

이온교환막을 통한 이온분리에 대한 총설

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A Review Based on Ion Separation by Ion Exchange Membrane

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요약: 이온교환막(IEM)은 다양한 종류의 단가이온과 다가이온을 분리하기 위해 사용되는 막의 한 종류로, 배터리, 연료 전지, 염화물-알칼리 공정 등에 사용된다. 이온교환막을 통한 막분리는 전기 구동력을 기반으로 한 녹색 분리 방식이며, 해수 담수화와 수처리 분야에서 떠오르는 방식이다. 전기투석(ED)은 양이온과 음이온이 이온교환막을 따라 선택적으로 이동하는 기술이다. 음이온 교환막(AEM)은 전기투석의 중요한 구성 요소 중 하나이며, 공정 효율을 향상시키는 데 상당한 역할을 한다. 이온교환막에 가교결합을 도입하면 자유 부피의 감소로 인해 이온 선택 분리 성능이 향상된다. 역삼투(RO) 공정을 통한 해수 담수화 시 RO 농축수에 용해된 염이 다량 존재한다. 따라서 1가 양이온 선택막으로 구성된 전기투석 공정은 오염을 줄이고 막 플럭스를 개선한다. 이 검토는 전기투석, 음이온 교환막, 그리고 양이온 교환막의 세 부분으로 나뉜다.

Abstract: Ion exchange membrane (IEM) is an important class of membrane applied in batteries, fuel cells, chloride-alkali processes, etc to separate various mono and multivalent ions. The membrane process is based on the electrically driven force, green separation method, which is an emerging area in desalination of seawater and water treatment. Electrodialysis (ED) is a technique in which cations and anions move selectively along the IEM. Anion exchange membrane (AEM) is one of the important components of the ED process which is critical to enhancing the process efficiency. The introduction of cross-linking in the IEM improves the ion-selective separation performance due to the reduction of free volume. During the desalination of seawater by reverse osmosis (RO) process, there is a lot of dissolved salt present in the concentrate of RO. So, the ED process consisting of a monovalent cation-selective membrane reduces fouling and improves membrane flux. This review is divided into three sections such as electrodialysis (ED), anion exchange membrane (AEM), and cation exchange membrane (CEM).

Keywords: *electrodialysis, anion exchange membrane, cation exchange membrane, reverse osmosis*

1. Introduction

The seawater desalination leads to overcoming the problem of shortage of freshwater due to various

factors. Reverse osmosis process is a well-established method for the desalination which leads to large presence of dissolved salt in RO discharge[1-5]. The treatment of the discharge by ED process using IEM re-

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duces membrane fouling as well as improves the membrane lifetime. Recently IEM based separation processes are widely researched due to its application towards sea water desalination by ED, chloride-alkali generation and various other processes. The electro-dialysis is driven by electrical field force in which cations and anions are separated present in the saline water[6-10]. There are several advantages of the ED process such as high recovery of efficiency and environmental friendly process. Wastewater can be treated by the ED process.

Electrodialysis, based on monovalent anion-selective membranes, has various advantages. The ED process based on a bipolar membrane supports the separation of ingredients which overcomes the formation of mixture[11-14]. This results in the preparation of pure products as well as a reduction in the cost of separation process. Improvement of IEM properties is done through modification of the membrane surface. Introduction of suitable function group on the membrane surface enhances the selectivity of ions by enhanced repulsion of multivalent ions. Functional groups present on the membrane surface are highly affected in harsh conditions leading to the shortened lifetime of AEM. Monovalent anion-selective membrane (MASM) is an alternative way to solve this problem.

Monovalent selective electro-dialysis (MSED) is an alternative process to replace RO for the freshwater generation to be used in irrigation. Dilute water contains divalent ions which are nutrients and harmful monovalent ions. In this review separation of ions is discussed in three different parts. Fig. 1 represents the schematic presentation of classification.

2. Electrodialysis

ED is important class of separation process of various ions by ion exchange membrane. The membranes with advanced selectivity of monovalent anions are extremely essential due to their broad possibility for usage in industrial spheres. To achieve the goal, the

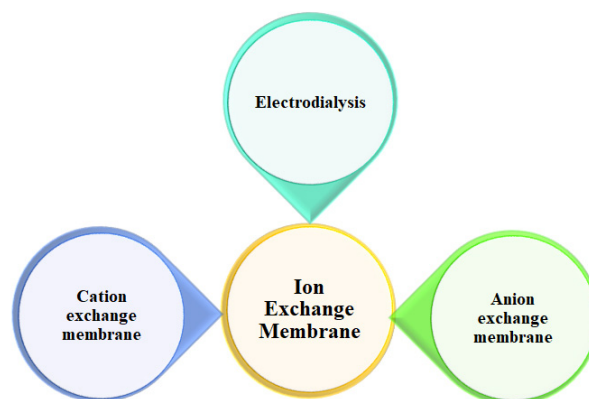


Fig. 1. Schematic representation of classification of the review.

membrane of amphoteric ion exchanges was prepared [15]. The membrane had advanced separation of both monovalent and divalent anions. The membranes were fabricated by poly (arylene ether sulfone) (PAES) which contained amino group with different percentages of sulfonated polysulfone. The blended polymer is grafted with imidazolium salt. Atomic force microscopy (AFM) showed that membranes had homogeneous structures and evenly distributed elements which illustrated the miscibility of entrails. The transmission electron microscopy (TEM) showed that even morphology lacked the state of splits. Through electro-dialysis, the density of the current, and perm selectivity between chloride and sulfate ions were identified to be 2.5 mA/cm² and 21.8 respectively. The properties enhancement of the modified membrane was due to the increased repulsion between sulfonate group on the membrane with monovalent and bivalent anionic ion present in the solution.

The trivalent and hexavalent chromium [Cr(III) and Cr(VI)] were simultaneously separated from soil contaminants through the “back-to-back” technique in the altered bipolar membrane scheme of electro-dialysis (ED)[16] (Fig. 2).

The analysis revealed that the pH of the soil mixture had a dramatic influence on the chromium elements’ desorption and follows Elovich kinetic model. The efficiency of removal was 99.8% whereas the recovery of

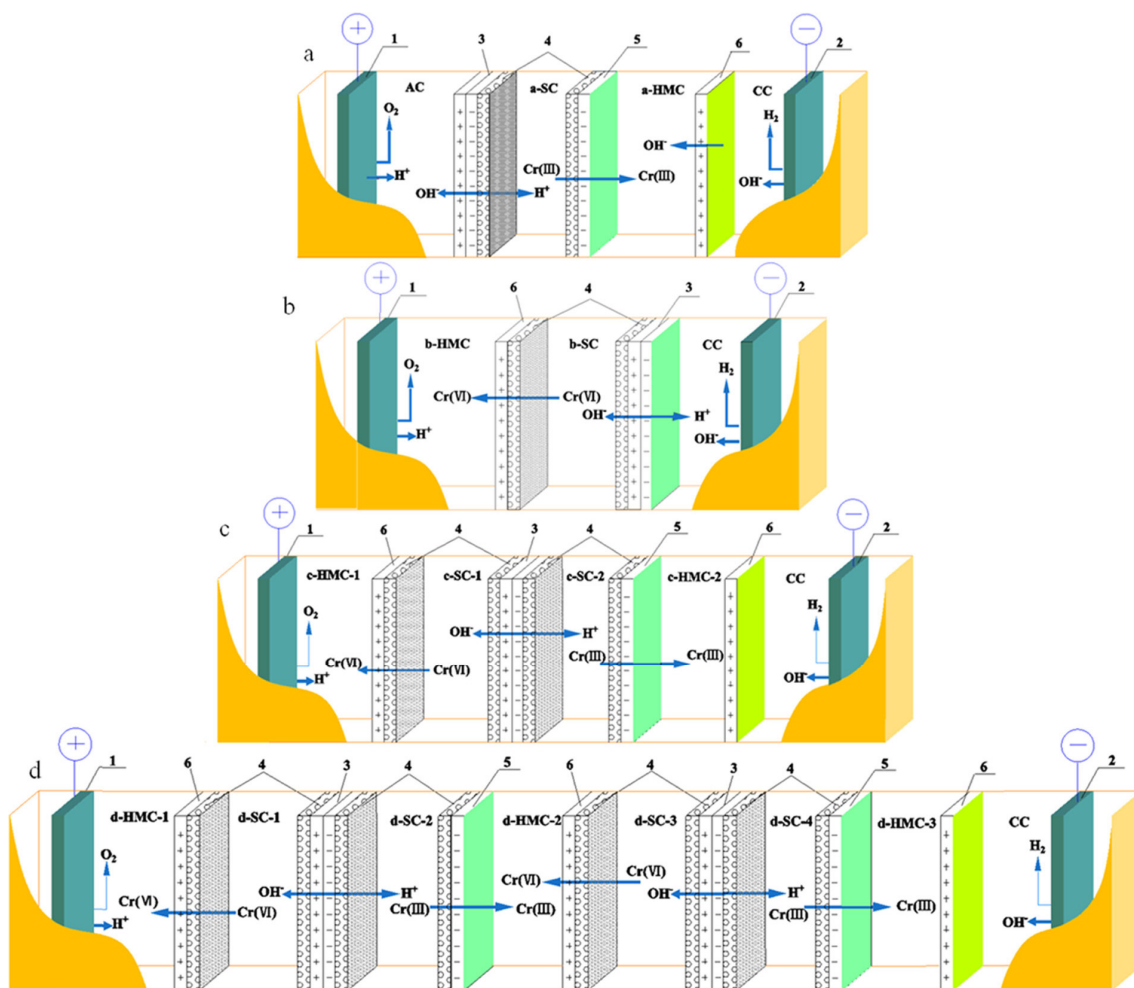


Fig. 2. Scheme of the experimental setup. (a) Cr(III) removal system, (b) Cr(VI) removal system, (c) one group “back-to-back” SC equipped system, (d) two group back-to-back SCs equipped system. AC: anode compartment; CC: cathode compartment; SC: soil compartment; HMC: heavy-metal compartment; (1) anode plate; (2) cathode plate; (3) bipolar membrane; (4) microfiltration membrane; (5) cation-exchange membrane; (6) anion-exchange membrane. (Reproduced with permission from Liu *et al.*[16], Copyright 2020, American Chemical Society).

elements was 87% for trivalent chromium and 90% for hexavalent chromium. The results confirm that the technique of the “back-to-back” compartment of soil increased the efficiency of current process with lower consumption of energy. When the scheme was applied, the efficiency of current went up by 28.8%, simultaneously dropping the consumption to 0.048kWh/g. The method of traditional electro dialysis called MSED uses ion exchange membrane where monovalent ions are separated from divalent one[17]. Due to possible applications of the latter, the process could be promising in the agricultural industry. Since monovalent selective

electrodialysis is an innovative method, the sources are restricted to the model of traditional electro dialysis where the prediction of the working process of MSED is calculated. The process consisted of more than 30 trials with various circumstances to be appropriate for the membrane with 6 and 8% information. Within one-tenth of the experiments, the voltage predicting was estimated. As well as perm-selectivity was also predicted among the plethora of compositions and salinities.

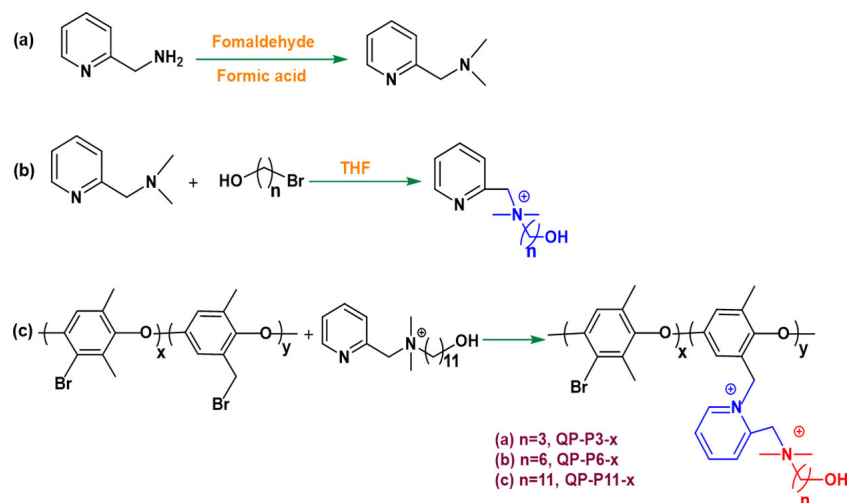


Fig. 3. Synthesis of (a) 2-(*N,N*-dimethylamino) methylpyridine, (b) QnP ($n = 3$, QPP; $n = 6$, QHP; $n = 11$, QUP), and (c) QP-P n - x AEMs (Reproduced with permission from Irfan *et al.*[19], Copyright 2019, American Chemical Society).

3. Anion Exchange Membrane

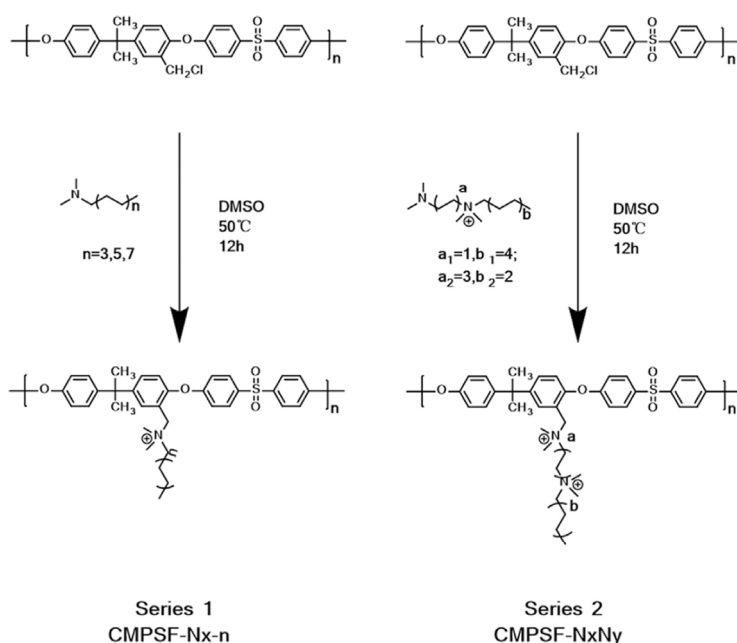
The membranes with great selectivity of monovalent ions were fabricated through cross-linkage of graphene oxide (GO) linked with 1,4-diazabicyclo [2.2.2] octane groups and chloromethylated polysulfone. The linkage of the former gives a membrane the matrix of dense polymer and with functional sites[18]. Through the properties of membranes, the most suitable one was CrPSf-3 which showed the best results in an ion exchange capacity of 2.01 mmol/g, water uptake of 31.2 % and swelling ratio of 9.9%. Separation factor of the membrane between chloride and sulfate ions was 5.7 in ED analysis which better than pristine membrane. Field emission scanning electron microscope (FESEM), was used to check the morphology of the membrane. The structure of the polymer matrix had a micro-sized interface and homogeneous dispersion. By controlling the compactness and transportation of ion channels in the membrane, the new monovalent anion-selective membrane was fabricated through organic-modified GO crosslinking.

Electrodialysis requires membranes that exchange ions without swelling effect whilst maintaining a high amount of selectivity of ions for cleaning resources as well as treating saline wastewater[19] (Fig. 3).

Hydrophobic properties of the membrane were tuned by linking to cationic ammonium group through alkyl spacer. The new membranes were able to separate monovalent anions from divalent through selectivity between chloride and sulfate anions up to about 13.07, in which spacer length plays a critical role. For usage in electro dialysis, the synthesis of the balanced membrane with excellent anion selectivity with better perm-selectivity between mono/multi-valent ions is very challenging[20]. Liao *et al.* fabricated new monovalent selective IEM with amphoteric properties.

The membrane was synthesized through imidazolium-functionalized poly(arylene ether sulfone) long chains that had been cross-linking with 4,4'-diazostilbene-2,2' - disulfonic acid disodium salt. The latter's percentage of mass was tuned, which led to better perm-selective and swelling ratio results of the new AIEM. The results of the membrane for perm-selectivity in anion was 8%, and the density of current was 2.5 mAcm⁻². In comparison with Neosepta ACS, the new membrane had higher perm-selectivity and a lower density of current. This can be explained by the size of pores that increase due to the sieving effect.

Metal-organic frameworks can be used as a separator due to their properties like the size of pores, ease of functionalization, and adjustment of the structure[21].



Note: "n" in CMPSF-N_x-n (n = 1 and 2) represents two groups of AEMs at different IEC value.

Fig. 4. Preparation route of CMPSF-N_x-n and CMPSF-N_xN_y AEMs (Reproduced with permission from Irfan *et al.*[22], Copyright 2021, American Chemical Society).

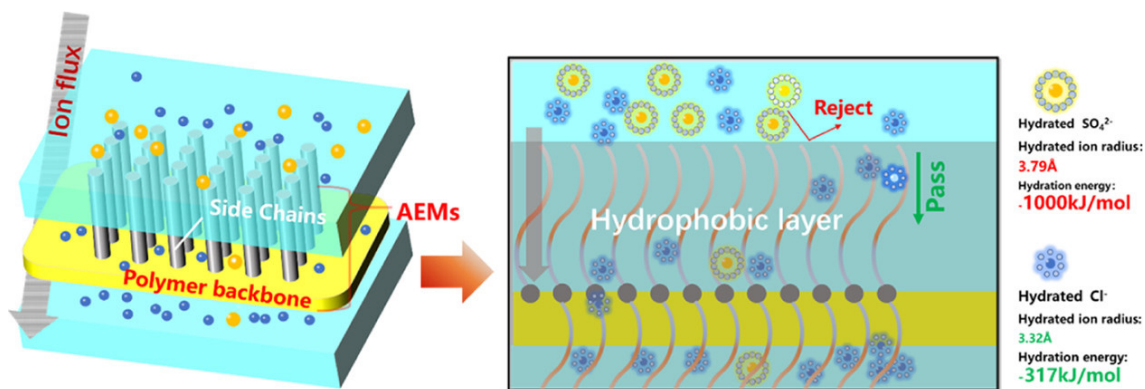


Fig. 5. Possible permselectivity mechanism of the prepared AEMs (membranes grafted with long alkyl chains) (Reproduced with permission from Irfan *et al.*[22], Copyright 2021, American Chemical Society).

Ruan *et al.* prepared UiO-66 membrane and then functionalized with various functional groups to be used in ED for the perm-selective separation of monovalent ions in the system. The effect on the density of current and original concentration of the solutions upon the perm-selective property UiO-66-NH₂ were studied. The MOF membrane layers were fabricated on the disks of anodic alumina oxide and then reacted with 1,3-propane sulfonate to prepare sulfonic acid terminated MOF.

UiO-66-NH₂ displayed better perm-selectivity of monovalent ions with highest value of 36.23 at 2.5 mAcm⁻².

In electro dialysis, AEM with high monovalent and divalent perm-selectivity have tremendous scope[22] (Fig 4 and 5).

AEM was modified with long side chain with cationic group in between by Menshutkin reaction. The hydrophobicity of the membrane surface was well controlled by varying the length of the carbon chain graft-

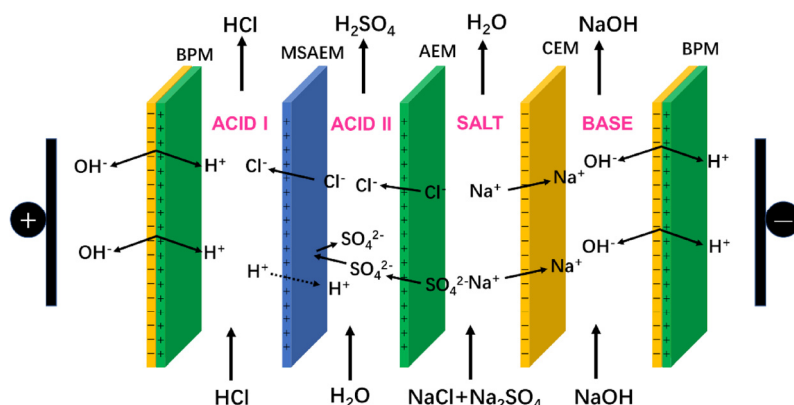


Fig. 6. Schematic diagram for the novel electrodiolysis stack (SBMED) process. BPM, bipolar membrane; AEM, anion-exchange membrane; CEM, cation-exchange membrane; MSAEM, mono-selective anion-exchange membrane (Reproduced from Wang *et al.*[24], 2021, MDPI).

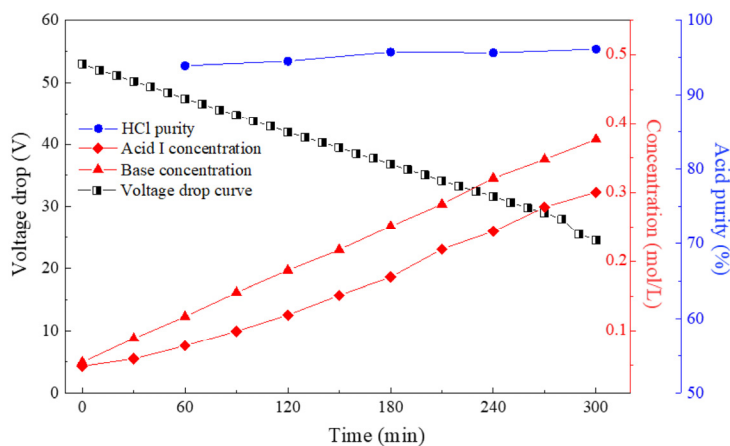


Fig. 7. The SBMED performances, i.e., voltage drop curve as a function of time, HCl purity in the acid I compartment, acid concentration curve in the acid I compartment and base concentration curve in the base compartment using simulated seawater (Reproduced from Wang *et al.*[24], 2021, MDPI).

ed onto the main chain polymer. The best performance of the modified membrane showed perm-selectivity of 60.1 for chloride/sulfate anions with 3.5% of water uptake. The optimized membrane has an ion exchange capacity value of 1.1 mmol. g⁻¹. The distribution of several cations present in side chain along with the length plays a critical role in perm-selectivity of the membrane.

The IEM with good perm-selectivity of monovalent ions is in demand due to various possible applications [23]. Various type of AEM were fabricated by modification of bromomethylated poly (phenylene oxide) (BPPO). Tertiary amine terminated long linear chain

alkyl group were grafted on to the main chain to tune the hydrophobicity of the polymer membrane. Alkyl chain length of 0, 5 and 15 are tried out of which BPPO grafted with 15 carbon group and molar ratio of 0.5 showed the best performance with perm-selectivity of 12.84 between chloride and sulfate anions. At the same time, it has lowest water swelling ratio. Performance of the membrane was enhanced by heat treatment method. Another method used to coat the membrane with conducting polymer like polypyrrole.

Due to the dangerous impact of mixed salts that have been crystallized, a new ED idea was proposed [24] (Fig. 6 and 7).

The SBMED was created through the assembly of monovalent selective anions into bipolar membrane electro dialysis (BMED). Separation of chloride from sulfate anions is possible through the monovalent selective anion-exchange membrane (MSAEM). Mixed salts are converted to monoprotic as well as diprotic acid. The purities of both acids were relatively high with ~80% while the density of current was 10 mA/cm. When the current was increased it affected the purity of the acids, which proves that they have an unproportionate relationship in the membrane. The purity, however, can be increased with the growth of divalent anions from monovalent. Through that, monoprotic acid with a purity of ~94-96% was achieved with the proposed method. Thus, SBMED was used as an effective technique for the transportation of a mix of salts into high-quality acids.

4. Cation Exchange Membrane

For the purpose of usage in ED, new membranes with perm-selectivity of monovalent cations (MCPMs) were synthesized for better results in the flux of cation, swell of membrane and broaden the possible applications in the industry like desalinating sea water, recovering the resources and treating the water[25]. The MCPMs were prepared through grafting of various alkyl spacers, to the cation with nitrogen center which had a connection to sulfonic acids and hydrophilic carboxylic groups, which were on the poly (2,6-dimethyl phenylene oxide). Those chains had the ability to tune the hydrophobicity and promote the separating microphases. Perm-selectivity of sodium/ magnesium ion was 25.26 which means that the improvement in hydrophobic properties of the membrane, which happened due to hydrophobic chains, enhanced the perm selective properties of monovalent cations. Same group prepared a similar MCPMs containing a zwitterion structure[26]. The prepared membrane has the structure of zwitterion which contained groups of quaternary ammoniums, sulfonic as well as carboxylic acids to

stabilize the flux of cations and perm-selectivity of the membrane. Perm-selectivity of sodium/magnesium ions (58.4) while for lithium/magnesium ion (16.5) is almost three times less. The effect of concentration of feed and density of current was investigated on the flux and perm selectivity. Moreover, the pH level was checked to see the influence on polarization concentration and split of water during electro dialysis. TEM results showed the uniform distribution of ionic clusters on the surface. Therefore, the MCPM structure of zwitterion was able to tune the membrane flux of cation as well membrane perm-selectivity. A commercial cation exchange membrane (CEM) made of crosslinked copolymer of vinyl monomer with sulfonic acid terminated group modified by surface coating with highly branched polyethyleneimine through epoxy terminated acrylic monomers[27]. Modification enhance the positive charge on the membrane surface but ion exchange capacity reduces very slightly. Transport rate of the divalent calcium ion through the modified membrane reduced as compared to monovalent sodium ion which is in accordance of the large scale pilot plant. Membrane modification enhance the selective separation capability monovalent ion but limitation of this process is that it is only valid only for feed solution with lower ionic strength. So the modified membrane is much suitable for electro dialysis of brackish water then concentrate water from RO.

5. Conclusions

Separation based on IEM is a well-established process but not so efficient for the separation of monovalent/divalent ions having similar ions. It is highly essential to develop IEM with monovalent selective ions for application in groundwater purification and desalination of seawater. The monovalent ion-selective membrane can be developed by a compact membrane separate based on the sieving mechanism. Secondly, by modification of the surface with a functional group that will have electrostatic repulsion. Thirdly, preparation of

an anion exchange membrane that will have an anionic functional group which will have tunable hydration properties based on the density of the charged group. This review is classified into three sections that deals with ED, AEM, and CEM.

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