International Journal of Advance Research in Engineering, Science & Technology(IJAREST),
ISSN(O):2393-9877, ISSN(P): 2394-2444,
Volume 2,Issue 10, October-2015, Impact Factor: 2.125

Study of Membrane Capacitive Deionization Technology – A Review

Dr. Archana Vyas[1]

[1]*Lecturer, Department of Chemistry, Govt. Polytechnic College, Jalore, Rajasthan, India*

Abstract *—The scarcity of fresh water due to the rapid growth of population and industries saline water (brackish and seawater) treatment through the desalination process has received increasing attention in recent years as an alternative solution. More than 17,000 desalination plants have been operated worldwide with an average production rate of 66.5 million m3 /day. There are two categories of desalination technology, namely thermal and membrane-based desalination. Specific energy consumption, water cost, operation and maintenance, and environmental impact are the set of parameters that are used to determine the most desirable processes among distillation technologies. Membrane-based technologies have increasingly been chosen in desalination processes, which are evidenced by the increase of large-scale plants constructed in recent years. Indeed, several appropriate strategies should be considered to minimize problems faced during the construction, such as membrane system designs, area requirement, energy requirement, operation and maintenance, and environmental impact, which are related to the economic view and process efficiency. This paper aims at understanding the membrane capacitive deionization technology for removal of pollutant ions from polluted water.*

Keywords*-Desalination, Membrane capacitive deionization.*

I. INTRODUCTION

One out of seven people does not have access to clean drinking water. Since the world population is still increasing, it is a major challenge to meet the drinking water demand of today and tomorrow. Because there are large resources with brackish water, that is, water with a moderate salt concentration, it is attractive to use these for drinking water production. Therefore, energy efficient and cost effective desalination technologies are of utmost importance. Membrane Capacitive Deionization is a robust, energy-efficient and cost-effective technology for the desalination of brackish water.

Capacitive deionization (CDI) is a desalination process that utilizes a capacitive electrode adsorption device and electrical field as a driving force. In CDI, ionic substances are removed when electrolyte solution is transferred through a cell with a couple of electrodes and the electrical field is established. The concept of ion transport in the CDI unit is presented in Figure 4 which is explained in literature. When the electrical field is established, counter ions in the solution migrate toward electrodes and are stored within the electrodes under electrostatic force. On the other hand, when the polarity reversal is applied, the ions are desorbed from the electrodes. The first operation produces desalted water, while the later regenerates each electrode. However, during the desalting step, ions that have been adsorbed on the electrode are brought back into the solution due to attraction from ions with an opposite charge near the electrode. Therefore, adsorption and desorption occur simultaneously, and thus reduce electrode capacity as well as current efficiency. To overcome the aforesaid problem, CDI is developed by including ion exchange membrane in front of the electrode, which is then called MCDI. The membranes act as barrier that block the co-ions to migrate from the electrode into the solution and are retained in the space between the electrode and the membrane. As a result, salt removal efficiency and current efficiency of MCDI are enhanced compared to CDI. MCDI is energy efficient desalination technology compared to RO and distillation especially for feed water with relatively low salt concentration. Additionally, MCDI is an environmentally friendly process since no contaminants or by products are produced during both the desalination and regeneration process.

II. REVIEW OF LITERATURE

2.1 Overview of Desalination

Membrane-based desalination processes that have been fully commercialized since 1987 up to the present time, involve pressure driven membrane, electrically driven membrane and recently, thermally driven membrane processes.

International Journal of Advance Research in Engineering, Science & Technology(IJAREST),
ISSN(O):2393-9877, ISSN(P): 2394-2444,
Volume 2,Issue 10, October-2015, Impact Factor: 2.125

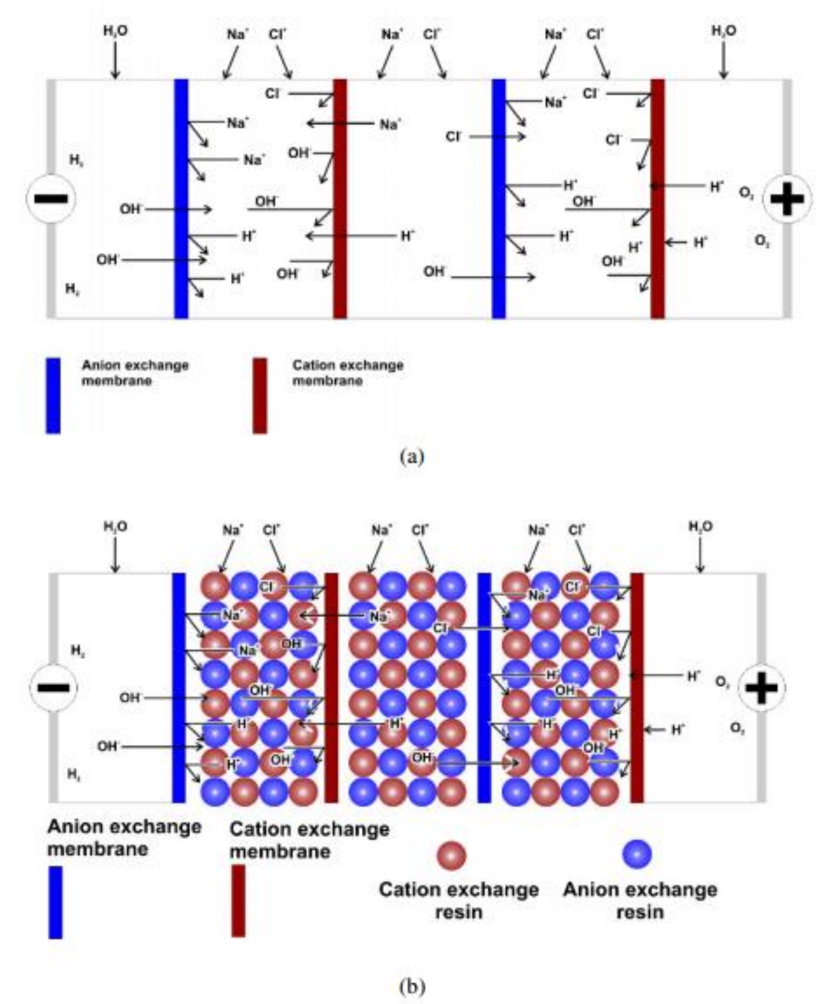

Figure 1: Schematic diagram of (a) ED and (b) EDI.

Those types of membrane processes can be categorized into two groups based on the components that are transported through the membrane, i.e. water or salt. Typically, seawater contains 3.5 g/L of salt components, which means that almost 97% of seawater content is water. Actually, the desalination process seems to be more economical and efficient by permeating salt components through the membrane. However, the enormous quantity of membrane developments, particularly reverse osmosis, is focused on the improvement of membrane hydrophilicity, which offers superior water permeability than other components in seawater. It is considered more efficient and less energy consuming compared with the early RO technology. In this sub-chapter, several membrane-based processes that were recently used in the desalination process are presented. The economics of each membrane process are also evaluated.

2.2 Capacitive deionization and membrane capacitive deionization (MCDI)

CDI works on the principle of electrostatic adsorption using porous electrodes. In a CDI transport of ion is due to electrostatic adsorption, not due to oxidation and reduction reactions. CDI has benefits of being eco-friendly, having less energy consumption and working costs than other desalination technologies, simplicity in regeneration and maintenance compared with other conventional techniques of desalination. In capacitive deionization techniques one or several pairs of oppositely charge electrodes are used as a capacitor for deionization of water. Electrodes used in CDI have a positive and negative pole under the application of external voltage. The salt solution contains positively and negatively charged ions, namely cations and anions, respectively. These ions are captured by oppositely charged electrodes due to electrostatic force under application of electric potential. Purification and regeneration are the two important operating steps used in CDI technology. In purification mode ions are captured or deposited on oppositely charged electrode under application of potential difference and pure water stream comes out from the CDI cell. When the electrodes getting saturated due to sorption of ions there is a necessity of desorption of ions from that electrode. In such conditions either reversed potential difference is applied or zero voltage is applied to the electrodes for removal of ions from electrodes and the outlet of CDI cell contains a highly concentrated solution. Schematics of purification mode and regeneration mode are presented in Fig. 2. Recently, ion exchange membranes are used in CDI systems that are called membrane capacitive deionization (MCDI) systems. Working mechanism is shown in Fig. 2(c). In MCDI ion exchange membranes are placed in front of porous electrode operated by applying a potential difference. Cation and anion exchange membranes are placed in front of negative and positively charged electrodes, respectively, and are separated by inserting a non-conductive spacer in between them to avoid short circuit. Ion exchange membrane role is to keep away counter ions. Finally, pure water comes out at the outlet of MCDI cell. In MCDI co-ion effect, i.e. co adsorption of ions with opposite charge because of e.g. specific interactions between ions is restricted.

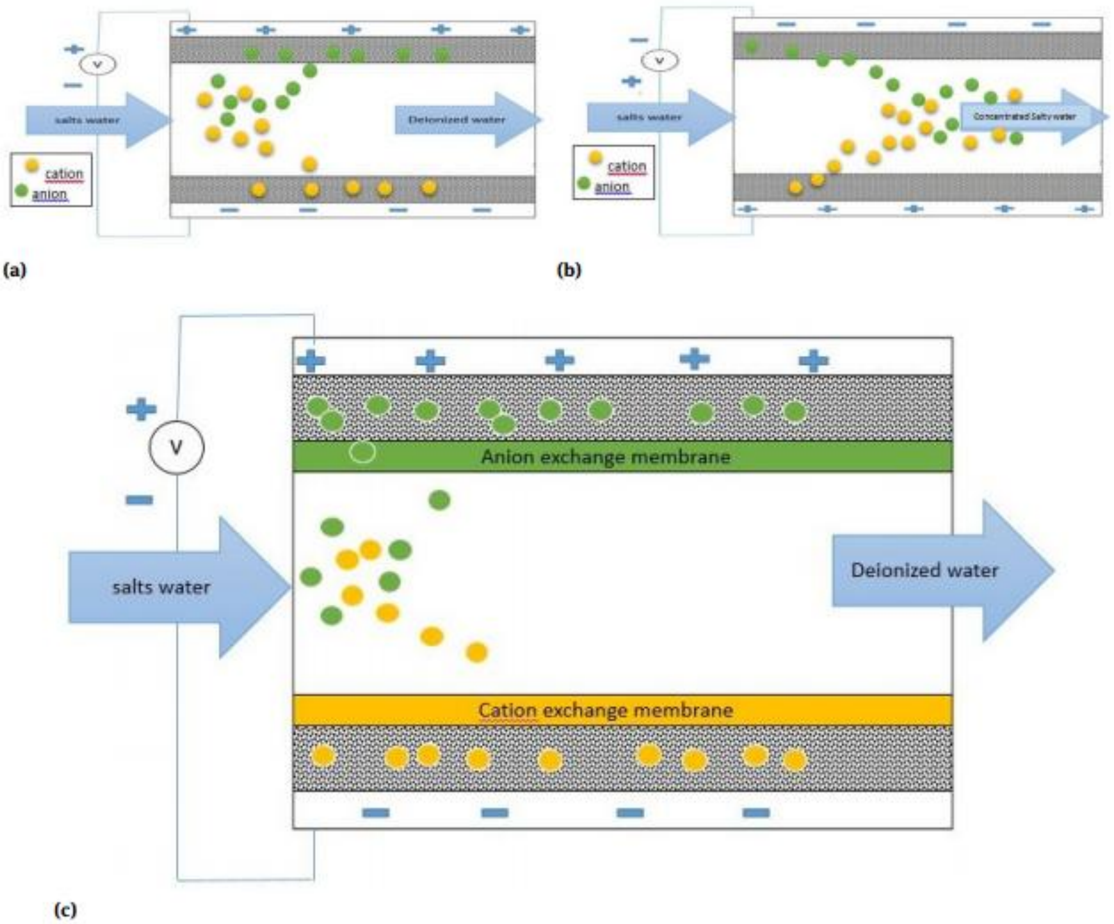

Figure 2: (a) CDI purification mode, (b) CDI regeneration mode, (c) membrane capacitive deionization.

Capacitive Deionization (CDI), often called capacitive desalination, electrochemical desalination or flow-through capacitor, is a fairly new desalination method. Over the past couple of decades, CDI has been promoted as a cheap, low-energy, high-yield competitor to reverse osmosis (RO) and electrodialysis (ED), with applications ranging from water softening to seawater desalination. CDI electrochemically removes ions from salty water. A saltwater process stream flows between two electrodes held at a potential difference of around 1.2-1.5 V. Ions in the solution are attracted to the oppositely charged electrodes. The ions are electrosorbed onto the electrodes, removing them from the process stream, and the deionization cycle continues until the electrodes are saturated with ions. Then, during the regeneration cycle, the two electrodes are discharged or the polarity of the electrodes is reversed. This releases the ions into a waste stream, which has a much higher salt concentration than the process stream. The major market advantage that CDI currently has over competing technologies is its ability to remove a wide range of ionic contaminants with high recovery rates. CDI can remove nearly all ionic contaminants – sulphates, nitrates, iron, arsenic and fluorides, along with sodium, calcium and magnesium salts. RO, which forces salty water through a nanoporous membrane, removes water from salt. By contrast, CDI removes salt from water. CDI has a much higher water recovery (up to 90% or more) than RO, which normally has a recovery rate of 50% or less. While CDI's high recovery rate is advantageous, it can also cause brine disposal issues. Brine injection back to source water can gradually increase total dissolved solids (TDS) in underground water, causing long-term environmental damage, which is a growing concern in developing countries such as India and Bangladesh. Meanwhile, CDI-based water softeners are being developed to compete with conventional resin technology, which, in contrast to CDI, requires the use and disposal of large amount of salty water, which can be environmentally unfriendly.

2.2.1 Energy use

During CDI's initial development, the potential for very high energy efficiency was seen as a major selling point. The more optimistic energy-use projections, however, require recovering energy during the regeneration cycle of operation; this requires a slow discharge to minimize losses due to polarization, and the electronics needed increase the cost and complexity of a CDI unit. Because fewer charge/discharge cycles can take place in a given time with energy recovery than without, the unit cost increases when using energy recovery. No currently commercially available CDI system uses energy recovery. In fact, most CDI systems reverse polarity during the regeneration cycle, speeding up kinetics and increasing throughput while consuming additional energy.

2.2.2 Cost challenge

The major challenge for CDI is its cost – both capital and operational costs are concerns. An RO system capable of treating 1,000 L/h costs between US$ 3,000 (INR 180000) and US$ 4,000 (INR240000), whereas a similar capacity CDI system costs about US$ 10,000. It is possible for CDI units to be sold at a premium price over RO, primarily because of CDI's low life-cycle cost and its ability to remove a wide range of ionic contaminants with substantially higher water-recovery than RO. In the future, CDI may become more cost competitive. No components in CDI (apart from membranes) are expensive; today's high costs are due to low manufacturing volumes and immature manufacturing processes.

2.2.3 Scaling issue

Electrode scaling is one of the biggest issues encountered in CDI. Virtually all source waters contains calcium and magnesium ions, which are innocuous in concentrations normally seen but can create precipitates at high concentration. During operation, the negative electrode electrosorbs positive ions indiscriminately, including calcium and magnesium ions. When the unit is discharged, a buildup of magnesium and calcium compounds can form when high concentrations of magnesium and calcium are released. To date, mild acids (such as citric acid) have been the preferred descaling method; however, process monitoring to determine when to descale the unit adds to complexity. According to Idropan's CEO, Mariella Servida, CDI unit cleaning is a major technical challenge. Idropan claims to have solved this problem using a patent-pending microinjection system that injects a citric acid-based solution on a daily basis. Other companies including AquaEWP and Enpar also have product literature and/or patent applications noting the use of citric acid to clean CDI units.

2.2.4 CDI and membranes

Historically, CDI has been touted as a membrane-free technology, and hence free from the issues facing membranebound processes such as RO and ED. Nonetheless, overcoming inefficiency and kinetic issues has generally required the use of membranes in practice. Marc Andelman of Biosource Inc first developed membrane CDI technology, and today most CDI units have ion-exchange (IX) membranes against their activated carbon electrodes to improve performance, while increasing cost. The IX membranes allow only positive ions to pass through to the negatively charged electrode, and only negative ions to pass through to the positively charged electrode. This solves two major problems: slow kinetics, and inefficiency due to counterion desorption with increased cost and decreased reliability. Counterion desorption refers to the expulsion of ions with the same sign as the electrode. When the electrodes are at the same potential, they have ions of both charges (positive and negative) adsorbed on their surface. Upon charging they expel same-charged ions (counterions) and attract oppositely charged ions. For instance, the positive electrode expels positive ions and attracts negative ions. This causes a net transfer of positive ions to the negative electrode, and negative ions to the positive electrode, independent of the deionization, reducing efficiency. With membranes in place, the need to maintain electroneutrality necessitates that ions from solution cross the membrane to balance out the counterions, so that counterion desorption no longer causes inefficiency. Charge transfer membranes also dramatically improve device kinetics. When a CDI unit goes in the regeneration cycle without a membrane, it takes a relatively long time for the ions to diffuse out into the waste stream. With a membrane, the need to maintain electroneutrality at each electrode forces the ions to travel through the membrane quickly during the regeneration cycle, improving device throughput. Despite the advantages of adding membranes, they are prone to fouling and degradation, and are expensive. While the continual charge transfer across the membrane is believed to help maintain the surface, prefiltration before the water reaches the CDI unit is necessary. Historically, ED units, which use ion-exchange membranes like those used for CDI, have had device lifetimes limited by membrane longevity. However, electrodialysis reversal (EDR), where the polarity of an ED system is periodically reversed, has shown improved longevity. Since in CDI the polarity is reversed every cycle, this lends credibility to the idea that the membrane will be more robust than in ED. CDI units appear to decrease in water recovery over time due to engineering/ design and membrane issues. It is believed that the space between electrodes increases with time, decreasing the flow resistance of water between the electrodes. This may be from the membrane wearing away during the repetitive charge and discharge cycling, pointing to the need for further membrane development work and improved device engineering. There are very few companies that manufacture membranes specifically for CDI; one notable company is Fujifilm's Netherlands operation. Little published research has focused on characterizing and improving membranes for CDI. CDI's reliability problems are design-related, and therefore can be solved as the technology matures.

2.2.5 Novel materials

While membrane development for CDI has seen little attention, much fundamental research has focused on novel carbon materials for use in CDI. Materials such as nanotubes, graphene and aerogel have been tested for use in CDI electrodes; the interest in novel carbon materials for CDI has been so high that Oak Ridge National Laboratories won an R&D 100 Award in 2011 for creating an ordered mesoporous carbon for CDI. However, activated carbon, at only US$ 4/kg for commodity carbon and US$ 15/kg for highly purified, specially selected supercapacitor carbon, remains much cheaper than the alternatives, which cost US$ 50/kg or more. Larger activated carbon electrodes are much cheaper than relatively small exotic carbon electrodes, and can remove just as much salt for a given current. The performance increase from novel carbons is insufficient to motivate their use at this point, especially since virtually all CDI applications under serious near-term consideration are stationary applications, where unit size is a relatively minor consideration. Figure 3 shows that CDI used as a point-of-entry system for treating incoming water for residential homes.

Figure 3: CDI used as a point-of-entry system for treating incoming water for residential homes.

International Journal of Advance Research in Engineering, Science & Technology(IJAREST),
ISSN(O):2393-9877, ISSN(P): 2394-2444,
Volume 2,Issue 10, October-2015, Impact Factor: 2.125

Figure 4: CapDI

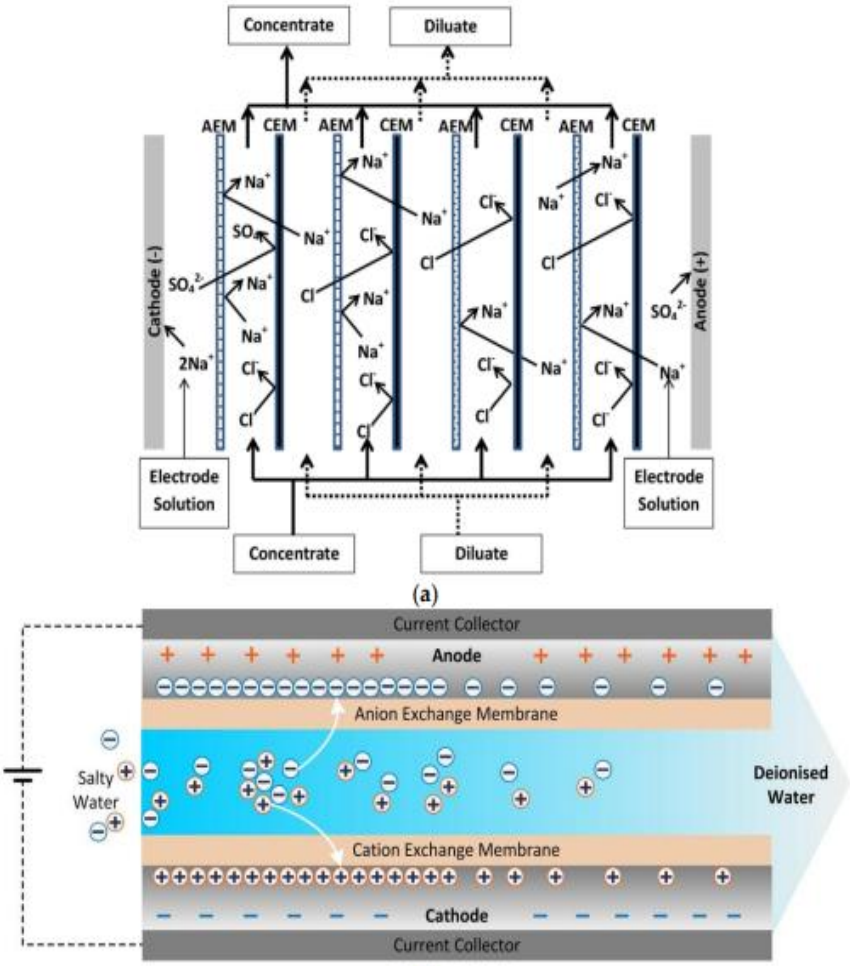

Figure 5: (a) Electro dialysis; and (b) Membrane Capacitive Deionization (MCDI) during adsorption.

Membrane Capacitive Deionization technology CapDI , ions are removed from the feed water by applying an electrical potential difference between two electrodes covered with selective ion exchange membranes. Electrodes are separated from each other by a mesh spacer, whereby water flows and the ions are removed from the feed water (purification step). These removed ions are temporarily stored in the electrical double layers formed at the electrode surface. When the electrodes become saturated with ions, they are regenerated by reversing the applied voltage and/or short circuiting (regeneration step). After the ions have been released from the electrodes, a concentrate stream is produced and captured ions are flushed from the module. It is important to note that ions are removed through membranes and water molecules stay behind.

2.3 Applications

CapDI technology is a chemical-free, low-cost, and environmentally friendly alternative to conventional water softening and brackish water desalination systems. CapDI offers the benefit of electronically adjusting the product TDS level. CapDI is used to deionize water with moderate levels of salt concentration (TDS <4000ppm).

- **Industrial and Commercial applications:** CapDI can soften feed water to boilers and cooling towers, polish tertiary wastewater effluent for reuse and desalinate brackish surface or ground water to make it suitable for industrial reuse. Industrial Systems employ a simple modular design providing flexibility to treat a few liters per minute (LPM) up to hundreds of LPM in a compact footprint. The IS series features real-time, remote monitoring and control capability. Modular designs allow flexibility to meet performance targets in a limited space.
- **Commercial Laundry:** CapDI removes TDS from laundry wastewater at laundering temperatures up to 60ºC/140ºF and recovers up to 90% of the treated water. Addition of CapDI to the treatment system allows recycling without ever reaching the standard operational TDS limit of 1,000 ppm. Reuse solutions work across all laundry intakes, industrial, food and beverage, healthcare and hospitality applications.
- **Consumer Appliance:** CapDI technology offers the freedom and flexibility to customize module size, shape and geometry. It allows consumers the benefits of no-salt softening combined with low TDS for higher water quality. Typical TDS removal is in the range of 50-90% at up to 90% water recovery.

III. CONCLUSIONS

Desalination technologies have become the key solution to overcome the increasing water demand of the population and industrial applications for several decades. Due to its intensive development and attractive features, membrane technology offers new options to achieve energy efficiency and a cost effective desalination process. Improvement in membrane technology including advances in membrane material, module and process design, pretreatment, and energy saving has led to cost reduction which in turn gains interest to its commercial applications compared to other desalination processes. Effective scale-up is a critical point of view to reproduce the success of the membrane-based desalination process from a small-scale experience into a larger one. Accordingly, it is desirable to keep operating parameters constant during scale-up for maintaining performance of the system as operated in a small-scale plant. Moreover, problems related to the process should be carefully investigated during lab scale and pilot scale experiments and considered for improvement of the system design.

REFERENCES

[1] Strathmann H. Ion-Exchange Membrane Separation Processes (Membrane Science and Technology Series 9). Amsterdam: Elsevier, 2004.
[2] Xu TW. Ion exchange membranes: state of their development and perspective. J Membr Sci. 2005;263:1–29.
[3] Pugazhenthi G, Kumar A. Chromium (VI) separation from aqueous solution using anion exchange membrane, AIChE J. 2005;51:2001– 2010.
[4] Huang CH, Xu TW, Zhang YP, Xue YH, Chen GW. Application of electrodialysis to the production of organic acids: state-of-the-art and recent developments (review). J Membr Sci. 2007;288:1–12.
[5] Saracco G. Ionic membrane technologies for the recovery of valuable chemicals from waste waters. Ann Chim. 2003;93:817–826.

[6] Huang CH, Xu TW. Cleaner production by using electrodialysis in organic or aqueous-organic systems. In: Loeffe CV, editor. Trends in Conservation and Recycling of Resources. New York: Nova Science Publishers, 2006:83–97.

[7] Audinos R. Ion-exchange membrane processes for clean industrial chemistry. Chem Eng Technol. 1997;20:247–258.

[8] Xu FN, Innocent C, Pourcelly G. Electrodialysis with ion exchange membranes in organic media. Sep Purif Technol. 2005;43:17–24.

[9] Kameche M, Xu FN, Innocent C, Pourcelly G. Electrodialysis in water-ethanol solutions: application to the acidification of organic salts. Desalination. 2003;154:9–15.

[10] Pourcelly G, Gavach C. Electrodialysis water splitting-application of electrodialysis with bipolar membranes. In: Kemperman AJB, editor. Handbook on Bipolar Membrane Technology. Enschede: Twente University Press, 2000:7–46.

[11] Anderson, M. A., Cudero, A. L., & Palma, J. (2010). Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete? Electrochimica Acta, 55(12), 3845-3856.

[12] Arras, W., N. Ghaffour, and A. Hamou. Performance evaluation of BWRO desalination plant- A case study. Desalination, 235, 170 (2009).

[13] Biesheuvel, P.M. Thermodynamic cycle analysis for capacitive deionization. Journal of Colloid and Interface Science, 332, 258 (2009).

[14] Biesheuvel, P.M., Y. Fu, and M.Z. Bazant. Diffuse charge and Faradaic reactions in porous electrodes. Physical Review E, 83, 061507 (2011).

[15] Cath, T.Y., A.E. Childress, and M. Elimelech. Forward osmosis: Principles, applications, and recent developments. Journal of Membrane Science, 281, 70 (2006)