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Study of monovalent ion selectivity of anion-exchange membranes: effect of surface modification and applied voltage

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ABSTRACT

Today, reduction of nitrate content is a great challenge not only in potable water production but also in food industry, especially in dairy products. In many applications, it is neither necessary nor desirable to remove all present ions from treated solution but, e.g., only as said nitrate. Nowadays, attention is paid to electrodialysis as a promising technique for selective demineralization. In this work, we deal with selectivity adjustment of heterogeneous anion-exchange membranes (AEMs) AM(H)-PES (MEGA, Czech Republic) using surface modification with polymer film based on perfluorosulphonic acid. In the next step, the influence of applied voltage on course of electrodialysis was investigated. For individual AEMs the batch desalination process of mixed equimolar solution containing $NaNO_3$, NaCl, NaH_2PO_4 and Na_2SO_4 was evaluated as well as selective transport of individual anions. The measurements suggest that there was a time extension in the case of modified AM(H)-PES. With respect to selectivity, all AEMs show slight decline of selectivity eventually unchanged values with higher applied voltage besides to lower voltage. Any AEM appeared to have no selectivity for same charged ions with similar size, regardless of applied voltage. However, it was confirmed that it is possible to increase somewhat the selectivity of monovalent and divalent ions as well as selectivity of $H_2PO_4^-$ and Cl^- or NO_3^- by voltage lowering.

Keywords: Anion-exchange membrane; Selectivity; Nitrates; Electrodialysis; Perfluorosulphonic layer

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1. Introduction

With an increase in industrial development, intensification of agriculture and tightening legislation requirements current demand are still growing to obtain a technology which enables recycling or selective removal of undesirable compounds, therefore, related lowering of environmental impact. Sustainable technologies for selective removal of nitrate are one of the current global requirements. Nitrates get into the water sources often due to excessive usage of fertilizers in agriculture and also by ineffective wastewater management of industrial and municipal water. Metabolism of nitrate in digestive tract of mammals leads to toxic nitrite and further to carcinogenic *N*-nitrosamines [1]. Selective removal of nitrate would, therefore, be useful in a wide range of industries, e.g., for groundwater and surface water sources treatment, in food industry for milk whey demineralization and for waste management of reverse osmosis (RO) brines [2–6]. According to WHO recommendation for potable water the maximum recommended concentration of nitrate is 50 ppm [1].

Treatment of water contaminated with nitrate can be realized through, e.g., adsorption, ion exchange, RO or electrodialysis (ED). In some cases there is also a possibility of partial nitrate removal by nanofiltration. Unlike pressure driven separation processes, ED used to be highlighted for high water recovery, because ED has no osmotic-pressure

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limitations and because of the longevity of membranes with respect to chemical and mechanical resistance. In the case of pressure and electrically driven membrane processes the concentrate is produced and is treated as waste. Attributable to concentrate management are: (1) direct discharge into sewage treatment plant, the amount of concentrate can be previously reduced, e.g., by ED or by evaporation, (2) direct biodegradation and (3) usage for irrigation [7]. Osipenko et al. [8] dealt with processing of RO brine rich in $NaNO_3$. They designed an ED concentrator for production of KNO_3, a valuable mineral fertilizer, this concentrator also prevented the formation of undesirable scaling in concentrate chambers, caused mainly by $CaSO_4$. Although the deeply concentrated KNO_3 was obtained, it was observed that with increasing the concentration of other anions in a treated solution, especially chloride, the concentration of nitrate declined [8].

Another possible way for nitrate removal is to use waste free technologies on the basis of chemical and biological treatment, which convert nitrate into harmless nitrogen compounds. These techniques, however, have not yet been realized on a large scale [9,10].

Nowadays, ED usage is on the rise for pure water production with minimal chemical consumption. In recent years, ED is preferred especially in brackish water desalination over RO for economic reasons. Generally, ED is economically sensible for water treatment with initial concentration lower than 5,000 mg L^{-1} [11,12]. However, Pirsaheb et al. [13] dealt with comparing operational cost and efficiency of ED and RO with respect to nitrate removal from drinking water. According to their work, better results were obtained using RO. Nevertheless, in general, for choosing the most suitable method for desalination it is necessary to proceed individually with respect to the technology scale and local conditions [13].

The principle of ED is ion removal using ion-exchange membranes (IEMs) whilst its efficiency also depends on the initial concentration of the substances contained in processed solution and the intensity of the applied electric field, respective to current density. The transfer of specific ion is dependent on its equivalent amount in processed water, ion mobility and depends on the choice of IEM [7]. The choice of an IEM is equally important and it is not always possible to make a choice on the basis of one characteristic. It is necessary to decide which parameters are essential for target process: maximum current limit, maximum transfer of nitrate, the highest degree of desalination, the best current efficiency and/or lowest specific energy consumption. Optimal adjustment of one of these parameters, however, does not guarantee the suitability of the remaining parameters [10]. Not all ED applications require the removal of all present ions. From the viewpoint of anion content, e.g., it is not physiologically appropriate to remove all the chloride during drinking water production, on the contrary, it is required for as low as possible nitrate content. The side effect of intensification of monovalent ions transfer compared with multivalent ions is the minimization of $CaSO_4$ creation at higher concentrations in concentrate chambers [14,15]. Although ED is a well-established method, the task of selectivity towards individual anions is still an ongoing topic of research. The development of anion-exchange membrane (AEM) selective towards nitrate would allow ED to become a more frequently used technique for water treatment [1]. Optimal AEM selective to nitrate suppresses the transport of other ions, particularly monovalent (chloride), as much as is possible, which are transported through AEM at the expense of nitrate [11]. In general, the selectivity of AEM is tailored based on the ionic size, mobility and anion affinity towards AEM (according to Gibbs hydration energy), which can be influenced by adjusting of hydrophobicity of AEM or by formation of a hydrophobic surface layer on AEM.

Manufacturing of nitrate selective AEM for ED is realized using general principles defined by Sata: (1) decrease of porosity by increasing of cross-linkage of AEM, typically by increasing divinylbenzene content, or by formation of compact surface layer, (2) formation of thin anionic polyelectrolyte surface layers on AEM for increase of electrostatic repulsion forces, (3) controlling hydrophilicity/hydrophobicity of AEM by introducing specific anion-exchange groups, inert fillers or by formation of specific layers on the surface of an AEM and (4) immobilization/grafting groups with specific affinity to the target anions [16,17].

Based on consideration in the third point, the affinity of anion with lower hydration energy (nitrate) towards AEM would rise with increasing hydrophobicity of AEM [1]. AEMs have naturally positive charge due to their functional groups, consequently AEMs preferably interact with multivalent anions comparing with monovalent anions. Vaselbehagh et al. [15] reported that AEM with surface modification by negatively charged layer exhibited lower values of resistance in solutions containing single monovalent anions comparing with solutions of single multivalent anions. The increase of selectivity towards monovalent anions was attributed to intensification of their flux [15].

The second of these principles is often used and simultaneously can also have a cross-linking effect mentioned in a first point. It has been described that the polycationic coating on cation-exchange membrane (CEM) or polyanionic coating on AEM is able to limit the transfer of polyvalent ions in favour of the monovalent ones [18]. This approach was used by Kikhavani et al. [1] who prepared heterogeneous AEM composed of strong base anion resin type I, dispersed in chlorinated polypropylene, moreover they prepared samples of AEMs containing activated carbon particles, for further enhancement of hydrophobicity. However, the AEMs with activated carbon particles showed worse nitrate selectivity than the commercially available heterogeneous AEM (AMI-7001S, Membranes International Inc., USA). This phenomenon was explained by the different structure caused by increased crystallinity [19]. Mulyati et al. [14] improved monovalent selectivity of AEM (AMX, Neosepta, Japan) by multilayer deposition by alternating coating with polyanion (poly(sodium 4-styrenesulphonate)) and polycation (poly(allylamine hydrochloride)) layers. In all cases, the top layer was formed by polyanion. They reported that with increasing number of layers the monovalent selectivity increased, and from a certain number of layers, it remained constant. The improvement of selectivity was attributed to the increase of negative charge density which caused a stronger repulsion of multivalent anions than the monovalent ones [14]. In Mulyati et al.'s [14] previous work, they prepared AEM modified only with one polyanion (poly(sodium 4-styrenesulphonate)) layer and they reported that the monovalent selectivity was not improved [14]. Their research showed that layer-by-layer deposition is more effective than single layer deposition for improving monovalent selectivity. Vaselbehagh et al. [15] modified AEM (AMX, Neosepta, Japan) by polydopamine coating and they reported improvement of monovalent selectivity, but the selectivity among single monovalent anions was not changed. This phenomena is caused by Donnan exclusion which is stronger for multivalent ions than for monovalent ones and due to the fact that Donnan exclusion of monovalent anions does not vary with ionic species [15]. Amara and Kerdjoudj [20] dealt with modification of AEM (ARA, Solvay, France) by electroadsorption of branched polyethyleneimine. They treated mixed salt solution of sulphate, nitrate and chloride and they suppressed the transport of sulphate. They observed that nitrate transport through AEM decreased in the presence of other anions but was still higher than sulphate transport [20]. Selmane Bel Hadj Hmida et al. [19] prepared homogeneous AEM, they investigated its selectivity in single salt solutions (nitrate and acetate) and in mixed solution of both salts. Whilst in single salt solutions the AEM behaved similarly, in the mixed salt solution the transport of acetate anion was very slow and after some time it stopped unlike the nitrate transport. The reason of this phenomenon can be explained by the presence of a diffusion layer close to the AEM surface in which water splitting occurs and it led to acetate protonation [19].

Other authors dealing with modification of AEM aiming to affect surface hydrophobicity are, e.g., Kikhavani et al. [21] who modified AEM with dipropylamine and Melnikov et al. who modified AEM with a perfluorosulphonic layer [5]. The principle of increasing separation efficiency after deposition of the surface layer is a separation of ions based on the hydrated ion radius and size of charge. Modification by the deposition of the surface layer is especially suitable as well as an approach, known as the cross-linking effect, when a separation of monovalent ions from multivalent is required, because affecting the selectivity of monovalent ions is insignificant [18,22,23].

Another way, which in some cases can affect selectivity of AEM is adjustment of applied voltage or current density [6,9,12,18,24,25]. For selective nitrate removal it is, therefore, necessary to optimize the AEM and also the setting of suitable conditions for the specific ED operation.

The aim of this work was to enhance the selectivity of commercially available AM(H)-PES (MEGA, Czech Republic) towards nitrate. In this work, the influence of applied voltage on the selectivity of various anions contained in a mixed salt solution has been evaluated, using ED stacks with different AEMs. Three types of AEMs were evaluated: AM(H)-PES (MEGA, Czech Republic), AM(H)-PES-C (C stands for additional surface coating by perfluorosulphonic layer) and AM(H)-PES-M (M stands for modification of composition using a different type of polyethylene matrix). AEMs were combined within the ED stack with CM-PES (MEGA, Czech Republic).

2. Materials and methods

2.1. Anion-exchange membranes

Typical properties of individual AEMs and their abbreviated names are listed in Table 1. The data for AM(H) were taken from producer's datasheet, for another two AEMs the data were determined using the same methods which are used by

Table 1
Typical values of AEMs properties

Type of AEM	AM(H)-PES	AM-PES-M	AM(H)-PES-C
Abbreviation	AM(H)	AM-M	AM(H)-C
Ion-exchange groups	R–$(CH_3)_3N^+$	R–$(CH_3)_3N^+$	R–$(CH_3)_3N^+$
Matrix	LDPE	mLLDPE + LLDPE	LDPE
Reinforcing fabric	Polyester	Polyester	Polyester
Thickness of dry membrane (mm)	<0.45[a]	0.38	0.44
Thickness of swelled membrane – DEMI water, 24 h, laboratory temperature (mm)	<0.75[a]	0.55	0.62
Surface resistance in NaCl 0.5 mol L^{-1} (under DC current) (Ω cm^2)	<7.5[a]	7.2	8.1
Specific resistance in NaCl 0.5 mol L^{-1} (under DC current) (Ω cm)	<120.0[a]	130.0	133.7
Weight difference after swelling in DEMI water (%)	<65[a]	51	49
Transport number in KCl 0.5/0.1 mol L^{-1}	>0.95[a]	0.97	0.96
Ion-exchange capacity (eq kg^{-1})	1.80	1.90	[b]

Note: DEMI: demineralized; LDPE: low-density polyethylene; LLDPE: linear low-density polyethylene; and mLLDPE: metallocene linear low-density polyethylene.
[a] Values from producer's datasheet.
[b] Unmeasured.

the manufacturer. AM(H) is industrially produced by MEGA (Czech Republic). AM-M was made in MemBrain (Czech Republic), unlike the AM(H), another polymer binder was used for production of AM-M. As the result, the weight change of AM-M after soaking in demineralized (DEMI) water is of 51% whereas AM(H) mentioned in this paper of 55%. Thanks to use of different polymer binder we received membrane with lower water content and thus we gently increased its hydrophobicity. The main advantage of AM-M is that comparing with AM(H), the cost of final product is almost the same. The AM(H)-C is based on AM(H) produced by MEGA onto which double layer of Nafion-like perfluorosulphonic layer was additionally chemically bonded. The modification was done according to a procedure described in reference [26]. The modification was one-sided and the coating was resistant to swelling and to chemicals at chosen ED conditions, so no leakage occurred. As it was mentioned above, it is possible to affect monovalent selectivity of AEMs by deposition of thin polyanionic surface layer. If the selectivity is better, higher manufacturing cost due to additional modification will be acceptable.

2.2. Electrodialysis equipment

Selectivity tests were carried out in batch mode in a laboratory ED unit P EDR-Z (MEGA, Czech Republic) with 10 paired stack (10 pieces of AEMs, 11 pieces of CEMs). Effective membrane area of one IEM was 64 cm^2, membrane spacers had a thickness of 0.8 mm. For each type of AEM two measurements of course of desalination were done. Between the two tests equilibration of the stack was performed: the output from depleted circuit was connected to the concentrate reservoir and the output from concentrated circuit into the depleted reservoir, in both circuits, as well as in electrode circuit, model mixed salt solution prepared by mixing of NaCl, $NaNO_3$, NaH_2PO_4 and Na_2SO_4 was placed. The flow in depleted and concentrated circuit was set to 72 L h^{-1}, in electrode circuit to 50 L h^{-1}, voltage was set to 1 V per membrane pair. Equilibration proceeded 30 min. AM(H)-Cs were oriented to depleted chambers by the modified side, thus tests with all AEMs were measured without polarity reversal.

2.3. Electrodialysis testing

Nitrate selectivity was tested by desalination of model mixed salt solution containing NaCl, $NaNO_3$, NaH_2PO_4, Na_2SO_4, every salt of concentration 0.05 mol L^{-1}. The temperature of solutions in depleted, concentrated and electrode solution was 25°C ± 1°C. Applied voltage was set at first to 0.5 V, after that to 1.2 V per membrane pair. Model mixed salt solution was put to concentrated, depleted and electrode circuit, the flow in concentrated circuit (V_C =1 L) and depleted circuit (V_D =1 L) was set to 60 L h^{-1}, in electrode circuit (V_E = 0.25 L) the flow was set to 50 L h^{-1}. Desalination tests were terminated upon reaching conductivity 0.7 mS cm^{-1} in depleted container. During ED automatic record of conductivity, temperature and pH in depleted and concentrated circuit was taken every 5 min together with electric current and total voltage. Terminal voltage adjusted at the beginning of the tests was maintained at constant value by automatic regulation.

The desalination using different AEMs types was evaluated based on the total mass flux of salts (J, kg h^{-1} m^{-2}, Eq. (1)), current efficiency (η, %, Eq. (2)) and specific energy consumption (W_{sp}, W h kg^{-1}, Eq. (3)). These parameters were evaluated according to relationships mentioned previously by Dlask et al. [27]:

$$J = \frac{\Delta m}{A t_d N} \tag{1}$$

where t_d (h) is the time needed for reaching total conductivity of diluted solution 0.7 mS cm^{-1}, Δm (kg) the overall weight of salts transported from depleted to concentrated circuit at time t_d, A (m^2) the effective area of membrane and N the number of membrane pairs in ED stack:

$$\eta = \frac{\sum_i \Delta n_i F \left| v_i^- z_i^- \right|}{N \int_0^{t_d} I(t)\, dt} \tag{2}$$

where Δn_i (mol) is an amount of individual salt (i = NaCl, $NaNO_3$, NaH_2PO_4 or Na_2SO_4), transported from depleted to concentrated circuit, F (C mol^{-1}) the Faraday constant, z_i^- the charge number of an anion in a salt i, v_i^- the stoichiometric coefficient of an anion in a salt i, t (s) the time and I (A) the electric current:,

$$W_{sp} = \frac{E\,Q}{\Delta m\, N 3600} \tag{3}$$

where E (V) is the applied voltage on membrane stack and Q (C) the electric charge.

2.4. Analytical method

All used chemicals were of analytical grade. During ED, samples of depleted solution were taken for analytical control at conductivities 20.5, 16, 12, 8, 4, 0.7 mS cm^{-1}, simultaneously the sampling time was recorded. Anions were analyzed using ion chromatography system (Dionex ICS-5000+ DC, column Dionex IonPac™ AS23 (4 × 250 mm), ICS-5000+ Analytical CD Conductivity Detector, Dionex, USA). The mobile phase was prepared by mixing of $NaHCO_3$ (0.8 mmol L^{-1}) and Na_2CO_3 (4.5 mmol L^{-1}). Anions were identified according to retention times of standard solutions (1,000 mg L^{-1}, Sigma-Aldrich, USA) and quantified on the basis of calibration curves. Samples of feed were taken before each desalination test and analyzed together with samples taken from depleted solution. Accuracy of method for measuring individual anions was ±5% as expanded uncertainty corresponding 95% confidence interval with coverage factor $k = 2$.

2.5. Data analysis

Selectivity of single AEMs was compared for a pair of anions contained in model solution. Formally, the selectivity was expressed like average separation efficiency relative to the entire course of the desalination which was calculated on the basis of partial separation efficiencies in the sampling times. For calculation of separation efficiency (Eq. (4)) and average separation efficiency (Eq. (5)) relationships mentioned by Van der Bruggen et al. [28] were used:

$$S(t)=\frac{\left({c_A(t)}/{c_A(0)}\right)-\left({c_B(t)}/{c_B(0)}\right)}{\left(1-{c_A(t)}/{c_A(0)}\right)+\left(1-{c_B(t)}/{c_B(0)}\right)} \tag{4}$$

where $S(t)$ is dimensionless value of separation efficiency, respectively, the selectivity between anions A and B in time t, $c_A(t)$, $c_B(t)$ are concentrations of anions A and B in time t, $c_A(0)$, $c_B(0)$ are initial ion concentrations in feed. Average separation efficiency S was calculated according to:

$$S=\sum_j \frac{\Delta t_j S_j}{\sum_j \Delta t_j} \tag{5}$$

where Δt_j is time interval between samples collection.

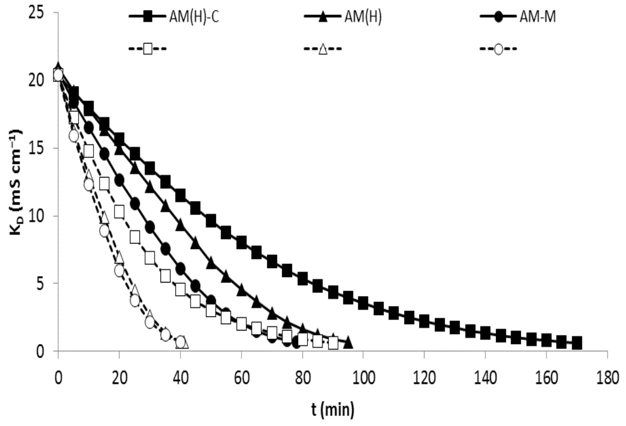

Fig. 1. Course of desalination of model mixed salt solution using different types of AEMs and applied voltage on membrane pair (solid symbols: 0.5 V per membrane pair, hollow symbols: 1.2 V per membrane pair).

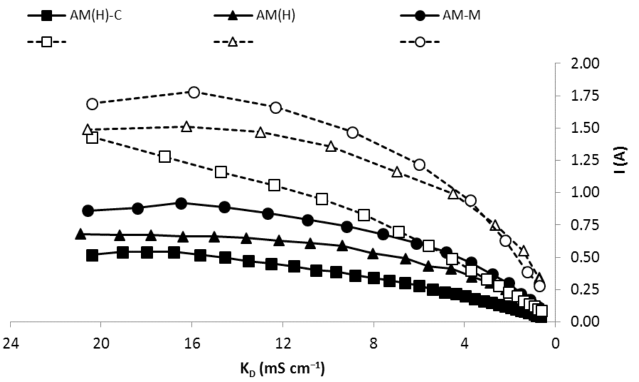

Fig. 2. Course of electric current according to conductivity of model mixed salt solution in depleted circuit using different types of AEMs and applied voltage on membrane pair (solid symbols: 0.5 V per membrane pair, hollow symbols: 1.2 V per membrane pair).

3. Results and discussion

Of the three tested AEMs, AM(H)-C should show increased selectivity to nitrate. The remaining two types of AEMs were used as comparative samples without declared selectivity to nitrate.

3.1. Electrodialysis

The courses for each pair of desalination tests for all AEMs matched very well, therefore, only results from the first tests are shown in Figs. 1 and 2. Fig. 1 depicts course of desalination of model mixed salt solution with initial conductivity 20.5 mS cm^{-1} using three tested stacks. When voltage was set to 0.5 V per membrane pair different desalination times for individual AEMs were observed. The fastest desalination of depleted solution was gained by AM-M (78 min), the slowest desalination was done by AM(H)-C (170 min). Desired reduction of time has been achieved by increasing the voltage to 1.2 V per membrane pair. Stacks composed of AM-M and AM(H) reached virtually identical times of desalination (40 min and 41 min, respectively). Desalination using AM(H)-C at voltage 1.2 V per membrane pair took 90 min. At both voltage values the desalination times using AM(H)-C were more than two times higher than using AM-M.

The current-conductivity dependence of depleted solution depicted in Fig. 2 corresponds to the course of desalination showed in Fig. 1. At the same time, Fig. 2 indicates the resistances of each AEM during desalination. AM(H) and AM-M both have lower area and specific resistances than AM(H)-C, thus higher electric current was observed, and therefore, shorter desalination time. The presence of cation-exchange layer is vital for AM(H)-C and causes slowdown of anions transfer due to repulsive forces. AM(H) has slightly better electrochemical properties than AM-M, nevertheless, reached slightly worse desalination times. This may be due to increased back diffusion of salts through AM(H), corresponding to its higher swelling capacity. The average weight increase caused by swelling in DEMI water at laboratory temperature after 24 h was 51% for AM-M whereas 55% for AM(H). At the same anion-exchange resin filling, ion-exchange capacity AM(H) in the working state is lower than the one for AM-M, thanks to higher water content. Both types of AEMs are composed of polymer matrix and anion-exchange resin on the basis of styrene–divinylbenzene. Used anion-exchange resin was the same in both types of AEMs, AM(H) and AM-M, but the polymer matrix differed. Membrane swelling is generally affected by the degree of cross-linking of ion-exchange resin. Highly cross-linked resins will swell lower than lower cross-linked resins. The binder itself does not swell because the nature of polyethylene is hydrophobic. However, it is possible to affect swelling of IEM, thanks to mechanical properties of binder related to mobility of polymer chains. If polymer matrix is more rigid and tough, swelling can be limited by its contractive elastic force. Consequently, AM-M has at the same applied voltage lower resistance to anion transfer in contrast to AM(H).

In Table 2, all results as a mean of a couple of desalination tests for each AEM are presented. The results are in agreement with the course of desalination showed in Figs. 1 and 2, and also with accordance to the electrical resistance of individual AEMs. As we mentioned above, reduced content of water in AM-M has an impact on apparent ion-exchange capacity of membranes during ED. Due to lower water content of AM-M we observed higher current efficiency and mass flux through the membrane per unit area and time, therefore, the desalination time was shorter and energy consumption was lower. On the contrary, AM(H)-C with the lowest current efficiency showed more or less a half mass flux at both values of applied voltage, comparing with AM-M and AM(H). With regard to AM(H)-C, the surface double layer got increased the resistance comparing with former AM(H). The surface tight layer also dramatically slow down the desalination rate comparing with two other investigated AEMs, which cannot be attributable only to the increased membrane resistance. All three types of ED stacks showed a decrease of current density with increase of applied voltage. The values of current efficiencies match the values of specific energy consumption very well. During all ED tests, we did not observe any external leakages.

The results, mentioned above, clearly show the negative influence of surface modification of AM(H)-C on the transport properties comparing with original AM(H), whereas the change of polymer binder in AM-M provided better result than original AM(H). Regarding to the time of desalination, the AM(H) and AM-M provided similar results, therefore, also the specific energy consumption of both membranes did not differ fundamentally. However, the time of desalination for reaching the same final conductivity using AM(H)-C was more or less two times higher. That means, two times higher electric consumption is needed for obtaining the product with the same conductivity, compared with AM(H) and AM-M.

3.2. Membrane selectivity

Depleted solutions had pH 3.5–5.2 ± 0.2 throughout desalination, thus phosphate contained in the solution was in the form of $H_2PO_4^-$ ($pKa_1(H_3PO_4) = 2.2$, $pKa_2(H_2PO_4^-) = 7.2$). So model solution contained three monovalent anions, two of similar size (NO_3^-, Cl^-) and one divalent anion (SO_4^{2-}). The results of anions analysis for a couple of desalination tests for each AEM matched very well, so only results from the first tests are listed. At first, desalination with individual AEMs was measured at voltage 0.5 V per membrane pair, after that the voltage was increased to 1.2 V per membrane pair.

Fig. 3 depicts the removal of anions from depleted solution depending on the course of desalination at two values of applied voltage ordered by the type of anion. The removal of an anion was expressed by the relationship in Eq. (6):

$$\text{Removal of anion} = 1 - \frac{c_A(t)}{c_A(0)} \quad (6)$$

Regardless of the selected voltage, it is evident that no AEM failed to show significantly increased selectivity towards NO_3^- comparing with Cl^- and all AEMs transported anions in the same order: the fastest NO_3^- and Cl^-, followed by SO_4^{2-} and $H_2PO_4^-$. AM(H)-C and AM-M gave slightly better selectivity towards monovalent ions with smaller size compared with $H_2PO_4^-$ and SO_4^{2-}. Preferential transport of NO_3^- and Cl^- manifested at all AEMs is consistent with the spherical effect which reflects the hydrated ionic radius (same charged ions are less hydrated when they are bigger comparing with smaller ones, NO_3^- less than Cl^- and monovalent ions are hydrated less than divalent ions). The effect of polyanionic coating of AM(H)-C provided, however, result comparable to AM-M.

Increasing the voltage from 0.5 to 1.2 V, the selectivity between monovalent and divalent anions of all AEMs has deteriorated. Similar trends observed by the desalination using AM(H) and AM-M were predictable because these AEMs differ only by the type of polymer binder, although in both types it is polyethylene. AM(H)-C was additionally coated with cation-exchange layer. Elevated transport rate of SO_4^{2-} at higher voltage corresponds to the suppression of repulsive forces of cation-exchange layer, thanks to the higher driving force of the electric field. The aim of AM(H)-C was also to interact preferably with less hydrated anions, and thus to favour nitrate desalination. Substantial restriction of Cl^- transport though AM(H)-C, however, did not manifest.

Courses of desalination for individual AEMs from the viewpoint of selectivity, did not differ too much. This match the data obtained in Table 3 summarizing the average separation efficiencies. The more the value of separation efficiency of the anion *A* relative to the anion *B* (marked *A*:*B*) approaches zero, the less the AEM is selective for that pair. If the value of *A*:*B* is equal to −1, the

Table 2
Desalination process characteristics achieved with different AEMs and applied voltage

Type of AEM	Voltage per membrane pair (V)	t_d (min)	J (kg h^{-1} m^{-2})	η (%)	W_{sp} (W h kg^{-1})
AM(H)	0.5	97.5	0.178	76	284
	1.2	43.0	0.399	73	698
AM-M	0.5	80.0	0.221	81	262
	1.2	41.5	0.417	72	712
AM(H)-C	0.5	170.0	0.107	75	284
	1.2	92.5	0.189	68	750

anion *B* is completely retained in the depleted solution, whereas if it is equal to +1, anion *A* is completely retained. From the above mentioned values it is apparent that no AEM is able to separate NO_3^- from Cl^-, since the value of the separation efficiency is lower than 0.10 (10%) and the selectivity was very little affected by changing the voltage. Overall, the highest separation efficiency reached NO_3^-:$H_2PO_4^-$, ranged about 30%–40%. The founded values indicate that all AEMs do not show particular selectivity against one of the anions. In the work of Zhang et al. [12], the values of separation efficiencies have been reported for monovalent selective AEM (MVA) for a pair of anions NO_3^-:$H_xPO_4^{y-}$ in the range of 50%–99% depending on the current and the pH of the solution. Selectivity for the pair NO_3^-:Cl^- in that work ranged from −3% to +8% for MVA, whilst non-selective AEM managed by adjusting the conditions to obtain the separation efficiency from −23% to 28%.

All AEMs types, which were compared in this paper, showed higher transport of NO_3^- comparing with Cl^-. This behaviour was also reported by Kikhavani et al., who increased selectivity of heterogeneous AEM by using hydrophobic chlorinated polypropylene as a binder [1]. As it can be seen from our results, also polyethylene is hydrophobic enough for increasing the hydrophobicity of AEM, and thus for increasing the transport of NO_3^-.

In the work of Amara and Kerdjoudj [20], who used electroadsorption of polyethylenimine on the surface of AEM (ARA), authors reported the decrease of SO_4^{2-} transport in a mixed salt solution (NO_3^-, Cl^-, SO_4^{2-}). The same effect was observed in our work using AM(H)-C and AM-M. Unlike Amara and Kerdjoudj [20], we used mixed salt solution containing moreover $H_2PO_4^-$. The $H_2PO_4^-$ was stronger detained in depleted solution using AM(H), but in according to suppression of divalent anion transport through AM(H)-C and AM-M, the intensification of $H_2PO_4^-$ transport was gained.

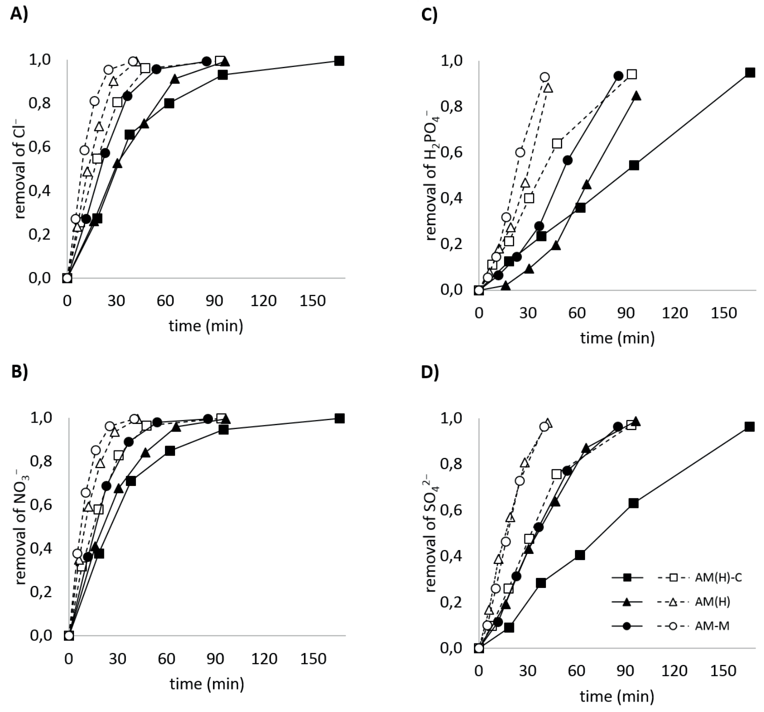

Fig. 3. Removal of individual anions according to Eq. (6): (A) Cl^-, (B) NO_3^-, (C) $H_2PO_4^-$ and (D) SO_4^{2-} as a function of time by AM(H)-C, AM(H) and AM-M (solid symbols: 0.5 V per membrane pair, hollow symbols: 1.2 V per membrane pair).

Table 3
Average separation efficiency for different types of AEMs and applied voltage on membrane pair

AEM type	Voltage (V/pair)	NO_3^-:Cl^-	NO_3^-:$H_2PO_4^-$	NO_3^-:SO_4^{2-}	$H_2PO_4^-$:SO_4^{2-}
AM(H)-C	0.5	−0.03	−0.33	−0.21	0.29
AM(H)-C	1.2	−0.02	−0.30	−0.15	0.30
AM(H)	0.5	−0.07	−0.40	−0.12	0.32
AM(H)	1.2	−0.06	−0.44	−0.10	0.39
AM-M	0.5	−0.04	−0.34	−0.22	0.16
AM-M	1.2	−0.04	−0.35	−0.22	0.20

Mulyati et al. [14] improved monovalent selectivity of AEM (AMX) by multilayer deposition of polyanion layers. They reported that with increasing number of layers the monovalent selectivity increased. The improvement of selectivity was attributed to the increase of negative charge density which caused stronger repulsion of multivalent anions than the monovalent ones [14]. It is possible that only two layers used for modification of AM(H)-C were not sufficient enough for increasing the monovalent anion selectivity.

Any post-modification of finished product increases its cost. In that case, the advantages of such a modification have to be higher comparing with non-modified products. In this paper, the modified AM(H)-C had worse transport properties, which causes higher energy demand. Although the transport of divalent comparing with monovalent anions was decreased, the selectivity between NO_3^- and Cl^- has not been improved. On the contrary, only by changing the type of polyethylene binder in AM-M, we obtained similar selectivity like using AM(H)-C, or the higher transport of monovalent anions comparing with divalent SO_4^{2-}. The main advantage was, that time of desalination, current efficiency and energy consumption of AM-M were similar or better than using the original AM(H).

4. Conclusions

Many authors deal with the problem of selective removal of NO_3^-. Their works are often inspired by customer requirements and they try to repeat the results obtained from desalination of model solutions even in the case of real media. Among these works a large diversity exists, because there are many types of commercial and developmental AEMs, electrodialyzer structures and ultimately different working conditions (voltage, current density, temperature, concentration and composition of solutions). Therefore, it is difficult to conclude, based on the available articles, the benefits of individual AEMs.

This work deals with the characterization of commercially available AM(H) and two developmental types derived from AM(H). The results show that it is possible to achieve better separation of polyvalent anions from monovalent by lowering voltage, however, in the case of studied AEMs the change was not essential. Under given conditions, the presence of surface modification of AM(H)-C by cation-exchange layer did not affect substantially the selectivity between monovalent anions. However, using AM(H)-C the transport of SO_4^{2-} comparing with Cl^- decreased to some extent, but only at a voltage of 0.5 V per membrane pair, because with the increase in voltage the effect of electrical repulsion dropped. The surface modification of AM(H) we used was not economically reasonable for desalination of mixed salt solution. On contrary, the obtained AM-M had similar or slightly better transport properties than the original AM(H). Although the selectivity among monovalent anions was not enhanced, the transport of SO_4^{2-} was slowed down. AM-M seems to be a viable alternative to AM(H) producible at the same price.

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Symbols

A — Effective membrane area, m^2
$c_A(0)$, $c_B(0)$ — Initial concentration of anion A/B in depleted circuit, mol L^{-1}
$c_A(t)$, $c_B(t)$ — Concentration of anion A/B in depleted circuit at a time t, mol L^{-1}
E — Applied voltage on membrane stack, V
F — Faraday constant, C mol^{-1}
I — Electric current, A
J — Salt flux, kg h^{-1} m^{-2}
N — Number of membrane pairs in ED stack
Q — Electric charge, C
S — Average separation efficiency
$S(t)$ — Separation efficiency at a sampling time
t — Time, s
t_d — Total desalination time, h
V_C — Volume of solution in concentrated circuit, L
V_D — Volume of solution in depleted circuit, L
V_E — Volume of solution in electrode circuit, L
W_{sp} — Specific energy consumption, W h kg^{-1}
z_i^- — Charge number of anion in a salt i
Δt_j — Time interval between sample collection, min
Δm — Weight change of salts in time t_d, kg
Δn_i — Amount of individual salt i, mol
η — Current efficiency, %
ν_i^- — Stoichiometric coefficient of an anion in a salt i
K_D — Conductivity of depleted solution, mS cm^{-1}

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