the development of effective techniques for the element removal from aquatic environment is required. It also includes desalination processes carried out for sea waters and other brackish waters [8].

The methods of boron removal can be separated into several categories. The first one involves not only coagulation and electrocoagulation [15,16] but also adsorption and ion exchange [4,6,8,17–22]. The last category is based on membrane separation including reverse osmosis (RO) and/or nanofiltration (NF) [4,6,23–44], electrodialysis (ED) [4,7,45–49], electrodeionization (EDI) [50,51] and Donnan dialysis (DD) [4,7,52] as well as ultrafiltration (UF) enhanced with polymeric complexation [4,8,53].

Unfortunately, not all available methods are simple and economically attractive. The main difficulty in choosing the method is the appearance of boron in various chemical forms as well as its changeable concentration [8]. Processes, which are commonly used in water and wastewater treatment, that is sedimentation, coagulation, natural beds adsorption and biochemical methods, are not always efficient enough [8]. Practically, every new technology of boron removal from water possesses some limitations. Adsorption/precipitation is effective only at high element concentrations and the final amount that can be reached is usually lower than 10 mg/L and it requires additional polishing [54]. The method based on ion exchange results in formation of strongly acidic side streams, utilization of which generates high additional costs. On the other hand, membrane separation results in the production of concentrate which usually contains high boron concentration and insignificant amounts of other substances, and as a result, other useful products can be formed [55]. Boron removal problems can also be solved by combination of particular unit operations into, so-called, integrated systems [3]. Some of them have already been operating, that is adsorption/co-precipitation and reverse osmosis, ion exchange—electrodialysis, reverse osmosis—ion exchange, adsorption—ultra/microfiltration and others [4,6,8,56]. In Table 1, the effectiveness of boron removal from different water streams with the use of various methods is presented [56–58]. It can be seen that the highest effectiveness is obtained for adsorption and complexation with ion exchange resins, 2-stage reverse osmosis and activated carbon adsorption.

Nevertheless, only two methods are nowadays applied on an industrial scale, that is reverse osmosis (RO) carried out at high pH conditions and ion exchange. The boron removal process should be both economically attractive and ensure almost complete element removal in order to enable the mixing of purified stream with the raw water.

2.1. Adsorption and ion exchange methods

2.1.1. The principle and the mechanism of boron complexation

Adsorption and ion exchange with the use of variety of sorbents seem to be one of the most effective methods of selective boron removal from water [4–6,8]. The process is carried out at ion exchange resins containing neighbouring hydroxyl group at *cis* configuration, which are able to bond (exchange) boron via formation of boric acids or borate ions complexes (Fig. 1) [5,8,20–22].

As the resin support macroporous polystyrene is usually used, the functional compound able to boron exchange is N-methyl-D-glucamine (NMDG). It possesses hydroxyl groups in *cis* configuration of tertiary amine (Fig. 2) [8,15]. The formation of complexes between –OH groups of ion exchange resin and boron does not require boric acid dissociation. Particles of polyoxide compounds reveal the tendency to form bidentate boric acid esters or borate anions complexes with a proton [4–6,8,20–22] (Fig. 1) [4–6].

The stability of formed complexes depends mainly on the type of applied diol. If the used applied possess –OH groups specifically suited to the structure of tetraedrical boron coordination, the stable complex is formed. In NMDG, there are five hydroxyl groups, while the main role of tertiary amine is the neutralization of proton revealed during tetraborate complex formation, which prevents the pH decrease. The most of synthetic resins are produced via modification of NMDG as copolymer of styrene and divinylbenzene (Fig. 2). Functional groups of those resins form covalent bonds with boron and as a result complex compounds are obtained [8,59].

2.1.2. Available sorbents

On the market, there are many of resins produced by different companies, for example PWA10 and IRA743 (Amberlite; Rohm & Haas Corporation), Dowex BSR-1 (Dow Chem.), DiaionCRB01, CRB02, CRB03 and CRB05 (Mitsubishi Corporation, Japan), S108 and S110 (Purolite) and others (Table 2) [4,6,8].

Table 1
The efficiency of various methods of boron removal from aquatic streams [56–58]

Technology	Water type	Removal (%)	Comments
Softening	Sea water	Insignificant	Precipitation of calcium carbonate
Coagulation	Drinking	<28%	Typical 10%
Adsorption on activated carbon	Simulated	Do 90%	High doses of activated carbon required
Reverse osmosis	Sea water	43–78%	–
Ion exchange resins	RO permeate	>99%	pH of effluent < 4.5
2-step RO with pH correction	RO permeate	40–100%	pH of raw water about 10.5
Electrodialysis	–	>90%	The high cost of disposal
Boron complexation	Simulated	>80%	For N-methylglucamine
	RO permeate	>98%	For mannitol

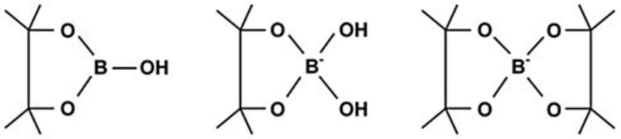

Fig. 1. Schemes of complexes (esters) of boron with sorbitol group [8].

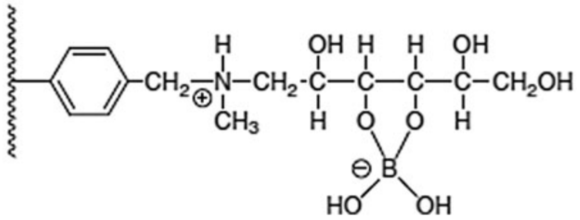

Fig. 2. Resins with NMDG group used to boron removal from water solutions [8,15].

These materials are able to remove boron with the efficiency up to 93–98%, even from highly mineralized solutions [59], and the final contaminant level in the purified stream is usually below 0.05 mg/L (even 0.02 mg/L). However, the process of ion exchange characterizes with high costs including investment and operation [13] related to resins regeneration with acids (1–10% HCl or H_2SO_4), neutralization with NaOH and utilization of side streams [3]. Nevertheless, ion exchange resins based on the system have already been tested in the pilot scale [60].

Conventional polystyrene sorbents are anion exchangers whose hydrophobic structure does not favour the mass exchange in water solutions, which has a negative impact on the boron removal effectiveness. The capacity of resins depends on many factors, that is a polymeric support type, its specific surface as well as the type of functional compounds and its active groups. Thus, many studies on the modification of already known resins or on the development of new materials are intensively carried out [4,6,8,61–66]. The exemplary modification of NMDG-based resin is the action with chromotropic acid [61] or sorbitol [59], which allows for removing boron from acidic solutions. Another example based on the synthesis of polymer with other functional groups is the introduction of a sulphonic group to the polystyrene matrix and its further interaction with glucosamine hydrochloride. The modified resin contains sulphonamide

Table 2
Commercial boron-selective resins [4,6,8]

Producer	Product name	Polymer structure	Functional groups	Diameter (μm)	Capacity (eq/L)
Amberlit	PWA10	Macroporous	N-methylglucamine	300–1,200	≥0.7
	IRA743	polystyrene		500–700	0.7
Dialon	CRB01	Macroporous	N-methylglucamine	300–1,200	≥1.2
	CRB02	polystyrene—DVB		300–1,200	≥0.9
Dowex	BSR-1	Macroporous polystyrene—DVB	N-methylglucamine	550 ± 50	0.7
Purolite	S108	Macroporous	N-methylglucamine	650 ± 70	0.6
	S110	polystyrene—DVB		600 ± 100	0.8

groups and long chains containing hydroxyl groups at *cis* configuration enabling selective bonding of orthoboric acid [60].

A series of studies focused on possible hydrophilic supports with a highly specific surface has also been performed [4,6,8,49]. Parschova et al. [64] have compared the characteristics of various supports (polypropylene—styrene, polypropylene—glycidyl methacrylate (GMA), viscose—GMA and commercially used styrofoam DVP (Purolite D-4,123) containing NMDG functional groups. The possibilities of investigated resins have been found to be much lower than commercial ones during their testing at the same experimental conditions. However, the sorbent based on viscose GMA mixture has revealed relatively high sorption kinetic and simplicity of regeneration even with the diluted hydrochloric acid (0.1 mol/L). There have also been some investigations involving terpolymer comprised of glycidyl methacrylate (GMA)—methyl methacrylate (MMA)divinylbenzene (DVB) as a support matrix for NMDG. Sorption and regeneration tests have shown satisfactory mechanical stability of particles during long term operation and better regeneration capability than commercial boron bonding sorbents. Senkal and Bicak [66] introduced imidodipropylene glycol to GMA-MMA-DVB terpolymer and proved its ability to complexation of boron. During batch sorption and the regeneration test it has been found that the resin characterizes with a great boron sorption capacity equal to 32 mg/g and it is easy to be regenerated.

Orlando et al. [67] proposed that several natural materials containing functional groups have able to boron-bonding and boron-revealing anion-exchange properties have been developed. For example, some polysaccharides as chitosan cross-linked with diglycidyl ethylene glycol ether have been found to remove boron from neutral solutions (pH 5–7) [62]. Moreover, cellulose fibres and powder have been tried to be used as a sorbent matrix [63,68]. The prepared materials are characterized with good affinity to boron and remove it from water solutions much faster than commercial resins. Other materials such as sawdust, MgO agglomerates [69,70], calcinated magnesite [71] or aluminium oxide cumulated in water treatment sludge [72] have also been tested in boron removal process. Polowczyk et al. [73] have tried to apply volatile dust agglomerates generated at a power plant in order to remove boron from water solution, and the maximum sorption capacity obtained has been at the level of 6.9 mg/g. Morisada et al. [74] have run tests with tannin gel modified with ammonia, but it has characterized with the low sorption efficiency at neutral environment, while the maximum value equal to 11.7–24.3 mg/g has been observed at alkali conditions. The removal of boron from wastewaters has also been carried out with the use of loam minerals, both natural and waste origin [75]. Those materials are layered metals hydroxides containing many bivalent cations which can be substituted with trivalent ones resulting in overall positive charge enabling the bonding of anions, including boron. Ferreira et al. [76] have used adsorbents containing Mg/Al and Mg/Fe, and the maximum effectiveness obtained during their studies was at the level of 14.0 mg/g. Kentjono et al. [77] have discussed the removal of boron from optoelectronic wastewater of high element concentration with the use of loams containing Mg/Al, and they have obtained the highest efficiency equal to 37.90 mg/g at pH 9.

The removal of boron from aquatic environment may also be performed via regular adsorption avoided ion exchange effect. Such a possibility has been checked for coal, breeze, zeolites and polymeric adsorbents as well as for combination of the process with co-precipitation using hydroxides of chosen metals [15]. Polat et al. [19] have studied the removal of boron from raw and desalinated sea water using carbon and volatile dust adsorption and show 95% effect of the contaminant removal at optimal conditions (pH 9, liquid/solid ratio L/S = 1/10, reaction time >6 h). The combination of this method with microfiltration can become an alternative solution for boron removal at areas, where both carbon and volatile dust are easily available. In the study on boron removal from chemical plant landfill leachates, granulated active carbon impregnated with tartaric acid and mannite have been used and the sorption capacity of 4.95 mg/g has been obtained [78,79]. In the case when powdered active carbon is applied, it can be separated from the treated solution by means of microfiltration.

To remove boron by means of adsorption/co-precipitation method, metal ions (Fe, Mg, Co, Ni, Zn) able to form both hydroxides of large specific surface or hardly dissolved borates in combination with low-pressure-driven membrane filtration for their separation can be used. In the study on boron removal from chemical plant leachates, nickel and aluminium hydroxides have been applied. However, only in the case of aluminium, the final concentration of boron has not exceeded the permissible levels established for wastewater distributed to the environment. At the investigated boron concentration range (5–300 mg/L), the obtained removal rate varied from 70 to 80% [15,58,79].

The modification of co-precipitation with hydroxides process is electrocoagulation, in which the electrolytic introduction of metal ions from electrodes composed of aluminium or iron to water solutions takes place [8,80]. The method is based on the electrochemical coagulants production, which removes contaminants from aqueous solutions. In this method, unlike co-precipitation, no additional anion is introduced to the solution and, as a result, the salinity increase is observed. The electrocoagulation process involves simple devices and it is easy to operate, and therefore, it generates low exploitation costs and insignificant additional chemicals requirements. Vasudevan et al. [81] have applied zinc hydroxide anode to remove boron with the efficiency of 93.2% at pH 7.0. However, higher removal rates reaching 95–96% can be obtained, but only in the case of highly concentrated solutions (1–5 g of boron/L), and the concentration of the contaminant in the purified stream is then usually from 40 to 250 mg/L [15].

2.1.3. The impact of operational conditions of the sorption effectiveness

The ion exchange process can be carried out at both static and dynamic conditions. At the former ones, a portion of sorbent is introduced to a boron-containing solution and an equilibrium state is supposed to be reached, usually at intensive stirring. At latter conditions, an ion exchanger (sorbent) is placed in a column as an immobilized phase through which a solution is flown at a given flow rate.

The effectiveness of boron removal depends not only on the type of applied sorbent, but also on process conditions. A volumetric ratio of resin/solutions, the initial boron concentration, solution pH and temperature and a speed of a mixture mixing need to be considered [6]. Boncukcuoglu et al. [82] have investigated the impact of those parameters on the boron removal via static sorption with Amberlit IRA-743 resin. An increase in temperature led to an increase in the reaction rate and, consequently, in higher boron removal rate [82]. The opposite tendency was observed by Ozturk and Kose [83] during their studies with water solution of boron concentration 600 mg/L and Dowex 2 × 8 resin at temperature range 25–45˚C. It has also been found that both the reaction rate and the boron removal effectiveness increases with an increase in the resin dose, and the process runs optimally at pH 9–9.5 [82,83]. A granulation of resin is another important factor of the operation. The small size of resin particles gives higher reaction and boron removal rates [84] due to the diffusion rate increase caused by a bigger surface. Moreover, higher the initial boron concentration is, lower the effective removal rate is. However, the speed of mixing which was in the range of 350–750 rpm, had no impact on the process performance [84]. Those dependences were confirmed by the study of Yan et al. [85].

The study on the effect of process parameters on the boron removal was carried out in the column system (Table 3). The breakthrough point of a column is found as a crucial parameter indicating on the effectiveness of the boron removal process as it is directly connected with a resin capacity. The results of those studies performed by several researchers are in agreement considering a solution flow rate and boron concentration, while differences can be found in the impact of pH and ionic strength on the process [6].

Considering the impact of a solution flow rate, it has been found that an breakthrough column capacity decreases with the parameter increase due to a shorter contact time of a resin with a boron-containing stream [84,85]. An increase in the height to diameter ratio (H/D) of the column can result in its higher breakthrough capacity as a contact time of a resin with a solution increases, and the distribution of a liquid in a column is improved [85]. The column breakthrough during the operation with highly concentrated solutions is faster as the column contains strictly given amount of a resin of a rigid sorption capacity. An increase in the ionic strength cases the boron removal rate decrease according to Yan et al. [85], while due to Simonnot et al. [22], the parameter has no impact on the process. This disagreement can be explained by differences in experimental conditions, that is pH a solution, an amount of added NaCl and boron selectivity of Amberlite IRA-743 and XCS-800 resins.

2.1.4. Boron recovery and sorbents regeneration

One of the main disadvantages of ion exchange and adsorption processes is necessity of resins and sorbents regeneration using additional chemicals. The regeneration process usually requires significant amounts of chemicals which significantly affects process economics. It is often necessary to use both, an acid (0.25 M HCl) and a base (0.25 M NaOH) of a volume corresponding to four-times volume of a column bed [6]. For example, a system with a bed of volume 10 m^3 used in boron removal from 3,800 m^3 of water of the contaminant concentration 5 mg/L requires 40 m^3 of HCl and 40 m^3 of NaOH for regeneration [22]. Thus, it is crucial to perform boron removal by sorbents at the most possible minimization of regenerating chemicals amounts.

The regeneration process generally comprises two steps, that is boron removal with an acid, HCl/H_2SO_4, which is followed by the bed neutralization with NaOH. Nadav [86] has compared the sorption

Table 3
Influence of process parameters on breakthrough capacity of boron sorbent resins

Process parameter	Boron rejection	References	Used resin	Experiments conditions
pH increase	Lack	[22]	Amberlite IRA743	pH 5.5–8, boron concentration 20 mg B/L, ionic strength 0–0.1 mol NaCl/L
	Increase	[85]	XCS-800	pH 4–12, boron concentration 40 mg B/L, flow rate 16 BV[a]/h, ratio H/D 15
Velocity increase	Decrease	[84]	Diaion CRB02	15 and 20 BV/h, B concentration 1.5–1.6 mg B/L
		[85]	XCS-800	5, 16 and 30 BV/h, boron concentration 40 mg/L, 293 K, pH 10
		[83]	Dowex 2x8	39 and 45 mL/h, boron concentration 600 mg/L, pH 5.8
Temperature increase	Increase	[85]	XCS-800	293–323 K, boron concentration 40 mg/L, flow rate 16 BV/h, pH 10, H/D ratio 15
Boron concentration increase	Decrease	[22]	Amberlite IRA743	1–5 mg B/L and 5–500 mg B/L
		[85]	XCS-800	40, 50 and 100 mg B/L, flow rate 16 BV/h, 293 K, pH 10, ratio H/D 15
Ionic strength increase	Lack	[22]	Amberlite IRA743	0–0.1 mol NaCl/L, boron concentration 20 mg B/L, pH 5.5–8
	Decrease	[85]	XCS-800	50, 75 and 100 g NaCl/L, boron concentration 40 mg B/L, flow rate 16 BV/h, pH 10, ratio H/D 15
Increase of H/D ratio	Increase	[85]	XCS-800	10, 12 and 15 H/D, boron concentration 40 mg B/L, flow rate 16 BV/h, pH 10

[a] BV(bed volume) = 1 m^3 solution per m^3 resin; H/D—height to diameter ratio of a column.

capacity of a resin regenerated by means of three different methods. It has been found that regeneration with H_2SO_4, and NaOH neutralization increases the sorption capacity of the sorbent in comparison with the regeneration made only with the use of H_2SO_4. Simonnot et al. [22] have run column regeneration tests using various acidic and basic reagents. It has been shown that the regeneration can be performed using a weak acid solution (CH_3COOH) and the regenerating solution volume needs to be 50 times higher than the bed volume. The regenerating acid, however, can be reused, which improves the attractiveness of the process, but the effectiveness of washing decreases from 94 to 78%.

Kabay et al. [87] have investigated the possibility of recirculation of chemicals used to boron-selective resin regeneration (Diaion CRB02). The resin has been used to the boron removal from geothermal water via 10 stepwise cycles: sorption–washing–eluation–washing–regeneration–washing. In the study, 5% H_2SO_4 solution and 4% NaOH solution have been involved. It has been observed that the breakthrough point decreases negligibly between 2nd and 7th cycle and reaches a constant level between 7th and 10th cycle. The decrease in a column capacity can be explained by the high temperature of treated geothermal water (ca. 70°C). Similar recycling tests have been performed by Ozturk and Kose [83] for strongly basic anionites Dowex 2x8. The washing of boron out of the resin has been made with 0.5 M HCl and the regeneration with 2 M NaOH. The increase in boron removal efficiency has been observed after the first cycle, while no change has been noted after 2nd and 3rd cycle.

2.2. Reverse osmosis application

The retention of boron by means of conventional RO in acidic or neutral environment is limited and usually equals to 40–60%, which does not guarantee the production of the permeate that fulfils regulations on drinking water quality [6,88]. It is especially important in the case of treatment of water containing high boron concentration (sea—oceanic water contains ca. 35 g/L of a salts and 5 mg/L of boron). The low retention of boron by RO membranes is caused by the appearance of the element in the form of orthoboric acid that can be transported through the membrane. Thus, the removal of boron by means of RO should be carried out at increased pH at which it is in ionic form [1]. On the other hand, such conditions lead to a significant membrane fouling (scaling) caused by precipitation of calcium and magnesium compounds, and thus, it required often chemical washing of membrane modules. RO permeate is usually alkalized to pH ca.

9.5 and undergoes the process one more time [3–6]. Such a solution results in the appearance of highly dissociated boron compound enhancing its retention by a RO membrane. Hence, in practice, the application of multistep RO systems is required in order to produce drinking water of a proper quality considering boron permissible level. Membranes applied in the second or third stage of the treatment are usually operated at lower salts concentration, and thus, the RO pressure can be lower (from ca. 0.6 to 1.3 MPa) [1]. Such a solution is especially recommended to the production of drinking water from sea water, and the possible boron retention rate reaches 98%, while the problem of salts deposition on a membrane surface is eliminated. Nevertheless, the necessity of multistage RO systems application increases the costs of the process because of both higher investment costs and significant water loses (ca. 10%). For example, the cost of boron removal via 2-stage system is estimated at 0.06 USD/m^3 [15,57]. One must also know that boron retention is affected not only by the pH, but also by the transmembrane pressure, while it is independent of the element concentration in the raw water [1,15,57].

Cengeloglu et al. [89] have investigated the removal of boron from water using single-stage RO system with RO membranes for sea water (SWHR) and brackish water (BW-30) desalination and AG (GE Osmonics) membranes for treatment of simulated brackish water (BW) and natural groundwater. The impact of pH, transmembrane pressure, boron concentration and membrane type on the boron removal rate has been analysed. Moreover, two natural groundwaters containing 24.8 and 9.4 mg of boron/L have been introduced to the treatment with SWHR membrane. Over 95% retention of the element has been obtained, which shows that RO process with membranes for sea water desalination can be effectively used already in a single-stage configuration for freshwater treatment.

Redendo et al. [90] have performed studies on the boron removal using different Filmtec membranes. The obtained retention has been at the level of 82–92% for most of sea water desalination membranes (SW) and between 30 and 80% in the case of BW membranes. In Table 4, usual boron retention coefficients of Filmtec membranes (SW3OHR-380, SW3OHR-320, SW30-380, BW30-400 and BW30LE-440) determined at standard conditions are shown [90].

The results on boron retention obtained for Filmtec membranes have been used to analyse several project concepts (multistage ones), due to their economic and technical aspects, which aimed at assuring the production of low boron content permeate from different types of treated water [90].

In recent years, many studies have been focused on an increase in boron removal using RO technology by the development of new membranes generation and improving a system configuration [1,4,5,90–92]. They have concerned the removal of boron to the level of ca. 0.5 mg/L from sea and BW of lower boron content by means of single-stage RO at the retention coefficient of 91–96%. This solution is mainly connected with the introduction of additives (or an additional layer) to a skin layer (an active layer) of a membrane in order to increase boron retention. Those modifications are mainly focused on an increase in membrane hydrophilicity, which recompenses an increase in membrane resistance caused by an increase in skin layer density [5]. The skin layer may contain one or several chemical substances. For example, Comstock [93] has achieved an increase in boron retention from 92.7% to 97.6% due to the coating of osmotic membranes for sea water desalination with polyhexamethylene biguanide. The author has observed an insignificant increase in boron retention (from 99.3% to 99.7%) and a decrease in membrane permeability from 54.1 L/m^2 h to 46.6 L/m^2 h [93]. Despite this fact, the improvement in boron retention using single-stage RO system for sea water treatment is advantageous considering investment and exploitation costs. However, further studies on the layer stability need to be carried out before its introduction to the practice. In Table 5, data on RO membranes with the increased boron retention are shown [1,4].

Majority of currently applied RO membranes characterize with low retention of boron, and therefore, they have to be combined with other treatment techniques. There are many solutions proposed for both sea and brackish water, which enables an increase in boron retention and consequently a decrease of its concentration in permeate. Those methods are as follows: [4–6,15]

(1) multistage reverse osmosis,
(2) reverse osmosis at increased pH conditions,
(3) the combination of both above-mentioned methods,
(4) the polishing of RO permeate on ion exchange selective to boron bed,
(5) the complexation of boron with polymers or adsorbents and their separation from water by means of low-pressure-driven membrane techniques.

Moreover, a series of other process configurations used to produce low boron content RO permeate is proposed [15,23,92,94]. In every specific case, the optimal technology should be chosen, which would be in

Table 4
Boron retention coefficients of Filmtec membranes for sea water (SW) and brackish water (BW) desalination at standard conditions [90]

Membrane	Module flux, m^3/h	Retention, %	
		Salt	Boron in neutral environment
FILMTEC SW30HR-380	0.95	99.7	90 (88–92)
FILMTEC SW30HR-320	0.79	99.7	90 (88–92)
FILMTEC SW30-380	1.43	99.4	88 (85–90)
FILMTEC BW30-400	1.67	99.5	65 (55–75)
FILMTEC BW30LE-440	1.81	99.0	54 (43–63)

Standard conditions: TDS 32,000 mg/L, Δp = 5.5 MPa, temp. = 25˚C, pH 8, recovery 8–10% for SW membranes. TDS 2,000 mg/L, Δp = 1.1–1.6 MPa, temp. = 25˚C, pH 8, recovery 15% for BW membranes.

Table 5
The comparison of RO membranes used to boron removal [1,4]

Membrane type	pH	Water type	The nature of the research	Maximum boron retention
UTC-80	8	32 g/L NaCl, 4–5 ppm B	Lab	90
SW30HR-380	8	32 g/L NaCl	Pilot	90
SW30HR-320	8	32 g/L NaCl	Pilot	90
SW-30-XHR-400i	8	32 g/L NaCl, 5 ppm B	Membrane producer	93
SW-30-HRLE-400i	8	32 g/L NaCl, 5 ppm B	Membrane producer	91
SW-30-XLE-400i	8	32 g/L NaCl, 5 ppm B	Membrane producer	88
SW-30-ULE-400i	8	32 g/L NaCl, 5 ppm B	Membrane producer	87
SW-30-2540	8–8.2	39 g/L NaCl	RO plant	85
SW-30-XHR-2540	8–8.2	39 g/L NaCl	RO plant	88
SW-30-HR-380	8	32 g/L NaCl, 5 ppm B	Lab	90
XUS SW30XHR-2540	5–5.4	8.8–11.4 ppm B	Pilot	88
SU-820	8	32 g/L NaCl, 5 ppm B	Lab	91
TM-820A-400	8	32 g/L NaCl, 5 ppm B	Membrane producer	93
TM-820E-400	8	32 g/L NaCl, 5 ppm B	Membrane producer	91
TM-820-370	8	32 g/L NaCl, 5 ppm B	Lab	91

agreement with a technical and economic analysis. Such a case study should consider all crucial parameters, that is raw water chemical composition, especially the boron content, required final boron concentration and all other factors which have an impact on investment and exploitation costs of either RO or other methods.

2.2.1. Multistage reverse osmosis systems

In order to adapt RO configurations to drinking water quality requirements, two-stage reverse osmosis systems are used. Sea water or any other water of increased boron content is desalinated during the first-stage treatment, permeate (of high boron content). It is partially or completely directed to second RO stage, at which the increased pH is applied (Fig. 3) [2,90]. Thus, membranes for sea water desalination (SWRO) are usually used in the first stage and those for brackish water treatment (BWRO) are involved in the second stage. The retentate obtained during the second-stage treatment is supersaturated with $CaCO_3$ and $Mg(OH)_2$ due to the high pH conditions. When the stream is mixed with raw water, the concentration of salts decreases and their microcrystals may appear during the mixing process. The phenomenon can be easily prevented by the retentate acidification.

Prats et al. [95] have shown the results of the study on boron removal from BW using pilot scale RO

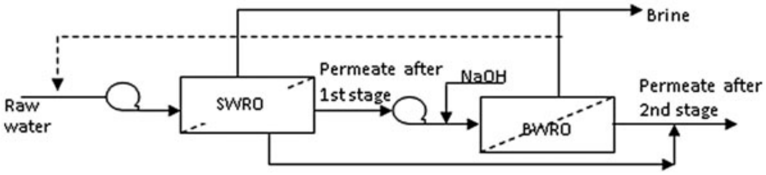

Fig. 3. Two-stage RO system for boron removal (SWRO—sweater desalination membranes, BWRO—brackish water desalination membranes) [2,90].

installation operated with three commercial membranes by Hydranautics (composite polyamide 4040-LHA-CPA2 type membranes of 99% salts retention arranged in a spiral wound module) and two composite cross-linked aromatic polyamide membranes by Toray (SU-710 and SUL-G10 of 99.4% salt retention also in spiral wound module). As a feed water, the permeate from BWRO treatment has been used (Fig. 3) and the process has been carried out at pH range 5.5–10.5. The boron retention significantly depends on pH of the treated solution, and at pH 9.5, it reaches ca. 50%, while at pH > 10.5, it can be 100% [95]. Composite aromatic polyamide membranes reveal good separation properties already at pH 9.5. Moreover, the elimination of boron increases with a transmembrane pressure increase. Pastor et al. [57] have also investigated the impact of pH on the removal of boron using pilot scale two-stage reverse osmosis system to treat BW (Fig. 3). In the first-stage of treatment, composite polyamide (Toray SUL-G10) spiral wound membrane of NaCl retention 99.4% at pH 3–9 has been used. It has been found that for water containing 1.5 to 2 mg/L of boron, single-stage RO is sufficient to produce drinking water quality permeate, while for its concentration >3.5 mg/L, two-stage system with no pH correction is required and finally, for higher contaminant concentrations pH should be increased to above 9 [57].

Redondo et al. [9] have proposed and technically and economically analysed four configurations of single-stage RO systems. Costs of desalination strongly depend on the demanded final boron concentration in the product. For single-stage treatment, costs for boron content 0.6–1 mg/L are 0.38 to 0.52 USD/m^3, while for 0.3–0.5 mg/L, they increase to 0.47–0.60 USD/m^3 (two-stage conventional system and with BSR). Additional costs of boron removal to the level of 0.4 mg/L have been estimated on 0.05–0.07 USD/m^3 for investigated systems and ca. 50% more for smaller systems.

In order to prevent membrane scaling in multistage systems, cascade configuration is proposed, especially in the case of sea water treatment [1,96–98]. Faigon and Hefer [2] have investigated the removal of boron using several full-scale multistage RO installations. The comparison of the two-stage system with the second stage of retentate recirculation with the cascade system (Fig. 4) has revealed many advantages of the latter one over the former one. For example, the use of the cascade system makes it possible to adjust process conditions to current needs and a decrease in water production costs. Four-stage cascade system (Fig. 4) covers desalination at the first stage and at increased pH in the second stage [2]. The retentate from that steps is treated in the first stage operated at low pH in order to remove salts causing membrane scaling ($CaCO_3$ and $Mg(OH)_2$). The fourth stage, operated at high pH, polishes permeate from the third stage. The finally produced water is the mixture of permeates from 2nd and 4th stages. In the first–stage, sea water desalination membranes (SWRO) are used, while in the remaining stages, BWRO is applied.

The cascade project has been involved in the modernization of the desalination plant in Ejlat, Israel. The modernization was made in 2004 and resulted in the capacity increase up to 10,000 m^3/d and a decrease in boron concentration to below 0.4 ppm [96].

Magara et al. [98] have applied three-stage RO system to remove boron in desalination installation for drinking water production (Fig. 5). In the first-stage, sea water desalination membranes Toray NTR-70SWC-S8 have been used, while in the second and third-stage BW desalination, that is low-pressure RO Toray ES1O-D4 membranes of 0.05% NaCl retention coefficient equal to 99.5% at 0.75 MPa have been applied. The second stage has aimed at treating permeate from the first stage, while in the third stage, two simultaneous solutions have been used. One line has been dedicated to the first-stage permeate, while the second line has directed the retentate to the treatment. Such a design solution enables high elasticity in both water recovery and an increase in the desalination rate. It also limits membranes scaling at higher pH conditions. The study (has) showed that the boron retention strongly depends on pH, and at pH 9, it starts to decrease to reach 90% at pH 10 and 99% and more at pH 11.

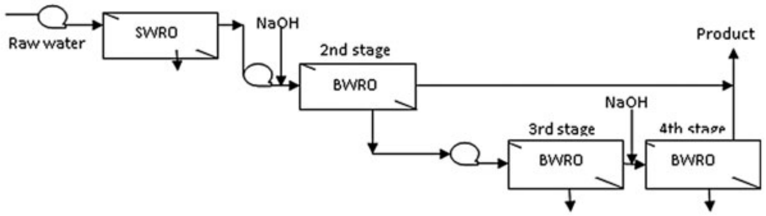

Fig. 4. Cascade RO system for boron removal (SWRO—sea water desalination membranes, BWRO–brackish water desalination membranes) [2].

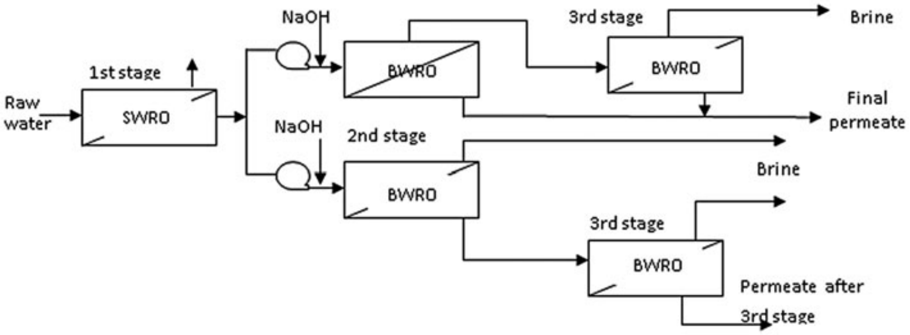

Fig. 5. Three-stage RO system for boron removal [98].

Three-stage RO system has already been operating at the full scale, for example the installation for drinking water production in the Netherlands Antilles [99]. The system comprises seven sea water treatment unit operations, that is multilayer filtration, 3-stage RO desalination, UV disinfection, remineralization, activated carbon filtration and final chlorination between the distribution systems. The maximum boron concentration in the treated water does not exceed 0.3 mg/L. The RO system is designed in such a way that the permeate from the 1st stage is directed to the 2nd stage, while the 3rd stage is fed with second-stage retentate (Fig. 5, upper line). Permeates from 1st and 2nd stage are mixed before UV disinfection.

At some circumstances in the case of highly loaded waters and strict produced water standards, the reverse osmosis system can be designed as a four-stage one. Such a solution (Fig. 6) has been applied to desalination of sea water containing 40,700 mg/L TDS in Aszkelon, Israel [100]. The required concentration of boron in permeate has been established on below 0.4 mg/L and for chlorides not more than 20 mg/L. The first step of the first and the second stage of the treatment is operated at low pH in order to remove TDS and to increase water recovery rate without membrane scaling. The second step involves an increase in pH conditions (>10) during which boron is effectively removed.

Dydo et al. [27] have investigated the removal of boron from municipal landfill leachates containing 25.4 mg B/L using nanofiltration and reverse osmosis with BW-30, TW-30, NF-90 and NF-45 (Filmtec) membranes. The obtained results have shown that the retention of boron depends on the membrane type and leachates pH and is almost independent of water recovery rate. A more detail analysis of the study results has revealed that boron is effectively removed at pH close to 11 and it is found to be the optimal for long-term RO membrane exploitation. The highest contaminant retention (ca. 99%) and its sufficiently low level in the permeate (<1 mg/L) have been observed for BW-30 membrane at the water recovery rate equal only to 50%. For TW-30 and NF-45 membranes, boron retention rates have been 97.6% and 97.2%, respectively. Thus, two-stage NF/RO system for boron removal from leachates at basic conditions has been proposed [27].

The use of nanofiltration to improve boron removal during water desalination by means of reverse osmosis has also been proposed by Mnif et al. [101,102]. In multistage sea water and BW desalination systems involving RO membranes at the first stage of the treatment, most of salts other than boron are separated, while boron removal is carried out on the 2nd and 3rd treatment stage at increased pH. The alternative solution is the simultaneous feeding of RO and

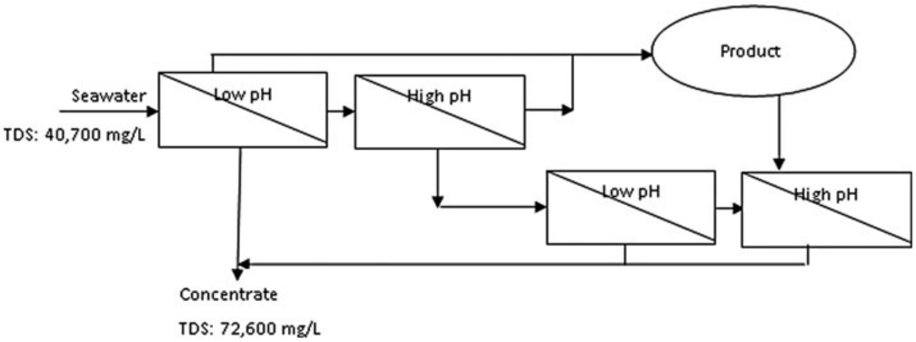

Fig. 6. The scheme of the water desalination plant in Aszkelon, Israel [100].

NF modules with raw water, and the direction of permeates mixed with raw water to further RO treatment [102]. The process performance partially eliminates the presence of ions responsible for membrane scaling and improves boron elimination.

2.2.2. *Reverse osmosis and ion exchange integrated systems*

As it has been already mentioned, ion exchange is a technology often used to selective boron removal from desalinated sea water. However, the method is expensive considering both investment and operational costs (column regeneration and eluate utilization costs) [86]. Thus, the removal of boron usually involves combined method, in which the first stage is the desalination of sea water and the second is the complete removal of boron using selective ion exchange resins [27].

Nadav [86] has carried out pilot scale selective boron removal from pre-desalinated water using ion exchange process. The feed water has been the permeate obtained at sea water desalination plant in Eilat (Israel) with the capacity of 10,000 m^3/d containing 1.8 mg B/L, which is much more than the permissible standard. The sea water usually contains 4–5 mg B/L. The costs of boron removal have been estimated at 0.04–0.06 USD/m^3 depending on the costs of the resin, chemicals and process exploitation.

Glueckstern et al. [92] have proposed the optimization of the hybrid system used to boron removal which involves two-stage RO and ion exchange, whereas first and second-stage RO permeates are polished at ion exchange column or, in parallel, the permeate from the 1st stage is polished in the 2nd stage with brackish water desalination BWRO membrane and at ion exchange column (Fig. 7). The study made by Taniguchi et al. [91] has confirmed the fact that the combination of SWRO, BWRO and BSR is an efficient method of limiting the costs generated by high boron concentration in raw water.

The same authors [97] have proposed 3-stage RO and ion exchange system for boron removal from brackish water (Fig. 8). During the study, the reduction of boron from 0.62 mg/L in the feed water to 0.3 mg/L in the purified stream was obtained. The tools of comparative costs analysis have also been presented [97].

Redondo et al. [91] have investigated the removal of boron from sea water using 2-stage system involving RO and ion exchange (Fig. 7) with desalination membranes by Filmtec. The obtained boron retention coefficients at natural sea water environment are as follows: SW30HR-380: 90%, SW30HR-320: 90%, SW30-380: 88%, BW30-400: 65% and BW30LE-440: 88%. It has been found that the best conditions to obtain such results are: temperature: 25°C, pH 8 for all membranes, while pressure and salt content: for SW30—5.5 MPa and 32,000 mg/L; BW30-400—1.6 MPa and 2,000 mg/L; BW30LE-440—1.07 MPa and 2,000 mg/L. The retention of salts has been 99.7–99.85%. Such results have been found to be economically successful boron removal from permeate obtained during desalination of sea water at neutral environment. Thus, the desalination of sea water at pure water recovery 40–60% at salt concentration up to 48 g/L and boron content 3.5–6.8 mg/L can be considered in real terms. The typical cost of drinking and irrigating water production at such conditions is estimated at 0.38–0.50 USD/m^3, when final contaminants level is 0.6–1.0 mg/L, and 0.47–0.60 USD/m^3 for produced water boron content 0.3–0.5 mg/L [90].

2.2.3. *Parameters determining boron retention during RO process*

The effectiveness of boron removal via RO method is affected by: temperature, pressure, pH, feed water

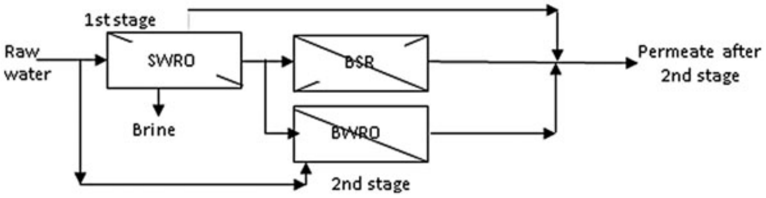

Fig. 7. Two-stage RO treatment system for boron removal integrated with the adsorption on ion exchange resins [92].

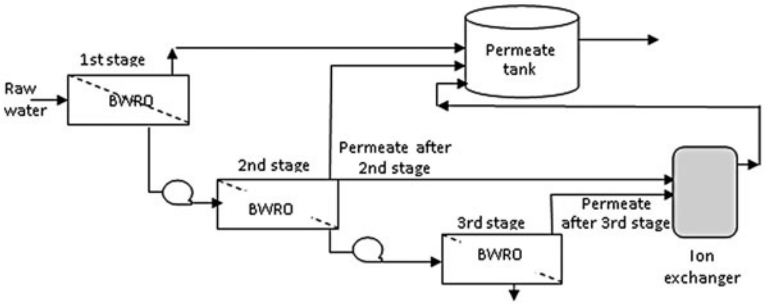

Fig. 8. Integrated RO and ion exchange system for boron removal [97].

velocity over a membrane, salt content (ionic strength), the initial boron concentration in feed stream and pure water recovery rate. The results presented in Table 6 indicate that regardless of membrane type applied every parameter similarly affects boron removal effectiveness [6].

The dominant parameter is pH. The boron retention coefficient increases from 50–75% at pH 7–8 to above 95% at pH 10.5. It is caused by higher share of borate ions whose amount increases with the pH increase [95,103,104]. The dependence of boron retention on feed pH can be connected with boric acid dissociation at high pH. When pH of a solution increases, boric acid reacts with water forming $B(OH)_4^-$ ions, which not only characterize with higher diameter, but are also negatively charged, which favours their retention due to electrostatic interactions with negatively charged membrane surface [5,90,98]. Moreover, most polyamide membranes are negatively charged and the charge density increases with the solution pH increase [5]. Higher charge density of the membrane surface can also improve the retention of negatively charged borates due to the repulsion effect. Moreover, it is suggested that boric acid is able to form hydrogen bridges with active groups of membrane material, and as a result, it diffuses through the membrane similarly as water particles [57]. The type of a membrane is found to have much smaller impact on the overall process performance.

Transmembrane pressure also influences boron retention, and its removal rate usually increases with the parameter value increase, which is confirmed by the most of performed experimental studies [9,89,95,103,104]. Exceptionally, in the case of using Filmtec SW30HR membranes, opposite tendencies, that is a decrease of boron removal at a pressure changes from 4.8 to 5.5 MPa, have been observed [104]. Even though the mass transport solution–diffusion model enables a very good prediction on pressure impact on boron retention, it does not consider the convective transport of the element. On the other hand, the irreversible thermodynamic transport model shows that the convective boron transport may be crucial for the explanation of the impact of the pressure on the element separation [5]. It is especially important at low boron concentration and high transmembrane pressure conditions, when the element transport is practically dominated by the convection rather than diffusion. The convection may also lead to the conjunction of water and boron fluxes, and as the permeability of water depends on pressure, in case of boron, the same effect is observed.

The high salt content in feed water and temperature growth also lead to the increased boron content in a produced permeate. Theoretically, higher salinity and temperature result in an increase in boric acid pKa, which leads to an increase in the borate ions content in a feed at a certain pH. Thus, it seems possible

Table 6
The impact of particular RO process parameters on the retention on boron

Parameters	Boron retention	References	Applied membranes	Comments
pH increase	Increases	[95]	Hydranautics CPA2 Toray SU-710, SUL-G10	pH 5.5–10.5
		[104]	Toray UTC-80-AB Filmtec SW30HR	pH 8.2 and 10.5
		[103]	Woongjin Chemical RE8040-SR, RE8040-SHN	pH 6.5–10.5
Pressure increase	Increases	[95]	Hydranautics CPA2 Toray SU-710, SUL-G10	Pressure for water recovery of 10, 20, 30 and 40 (Brackish water)
		[104]	Toray UTC-80-AB Filmtec SW30HR	600–800 psi; No effect for SW30HR (low decrease) 15–35 bar
		[89]	Filmtec SWHR, BW-30 GE membrane AG	
Temperature increase	Decreases	[106]	Hydranautics SWC4+, SW30 HR LE Toray TM820, TM820A	15˚C, 25˚C, 35˚C at pH 6.2 and 9.5)
		[103]	Woongjin Chemical RE8040-SR, RE8040-SHN	15–35˚C at pH 8.1–8.3
Cross-flow velocity increase	No effect	[95]	Toray UTC-80-AB Filmtec SW30HR	Cross-flow velocity 0.5–1.0 m/s
Initial boron concentration increase	No effect	[98]	Nitto Denko NTR-70SWC, ES10-D4	No effect below concentration of 35 mg/L
		[104]	Toray UTC-80-AB Filmtec SW30HR	No effect below concentration of 6,6 mg/L
Feed salinity increase	Decreases	[103]	Woongjin Chemical RE8040-SR, RE8040-SHN	20,000–45,000 ppm
		[105]	Hydranautics ESPA1, LFC1, CPA2	500–15,000 ppm (Brackish water)
Water recovery increase	Decreases	[98]	Nitto Denko NTR-70SWC, ES10-D4	Recovery: 50%, 80%, 90%; High recovery when pH increases

to improve boron retention at low pH conditions via salinity and the temperature increase.

The experimental results, however, clearly indicate that the removal of boron is improved by the salinity increase. According to Oo and Song [105], it can be explained by the charge neutralization effect and limitation of boron access to a membrane surface due to the high content of other salts. The electrostatic repulsion between the membrane surface and borates ions as well as charge density of the membrane surface plays much less important role in the boron retention, and as a result, the diffusion of contaminant ions through the membrane is easier and faster. An increase in boron concentration in permeate caused by both salinity and the temperature increase can also be explained by the fact that the permeate flux through RO membranes, and the same, salts flux, increases with the temperature increase.

According to both models of mass transport during membrane separation based on irreversible thermodynamics and solution-diffusion, the concentration of dissolved substances has no impact on boron RO or NF retention. This independence has been confirmed by some experiments [89,98,103]. The formation of polymolecular ions of high boron content should not affect boron retention during water desalination due to its low concentration in natural waters.

2.3. The application of low-pressure-driven membrane processes

Hybrid methods combining sorption on powdered sorbent and low-pressure-driven membrane techniques, that is micro- and ultrafiltration, can also be applied to remove boron from aqueous solutions (AMF process) [1,3,4,107]. Additionally, other boron-bonding substances, for example soluble polymers (PEUF process), can be used in hybrid methods. Hybrid separation techniques have been recently of a high interest in the process engineers group as they can be applied to remove even small amounts of harmful substances present in treated water.

2.3.1. The treatment of water via integrated sorption–membrane system

An interesting modification of ion exchange is a sorption–membrane hybrid process used to remove boron from sea water and from the permeate obtained during RO desalination process. In this method, boron is bonded by commercial ion exchange resins of a very small granular size (20 μm) and polymeric microspheres present in the suspension, and next, the ionite is separated from the solution by means of micro- or ultrafiltration. Due to a small resin granulation, an increase in the boron content from 2 mg/L to 0.243–0.124 mg/L depending on the ion exchanger dose (0.25–1.0 g/L) can be obtained already after 2 min of contact time. The characteristic feature of the resin, similarly as in the case of anionites, is the presence of N-methylglucamine groups able to boron sorption [58]. The removal of resin-boron complexes can be made using immersed microfiltration membranes (e.g. 0.4 μm polypropylene ones). MF does not require high pressure and can be operated below critical flux conditions, which significantly limits fouling [107].

The main advantage of a hybrid process regarding the conventional column sorption is the possibility of the usage of powdered resin form. It is known that the kinetics of the process is improved when small sorbent particles are present, which decreases the required amount of the sorbent for a given boron concentration and improves the process costs. In the case of sorption processes integrated with membrane separation, a decrease in pressure, which usually affects energy costs, is independent of particles size and results only in membrane resistance [107]. Overall, it leads to an increase in the process effectiveness. The use of fine particles in conventional column sorption process is impossible because of the pressure decrease on a column bed. According to Kozen–Carman equation, the pressure drop during solution flow through a packed bed is indirectly proportional to the square of particles radius [6]. Kołtuniewicz et al. [107] have compared the total operational cost of a hybrid system with two systems based on packed beds of the packing particles sizes 1 mm and 1 μm, respectively. It has been found that AMF operational costs are much lower than ones of conventional system due to the smaller amount of sorbent and lower pressure drop.

The efficiency of AMF method to boron removal from aquatic solutions has also been investigated by Kabay et al. [56,58,108–111,113–116]. The authors have applied two commercial resins containing N-methyl-D-glucamine groups (Diaion CRB02 (Mitsubishi) and Dowex XUS 43594.00) as well as those synthetized from polymeric microspheres [115]. The membrane filtration has been performed with the use of microfiltration polypropylene capillary membranes (0.4 μm) and Teflon membranes (0.2 μm). The authors have checked the effectiveness of boron removal from geothermal water [110,111] as well as boric acid removal from simulated solutions [110–113,115] and SWRO membrane permeate [56,110,116]. The impact of the size and concentration of sorbent particles and the suspension flow rate on the membrane capacity has been determined. It has been found that the size of sorbent particles affects the AMF water treatment hybrid system to the highest extent. Kabay et al. [108] have developed the concept of a hybrid process to boron removal from water solutions which comprises 5 steps as follows:

(1) sorption of boron on a resin,
(2) membrane separation of boron saturated resin from water solution,
(3) desorption of boron using an acid,
(4) membrane separation of regenerated resin from the suspension,
(5) regeneration of the resin with a base.

During the separation of the regenerated sorbent from the suspension, the volumetric permeate flux is relatively low due to the high concentration of the suspension. Additionally, the introduction of an acid increases pH, and thus, the applied pH must characterize with high resistant to both acid and suspended solids content.

Blahusiak et al. [117] have investigated the usability of immersed membranes to separation of suspended solid from the suspension of high boron-bonding ionite concentration (Dowex XUS-43594.00). It has been found that sorbent can be successively concentrated up to 11% w/w using hydrophilic capillary immersed microfiltration membranes and hydrophobic propylene ones. An increase in transmembrane pressure results in an increase in the permeate flux, and at 40 kPa, it is equal to 72 and 14 dm^3/m^2 h for concentration of suspended solids (SS) below 7 and 4% w/w for hydrophilic and hydrophobic membranes, respectively. The observed dependence allows one to conclude that hydrophilic membranes are more favoured to be used in AMF process. Onderkova et al. [118] have studied the use of tubular ceramic microfiltration membranes Membralox of internal diameter 7 mm and 0.25 m length. A decrease in the permeate flux has been tolerable at the SS concentration range from 4 to 16% w/w, while for solutions of SS content above 20% w/w/, it has been independent of the concentration. It has been concluded that ceramic membranes can be successfully used in AMF process as they reveal satisfactory permeate flux even at high SS content up to above 20% w/w and they can be operated at wide pH range.

As it has already been mentioned, AMF should be carried out with the use of fine sorbent particles resistant to abrasion and crushing, of a small diameter and a low dispersity. Unfortunately, commercially available polymeric sorbents are prepared to be used in column systems and the size of their particles varies from 300 to 500 μm [8], which practically eliminates their usage in hybrid systems. Trials on their crumbing usually result in ununiformed sized and creation of sharp edges, which can destroy membrane surface. Thus, many studies on the development of novel sorbents [119] with monodisperse diameter size from few to 50 μm are carried out. Polymeric microspheres can be obtained from both natural and synthetic polymers [85,86] by means of crystallization and precipitation procedures [120]. They can be prepared directly during emulsion [121–124] or suspension [125] polymerization or membrane monomers emulgation proceeded with emulsion polymerization [126,127]. Wolska and Bryjak [126] have produced polymeric microspheres from the mixture of monomers of vinylbenzene chloride–styrene–divinylbenzene (VBC–S–DVB), after which suspension polymerization and modification with N-methyl-D-glucamine have been performed. Wolska [8] has checked the stability of the developed material after ten sorption–desorption cycles confirming that ligands have become covalently bonded with polymeric matrix, and the produced polymeric balls are resistant to the change of treated solutions properties with no impact on their borate affinity. Samatya et al. [128] have prepared porous polymer comprised of glycidyldimethacrylate/ethylene dimethacrylate (GMA/EDM) using seed polymerization, the surface of which has been next modified with a dextran. The obtained sorbent has characterized with very good boron sorption, which, according to authors, has resulted in the brushing structure of dextran chain on the polymer surface. Similar adsorption properties have been observed by Gazi et al. [129] for a sorbent of approximate structure, which has been produced from glycidyl methacrylate modified with 2-hydroxyethyloamino-2,3-propanodiol.

2.3.2. Application of polymer-enhanced ultrafiltration

Many researches on boron removal from water by means of polymer-enhanced ultrafiltration (PEUF) process have also been carried out [53,130,131].

Polymer-enhanced ultrafiltration is based on the complexation of water-soluble metal ions and polymers, and the formed complexes are separated by ultrafiltration membranes due to the sieving mechanism. The process has already been applied to remove metals from diluted solutions Thus, UF can be used to produce drinking water, treat waste-, ground- and sea waters [3]. Its advantage is low energy consumption (UF) and the high ability of impurities complexation by water-soluble polymers [3]. UF process requires lower transmembrane pressure than nanofiltration, which enables to obtain higher permeate fluxes. Boron-selective polymers are produced via bonding of carbohydrate ligands with polymeric chains [8]. Their concentration in the solution does not usually exceed 1% [5]. In PEUF process, usually following polymers are used: polyvinyl alcohol, glucoheptanamide derivatives of poly(amidoamine) and poly(ethyleneimine), poly(glycidyl methacrylate) and poly(N,N´-diallylmorpholinium bromide) modified with hydroxyethylaminoglycerol, hydroxyethylaminoglycerol functionalized to poly(glycidylmethacrylate) and poly(4-vinyl-1,3-dioxalan-2-one-co-vinyl acetate), alkyl monol, diol, or triol containing polyethylenimines [8]. In order to obtain boron-bonding properties, the applied polymers are modified with N-methyl-D-glucamine (NMDG)..

Boron retention coefficient observed during PEUF process performance decreases with the process run (starting from ones equal to 100%) as active sites of the chelating polymer become occupied. The retention depends also on pH, boron and polymer concentration in the feed. The very important feature of applied polymers is that they have to be non-toxic.

In pilot scale studies on the impact of process parameters on boron, removal by means of PEUF is discussed [53]. Polyvinyl alcohol has been used as a boron-bonding agent, while spiral wound cellulose ultrafiltration membrane of cut-off 10 kDa has been used as a boron–polymer complexes barrier. The investigated parameters have covered: boron/polymer ratio (load) (0.1–0.5), pH (7–10) and polymer characteristics, that is molecular mass (M_n) and hydrolysis rate. Regardless of the process parameters, the permeate flux has stabilized after 1 h of the process run and kept on the same level until the separation is finished (ca. 19 L/m^2 h). It indicates that any disadvantageous phenomena affecting UF process, that is concentration polarization, fouling and gel layer formation, has appeared. The retention of boron has increased with a decrease in boron/polymer ration (load) and pH increase [53].

Recently, Zerze et al. [13] have synthesized the copolymer, polyvinylamino-N–N-bis-propane diol co-DADMAC) (GPVA-co_DADMAC), at three various co-monomer ratios (2, 5 and 10%). 92% removal of boron from a solution on initial concentration 10 mg B/L at pH 9 has been obtained. The same authors [131] have developed another chelating polymer polyvinylamino-N,N-bispropanediol) (GPVA) to boron removal, for which the observed removal rate using PEUF recirculation system at pH 9.0 has been up to 96%.

Thus, PEUF can be found as an efficient and alternative method for boron removal whose main advantages are effective separation and satisfactory kinetics. However, there are some limitations, that is the necessity of water-soluble polymers preparation of molecular weight higher than applied UF membrane cut-off, polymers regeneration and membranes fouling.

2.4. The application of methods with ion exchange membranes

This group of processes comprise an electrical current separation techniques in which mass transport through ion-exchanging membranes is caused by a difference in an electric potential as well as non-current separation driven by a difference in concentrations at both membrane sides. In the first group, electrodialysis and electrodeionization can be found, while in the other, Donnan dialysis and diffusive dialysis are placed [3]. Ion-exchanging membranes comprise polymeric matrix containing immobilized ion-active groups of a proper charge and mobile counter-ions (ions of a charge that is opposite to the one of immobilized groups), which participate in the ion exchange between solutions separated by a membrane. Cation-exchange membranes (CEM) contain immobilized negatively charged ion-active groups, while cations are counter-ions, while in case of anion-exchange membranes (AEM), immobilized groups are positively charged, while anions are mobile groups [3]. Due to the principle known as the Donnan exclusion, immobilized ion-active groups localized inside a membrane eliminate—by means of the electrostatic repulsions—the possibility of permeation of ions of the same charge (co-ions) through the membrane. Counter-ions are the only ones which are able to permeate through the membrane.

In boron removal process, electrodialysis (ED) and Donnan dialysis (DD) are usually applied [3,4,7].

2.4.1. Electrodialysis (ED)

In the electrodialysis (ED) process, cation-exchange and anion-exchange membranes are installed in parallel and/or alternately and are separated by distance spacers. The whole construction is placed in an electrical field and limits the transport of cations or anions. To perform the electrodialysis process, so-called, electrodialyser consisted of several hundreds of membranes is arranged in such a way that dialysate and concentrate chambers can be distinguished within the device. The idea of the process is based on the directed transport of ions at the constant electric field. Ions migrate to proper electrodes through membranes of which one permits and other blocks ions transport, and, as a result, salt-rich concentrate and desalinated dialysate are produced in the proper electrodialyser chambers. Feed solutions introduced to every chamber type (including electrode-containing chambers) are circulated in order to equalize concentration in those chambers and to limit the impact of concentration polarization on the process capacity.

Similarly as in the case of reverse osmosis, the process needs to be performed at $pH > 9$ as borates, oppositely to boric acid, are transported through anion-exchange membranes at a higher rate [45–47,59,132–135], and fluxes of those ions are found to be in the range 80–420 $\mu g/m^2$ s [7]. In the literature, following boron removal rates in the dependence of pH can be found:

(1) from 12.4% at initial diluate pH equal to 8.31 to 17.8% at pH 10.5 [47];
(2) from 0.8% at initial diluate pH equal to 3.2 to 97% at pH ca. 10 [47];
(3) from < 20% at diluate pH equal to 9.0 to ca. 80% at pH 10.5 [133];
(4) from ca. 20% at $pH < 7$ to 60% at pH 12 [134];
(5) from 33% at pH 3.6 to ca. 75% pH 12, 8 [59].

It shows that the increase of pH results in the increase of borates in concentrate chambers which favours both the effective transport and the removal of boron by means of ED.

The main advantage of ED in refer to RO is the lower sensitivity of ion exchange membranes to high pH. However, event at high pH conditions (pH 9–10), the transport of chlorides is the preferable one, while sulphates are transported with the same rate as borates [15,45]. The low mobility of borates in comparison with other ions is ED process disadvantage as boron can be favourably transported only after the decrease of other salts content in the diluate [45]. In order to prevent deep diluate demineralization at alkali conditions (pH 9–10), monopolar membranes are used [47]. Moreover, the application of such a high pH in practice may lead to precipitation of $Mg(OH)_2$ and $CaCO_3$. However, ED systems are less sensitive to fouling and its results than systems operated on the basis of RO.

Melnik et al. [45] have investigated parameters influencing boron removal by means of ED method from desalinated water using a series of ion exchange membranes: heterogeneous (MK-40 and MA-40—Russia), homogeneous (MK-100 and MA-100—Ukraine) and IONICS [CR67-HMR and anion-204–8XZL-366 (5188C) (USA)] ones. The study has shown that the removal of boron has been dependent on the membrane type, solution pH, the salinity content and the initial boron concentration. The maximum removal rate has been observed for $pH > 10$, especially in case of MK and MA membranes. If the concentration of boron in the raw water had exceeded 4.5 mg/L, then even optimal process conditions (alkali solution, salinity content <0.2 g/L) would not have made it possible to decrease the contaminant concentration below 0.3–0.5 mg/L. Thus, it can be concluded that the use of ED to boron removal in a single-stage configuration is undesired, and it is recommended to polish the treated stream via, for example, ion exchange. Kabay et al. [133] have studied the removal of boron from water by means of ED with Neosepta CMX and AMX membranes. The effectiveness of the process has also increased with the pH increase and higher initial concentration of boron in the feed water, while it has decreased at the presence of chlorides. The appearance of sulphates in the raw water has not affected the removal of boron, but it has elongated the process run. Yazicigil et al. [46] have found that for Neosepta-AC membranes, the maximum boron retention during ED is obtained at $pH > 9$ and the transport rate is affected by other salts presence at a following series: $NaCl > NaNO_3 > Na_2SO_4$. Turek et al. [47,132] have run some experiments on the electrodialytic boron removal from solutions simulating permeates after RO sea water single-stage desalination. Two types of waters have been used. First of total dissolved solid content of 604 mg/L and boron concentration 2.25 mg/L simulated the permeate after RO with SW30HR-320 and 40% water recovery rate, while the second have contained TDS at a level of 400 mg/L and boron at 1.3 mg/L. The electrodialyser has been equipped with Neosepta AMX and CMX membranes (Tokuyama Co.) and spacers of thickness 0.4 mm. In both cases, ED process has been carried out until the boron concentration reached 0.4 mg/L. Thus, the obtained diluate has been almost completely demineralized (specific conductivity of 0.7 μS/cm), and the boron flux has been equal in the former case to 15.2 $\mu g/cm^2$ h and 11.3 $\mu g/cm^2$ h in the latter one. The energy consumption has been very low and equal to 0.237 kWh/m^3 (0.186 kWh/m^3).

The laboratory studies on the electrodialytic removal of boron from wastewater (industrial landfill leachates) containing 63.5–76.5 mg B/L have been performed by Turek et al. [47]. The electrodialyser has been equipped with Neosepta AMX and CMX membranes (Tokuyama Co.) and spacers of thickness 0.19 mm. The leachates have been treated via two-stage process. During the first one, slightly acidified leachates have been partially desalinated until ca. 80% of salts have been removed, while in the other one, the alkali conditions (pH 9–10) have been applied, and the obtained boron retention of 97% have been obtained. However, it has been found that high initial pH of the diluate does not result in the better transportation of boron through the membrane, which can be explained by the higher mobility and content of hydroxyl ions, which at such conditions are preferably transported through the membrane.

The electrodialysis has also been considered to treat post-regeneration solutions generated during ion exchange as well as to treat wastewater containing boron with the use of monoselective membranes [47]. A high flux of boron for monoselective Neosepta CMS and ACS membranes has been obtained.

The discussed cases show that boron can be effectively removed from water only at alkali conditions. However, at such high pH values, a serious possibility of membrane scaling (i.e. the precipitation of insoluble calcium and magnesium salts on a membrane surface) occurs. Thus, the removal of boron from water via ED should be preceded by desalination at $pH<9$. From such a preliminary desalinated water, borates can be effectively removed with a high rate and the highest possible, but limited, current capacity.

Recently, Nagasawa et al. [136] have presented promising results of the removal of borates by means of ED method with bipolar membranes (BPM). Such membranes consist of anion-exchange and cation-exchange membranes connected in a form of a bilayer. The distance between them is obtained by a thin layer of water (of a thickness ca. 2 nm). At the constant electric field, water particles dissociate to H^+ and OH^- ions which are transported by proper membrane layers to neighbouring electrodialyser chambers. As a result, in the surrounding of anion exchanger of BPM, a solution becomes alkali, which is caused by the formation of borates in the boron-containing feed solution. Next, borates are transported through AEM to a concentrate solution which sticks to cation-exchange part of BPM. In this part, hydrogen ions are revealed to the solution, which causes borates neutralization. Thus, the feed solution is deprived of boron, while the concentrate contains boric acid. Nagasawa et al. [136] have informed that the use of ED with BPM enables the removal of more than 90% of boron present in water at its initial concentration 100 mg/L and NaCl content of 0–20 mmol/L. Such results have been obtained at the wide pH range (2.3–12) of the feed. In most cases, the current capacity has been similar to one observed for conventional ED systems.

In [50,51], the use of electrodeionization (EDI) for boron removal from water undergone demineralization is discussed. The electrodeionization is the combination of electrodialysis and ion exchange [3], and chambers separated by membranes are filled with ionite and fed with raw water, and thus, the demineralized water leaves the system. The applied current causes the flow of ions to proper electrodes and, consequently, to the concentrated stream. Secondly, the constant electric field assures the dissociation of water to H^+ and OH^-, which enables the regeneration of ion exchange resin. Thus, the additional chemical regeneration of the resin is eliminated. The obtained demineralized water characterizes with a very high quality and specific conductivity not higher than 0.1 μS/cm [3]. Differently as in the case of the conventional ion exchange process, EDI is a continuous method. Hydroxide ions formed during water electrodeionization ionize boron present in purified water, and as a result, its removal is enabled.

In studies discussed in [51], the optimal conditions of silica and boron removal by means of EDI method, that is electric current intensity, electric conductivity, the flow rate of raw water in diluate and concentrate chambers as well as pH, have been found. A decrease in boron concentration from 50 μg/l to 1 μg/L, while of silica from 1,000 μg/l SiO_2 in raw water to 2.66 μg/l SiO_2 in the final product has been obtained, which corresponds to the demand on ultrapure quality water. The retention coefficients of both silica and boron have been over 99%. An increase in the current intensity favours the removal of boron and silica; however, above a certain value, it causes ionic polarization and reverses diffusion. The increase of the conductivity in the diluate chamber increases boron and silica concentration in the ultrapure water stream, and thus, the efficiency of their removal decreases. On the other hand, the electric conductivity increase in the concentrate chamber firstly leads to a decrease in those contaminants in the product stream, next the concentration is stabilized and finally, it increases. The removal of both silica and boron is found to be strongly pH dependent and the optimal parameter range is 6–8.

Arar et al. [50] have investigated the removal of silica and boron from geothermal water using hybrid system comprised of RO and electrodeionization. The impact of the current voltage, the flow rate, Na_2SO_4 in electrode chambers, membrane and ion exchange resin types on the contaminants removal effectiveness has been checked. RO system has consisted of two membranes for brackish water desalination (BW-30-2540, Dow FilmTec) arranged in parallel. The concentration of boron has decreased from 5.9 mg/L to 0.4 mg/L, while of silica to 0.4 mg Si/L in the second EDI stage.

2.4.2. Donnan dialysis

Unlike the ED, Donnan dialysis (DD) process does not require any external current source, but it also involves only cation- or only anion-exchange membranes. During DD, borates are transported from a feed stream to a concentrate by AEM. However, in order to fulfil the electroneutrality condition, an equal amount of another ion must be transported to the feed solution from the boron-rich solution. That ion is known as a driving one, and usually, chloride, sulphate or even hydroxyl ions are used. The process runs as long as a certain ratio of borates to driving ions concentrations in both solutions is reached. The ration is known as the Donnan equilibrium. Due to the equilibrium character of the process, a significantly excessive amount of the driving ion to the removed ion is required.

DD can be found as an alternative solution to borates removal from water. Ayyldiz and Kara [52] have studied the efficiency of borates transport through anion-exchange membranes using DD process with Neosepta AHA, AFN and AMH membranes. They have observed that boron flux during DD depends on the membrane type, boron concentration in the feed, pH of both raw water and boron-accepting solution, accompanying ions presence in the feed solution and type of a driving ion. At high boron concentration (0.1 mol/L), its maximum flux has been obtained at pH 9.5, while in the case of diluted solutions (0.001 mol/L), it was obtained at pH 11.5. The phenomenon can be explained by the formation of polyborate ions at high boron concentration conditions and their absence in the diluted solution. Similar tendency has also been observed during ED process. Moreover, accompanying ions such as chlorides, hydrocarbonates and sulphates have also affected borates transportation rate during DD. The maximum element flux ca. 3,500 μg/m^2 s has been observed at the presence hydrocarbonates and chlorides. The impact of a membrane type on the boron removal efficiency can be arranged in the following series: AFN > AMH > AHA. Use of Neosepta AHA and AMH membranes has resulted in the similar boron fluxes, while it has been significantly higher in the case of AFN membrane. It can be explained by the higher water content in AFN layer than in other membranes.

The choice of the proper membrane type is crucial for the effective Donnan dialysis performance. In literary sources, several methods of preparation of such materials can be found. The first one is the mixing of standard polymers containing functional groups and processing of such mixtures. The second one covers the usage of porous polymeric support, for example ultrafiltration or microfiltration membranes and introduction of gel-ion exchanging polymers inside their pores [137]. A very important feature of such membranes is a good ions permeability, which influences the localization of functional group containing polymers in the pore network and an increase in their stability. Kir et al. [138] have shown that plasmatic modification of AEM membranes may cause a significant improvement in boron transportation rate during DD. The maximum parameter value obtained has been at the level of 410 μg/m^2 s.

Bryjak et al. [139] have proposed the method based on DD to regeneration of fine-powdered boron-selective resin (BSR) DOWEX XUS 43594.00. In the process, a suspension with BSR containing adsorbed boron is underdone to DD feed chamber. The authors have assumed that borate present in feed water is always in equilibrium with BSR, and as a result, those amounts are transported to the accepting solution causing the final complete boron removal from BSR. The netto effect of the process is the regeneration of the resin to its chloride form and the boron-enriched concentrated solution. Moreover, high fluxes of boron during the process, up to 1,500 μg/m^2 s, have been observed. The method can be an interesting solution for BSR regeneration after AMF-based boron removal process [56].

3. Final remarks and conclusion

Boron is emitted to the environment via natural (rock) and anthropogenic (industry, agriculture) pathways. That microelement is necessary for plants and animals, but it is also widely used in many industrial branches. However, the overdose of boron is much harmful to both plants and animals. The boundary between the required dose and an overdose of boron is very narrow. Boron needs to be frequently removed from water and wastewater. The permissible level of boron in both drinking water and wastewater deposited to the environment is established at 1 mg/L. The detailed review of the literature on various boron removal methods is presented as follows:

(1) ion exchange and adsorption on boron-complexing resins,
(2) reverse osmosis, including multistage systems comprised of RO and sorption,
(3) hybrid methods combining sorption and complexation with polymers together with low-pressure-driven membrane separation,
(4) ion-exchanging membrane methods.

The removal of boron by means of ion exchange using boron-selective resins (BSR) shows a high effectiveness when arranged in a conventional column system at the exploitation mode. The disadvantage of the method is the requirement of high amounts of the acid and the base used to the BSR regeneration. Thus, development of an efficient regeneration method involving low volumes of additional chemicals, together with the improvement of boron sorption capacity, is required. The study on the optimum process conditions shows that the contact time between BSR and boron is crucial for the effective process performance, while the active BSR surface is responsible for the sorption kinetics. Additionally, the powdering of BSR particles, an increase in the column height to diameter ratio and a decrease in the raw water flow rate improve the overall effectiveness of the method.

Studies on the removal of boron by means of the reverse osmosis method are focused on developing a proper system configuration and process parameters optimization. The main disadvantage of the method is the necessity of multistage RO systems application as the proper removal rate of boron can be obtained at pH above 9. Thus, intensive researches on novel osmotic membranes with a high boron retention that can be operated at the wide pH range and prepared at a low costs are carried out. It is found that pH is the most important parameter that influences the retention of boron, regardless of the applied RO membrane type. The effectiveness of the contaminant removal also increases with the temperature decrease and at low feed water salinity.

The hybrid process of adsorption-low-pressure membrane filtration (AMF) is found to be a promising method of boron removal, including high capacity and low exploitation costs. The main advantage of AMF is the possibility of using fine BSR particles, which improves the capture of boron by resin and decreases the required BSR dose, consequently, lowering the overall cost of the process. However, the process is not fully investigated and requires further intensive studies, similarly as in the case of novel polymer-enhanced ultrafiltration. Differently as in AMD, PEUF involves water-soluble boron-bonding polymers which are separated by a membrane. The advantage of the method is the high separation efficiency accompanied with satisfactory bonding kinetics. The studies in this field are focused on developing some novel polymers, membrane fouling prevention and chelating polymers regeneration.

Investigations on boron removal using ion exchange membranes reveal that ED method is the most popular. The transportation rate of boric acid observed for ED system is low ($<150\ \mu g/m^2s$) in comparison with borates fluxes noted for EDI and DD systems. Besides it creates the possibility of separating borates from other acids and salts. On the other hand, the removal of boron via ED is sufficient only at high pH at which there exists a serious risk of membrane scaling with calcium and magnesium compounds. Hence, the demineralization of the diluate is required before the removal of boron with ED. The preliminary studies on borates transport in Donnan dialysis (DD) systems indicate on the possibility of the use of this process in order to remove boron from water solutions. Fluxes of boron that can be found in the literature regarding DD system are comparable with the ones referring to ED and EDI. Thus, the required membrane areas and exploitations costs should be at the same level. However, the limitations of those methods in the field of boron removal are similar to for example the need of preliminary deep demineralization of the feed water.

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