Diffusion Permeability of Cation-Exchange Membrane in Different Solutions

Mohammed Qader Gubari[1,3*], Abdullah Adnan Abdulkarim[2], Nadezda Vyacheslavovna Alekseeva[3]

[1] Department of Fuel and Energy Engineering technologies, Technical college Kirkuk, Northern Technical University, Mosul, Iraq

[2] Commission for Research and Industrial Development, Ministry of Industry and Minerals, Baghdad, Iraq

[3] Department of Technological Processes, Devices and Technosphere Safety, Tambov State Technical University, Tambov, Russia

* Corresponding author's e-mail: mohammedqader1983@gmail.com

ABSTRACT

This work is devoted to study the effect of thermal conditions and concentrations on the diffusion permeability of a cation exchange membrane (MK-40) using sodium chloride (NaCl), sodium acetate ($C_2H_3NaO_2$) and acetic acid (CH_3COOH) solutions, which are usually highly concentrated components of pigment yellow 13 of industrial wastewater. A cell containing two compartments was used to analyze the properties of membrane. The results showed that the maximum diffusion permeability coefficients for NaCl, $C_2H_3NaO_2$, and CH_3COOH were 6.08×10^{-9} m^2/s, 13.29×10^{-11} m^2/s, and 25.95×10^{-11} m^2/s, respectively. The increase in the CH_3COOH solution concentration was found to improve the diffusion permeability. However, the NaCl and $C_2H_3NaO_2$ solutions exhibited decreases in diffusion permeability with solution concentration. There was a significant increase in diffusion permeability with temperature.

Keywords: cation exchange membrane, temperature, concentration, diffusion permeability.

INTRODUCTION

Pigments are available in a wide range of colors, consisting of small molecules that are practically insoluble in the medium and they are known to be unique compounds for many industries [Nigam et al., 2009; Malik et al., 2012]. They are widely used in dyestuff, cosmetics, food products, pharmaceutical, manufacturing processes, etc. [Durán et al., 2002]. Basically, azo dyes are the most commonly used dyes and account for about 60% of the total amount of dyes. Approximately 70% of all dyes used in industry are azo dyes. These compounds are characterized by a functional group (- N=N -) [Benkhaya et al., 2020]. According to Bogacki et al. [2004], pigments can be divided into two categories: homogeneous pigments and mixtures. In addition, pigment yellow 13 belongs to the azo group and is one of the important products of PJSC "Pigment" in (Tambov/Russia), a manufacturer of chemical products.

The removal of color, especially from pigment industrial wastewater, is known to be a difficult task, and can be overcome with a single and cost-effective treatment technique. The industrial wastewater treatment plants were commonly used ion exchange membranes in the removal of dye pollutants using different techniques such as electrodialysis, electrodeionization, diffusion dialysis, membrane electrolysis, and Donnan dialysis [Strathmann et al., 2013]. Recently, ion exchange membranes (IEMs) have attracted attention in membrane technologies due to their chemical stability and ions selectivity with excellent water transport properties [Geise et al., 2014].

In 1950s, Ionics Inc. offered the first cation exchange membranes (CEMs) suitable for membrane electrolysis. Such a membrane has a high exchange capacity, good electrical conductivity and stability in the presence of both concentrated alkali and

chlorine, as well as operates at elevated temperatures [Jaroszek & Dydo, 2016]. Melnikov et al. [2018] studied the diffusion permeability of MK-40 and MA-41 using an equilibrium salt or acid solution. The MK-40 composites were formed by the KU-2 cation-exchange resins (a polystyrene matrix (PS) crosslinked with divinylbenzene (DVB) and fixed groups), polyethylene, and nylon [Berezina et al., 2008]. In addition, the MK-40 membrane bulk contains 35% polyethylene. At the same time, approximately 80% of the polyethylene covered the wet surface area of the MK-40 membrane [Pismenskaya et al., 2012]. It was established that the distribution of ion exchanger portions on the surface of heterogeneous membranes is complex stochastic; their sizes for MK-40 are 5–30 µm [Vasil'eva et al., 2013]. In several research works, the diffusion permeability of MK-40 in the NaCl solution were also investigated and demonstrated high efficiency [Sarapulova et al., 2019; Izquierdo-Gil et al., 2020]. For example, in the case of concentrated NaCl solutions (C = 1.5 M), the diffusion permeability of MK-40 was 8.3×10^{-12} m²/s [Izquierdo-Gil et al., 2020].

Despite significant progress in understanding the response of the MK-40 membrane characteristics, there are shortcomings and significant gaps in knowledge of understanding its behavior at different operating temperatures. Thus, the aim of this work was to study the effect of feed solution concentration and its temperature on the diffusion permeability of cation exchange membranes using sodium chloride (NaCl), sodium acetate ($C_2H_3NaO_2$) and acetic acid (CH_3COOH), which are usually the highest components existing in the wastewater of pigment yellow 13.

MATERIALS AND METHODS

Materials

Commercial heterogeneous cation exchange membrane (MK-40) was supplied by "Shchekino-azot" (Russia) [Pismenskaya et al., 2012]. The main properties of commercial MK-40 membrane are summarized in Table 1. NaCl, $C_2H_3NaO_2$, CH_3COOH were supplied from pigment plant in Tambov (Russia) and used as received. Table 2 shows the main composition of wastewater discharged during the production of pigment yellow 13.

The initial feed solutions were prepared using distilled water in the concentration ranged from 0.1 to 1.0 M for NaCl, from 0.05 to 0.5 M for $C_2H_3NaO_2$, and from 0.025 to 0.25 M for CH_3COOH.

Method

Two-compartment cell was used to study the permeability characteristics of MK-40, as shown in Figure 1. The concentrated solutions of NaCl, $C_2H_3NaO_2$ and CH_3COOH were used with distilled water to characterize the MK-40 membrane.

Table 1. Properties of commercial MK-40 membrane

Membrane properties	Cation exchange (MK-40)
Ion exchange groups, bulk	$-SO_3^-$
Idem, surface	$-SO_3^-$
Thickness, µm	480 ± 10
Ion exchange capacity, mM·cm⁻³ wet	1.7 ± 0.1
Ion exchange material surface fraction of, %	22 ± 3
Contact angle, degrees	55 ± 3
Particular electrical conductivity in 0.5M NaCl solution, mS·cm⁻¹	7.7 ± 0.3
Diffusion permeability, 10⁻⁸ cm·s⁻¹	6.7± 0.4

Table 2. Main components of wastewater discharged from the production of yellow pigments 13

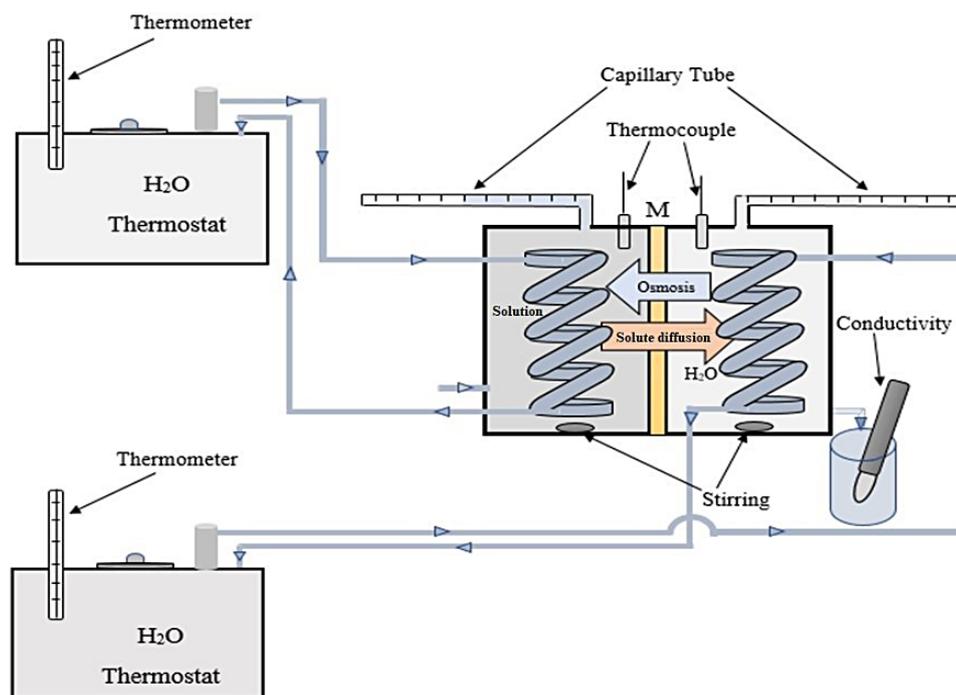| Composition	Concentration (M)
Orthoxylene	0.0263
Acetic acid	0.017
Sodium chloride	0.25
Sodium sulfate	0.0016
Sodium acetate	0.093
Water	55.5

Figure 1. Schematic experimental setup of membrane permeability measurement

The volumes of the left compartment contained a concentrated solution, while the right compartment contained distilled water. The volume of each compartment was 570 cm^3. The area of the membrane was 31.4 cm^2 and its thickness was 1 mm. Each compartment cell was connected to a thermostat box to control the temperature of the solution and the distilled water.

Different concentrations of NaCl, C$_2$H$_3$NaO$_2$, and CH$_3$COOH were selected to study the diffusion permeability of the membrane at different cell temperatures (25, 35, 45, and 50 °C). The experimental time during each test was 100 min.

Before starting the measurement of diffusion permeability of membrane, the MK-40 membrane was soaked in a solution of carbon tetrachloride and then with an ethanol solution; afterwards, it was left for a few minutes to dry in air. Then, the membrane was immersed in a saturated solution of NaCl for 24 hrs, followed by immersion in distilled water for 24 hrs. After that, the membrane was placed in 0.1 M NaOH solution for 24 hrs and then in distilled water for 24 hrs. The membrane was subsequently placed in 0.1 M hydrochloric acid (HCl) for 24 hrs and washed in distilled water until a neutral pH and pseudo-stable diffusion and osmosis were achieved.

After preparing the membrane for operation, it was placed in a cell, between two compartments, one of which is filled with the necessary

concentrated solution, and the other with distilled water. Both compartments were stirred at 300 rpm using magnetic stirrers. As a result of the concentration gradient caused by the diffusion of solution from highly concentrated solution chamber to distilled water chamber, the diffusion coefficient of the solution was determined. The two-chamber cell was tightly sealed and connected to a capillary tube, enabling the volume change in the chamber to be measured with high accuracy.

In order to find the calibration curves of the solution, a series of standard solutions of sodium chloride, sodium acetate, and acetic acid solution was prepared. The electrical conductivity of these solutions was measured and converted to a concentration.

The diffusion permeability coefficient of membrane was determined by calculating the self-diffusion of initial feed solution from the concentrated compartment side to the diluted part (distilled water). The movement of water from distilled water compartment over time reduces the concentration of the concentrated compartment, which leads to a decrease in the driving force of diffusion and osmosis [Kingsbury et al., 2018]. After 100 min of operation time, the diffusion permeability coefficients of membranes (P_s) can be determined by the formula given in equation (1) [Alekseeva et al., 2012].

$$P_S = \frac{C_1 \cdot V_2 \cdot X}{(C_1 - C_1) \cdot S \cdot t} \qquad (1)$$

where: C_1 is concentration of initial feed concentration (kg/m³); C_2 is concentration of feed in the distilled water compartment at the end of the experiment (kg/m³); V is the volume of water at the end of the experiment (m³); S is membrane operating area (m²); X is thickness of the membrane (m); and t is the operating time (s).

RESULTS AND DISCUSSION

The diffusion permeability coefficients of NaCl at different temperatures (25, 35, 45 and 50 °C) during 100 min of experimental time were shown in Figure 2. This figure shows that the maximum NaCl diffusion permeability coefficient was 6.08×10^{-9} m²/s at feed concentration of 0.1 M at an operating temperature of 50 °C. In turn, the minimum NaCl diffusion permeability coefficient was 1.7×10^{-9} m²/s obtained at concentration of 1 M at 25 °C.

The drop in the diffusion permeability coefficients of NaCl can be caused by the flow of water from the distilled water compartment to the salt solution compartment, which reducing the driving force of diffusion and osmosis [Kingsbury et al., 2018]. The increase in concentration polarization of NaCl at the boundary layer on the membrane surface could also result a decrease in the diffusion permeability of membrane [Melnikov et al., 2018].

It was also observed that the increase in the temperature of the NaCl solution leads to an increase in permeability of membrane. This may be due to increase in the penetration rate and thus
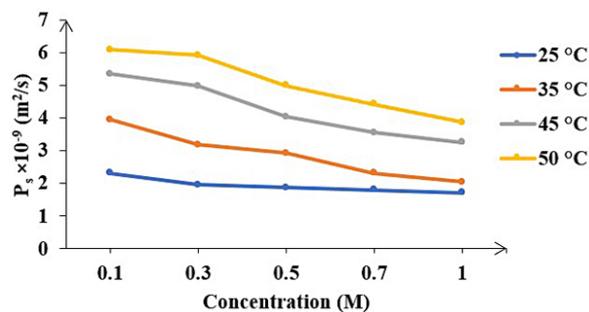
accelerate the transfer of ions through membrane [Zhang et al., 2011]. As such, Gatapova et al. [2020] investigated the diffusion permeability coefficient of MK-40 membrane for the NaCl solution using two different temperatures (25, 50) °C for both sides of the compartment under thermodynamic and thermostatic conditions. They found a significant difference in the values of the diffusion permeability coefficient when both sides of the compartment are operating at the same temperature, compared to working with different temperatures on both sides.

The diffusion permeability coefficients of sodium acetate ($C_2H_3NaO_2$) using different concentrations and temperatures (25, 35, 45 and 50 °C) were calculated using equation 1 and plotted as shown in Figure 3.

Figure 3 showed that the increase in the concentration of $C_2H_3NaO_2$ reduces the membrane diffusion permeability. This is due to the fact that the water content of membrane in the polymer decreases with increasing salt concentration [Geise et al. 2014]. It was shown that the maximum diffusion permeability coefficient was 13.296×10^{-11} m²/s when the concentration of $C_2H_3NaO_2$ was 0.05 M at an operating temperature of 50 °C. However, the minimum diffusion permeability coefficient was 2.0541×10^{-11} m²/s when feed concentration was 0.5 M at 25 °C operating temperature.

It was also noticed that the diffusion permeability was decreased when the concentration of sodium acetate was increased. However, there was insignificant change in the diffusion permeability of the membranes at concentrations of 0.3 and 0.5 M. According to Beckingham et al. [2018], the diffusion permeability of sodium acetate through the Nafion* 117 membrane
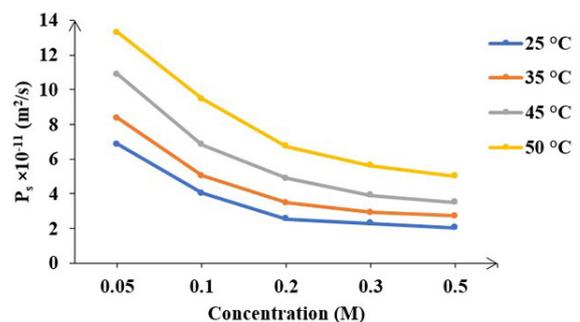
Figure 2. Diffusion permeability coefficients for MK-40 membrane at different temperatures, using different NaCl concentration, 0.1, 0.3, 0.5, 0.7, and 1 M, over 100 min operational time

Figure 3. Diffusion permeability coefficients for MK-40 membrane at different temperatures, using different $C_2H_3NaO_2$ concentration, 0.05, 0.1, 0.2, 0.3, and 0.5 M, over 100 min operational time

was $(5.0 \pm 0.4) \times 10^{-12}$ m²/s. Wagner & McGinity [2002] investigated the permeability of the cationic acrylic copolymer Eudragit RS 30 D for sodium acetate. They observed that 0.1 M of sodium acetate has a lower permeability compared to 0.01 M and 0.001 M of this compound.

Wang et al. [2020], studied the diffusion permeability of two anion exchange membranes (AR103 and AR204) and found that at the same concentration, the diffusion coefficient of sodium acetate is lesser than the value of sodium chloride (NaCl). This can be explained by their Stokes radius (i.e., Cl^- (0.121 nm) is less than Ac^- (0.194 nm)). It was also found that diffusion coefficients for these membranes was relatively constant, but slightly decrease with an increase in the concentration of the external solution of sodium acetate and sodium lactate solutions due to osmotic deswelling. Thus, it could be concluded that MK-40 has a lower diffusion permeability coefficient for a solution of sodium acetate compared to sodium chloride. This indicates that its MK-40 membrane efficiency in removing $C_2H_3NaO_2$ ions is better than NaCl and requires lower energy.

The results of diffusion permeability coefficients of different concentrations of acetic acid (CH_3COOH) at different temperatures (25, 35, 45 and 50 °C) were shown in Figure 4. It was shown that the increase in concentration of CH_3COOH from 0.025 M to 0.25 M improved the diffusion permeability of the membrane. The results showed that the maximum diffusion permeability coefficient was 25.95×10^{-11} m²/s for 0.25 M of CH_3COOH solution at the operating temperature of 50 °C. At similar concentration with different operating temperature (25 °C), the maximum diffusion coefficient was 13.3×10^{-11} m²/s. According to a study by Kawaguchi et al. [1997], it was found that the cation exchange permeability coefficient of membrane (K101) for acetic acid is 1.69×10^{-9} m²/s. MK-40 membrane has a lower diffusion coefficient for acetic acid, which means a higher removal efficiency of the acetic acid solution. Similarly, Han et al. [2006] found that the ion-exchange membrane works efficiently in removing acetic acid from wastewater. It can be noticed that the diffusion permeability of the MK-40 membrane for the CH_3COOH solution was lower than for NaCl and $C_2H_3NaO_2$ solution. This means that MK-40 has a high CH_3COOH ion removal efficiency.
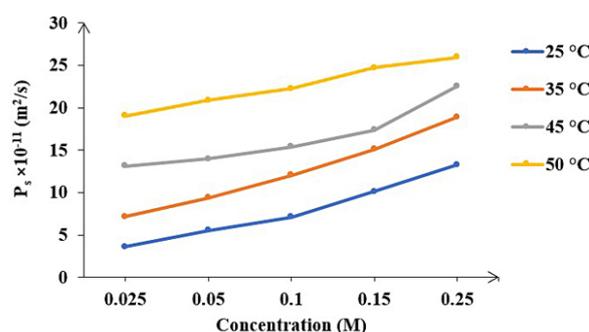

Figure 4. Diffusion permeability coefficients for MK-40 membrane at different temperatures, using different CH_3COOH concentration, 0.025, 0.05, 0.1, 0.15, and 0.25 M, over 100 min operational time

CONCLUSIONS

In this work, the membrane diffusion permeability of cationic exchange membrane (MK-40) was characterized using different concentrations of sodium chloride, sodium acetate, and acetic acid. An increase in temperature of the NaCl solution led to an increase in the rate of membrane permeability coefficient due to the acceleration of ions transport through membrane with an increase in temperature. The membrane diffusion permeability decreases with increasing concentration of sodium acetate. An increase in the acetic acid concentration led to an increase in the diffusion permeability of the membrane. It was observed that the diffusion permeability coefficient of the MK-40 membrane was increased with increase in solution temperature. The tested membrane showed low permeability to sodium acetate and acetic acid compared to sodium chloride, which means that the energy loss for sodium acetate and acetic acid is lower than that for sodium chloride.

REFERENCES

1. Alekseeva, N.V., Arkhipov, A.I., Borisov, P.A. 2012. Study of Diffusive and Osmotic Permeability of MK-40 and MA-40 Electrodialysis Membranes in Two-Component Solutions of Copper, Zinc, Nickel and Sodium Salts. Transactions of the TSTU, 18(4), 923–927.

2. Beckingham, B.S., Lynd, N.A., Miller, D.J. 2018. Monitoring multicomponent transport using in situ ATR FTIR spectroscopy. Journal of Membrane Science, 550, 348–356.

3. Benkhaya, S., M'rabet, S., El Harfi, A. 2020. Classifications, properties, recent synthesis and applications of azo dyes. Heliyon, 6(1), 1–26.

4. Berezina, N.P., Kononenko, N.A., Dyomina, O.A., Gnusin, N.P. 2008. Characterization of ion-exchange membrane materials: Properties vs structure. Advances in Colloid and Interface Science, 139(1-2), 3–28.

5. Bogacki, M.B., Michalska, I., Krysztafkiewicz, A. 2004. Application of experimental design for optimization of physicochemical properties of the inorganic pigment, iron (III) silicate. Dyes Pigments, 61(2), 149-164.

6. Durán, N., Teixeira, M.F.S., De Conti, R., Esposito, E. 2002. Ecological-Friendly Pigments from Fungi. Critical Reviews in Food Science and Nutrition, 42(1), 53–66.

7. Gatapova, N.T., Dzhubari, M.K., Alekseeva, N.V. 2020. A Study of Diffusion Permissibility of MK-40 Membrane in Thermodynamic Conditions. Transactions of the TSTU, 26(4) 619–628.

8. Geise, G.M., Paul, D.R., Freeman, B.D. 2014. Fundamental water and salt transport properties of polymeric materials. Prog. Polym. Scie, 39(1), 1–42.

9. Han, B., Carvalho, W., Canilha, L., da Silva, S.S., Almeida e Silva, J.B., McMillan, J.D., Wickramasinghe, S.R. 2006. Adsorptive membranes vs. resins for acetic acid removal from biomass hydrolysates. Desalination, 193(1–3), 361–366.

10. Izquierdo-Gil, M.A., Villaluenga, J.P.G., Muñoz, S. Barragán, V.M. 2020. The Correlation between the Water Content and Electrolyte Permeability of Cation-Exchange Membranes. International Journal of Molecular Sciences, 21(16), 1–11.

11. Jaroszek, H. & Dydo, P. 2016. Ion-exchange membranes in chemical synthesis – a review. Open Chemistry, 14(1), 1–19.

12. Kawaguchi, M., Murata, T., Tanioka, A. 1997. Membrane potentials in charged membranes separating solutions of weak electrolytes. Journal of the Chemical Society, Faraday Transactions, 93(7), 1351–1356.

13. Kingsbury, R.S., Zhu, S., Flotron, S., Coronell, O. 2018. Microstructure Determines Water and Salt Permeation in Commercial Ion-Exchange Membranes. ACS Applied Materials & Interfaces, 10(46), 39745–39756.

14. Malik, K., Tokkas, J., Goyal, S. 2012. Microbial pigments: A review. Int. J. Microbial. Resour. Technol, 1(4), 361–365.

15. Melnikov, S, Kolot, D, Nosova, E, Zabolotskiy, V. 2018. Peculiarities of transport structural parameters of ion-exchange membranes in solutions containing anions of carboxylic acids. Journal of Membrane Science, 557, 1–12.

16. Nigam, P., Pandey, A., Babitha, S. 2009. Microbial pigments biotechnology for agro-industrial residues utilisation, ed: Springer, Dordrecht, 147–162.

17. Pismenskaya, N., Melnik, N., Nevakshenova, E., Nebavskaya, K., Nikonenko, V. 2012. Enhancing Ion Transfer in Overlimiting Electrodialysis of Dilute Solutions by Modifying the Surface of Heterogeneous Ion-Exchange Membranes. International Journal of Chemical Engineering, 2012, 1–11.

18. Sarapulova, V., Shkorkina, I., Mareev, S., Pismenskaya, N., Kononenko, N., Larchet, C., Dammak, L. Nikonenko, V. 2019. Transport Characteristics of Fujifilm Ion-Exchange Membranes as Compared to Homogeneous Membranes AMX and CMX and to Heterogeneous Membranes MK-40 and MA-41. Membranes, 9(7), 1–23.

19. Strathmann, H., Grabowski, A., Eigenberger, G. 2013. Ion-Exchange Membranes in the Chemical Process Industry. Ind. Eng. Chem. Res, 52(31), 10364–10379.

20. Vasil'eva, V.I., Akberova, E.M., Zhiltsova, A.V., Chernykh, E.I., Sirota, E.A., Agapov, B.L. 2013. SEM diagnostics of the surface of MK-40 and MA-40 heterogeneous ion-exchange membranes in the swollen state after thermal treatment. Journal of Surface Investigation. X-Ray, Synchrotron and Neutron Techniques, 7(5), 833–840.

21. Wagner, K.G., McGinity, J.W. 2002. Influence of chloride ion exchange on the permeability and drug release of Eudragit RS 30 D films. Journal of Controlled Release, 82(2-3), 385–397.

22. Wang, Q., Chen, G.Q., Kentish, S.E. 2020. Sorption and diffusion of organic acid ions in anion exchange membranes: Acetate and lactate ions as a case study. Journal of Membrane Science, 614, 1–10.

23. Zhang, X., Li, C., Wang, Y., Luo, J., Xu, T. 2011. Recovery of acetic acid from simulated acetaldehyde wastewaters: Bipolar membrane electrodialysis processes and membrane selection. Journal of Membrane Science, 379(1-2), 184–190.