A brief review on operation of flow-electrode capacitive deionization cells for water desalination

Khadijeh Dehghan, Seyed Ahmad Mirbagheri, Mahdi Alam*

Department of Civil and Environmental Engineering, K.N. Toosi University of Technology, No. 1346, Vali Asr Street, Mirdamad Intersection, Tehran, Iran, Tel. +98(21)88779474; Fax +98(21)88779476; emails: maalam@mail.kntu.ac.ir (M. Alam), khdehghan@mail.kntu.ac.ir (K. Dehghan), mirbagheri@kntu.ac.ir (S.A. Mirbagheri)

ABSTRACT

Since a huge part of the world's population is facing serious fresh water shortage, numerous researchers are working on efficient, cost-effective and environmentally friendly approaches for desalination of seawater (SW) and brackish water (BW) to overcome this problem. The article is focused on flow-electrode capacitive deionization (FCDI), which is considered as an advanced electrochemical desalination method. After reviewing its history, the components and materials used in this system were discussed in detail. The assembling process and the performance of the FCDI system were also addressed. In the end, a prototype of an FCDI system working in batch-mode was assembled. The system performance and the effective parameters on the system efficiency were also introduced by several experimental tests.

Keywords: Electrochemical water desalination; Capacitive deionization; Flow-electrode capacitive deionization; FCDI cell assembling

1. Introduction

Water is the most essential element of life with a significant role in all aspects of human lives including socio-economic development. While about 75% of the earth is covered by water, 97% of these waters are in the seas and oceans; according to volume of stored water in glaciers, and saline surface and groundwaters (inaccessible), leaving only less than 0.5% as the ready-to-use fresh water [1,2]. On the other hand, about 25% of the world's population do not access potable water at proper quality and quantity; and more than 80 countries are dealing with water crisis [3]. Furthermore, water resources of the world are diminishing due to the population growth–induced rising global demand for water, insufficient fresh water in various regions, industrial and agricultural developments, and contamination of the surface and groundwater. In this way, providing healthy, safe, inexpensive, and energy-effective water has been considered as one of the serious challenges

of the human societies, and in this regard, the 21st century is named the century of water [4].

Rising demand for water and reduction of the fresh water resources have guided the human to develop various wastewater treatments and re-usage of water (treated urban and industrial wastewaters) as well as the desalination of seawater and brackish water [5,6]. Conventional wastewater treatment processes separate the nutrients and organic matters from the wastewater, but they cannot eliminate the dissolved salinity of the treated effluent. The application of these treated effluents in the agriculture sector will increase the soil salinity and damage the crops. Therefore, to achieve usable water from the treated effluents, desalination should be conducted in addition to the conventional wastewater treatment methods. Furthermore, the desalination of sea and ocean waters can significantly contribute to the worldwide supply of fresh water as these two (seas and oceans) account for the highest portion of the available water. Desalination of the underground brackish water and

* Corresponding author.

industrial wastewater can also help in the combat against the shortage of natural healthy water.

In this paper, different desalination technologies are introduced at first. Then, among them, one of the newest desalination technologies with the very low energy consumption, known as flow-electrode capacitive deionization (FCDI), will be presented and its various components will be described. In the end, one prototype of this system will be assembled and its deionization (i.e., desalination) process will be examined.

1.1. Desalination technology

Desalination means the elimination of different types of salinities and minerals from salt and brackish waters. In fact, desalination is aimed to transform salt and brackish waters into the suitable waters for human uses. Evaporation of the seawater and its conversion to rain is one of the natural examples of desalination with millions of years old. Another natural desalination process occurs near the polar regions of the earth; where the seawater is frozen giving rise to the growth of ice crystals. As the ice crystals are produced from pure water, their salts will be eliminated giving rise to a desalination process. The history of man-made desalination dates back to 300 BC–200 AD [7]. At that period of time, sailors employed the distillation process (boiling seawater, its evaporation, cooling and finally condensation) to provide their required fresh water. This method has been used for many centuries. In 1565, Jean De Lery reported seawater desalination during his sea travel to Brazil [7]. In 1627, Sir Francis Bacon employed sand filters to desalinate seawater; his attempts later significantly helped the subsequent developments in water treatment and desalination [8]. In the mid-18th century, steam power provided the platform for the development of desalination and evaporation–condensation became a common desalination technique at the early 1900 [7].

Desalination plants became commercialized in 1960 most of which relied on thermal processes. Multi-stage flash (MSF) distillation was one of the most applied thermal procedures in the commercialized desalination units. In the late 1960s, membranes entered into the desalination market and reverse osmosis (RO) emerged one decade later [7]. Till 1980, both thermal and membrane-based desalination had become commercialized giving rise to a substantial increase in the global fresh water production capacity [7]. In 1960, only five desalination units could be found throughout the world; while in the year 2000, 16,000 desalination units worked in more than 120 countries [9]. This indicates the increasing significance of desalination in water provision during the last decades. Currently, more than 75 million people supply their potable water through desalination of salt or brackish water [2].

Nowadays, the desalination procedures are of crucial significance in some parts of the world in a way that its application is more cost-effective in comparison with the other conventional water resources and water transfer techniques. For instance, over-extraction from the groundwater (wells) has resulted in the penetration of seawater into the wells in several countries such as Bahrain, Qatar, UAE, Oman, Saudi Arabia and Kuwait. These countries are now supplying their water from wastewater treatment and seawater desalination [2,7,10]. In numerous countries such as India, China and African countries, aquifers are the major source of potable water. By increased application of groundwater, the entrance of seawater to these aquifers is one of the major issues of these countries. In this regard, desalination can serve as one of the undeniable solutions for fresh water provision [7,9,11–13].

Currently, various types of desalination processes can be found worldwide. Regarding the World Health Organization (WHO) allowed amount of total dissolved solids (TDS) for drinking water (500 mg/L), desalination techniques should decline TDS of the water to 500 mg/L or lower [4]. The desalination techniques can be classified into four groups:

- Phase change processes including evaporation, distillation and freezing methods (thermal processes): these processes mainly include MSF distillation, multi-effect distillation (MED), mechanical vapor compression (MVC), thermal vapor compression (TVC), solar distillation (SD), humidification–dehumidification desalination (HDH) and freezing–melting (FM). This class of desalination processes uses heat transfer to convert sea and brackish water to fresh water. In other words, these processes exploit heating of the feed water to the boiling point or heat extraction from feed water to the freezing point to transform the feed water into steam or ice, respectively. In this way, salts will be separated from the feed water for the production of fresh water.
- Non-phase change processes (single-phase or membrane processes): this class of processes refers to the separation processes in which the dissolved salts will be separated by mechanical or chemical/electrical means. In these apparatuses, a membrane is placed between the feed water (sea or brackish water) and the product (fresh water). Electrodialysis (ED) and RO are among the most well-known techniques in this field. Forward osmosis and nanofiltration (NF) could be also classified in this group.
- Chemical desalination processes: ion-exchange desalination (I.Ex), liquid–liquid extraction (LLE) and gas hydrate (G.Hyd) are among the processes in this group.
- Hybrid processes: these processes are a combination of the phase change and separation techniques. Membrane distillation and RO in combination with MSF distillation or MED are among the methods of this group.

RO process accounts for more than 60% of the global desalination capacity [3,14,15]. After that, MSF distillation (23%–26%), MED (8%) and ED (3%–4%) have gained the next ranks [7,16–19]. Desalination processes are generally high energy-consuming. This energy is mainly supplied by fossil fuel, which will result in environmental consequences such as greenhouse gas emission, production of harmful gases, and air pollution. For seawater desalination, although thermal processes have high fresh water production capacity, their high energy consumption has increased their associated cost. Moreover, their contamination is also higher compared with the methods with lower energy consumption (such as RO, 1–3 kWh/m³) [20].

TDS is another important effective factor in the cost of seawater desalination [3]. The lower the TDS of water, the lower the energy consumption of its desalination process will be. Thus, the cost and environmental consequences will be declined for low-TDS waters [13]. Therefore, in the regions with brackish groundwater, desalination of low-TDS waters has priority over the seawater desalination. Membrane processes such as RO are mainly used for the desalination of brackish water. Besides the superiorities of the membrane methods (such as RO), these systems have their own drawbacks. As these systems involve compressive passing water through the osmosis membrane (the filter separates impurity ions from the feed water), these methods are highly energy demanding. On the other hand, these membranes have a limited lifetime and must be replaced in 2–5 years. Moreover, their maintenance is costly and troublesome [21].

Currently, in addition to RO, ED (as another membrane process) is extensively employed in commercial water treatment processes. An ED cell includes several pairs of anion and cation exchange membranes (CEMs) placed between a pair of planar electrodes (anode and cathode). Similar to the RO process, ED also requires pre-treatment to decrease the fouling and membrane deterioration. In addition, regarding the high electrical voltage of this process, the ED can result in high gas emission. Although the mentioned processes are currently employed in the desalination sites worldwide, their high energy consumption combined with their high costs (initial costs, implementation, and maintenance) and environmental impacts have resulted in intense studies on the innovative desalination technologies.

Capacitive deionization (CDI) is one of the promising methods with low energy consumption. In this context, the first part of this paper is devoted to the introduction and history of this process and its different modes of application, the second section addresses the different components of a pilot set up flow-electrode capacitive deionization (which is one of the latest processes of this innovative technology). The final section of this paper presents the results of some basic experiments on the developed pilot.

1.2. Capacitive deionization

CDI process is one of the electrochemical processes in sea and brackish water desalination, which has recently attracted a huge deal of interest. Its low energy consumption is one of the most important features and the major reason for its superiority over the other desalination processes such as RO, ED and thermal processes [15,22–24]. In addition to desalinating sea and brackish water, CDI has some other applications such as electrochemical desalination of wastewater [12], water softening [22,25] and eliminating weak acids such as boric acid from the treated water [22].

CDI is a water treatment method (eliminating the ions in water) with no need for chemicals and high energy consumption, and no production of secondary pollution. Therefore, CDI has been regarded as an innovative, cost-effective, and environmentally friendly technology with a high recovery rate and energy efficiency (0.5–1 kWh/m^3) [20], which can be employed to remove charged ionic species from the aqueous solutions. In electrochemical desalination methods (such as CDI), the minority compound (salt ions) of the feed water will be removed from the solution. However, the other desalination methods eliminate the majority phase (water) from the salt–water solution [18,22]. In continue, first, the formation and development of the CDI technique will be investigated, then the features of this technology, as well as its performance, will be addressed.

Faraday started the electrochemical experiments in the liquid environment in 1833–1834 [26,27]. Later, in 1900, Gibbs invented an electrolyte apparatus capable of producing chlorates from the aqueous solutions using electrical current [14]. This invention provided the platform for the development of CDI. The concept of CDI was first introduced by W. Blair, Murphy and their colleagues under the title of electrochemical demineralization of water [28,29]. Several years later, Evans and Hamilton (1966) investigated this mechanism; the demineralization process was first mathematically described by Murphy and Caudle in Oklahoma university in 1967 [29]. In this regard, the highest development in the field of CDI can be assigned to the works done by Caudle and Johnson (with Newman) in the 20th century. They were the first group to establish the concepts of flow-through capacitor system and electrochemical demineralization of water using porous carbon electrodes in 1966 and 1971, respectively [14,28]. In the early 1970s, Oren and Soffer [30], Oren and Folman [31] and Oren and Softer [32] further studied this topic following the EDL theory concept, which is still going on. Besides the extensive researches to improve the CDI system performance and updating that, huge efforts have been devoted to commercializing this technology.

The initial commercialization attempts date back to the 1990s [22]. At that time, numerous studies were aimed to develop and improve the effective carbon-based materials used in the water deionization process. Among these works, Farmer et al. [33,34] in LLNL (Lawrence Livermore National Laboratory, USA) managed to develop carbon aerogel-based materials, which can be applied as the electrode in CDI system; although they had low salt adsorption capacity (SAC) [33,34]. Carbon aerogels have considerable properties among which monolithic structure, large internal surface area, and good conductivity can be mentioned. As a result, carbon aerogel electrodes are considered superior to activated carbon electrodes and have attracted a lot of scientific and technical interests. The title of CDI was also proposed by Farmer et al. [33,35] in 1996; since then, the CDI process has gained considerable attention. One of the largest and most comprehensive experiments on the CDI process was conducted by Welgemoed and Schutte with a daily capacity of 3,785 m^3 [36].

Generally speaking, CDI technology can be very helpful in the separation processes. Voltea (The Netherlands) is one of the major producers of the CDI system which declared its commercialized version before 2012 [14].This company developed membrane capacitive deionization (MCDI) systems for domestic and commercial applications [37]. EST water and Technology also develops large-scale CDI systems for industrial applications (such as power plants, petrochemical industry, urban groundwater treatment, fluorine and arsenic elimination from brackish water, and paper, steel and fertilizer factories). In addition, more

than 30 industrial CDI systems were installed in China [22]. Currently, CDI technology is one of the innovative desalination techniques, which has gained a huge deal of attention. This technology does not require membrane replacement (due to membrane fouling and deterioration), has no secondary pollution and is energy-effective (consumes lower electrical energy compared with the conventional desalination techniques) [1,21,22]. Thus, CDI can be regarded as an environmental friendly process with no secondary pollution.

CDI is an effective electrochemical process for elimination of anions (such as nitrates (NO_3^-), sulfates (SO_4^{2-}), chlorides (Cl^-), fluorides (F^-) and arsenates (AsO_4^{3-})), and cations (e.g., calcium (Ca^{2+}), potassium (K^+), magnesium (Mg^{2+}) and heavy metal ions such as chromium (Cr^{3+}), lead (Pb^{2+}) and cadmium (Cd^{2+}) from aqueous solutions [12,17,38]. In fact, capacitive deionization involves two sections: deionization and capacitive parts. The deionization section deals with atoms and charged molecules elimination (in the form of ion); while the capacitive part is related to the capacitive properties of the electrodes, which can help in the ions elimination.

A capacitor includes one or more pairs of oppositely charged electrodes. In conventional CDI technology, the feed water passes through the spacer channels and an electric potential difference is applied to the porous carbon electrodes (anode and cathode forming the positive and negative poles, respectively). In this way, the dissolved salt molecules with positive and negative ions will be adsorbed to the negative and positive electrodes, respectively. These undesirable ions will be then collected in the carbon material pores [12,14,21,38]. In fact, CDI technology relies on the ions adsorption in the electrical double layers (EDLs). In other words, when the electric field is applied to CDI cell, electrodes produce EDLs around their surface (in the electrode–solution interface) [21,39,40]. The charged ions in the feed water will be transferred to EDLs and stored within them (the porous electrode), which this process is known as the electromigration. This will ultimately deionize the saltwater [16,18,41,42]. The motion of the ions from the feed water to the charged electrodes is called ion electrosorption.

The interesting point in conventional CDI technology is that the applied electrical potential difference to EDLs should not exceed 1.23 V (Nernst voltage) as the higher voltages will break down the H–O bonds in the water molecule (hydrolysis) [14]. To compensate for the circuit system resistance, the electrical voltage applied to the CDI cell may exceed 1.23 V but no hydration reaction (i.e., hydrolysis) occurs. This could be due to the fact that the threshold of Nernst voltage is specific to the local potential difference experienced by the water molecules [14]. Based on the previous works on conventional CDI, the porous electrode pairs are generally charged by the DC voltage in the range of 0.6–2 V [12,22]. So far, various cell architectures of capacitive deionization have been developed to be applied in CDI cells: (1) flow-by: this architecture includes two electrodes separated by a spacer channel (the feed water pathway). This is the most common architecture for the CDI reactors. (2) flow-through architecture in which the feed water is directly flown through the electrode macropores. (3) membrane CDI (MCDI) is a combination of CDI with ion-exchange membranes, and (4) flow-electrode capacitive

deionization where flow-electrode technology is used instead of fixed electrode.

In general, the water desalination by conventional CDI involves two periodic stages: ion electrosorption (deionization) and the second stage which includes the desorption step. The first stage involves the adsorption and charging of the ions within a pair of porous carbon electrodes. After a while, the accessible pores of the electrodes will be saturated by the adsorbed ions and their storage capacity will end. In the second stage (discharging), the ions will be discharged from the electrodes by declining the applied voltage or reversing that. The discharged ions will then immediately enter the CDI effluent; this stage is the desorption stage, which will regenerate the carbon electrodes. Therefore, a salt-containing stream (known as brine stream) will be generated and the ion adsorption capacity of the electrodes will be returned to their initial value. This reversibility is merit against the other desalination techniques. Fig. 1 schematically illustrates the conventional CDI process.

1.2.1. Electrode materials and features

The material used for the fabrication of the electrode plays a crucial role in the electrochemical separation processes (e.g., CDI) as it can affect the desalination and fresh water production capacity [17]. Application of the porous carbon electrodes for water desalination dates back to the 60s and 70s when the initial studies on CDI were started. At that time, activated carbon (AC) was employed for the fabrication of the porous electrodes [18]. As mentioned before, Farmer et al. [33,35] in Lawrence Livermore National Laboratory (LLNL), California, were the first group who applied carbon aerogel in the electrode for water deionization. They showed that the electrosorption process by the carbon electrodes is capable of removing different ions such as sodium and chloride from the aqueous solutions.

High specific surface, proper electrical conductivity, high porosity, capacitive properties and good particle size distribution are among the most prominent characteristics of the carbon electrodes in CDI process. Various carbon-based materials have been employed as the electrodes in CDI such as activated carbon [23,43,44], mesoporous carbon [23,44], graphene [24,44] and carbide-derived carbon [17] can be mentioned. Owing to their high specific surface area and porosity as well as proper electrical conductivity, these materials possess high ion adsorption capacity. Among them, AC has been widely used for the fabrication of the CDI electrode. This material, however, suffers from several drawbacks such as not high conductivity and irregular porous structure.

Since electrodes could have a substantial influence on the performance of CDI cell, some innovative materials such as nanoporous carbons, carbon aerogels (CAs), fullerenes, carbon nanotubes (CNTs), multi-walled CNTs, graphene oxide, modified composites including TiO_2 and carbon nanofibers can be exploited in the fabrication of the electrodes [12,22–24,45]. These materials have high specific surface area and high conductivity along with regular porous structure, which can improve the performance of CDI cells.

According to the studies, carbon aerogels are highly porous with high surface area and low electrical resistivity
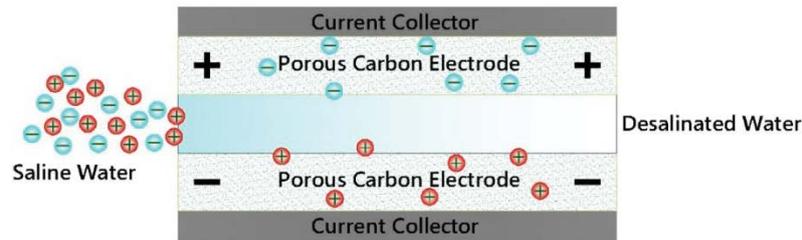
Fig. 1. Schematic view of conventional CDI process.

and controllable pore size distribution. As mentioned earlier, CNTs are among the modern materials used in the fabrication of the electrodes. Zhang et al. [46,47] fabricated a new type of CNTs that can be employed in the desalination of saltwater. They combined activated carbon with CNTs and employed them in the fabrication of the electrode [46,47].

In order to improve the carbon-based materials for the fabrication of electrodes and enhance the CDI performance, Ryoo and Seo [48] modified the activated carbon cloth with titania. Concerning electrosorption deionization technologies, high fabrication costs of electrodes have limited the transformation of the experimental systems into the industrial-scale systems. At large-scale applications, activated carbon has found an extensive application in the commercialized systems due to its cost-effectiveness [17,18,21,44]. For instance, the fabrication cost of the commercial ACs is lower than the carbon aerogels. Thus, the use of ACs can facilitate the transformation for the experimental systems into the industrial scale [21]. In the meantime, some attempts have been devoted to modifying the carbon aerogels synthesis to lower their fabrication cost; among which the work by Alam et al. [49,50] for preparing carbon xerogel (a subcritically dried carbon gel) can be mentioned.

1.3. Membrane capacitive deionization

Conventional CDI process is challenged by the co-ion effect, which can restrict its industrialization [23,42]. Due to the electrostatic force, the counter-ions will be temporarily adsorbed to the pores on the electrode surface upon the application of the electrical potential to CDI cell in the ion adsorption stage. Co-ions will be simultaneously desorbed from the electrode. This indicates that adsorption–desorption processes simultaneously occurred in the EDL (on the CDI electrode surface). Mobility of the undesirable ions results in high energy consumption, low electrosorption capacity and leading to declined salt removal efficiency [19,23,41,45,51]. To solve this problem, a CDI system was proposed by Andelman and Walker in 2002 [52], which was then scientifically developed by Lee et al. in 2006 [53] and named MCDI. In fact, by adding ion-exchange membranes to conventional capacitive deionization system, they modified the CDI cell.

Similar to conventional CDI process, in MCDI, counterions will be adsorbed within the EDLs (inside the micropores formed in the porous carbon electrodes) due to the application of the electrical voltage in the ion adsorption stage; the co-ions are, however, desorbed from these micropores. In conventional CDI process, these co-ions

enter the spacer channel and decline the desalination performance; while in MCDI, ion-exchange membranes are placed in the vicinity of the electrodes and hinder the release of the repelled co-ions from the surface of electrodes (i.e., micropores). Therefore, these co-ions enter the macropores of the electrode and could be stored there. The concentration of these co-ions is higher than those of conventional CDI process entering the spacer channel. Co-ions of macropores should be neutralized. Thus these co-ions lead to the accumulation of counter-ions inside the macropores.

During MCDI, in addition to the adsorption of counterions in the micropores, their excess amounts will be accumulated in the macropores; therefore, its salt concentration will be higher than that of the spacer channel. Therefore, in the MCDI process, macropores are the most important factor in the increase of ions adsorption capacity relative to conventional CDI process that during the ion adsorption stage, macropores have no salt-storing capacity [18]. Therefore, in MCDI, the ion-exchange membranes will cause higher salt storage in the electrode macropores relative to conventional CDI process; they also enhance the desalination efficiency and save energy.

In the MCDI process and in the ion desorption stage, counter-ions can completely detach from the electrodes. In this process, the membranes generally inhibit the co-ions transfer while the counter-ions are free to move toward or from the electrodes [51]. An MCDI system is generally composed of two solid porous electrodes, anion exchange membrane (AEM) and CEM. MCDI electrodes are often static and plate-shaped; the AEM and CEM are placed near the porous anode and cathode, respectively. Ion-exchange membranes can select between the ions penetration based on their type (cation or anion); in other words, ion-exchange membranes are ion-selective. This means that a CEM only allows for cations penetration while the AEM only permits anions exchange. Similar to ED, in an MCDI cell, the feed water channel is surrounded by the anion and CEMs and the feed water passes through a spacer between the two membranes. Upon applying electrical voltage to MCDI cell (between the two electrodes), the cations and anions of the electrolyte will be adsorbed to the porous carbon electrodes and stored inside them. Fig. 2 presents the schematic view of MCDI system.

1.4. Other architecture of CDI

As mentioned before, the CDI system has immobile electrodes. During desalination operation, the salt ions will be adsorbed on the surface of the electrodes until their
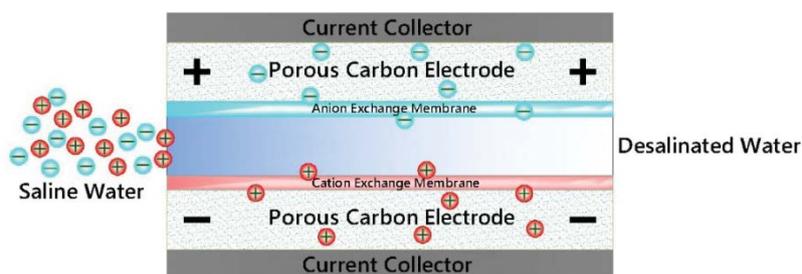
Fig. 2. Schematic representation of MCDI process.

saturation. Regarding the limited volume of the pores and size distribution of the active particles in the fixed electrode, the performance of conventional CDI process is limited. When the pores are saturated by ions, the electrodes should be regenerated to be able to remove the ions again. In other words, the conventional CDI cell can continue desalination operation until the saturation of the electrodes pores. The important point is that during a discharging step (ion desorption), the desalination process should be stopped to prepare the CDI cell for the subsequent cycles. In other words, conventional CDI systems periodically perform the electrical voltage application stage (ion adsorption) followed by a short circuit stage (regeneration or ion desorption). Due to electrodes regeneration inside the same cell, conventional CDI systems have semi-continuous or discontinuous performance [43].

As mentioned earlier, initial conventional CDI systems do not operate in continuous mode. Thus, huge efforts have been devoted to resolving this issue while maintaining the overall architecture of the process [54–62]. Among these attempts, the works by Smith and Dmello [63] in 2016 and Arulrajan et al. [64] in 2019 could be mentioned.

In the conventional capacitive deionization processes, cation and anion porous carbon electrodes are often used. In 2016, Smith and Dmello [63] proposed a novel design for CDI cell in which two cation-selective electrodes and one AEM were employed between two flow channels. In the mentioned CDI cell, when anions passed the AEM, cations are simultaneously adsorbed in one electrode while the cations release occurs in another electrode. Therefore, in the first instant, the first and second channels produce desalinated and concentrated streams, respectively. For reversed current direction, the first channel will produce brine water while the second one will generate water of lower salinity. Thus, this CDI cell continuously produces desalinated water [63].

In 2019, Arulrajan et al. [64] extended the work of Smith and Dmello and used another design of CDI cell comprising two anion-selective electrodes and one CEM, which was capable of continuous desalination.

In their work, they fabricated new anion-selective electrodes through chemical modification of the carbon electrode. Using this electrode, they managed to achieve excellent CDI performance. In other words, Arulrajan et al. showed the effectiveness of the low-porosity carbon electrodes in improving the efficiency of the CDI process [63,64].

In addition to the studies conducted by Smith and Dmello and Arulrajan et al. to improve the CDI process to transform the conventional CDI system into continuous ones, another capacitive deionization process known as FCDI can be employed which also works in continuous mode.

1.5. Flow-electrode capacitive deionization

As mentioned before, to overcome the periodic performance of the conventional CDI system (charging/discharging), a system was investigated, designed and evaluated based on flow-electrodes, which was entitled FCDI [22,42,43,65,66]. FCDI is a new, energy-efficient, and sustainable saltwater desalination technology with high effectiveness in the ion transfer and adsorption inside the EDLs (formed inside the electrode materials such as AC particle).

Serious studies on FCDI started in 2013. Gendle, Rommerskirchen, Hatzell, Hatzell, Porada, Doornbusch and Yang et al. have studied FCDI systems [10,51,67,68]. Jeon et al. [66] also conducted some studies on FCDI to overcome the limitations of the CDI process. They investigated flowable suspension electrodes as an alternative for the electrodes of MCDI systems [66]. FCDI system includes anode and cathode flow-electrodes in the pathway carved on the current collector plates. These electrodes are a suspension containing carbon materials (usually AC), which play the role of fixed porous carbon electrodes on the current collectors of conventional CDI processes. Thus, contrary to the electrodes in the conventional CDI and MCDI systems (made from solid porous carbon), the electrodes in the FCDI system are slurry-type and hence mobile.

The application of flow-electrodes can increase accessible carbon materials for salt ion adsorption. This can explain the substantial ion-adsorption capacity of the FCDI system (due to the presence of flow-electrodes) compared with the conventional CDI systems with limited-capacity fixed electrodes [66,69]. In fact, the FCDI system can desalinate feed waters with higher salt concentration as compared with the static CDI systems. Therefore, the desalination capacity of FCDI is higher than that of the conventional CDI and MCDI processes.

FCDI has a continuous desalination system with high desalination efficiency. For example, Jeon et al. [66] achieved more than 95% sodium chloride removal efficiency for the feed water with NaCl concentration of 32.1 g/L [66]. The continuous performance of FCDI has numerous advantages such as optimized system performance, simpler system design (relative to the classical systems), simpler system operation, higher energy efficiency, and a more sustainable system at lower costs [69].

In contrary to conventional CDI, in the FCDI, the deionization and regeneration do not occur in a single unit. In fact, in an FCDI system, instead of discharging the ions in the same cell, the suspension carbon electrodes can be directly and continuously mixed with each other outside the FCDI cell, which will result in spontaneous discharge and release of salt ions and hence electrodes neutralization. Therefore, in the FCDI system, water desalination and anode and cathode regeneration are continuous and simultaneous. This feature has made the FCDI a proper technology for large-scale industrial applications (i.e., FCDI is highly scalable). As mentioned before, the geometrical design of the FCDI cell is similar to the MCDI cell; the only difference is the distribution of the flow-electrodes (aqueous suspension containing carbon materials) in two channels instead of the fixed electrodes in the conventional MCDI systems. Each of these two electrodes flows between an ion-exchange membrane and a current collector. Moreover, a spacer channel is embedded in the middle part of the FCDI cell to prevent the mixing of the three fluids (anode, cathode and feed water). In order to create a pathway for the flow-electrodes, meandering flow channels are carved on the current collector plates.

Numerous attempts have been devoted to improve the desalination rate of the FCDI process. For instance, modifying the chemical properties of the electrodes surfaces, using fluidized bed electrodes to increase the weight percentage of carbon electrodes, optimizing the salt concentration of the flow-electrode electrolyte, and also the residence time of saltwater in the system [42]. Enhancement of the electrical voltage applied to an FCDI cell can substantially increase its desalination rate [42].

The studies on FCDI were further extended by Hatzell et al. [10] who developed a new type of FCDI system to desalinate sea and brackish water. In fact, they proposed an innovative CDI process that was completely based on ion removal using the flowable carbon suspensions without the presence of the ion-exchange membranes, which includes filtration step (application of porous separator instead of the ion-exchange membranes) [10,40,70]. Based on the abovementioned discussions, it can be said that the FCDI technology is one of the latest architecture of the CDI technology for water deionization.

In continue, the assembling of an FCDI system operating under batch-mode will be described in detail; then the stages and components of our FCDI system will be completely explained. At the end of this paper, we tried to evaluate the performance of this FCDI system by several simple and basic tests.

2. Different parts of an FCDI cell

A lab-scale FCDI system generally includes a pair of current collectors, ion-exchange membranes, middle silicon-based gaskets and spacer, a pair of end plates, flowable suspension electrodes, peristaltic pumps, DC power supply, feed water and electrodes reservoirs and several joints (e.g., screws, nuts, washers and hoses). The mentioned components are often assembled as an FCDI cell as shown in Fig. 3.

2.1. Current collectors

The current collector plates should have two major properties: sufficient conductivity to pass electrical current and transfer the electrical charges to the flowable suspension electrodes; and resistance to corrosion due to application of electrical current. If the current collector plate is
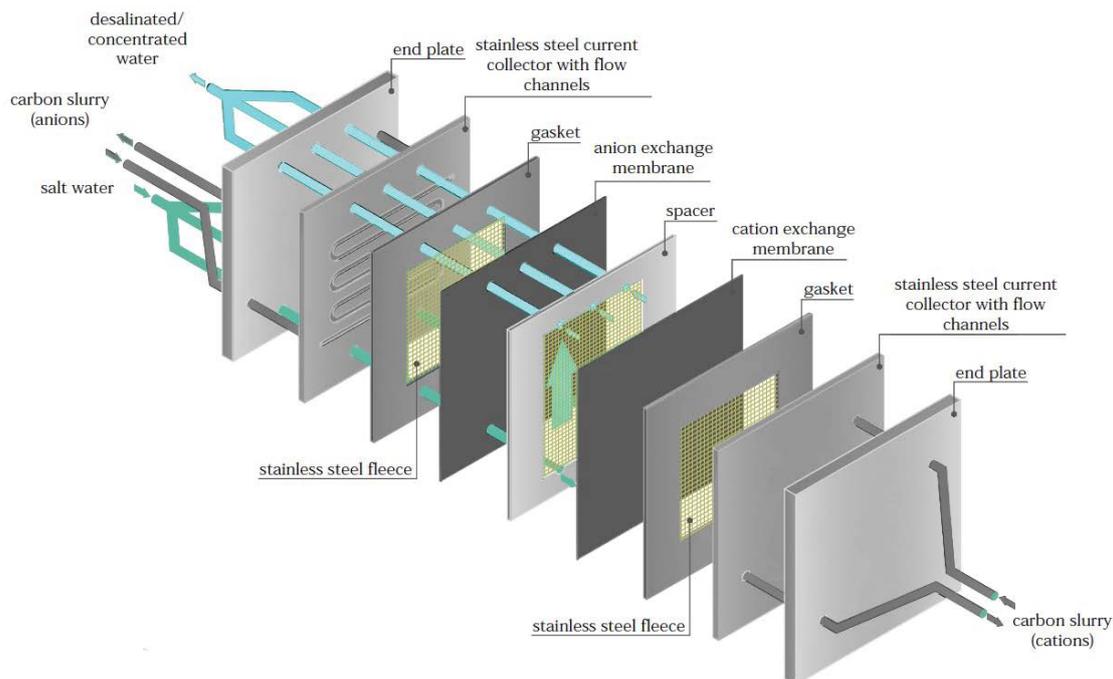

Fig. 3. Structure of an FCDI cell.

made of porous materials, its porosity percentage should be adjusted in a way to prevent leakage and water penetration from the FCDI cell. The material of these plates should be selected carefully to provide sufficient strength against the applied pressure during pathways carving and the components assembly. Graphite current collectors [67,71–77], stainless steel plates [15,66,68,78], composite current collectors that were made of graphite paper and acrylic sheets [79] and titanium plates [80] are among the current collectors, which have been applied so far. The majority of the lab-scale FCDI systems use graphite plate as the current collector since the electrical conductivity and corrosion resistance of graphite are higher than the stainless steel. In the case of using graphite plates as the current collectors, the water leakage and penetration should be avoided from the pores of these plates.

2.2. Flow-electrode channels

In the FCDI process, meandering flow channels (serpentine flow channels) are carved on the current collector plates as a pathway for flowable suspension electrodes. The design of these channels is of crucial significance. For instance, if the depth of the flow channel is so high, the lower effective surface of the active electrode materials will be in contact with the membranes. In other words, the electrodes may lose the deionization chance at high depths, which will decline the desalination efficiency. Increased flow channel width or the enhancement in the area of the flow-electrode current pathway may decrease the current velocity and increase the sedimentation chance of the flow-electrode particles, which will reduce the desalination efficiency. The dimension of the channels should be also compatible with the size of flow-electrode particles and the electrodes flow rate to avoid the particles sedimentation and channels fouling. Since the effective contact surface of the flow-electrode and ion-exchange membrane is directly related to the desalination efficiency; we defined a parameter as the coefficient of the effective area between the flow-electrode and ion-exchange membrane according to Eq. (1).

$$C_A = \frac{A_{eff}}{A_c} \tag{1}$$

In the above equation, A_{eff} shows the effective contact area between the ion-exchange membrane and flow-electrode; A_c denotes the area of the current collector on which the flow-electrode channels are carved (if the current collector surface dimension is defined as width × length, the flow-electrode channels are carved on this rectangular surface (A_c); and C_A represents the effective area coefficient. The effective area between the ion-exchange membrane and flow-electrode is a function of the carved channels' width and length. For instance, Yang et al. [77] considered this coefficient as 0.67. This coefficient can be regarded as a measure of the net effective surface involved in the ion exchange process between the feed water and the flow-electrodes.

2.3. Ion-exchange membranes

Ion-exchange membranes include the anion and cation exchange membranes and have been widely used in the separation processes. These membranes are ion-selective; this means that only cations can penetrate through the CEM; while the AEM only allows for anions penetration. Therefore, in the FCDI process, the ion-exchange membranes located near the flow-electrodes are selective toward the ions penetration during the charging and discharging stages.

In FCDI desalination, IEMs can enhance desalination efficiency. In this process, electrical insulator ion-exchange membranes are placed at both sides of the feed water pathway (between the feed water and electrodes) and prevent mixing of the three streams (anode and cathode electrodes and feed water).

Various IEMs with different properties, thickness and qualities have been produced for diverse applications. According to the previous studies, the CDI membranes are often the products of companies such as Fumatech (Germany) (thickness of 90–120 μm) [15,43,68,70,81–84], Astom Co., Japan [76,85,86], Tianwei Membrane Technology Co., Ltd., Shandong, China (thickness of 280 μm) [42,80,87,88], FUJIFILM Europe (thickness of 125, 135 and 160 μm) [72,77,79,89,90], Asahi Glass, Japan (thickness of 110–150 μm) [65,67,81], Tokuyama Co., Japan (thickness of 110–200 μm) [40,41,51,66,69,73,81,91–94] and Beijing Ting run Membrane Technology Development Co., Ltd. (thickness of 160–230 μm) [95].

2.4. Gaskets and spacers

The spacer chamber is one of the essential components in the assembly of the FCDI cell. It is composed of a silicon gasket and a spacer with a definite thickness placed between the cation and anion exchange membranes. The purpose of placing this middle silicon gasket is to prevent short circuit between the two current collectors after application of the electrical voltage. This gasket provides space for water circulation (water chamber) and also insulates the two cation and anion exchange membranes as well as sealing the FCDI cell. The spacer also serves as the feed water pathway. The samples used as gasket are often made of silicone rubber [40,72,76,77,79,88–90], rubber [45,68], latex [78,96] and nylon [87]. The spacers of the gaskets are often made of polyester [40,72,76,77,88,89], nylon sheet [79,90], polyvinyl chloride (PVC) [68], rubber/nylon [45] and polyurethane sponge [91].

2.5. End plates

Similar to the CDI and MCDI processes that use end plates, in FCDI, the components are assembled beside each other by two plates. In fact, end plates serve as the holders of the cell components. Various materials have been employed as the end plate among which PVC [40,68,72,76,83,87,88], stainless steel [77], rigid plates of high-density polyethylene (HDPE) [65], acrylic end plate [79], polyethylene end plates [84] and polycarbonates [75] can be mentioned. If the current collector plate has sufficient strength (e.g., when the current collector is made of stainless steel), it can serve as the end plate as well.

2.6. Peristaltic pumps

In the FCDI system, the feed water flow rate is an effective parameter in the desalination efficiency of the

system and its performance. Porada et al. [69] investigated the effect of residence time on the salt removal efficiency and salt removal rate. They found out that salt removal efficiency could be increased by declining the feed water flow rate (enhancing the residence time of the feed water) [69]. They also revealed that extremely low flow rates could decrease the salt removal rate. Therefore, the choice of the flow rate in a reliable range can significantly affect system efficiency. Fig. 4 represents the results obtained by this research group.

The results obtained by Lee et al. [53] on the MCDI system in 2006 also indicate that the salt removal rate depends on the residence time of the solution on the electrodes, and higher removal rate requires more residence time [53]. The feed water flow rate of the studies on CDI, MCDI and FCDI was less than 100 mL/min [15,22,43,53,74,77,86,93,94,97–101]. In FCDI, in addition to the feed water flow rate, the flow rates of the flow-electrodes can also affect desalination efficiency. During the FCDI processes, the flow rates of the flow-electrodes were up to 250 mL/min. This value could be further extended but as a general conclusion, it can be said that in most of the FCDI studies, the flow-electrode flow rate should be higher than that of the feed water [15,22,43,70,77,83,94,102].

Regarding the flow rates considered for the feed water and flow-electrodes in the lab pilot scale, such flow rates should be provided by high-precision laboratory pumps. The peristaltic pump is one of the best pumps for this purpose. This pump can be classified as a positive displacement pump capable of pumping various fluids. In these pumps, the fluid is trapped in a flexible tube placed within the circular chamber of the pump. The rotor of the pump is responsible for compressing the tube. A rotor with two or more rollers attached to the external circumference of the rotor, compresses the tube. When the rotor turns, a part of the tube under compression will be occluded that results in fluid motion within the tube. This process is called peristalsis. The fluid circulation rate inside the peristaltic pump can be adjusted. This type of pump is benefited from several advantages: (1) capable of operating under dry condition, (2) high suction, (3) able to pump highly toxic and corrosive materials, (4) low-cost and simple repair and maintenance, (5) facile installation and implementation, and (6) high precision at any flow rate. These pumps have been developed for diverse flow rates.

2.7. Power supply

In the FCDI process, DC power supply is considered as the source of electrical energy to provide the cell voltage. A controllable power supply can adjust the output voltage or the current at a specific value. In fact, in this process, an electrical voltage could be applied to the current collector plates by an external power supply to charge the current collectors and electrodes, hence move the ions from the aqueous solution to their counter-flow electrodes (cations to the cathode and anions to the anode). In general, the electrical voltage applied to the FCDI cell should not exceed 1.23 V as it can hydrolyze the water [42,45,101].

Liang et al. [42] applied voltages higher than 1.23 V to the FCDI cell to achieve higher desalination rates. These electrical voltages reinforced the driving force of the ions and their adsorption in the FCDI system. Such an increase in the applied voltage will also elevate the energy consumption. When the electrical voltage was raised from 0.6 to 4.8 V, the desalination rate showed a seven-fold enhancement. As anticipated, charge efficiency was reduced from 92% to 69.5% due to the Faradaic reactions (e.g., electrolysis and oxidation of carbon electrode). To improve the charge efficiency, Liang et al. added carbon black (CB) with a mean diameter of 12 μm to the activated carbon-containing flow-electrode as the weight percentage of 1.5. In this way, they managed to enhance the charge efficiency of the FCDI system to 96.5% at the voltage of 2.4 V. At high electrical voltages, CB can help in maintaining high charge efficiency due to its excellent electrical conductivity. In fact, excellent conductivity of CB has provided the proper condition for efficient electric charge transfer between the activated carbon particles as well as facilitating the ion adsorption process [42].

Xu et al. presented an asymmetric FCDI system known as AFCDI for the first time [101]. They employed AC/ MnO_2 and AC suspension as the positive and negative electrodes, respectively. They managed to increase the electrical voltage to 1.8 V due to the expanded potential window between the positive and the negative electrodes. At 1.8 V, the AFCDI system exhibited no unwanted electrochemical reactions such as water decomposition. Xu et al. [101] achieved the salt removal efficiency of 78% for NaCl solution (0.1 M) after 2 h; while the salt removal efficiency of the conventional FCDI reached 59%.

It must be noted that at voltages above 1.2 V in FCDI system, desalination included electrosorption process of active materials and electrodialytical desalination mechanism. According to Gendel et al. [68] research in the FCDI process, additional electrodialytical (EDI) desalination mechanism within capacitive deionization occurs in parallel with the electrosorption mechanism. Xu et al. [103]
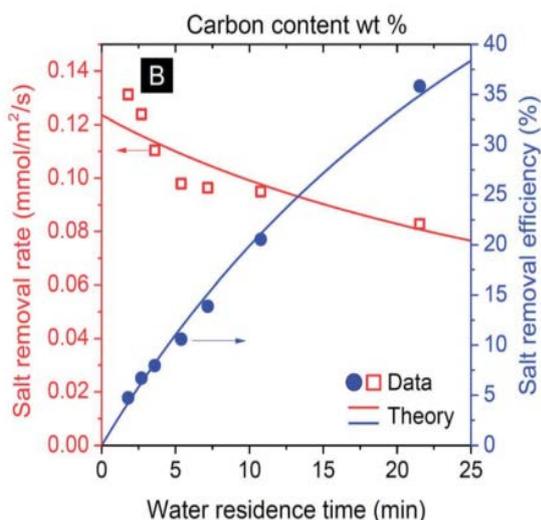

Fig. 4. Influence of water residence time on salt removal rate (red squares) and efficiency (blue dots) measured for carbon flow electrode containing 20 wt.% of activated carbon [69].

also stated the significant role of the electrodialytical desalination in the performance of their AFCDI system. They investigated the desalination process using EDI in an FCDI system without electrodes at voltage values of 1.2 and 1.8 V. The desalination efficiency of EDI process was 0.38 at 1.2 V; while the desalination efficiency under the same condition was calculated as 0.59 for the FCDI process with electrodes. Thus, they realized that EDI desalination plays a pivotal role in the FCDI process. Moreover, when the EDI process was conducted at the voltage of 1.8 V (FCDI without electrodes), the EDI desalination efficiency reached 0.92, which is higher than that of the AFCDI process (0.78). The reason could be explained as follows: in the EDI process at voltages above 1.2 V, water electrolysis becomes violent, and the high electrolytic current can drive excess ionic flux across the ion-exchange membranes, thus enhancing the desalination efficiency; therefore, higher amounts of O_2 and H_2 will be produced. In the AFCDI system developed by Xu et al. [103], however, these gases were not produced at the voltage of 1.8 V.

2.8. Flow-electrode materials

The electrode plays a significant role in CDI processes since it serves as the ion-storage site. Theoretically, electrodes can be made out of conductive and porous materials. However, the choice of electrode materials often relies on their costs, porosity, specific surface area, and availability. In an FCDI system, the flow-electrode plays a crucial role in maintaining the continuous activities of the system. This slurry-type electrode is constituted from a porous material (e.g., porous activated carbon), a conductive additive and an aqueous electrolyte [40,69,104,105]. In fact, carbon slurry is a capacitive suspension of charged carbon particles in an electrolyte. Regarding the very high ionic capacity of flow-electrodes compared with fixed electrodes, they are widely employed in the continuous deionization of saltwater.

The concept of the movable electrode was first introduced by Faris. His proposed electrode was a solid movable electrode operating through a movable belt or a roller. Whereas the flow-electrode in an FCDI system is a flowable carbon suspension working by a pump [40]. Flow-electrode was first investigated by Micka in 1960 [69] and then reported by Kastening. This electrode included a suspension of charged carbon particles in an electrolyte [106–108]. The particles used in the flow-electrodes are often benefited from a high specific surface area (e.g., activated carbon). Sodium chloride solution has been also utilized as the electrolyte in this type of electrodes [67]. Desalination operation by FCDI system is mainly based on the electrostatic adsorption of ions on the porous materials under an electrical potential. Therefore, desalination efficiency depends on the osmotic phenomenon arisen from the salt concentration difference between the flow-electrode and saltwater [66]. This means that a slight decrease in the electrical conductivity (concentration of the feed water) before applying an electrical voltage to the FCDI cell could be ascribed to the presence of sodium chloride in the electrolyte of the flow-electrode (activated carbon-containing suspension). The impact of this ionic chemical adsorption is negligible in comparison with the electrical voltage-induced

desalination. Thus, adding a proper amount of salt to the flow-electrode can effectively maximize its desalination performance.

Electrical conductivity is one of the major characteristics of activated carbon suspensions. In spite of the mechanical motion of the charged particles and their flow within the suspension, EDL still serves as the electrosorbed ions storage site [69]. Therefore, a conductive carbon network (i.e., flow-electrode) can be employed as a source of ions and charged particles transfer and storage in EDL. In fact, carbon substances are able to adsorb ions and store charges, which are directly related to their porosity and conductivity [78]. A direct correlation also exists between the electrolyte's salt concentration in the flow-electrode and the FCDI desalination rate [42].

Active materials loading can be determined according to the intended application. An increase in AC loading can elevate the electrical conductivity of the flow-electrode and hence augment its desalination rate [69]. To make sure on the suspension flowability, AC loading could be at most raised up to 20–25 wt.%, since higher carbon mass loading, due to elevated viscosity, makes the flow-electrode prone to fouling and can disrupt the flow [67,94]. Most of the studies in this field have considered AC particles loading in the range of 5–15 wt.% [65–67,69,77,90,91,97,109].

The flow capacitive suspension electrode can resolve the challenges of CDI processes. For instance, in the CDI process, desalination and electrodes regeneration processes occur in one cell, but thanks to flow-electrode, the FCDI process is able to separate the brine and deionized water flows. Therefore, the output water of the FCDI cell will have a definite and controllable concentration. Energy recovery is one of the other superiorities of FCDI technology over CDI, which can be assigned to the presence of flow-electrodes (FCDI technology has the energy harvesting potential) [67,69].

The precise selection of the dimension of the activated carbon particles in the FCDI process can dramatically decline the fouling in the flow channels. Yang et al. [40] addressed the challenge of minimizing the flow-electrode channels fouling. They attributed the flow channels fouling to the size of the activated carbon particles. Accordingly, the proper size of the activated carbon particles should be employed in the flow-electrodes structure regarding the dimension of the flow channels carved on the current collector plates.

2.9. Other instruments

2.9.1. Conductivity meter

The electrical conductivity (EC) of the electrolyte can be measured by a conductivity meter (or TDS meter). EC has a direct relationship with the salts present in the electrolyte. The higher the dissolved salts of the water, the higher its EC and the lower its electrical resistance. EC measurement is always employed for the production of pure water or determination of the salt concentration. The simplest EC measurement cell includes two platinum electrodes (electrodes are usually made of Pt) with definite surface and distance. The electrical potential applied to the electrodes will cause the ions to migrate toward the

electrodes. By increasing the ions population in the electrolyte, the electrical current between the two electrodes will be increased as well. Conductivity meter can measure this electrical current and determine EC using the Ohm's law. EC unit is ohm^{-1}, mho or S (Siemens) while the specific conductivity can be presented in mmho/cm or μmho/cm whose SI representation is mSiemens/cm or μSiemens/cm, respectively.

In an FCDI system, by application of the electrical voltage to the flow-electrodes, the electrical conductivity of the feed water will dramatically drop by passing of time. In such a system, an EC meter is placed at the outlet of the FCDI cell to measure the variations in the salt concentration of water. In fact, by continuous measurement of the electrical conductivity of the FCDI cell output solution (the deionized solution), it is possible to assess the salt concentration of the solution. For highly dilute solutions, the salt adsorption of the FCDI system will approach zero. The higher the initial salt contents of the feed water, the higher the salt removal; this could be due to the increased ion mass transfer rate inside the micropores [45]. Using a conductivity meter, it is also possible to calculate the salt removal efficiency according to the following equation:

$$\text{Salt removal efficiency}\,(\text{SRE})\,(\%) = \frac{C_0 - C_f}{C_0} \times 100 \qquad (2)$$

in which, C_0 and C_f are the initial and final concentrations, respectively.

In an FCDI system, EC or salt concentration of the solution can be evaluated by inline or online methods. Inline conductivity meter is placed in the pathway of the solution flow and instantly measures the EC of the electrolyte passing through the tube. This type of conductivity meters is highly sensitive to the changes in the electrical conductivity of the solution. This sensitivity results in a high precision in measurements. When this type of EC meter is not in hand, the solution exiting the FCDI cell (the deionized solution) can be collected in a container and an online conductivity meter probe could be placed in that to measure the EC variations of the solution.

2.9.2. Bolts and nuts

Bolts and nuts are used to assemble the FCDI cell components. In the cases using metallic bolts and nuts, they should be completely covered and sealed by Teflon tape (thread seal tape or PTFE tape) to insulate the bolts and prevent the short circuit and corrosion. These bolts are in direct contact with the current collector plates and will corrode due to the application of the electrical potential difference to the current collector plates. Moreover, their contact with salt water can further intensify the corrosion. To prevent these problems, corrosion-resistance bolts and nuts (e.g., stainless steel) can be applied.

2.9.3. Silicon and pneumatic hoses

Proper hoses should be employed to connect the feed water and electrodes reservoirs, FCDI cell and pumps. The suction and deriving sections of the peristaltic pumps are usually made of silicone hoses. Therefore, these silicone hoses are a proper candidate to connect the components. Pneumatic hoses have also exhibited acceptable performance. In comparison with the pneumatic hoses, the silicon hoses are more elastic; however, silicone hoses are more prone to fouling due to their internal surface roughness.

3. Different modes of water desalination using the FCDI cell (batch and continuous)

FCDI experiments can be carried out in two operational modes: batch and continuous. In an FCDI batch-mode operation, water desalination, electrodes regeneration, and brine water production occur in one electrosorption system under continuous cycles until the salt concentration of the feed water is reduced to the intended value. In each experiment, a fixed volume of feed water (with definite salt content) is continuously pumped by a peristaltic pump into the FCDI cell and the output deionized water (the product of deionization process) is re-pumped to the FCDI cell. This cycle continues throughout the experiment. In fact, the feed water flows at a definite rate through the spacer chamber and between the ion-exchange membranes in a closed-cycle with one reservoir. The flow-electrodes are also operating with a fixed volume and definite flow rate under a closed-cycle with the electrodes reservoir. The flow cathode and anode electrodes are pumped to the FCDI system from the same reservoir; these two electrodes return to the flow-electrodes reservoir after passing the flow channels carved on the current collector plates. This method is based on the automatic release of the adsorbed ions by the flow-electrodes through simple mixing of the charged flow anode and cathode electrodes and hence neutralization of the electrodes after desalination stage. In this way, flow-electrodes will achieve its initial desalination ability [40,45].

In an FCDI batch-mode operation system, the ions trapped in electrodes can be discharged by polarity reversal, which can discharge the adsorbed ions to the water channel. Fig. 5 shows an FCDI system working under batch-mode (closed-cycle).

For instance, Gendel et al. [15] used this desalination system (FCDI batch-mode operation system) in 2014. In their study, they investigated high apparent SAC[1] value for flowing electrodes. As shown in Fig. 6, they successively recirculated each electrode (volume of 50 mL) between the reservoirs and FCDI module using a peristaltic pump with a flow rate of 60 mL/min. Under the same condition, NaCl solution was also recirculated between the FCDI cell and feed water reservoir with a flow rate of 9 mL/min. Using this desalination system, they achieved salt removal rate above 99% from the feed water with the initial concentration of 1 g NaCl/L after 4 h. They also achieved apparent salt adsorption capacity value as high as 260 mg/g for the activated carbon slurry electrodes for the first time for the initial NaCl concentration of 15 g/L in about 70 h [15].

In order to investigate the significance of Faradaic reactions in the FCDI process, Nativ et al. [68] designed an FCDI system for which flow-electrodes and feed water

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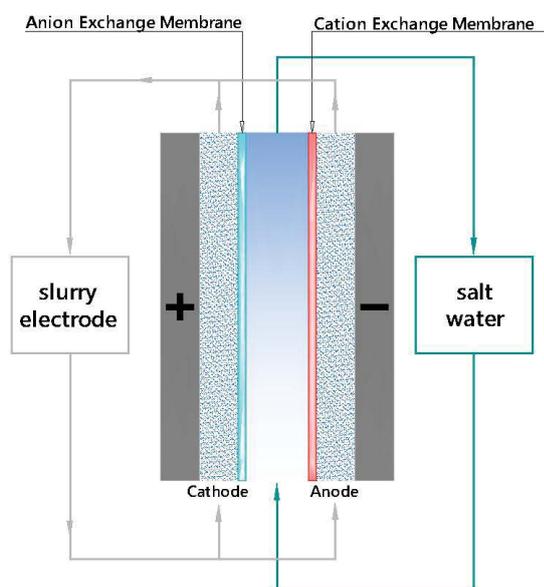1 Weight of adsorbed ions per dry weight of adsorbent.

Fig. 5. Schematic of an FCDI system operating under closed cycles (batch-mode FCDI system).
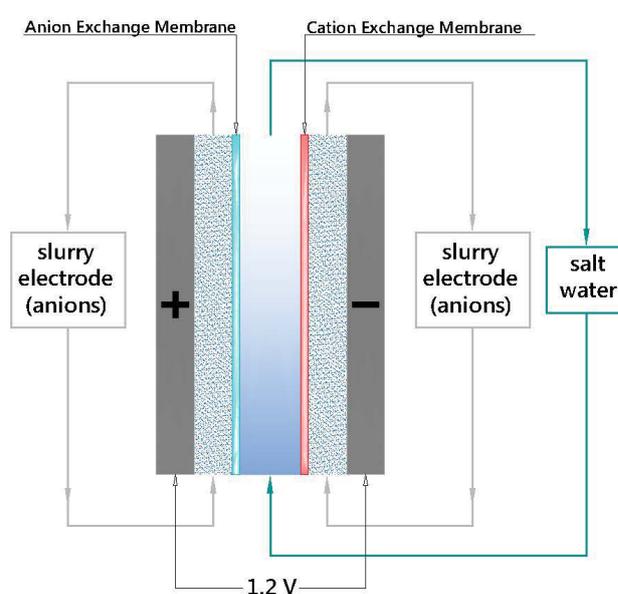
Fig. 6. Schematic view of the batch-mode FCDI system in desalination of water.

operated in batch-mode. The feed water was recirculated through the FCDI module at the flow rate of 60 mL/min. The feed water volume was 150 mL. They revealed that the FCDI desalination process could produce H⁺ and OH⁻ in the anode and cathode electrodes, respectively. Therefore, it seems that the electrodialytical and electrosorption mechanisms in the FCDI process need further investigation. According to their obtained results, Nativ et al. [68] found that the FCDI process could be exploited for the production of HCl and NaOH from NaCl. Fig. 7 presents the schematic view of the batch-mode FCDI system of Nativ et al. [68].

All the mentioned studies evaluated the batch-mode FCDI process. However, the continuous-mode operation system is one of the other operation modes of the FCDI process. In contrary to the batch-mode in which the feed water and flow-electrodes pass several repetitive cycles, the feed water could be desalinated in just one cycle during the continuous-mode of FCDI.

For instance, Yang et al. [40] passed the SW (seawater) with the initial concentration of 35 g NaCl/L with the flow rate of 3 mL/min through the spacer and between the ion-exchange membranes in a continuous FCDI system. In this process, the SW worked under an open-cycle with two reservoirs (desalinated water and saltwater). Moreover, each of the flow-electrodes worked under a closed-cycle with a flow rate of 25 mL/min. Both flow-electrodes entered the FCDI cell from a common reservoir, adsorbed the ions and then returned to the same reservoir. The adsorbed ions were stored and neutralized in that electrodes reservoir. Fig. 8 represents the schematic view of this deionization system [40].

In addition to the previously mentioned batch FCDI process, Gendel et al. [15] also studied the continuous operation of an FCDI system. Their continuous system included a desalination module and a regeneration/concentration module. Each of the flow-electrodes (100 mL) was

continuously recirculated in a closed-cycle at the rate of 250 mL/min between the two reservoirs (containing carbon suspension) and FCDI modules. The feed water (1 g NaCl/L) was also split between the two FCDI modules. In the desalination module, the salt ions of the feed water were adsorbed to the flow-electrodes; these ions were then desorbed from the charged electrodes to the regeneration/concentration module under reverse potential to the second module. In this way, the feed water could be split into diluate and concentrate streams. Under optimal conditions, they achieved desalination rate above 99% for the feed water with initial NaCl concentration of 1 g/L. As suggested by Fig. 9, in the continuous FCDI process of Gendel et al. [15], the water desalination, production of concentrated and desalinated water, and regeneration of the electrodes were performed continuously [15].

Rommerskirchen et al. [43] designed an FCDI system based on a single, continuously regenerated flow-electrode and a single module for continuous water desalination in 2015 (Fig. 10).

They split the cell inlet feed water (1 g NaCl/L) into two parallel streams (desalination and concentration). They also placed an ion-exchange membrane (anionic or cationic) between these two streams to separate them. According to Fig. 10a, the membranes near the electrodes had equal fixed charge (anionic or cationic) while the charge of the middle membrane between these two parallel streams was opposite with the two other membranes (in this system, it is not important which type of IEM is near the two electrodes). By applying a voltage to the FCDI module, the flow-electrodes flowing at both sides of the symmetric module are oppositely charged. In this way, one ion type (depending on the type of the membrane applied between the two parallel streams) can penetrate from the diluate water compartment through the middle membrane and enter the concentrate water. In the meantime, the opposite
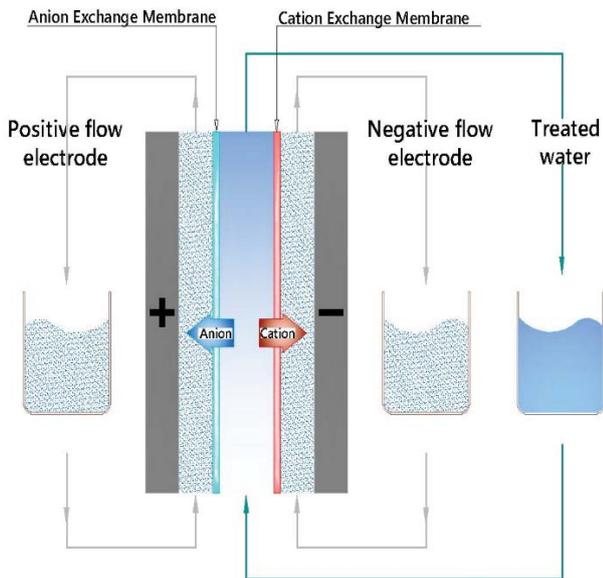
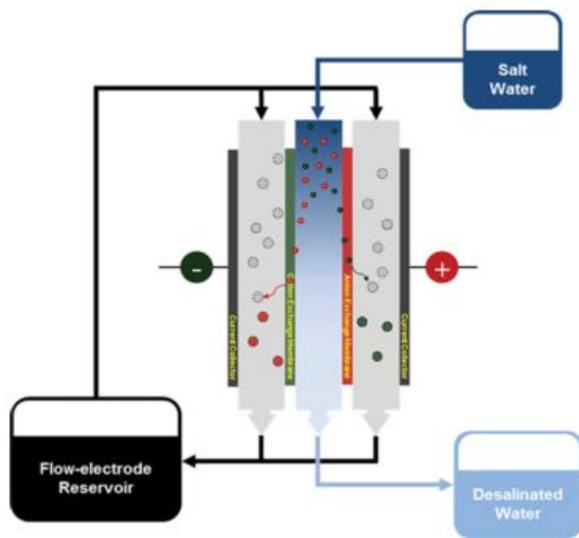Fig. 7. Schematic structure of a batch-mode FCDI process.

Fig. 8. Schematic view of an FCDI process employed by Yang et al. [40] for desalination of saltwater. The flow-electrodes worked under a closed-cycle with a common reservoir while the salt-water operated under open-cycle (saltwater and desalinated water reservoirs) [40].

ions will enter from the diluate water compartment into the adjacent electrode where they can be adsorbed on the carbon particles of the suspension electrode.

In this type of FCDI system, a single flow-electrode flows in the flow channels and works under a closed-cycle. In this way, the adjacent electrode of the diluate water compartment will transfer the adsorbed ions to the concentrate water compartment (which has an equal potential as the adsorbed ions) and desorb them in the concentrate water compartment (deionization process). They finally reached two parallel streams (desalination water and concentration
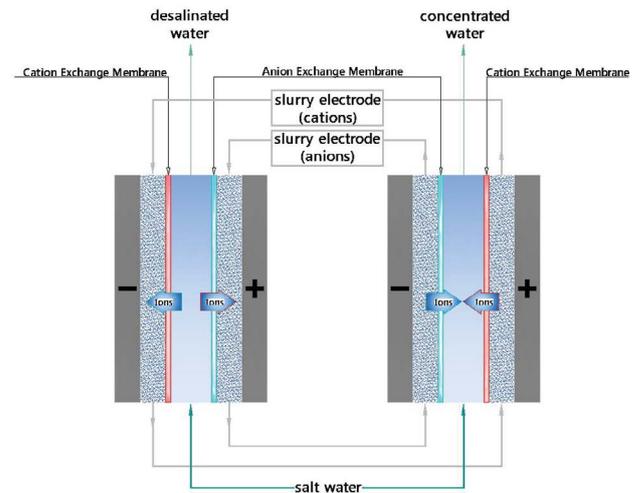

Fig. 9. Schematic structure of a continuous two-module FCDI process.

water) outside the symmetric FCDI module and managed to achieve the desalination rate above 70% for the feed water (1 g NaCl/L) and over 80% water recoveries during the continuous operation of the system. The system presented by Rommerskirchen et al. [43] only included one pair of monopolar electrodes, which simultaneously combined continuous desalination, flow-electrode regeneration, and concentration of salt water in a single module. They also exploited carbon particles to decrease the chlorine production and hence reduce the electrode corrosion and membrane deterioration [43]. Fig. 10 illustrates a schematic view of the system investigated by Rommerskirchen et al. [43].

Two operation modes of FCDI systems were explained in this section. In the next section, a pilot-scale FCDI system will be described, fabricated and evaluated as an example.

4. Assembling a pilot-scale FCDI system

This section is aimed at describing an example of a pilot-scale FCDI system, investigating its performance and examining the results of its desalination tests. In the assembly of the unit cell of this system (according to Fig. 11), two current collector plates (made of stainless steel type 316) were employed. The length, width and thickness of these two rectangular current collector plates were 200, 150 and 10 mm, respectively. In this FCDI system, flow-electrodes flew in the meandering flow channels (grooves carved by a CNC apparatus on the current collector plates). The width and depth of the flow channels were 2.5 mm while the length of each column of flow channels was 102.4 mm. Overall, 17 columns were carved on each current collector plate. Moreover, the total width of the space occupied by the flow channels on each current collector plate was measured to be 110 mm. In this system, each of the flow-electrodes entered the FCDI cell from the top of the current collector plate in which it flew. After passing the meandering flow channels, the flow-electrodes exited from a section below the stainless steel plates. The contact area between the IEMs and the flow-electrodes was about 4,352 mm^2.
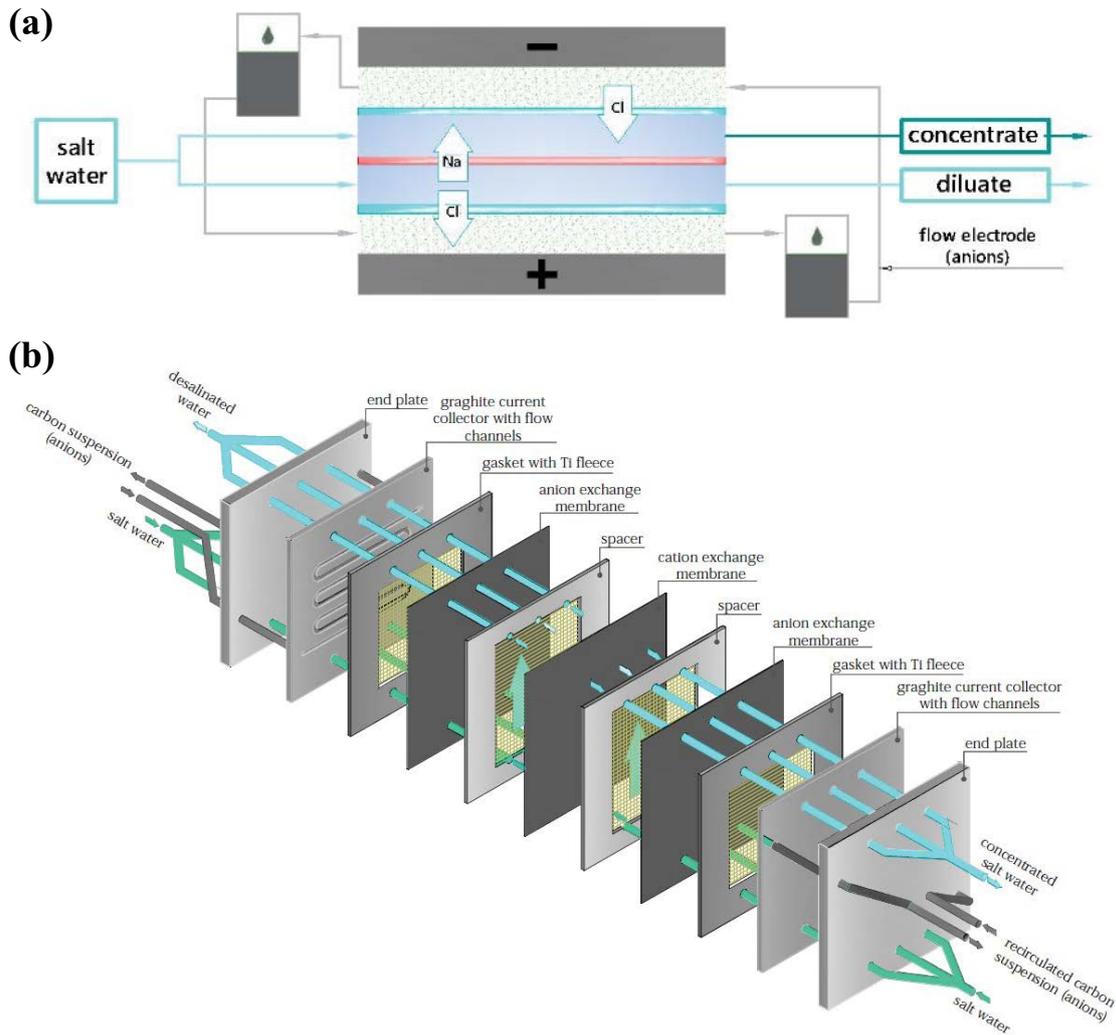
(a)

(b)

Fig. 10. Schematic of single module FCDI concept (a) and structure of single FCDI module (b) for continuous water desalination.
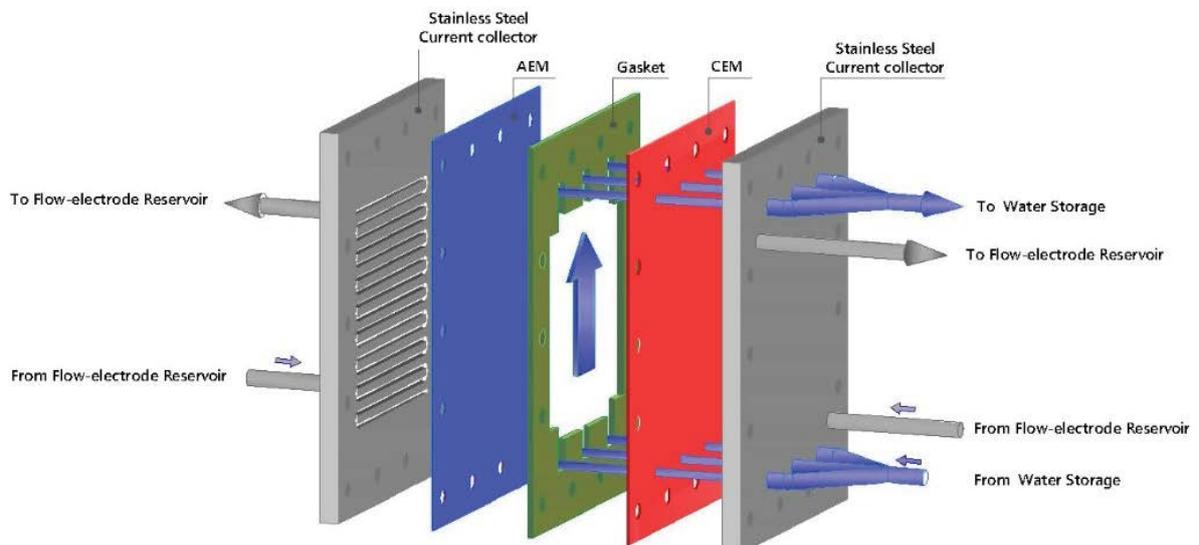

Fig. 11. Schematic arrangement of our FCDI cell components.

Cation and anion exchange membranes with thicknesses of 130 μm (Fumasep FKS-PET-130/ED-100 and Fumasep FAS-PET-130/ED-100, Fumatech, Germany) were employed in the assembly of this lab-scale system. In this cell, the CEM is placed after the cathodic current collector and in its vicinity (Fig. 11). By applying an electrical voltage to the FCDI cell, the cathodic current collector will have a negative electric charge; thus, the flow-electrode flowing in its flow channels (cathodic current collector) will serve as a cathode. Cathode flow-electrode has the potential to adsorb cations (Na+); therefore, cations can penetrate from the CEM and be adsorbed to the cathode flow-electrode. In this deionization system, the spacer chamber is placed after the CEM. The spacer chamber (water chamber) includes a polyester paper (polyester spacer) along with two silicon gaskets (thickness of 1.5 mm). These two gaskets surrounded the water chamber. Then AEM is placed for anions (Cl⁻) penetration and their entrance to the anode flow-electrode. After that, the anodic current collector is placed. In the end, all the components of the FCDI cell are assembled beside each other using stainless steel bolts and nuts (Fig. 11).

After assembling the FCDI cell, this system was completed by the use of the silicon and pneumatic hoses, peristaltic pumps (for pumping the feed water and electrodes), DC power supply and the feed water and electrodes reservoirs. In the CDI processes, two charging modes are often used: constant voltage (CV) and constant current (CC) [92,110]. In our system, the voltage of 1.2 V was applied to the FCDI cell under constant voltage mode. Under this condition, the salt concentration of the output solution will decrease over the time. In the present pilot, GPS-3000 series constant voltage/current digital DC power supplies were used to apply a constant voltage to the anodic and cathodic current collectors. The salt concentration and electrical conductivity of the output water of our FCDI cell were continuously measured by AZ 8603 Water Quality Meter (Taiwan). In this system, silicon and pneumatic hoses (external and internal diameters of 4 and 2 mm, respectively) were also employed to connect the feed water and electrodes reservoirs, peristaltic pumps and FCDI cell. To resolve the leakage, seal the system and prevent short circuit as the result of applying an electrical voltage to the current collectors, in addition to using stainless steel washers, Teflon (polytetrafluoroethylene [PTFE]) washers with the thickness of 4 mm were also used at the bolts location. One bolt was used in the cathodic current collector and one was employed in the anodic current collector without the Teflon washer, so the electrical voltage could be applied to the stainless steel current collector plates through these two bolts. Moreover, the short circuit was avoided by using the Teflon (PTFE) tape throughout the bolts.

In this experimental work, as mentioned before, an FCDI system was employed in the batch mode. In other words, the feed water and carbon flow-electrodes repeated the continuous cycles in this system.

Flow-electrodes were pumped to the flow-electrode inlets (as shown in Fig. 12, above the current collector plates) from a reservoir (with an approximate volume of 250 mL) using one peristaltic pump and silicon and pneumatic hoses. Both flow-electrodes exited the cell after
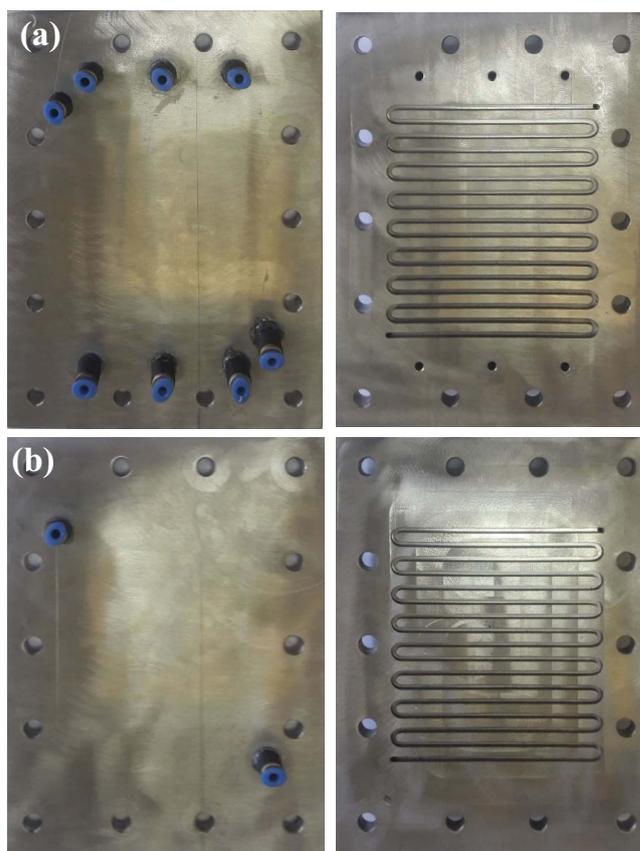

Fig. 12. (a) Cathodic stainless steel current collector plate, flow channels carved on the cathodic stainless steel current collector plate, inlet and outlet of the cathode flow-electrode and inlet and outlet of the water (manifold) (both surfaces of the cathodic stainless steel current collector plate can be observed). (b) Anodic stainless steel current collector plate, flow channels carved on the anodic stainless steel current collector plate and inlet and outlet of the anode flow-electrode (both surfaces of the anodic stainless steel current collector plate can be observed).

passing the flow channels from the designed outlets (as shown in Fig. 12, below the current collector plates) and returned to the electrodes reservoir. At the upper part of the electrodes reservoir, the electrode inlets were placed while the electrode outlets were placed on the bottom of the reservoir. The suspension electrodes included 5 wt.% activated carbon powder (Norit, Netherlands). To avoid fouling and sedimentation in the system and provide desirable homogeneity in the flow-electrodes, carboxymethyl cellulose (CMC) was employed as the dispersing agent or dispersant. The suspension electrodes contained 250 mL distilled water, 12.5 g activated carbon powder, 1.45 g NaCl (0.1 M) and 0.5 g CMC.

Simultaneously, the feed water (100 mL) was pumped to the inlet (according to Fig. 12a, it includes three inlet tubes at the bottom of the cathodic current collector plate or the manifold) using a peristaltic pump and silicon and pneumatic hoses. After passing the water channel, it exited from the outlet (including three outlet tubes on the top of

the cathodic current collector plate or manifold; Fig. 12a) and returned to the reservoir. For continuous measurements of salt concentration of the feed water, a place was considered on the upper part of the feed water reservoir to enter the conductivity meter probe.

In order to evaluate the operation of assembled FCDI cell, we conducted four experiments. The first experiment was aimed to investigate the desalination efficiency of the system for feed water at low initial NaCl concentration. In this regard, 5 wt.% suspension electrode with the flow rate of 25 mL/min and 100 mL NaCl solution with initial concentration of 500 mg NaCl/L and flow rate of 10 mL/min were used. The second and third experiments were employed to investigate the effect of the initial concentration of the NaCl solution on the desalination efficiency of the FCDI process. These two experiments were carried out using 5 wt.% suspension electrodes with a flow rate of 25 mL/min and two NaCl solutions with initial concentrations of 500 and 3,000 mg NaCl/L (100 mL and flow rate of 10 mL/min) for 6 h and 30 min.

At the end of each test and reaching the intended salt removal, a reverse-voltage (polarity change) could be applied to the system to evaluate the reversibility of our FCDI process. In this way, by adding a stage to the end of the fourth test, this test included two stages. In the first stage, 100 mL feed water with an initial concentration of 3,000 mg NaCl/L and flow rate of 10 mL/min was desalinated in 7 h and 30 min. The second stage involved a reverse-voltage to the flow-electrodes. In fact, in the second stage, the FCDI system had the opportunity to return the adsorbed ions of the electrodes to the water channel and then the water reservoir. In this way, the NaCl concentration of solution will be returned to its initial value. In this experiment, the 5 wt.% suspension electrode with the flow rate of 25 mL/min was employed as well.

5. Results and discussion

Our FCDI test diagrams and determining the salt removal efficiencies are provided in the following sections.

5.1. Salt removal efficiency of the FCDI system for low-initial concentration feed water

As mentioned earlier, the first experiment was aimed to remove salt from feed water with low initial concentration. As suggested by Fig. 13, the salt removal efficiency of this experiment reached 90% in 7 h. The salt removal efficiency remained constant in the last 30 min. In other words, the diagram reached the steady state and the slope approached the horizontal condition. During this test, the salt concentration of the feed water gradually declined and the test was continued until the salt concentration of the water reached a constant value (salt removal process got very slow). This test indicates the NaCl removal potential of our FCDI system. In this experiment, 3.44 mg NaCl was removed per each gram of activated carbon powder (salt adsorption capacity [SAC] value). To examine the ability of this system in removing NaCl from solution at higher initial concentration, the second and third experiments were conducted.
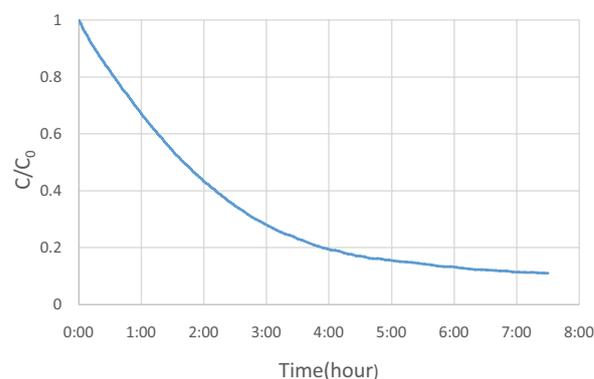

Fig. 13. Test diagram of the FCDI system including 5 wt.% suspension electrode with the flow rate of 25 mL/min and low-initial concentration feed water (500 mg NaCl/L) at the flow rate of 10 mL/min.

5.2. Effect of initial concentration of feed water on the FCDI performance

As mentioned in the previous section, this FCDI system is theoretically capable of treating solution with higher initial NaCl concentration. For further investigations, the results of the second and third tests on the feed waters with respective initial concentrations of 500 and 3,000 mg NaCl/L were compared in one diagram (Fig. 14). In both experiments, 5 wt.% suspension electrode with the flow rate of 25 mL/min was applied. These two experiments took 6 h and 30 min each. The results of these two experiments are compared in Fig. 14.

As anticipated, the second test which involved the feed water at an initial concentration of 500 mg NaCl/L had higher salt removal efficiency (87%) compared with the third one (58%), which treated the feed water at an initial concentration of 3,000 mg NaCl/L. Therefore, the diagram of the third test will be above the second one. In the third experiment, 12.4 mg NaCl was removed per each gram of activated carbon powder (SAC value), which is significantly higher than the first experiment with the SAC value of 3.44 mg NaCl/$g_{activated\ carbon}$. This indicates the acceptable ability of this FCDI system in removing salt for the feed waters with initial concentrations higher than 500 mg NaCl/L.

As expected, an increase in the initial concentration of the feed water resulted in a decline in salt removal efficiency. In fact, the salt ions adsorption process could continue until the saturation of the ion adsorption capacity of the flow-electrode (the ion adsorption capacity of the activated carbon suspension). In the batch-mode FCDI system, more ions will be generally adsorbed and stored in the EDLs by passing of time. Thus, the electrodes' ion adsorption capacity will be reduced gradually. Now, if we consider two batch-mode FCDI tests with feed water initial concentrations of 500 and 3,000 mg NaCl/L under similar conditions, the ions of the feed water with an initial concentration of 500 mg NaCl/L will evidently require shorter time to be adsorbed in the EDLs as compared with the one at an initial concentration of 3,000 mg NaCl/L. Moreover, the electrodes still have the capacity to adsorb more ions.
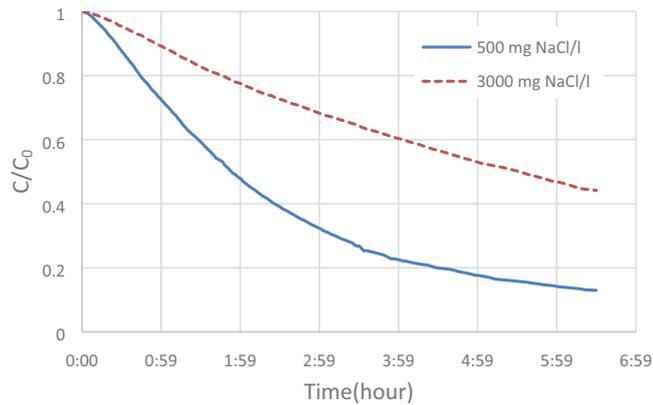
Fig. 14. Comparison of the results of two experiments; FCDI system with 5 wt.% suspension electrode at the flow rate of 25 mL/min treating feed waters with initial concentrations of 500 and 3,000 mg NaCl/L and flow rate of 10 mL/min.
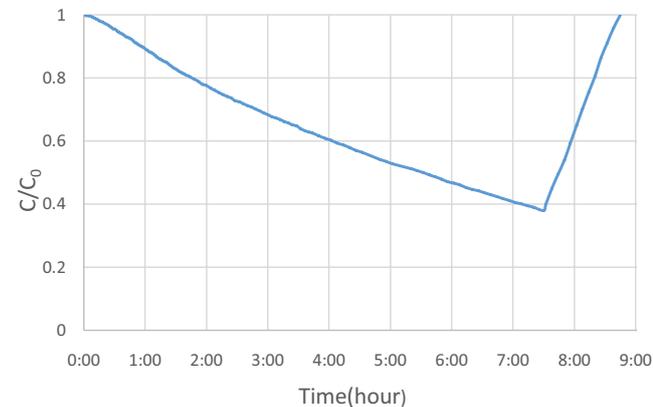

Fig. 15. Result of our FCDI test with 5 wt.% suspension electrode with the flow rate of 25 mL/min and the feed water at an initial concentration of 3,000 mg NaCl/L and flow rate of 10 mL/min with polarity reversal.

In this way, if solutions with higher initial salt concentrations are used, more ions will be adsorbed in the EDLs at shorter time periods; or better to say more SAC values can be achieved.

5.3. FCDI test with reverse-voltage

In this stage, 100 mL feed water (initial concentration of 3,000 mg NaCl/L and flow rate of 10 mL/min) and 5 wt.% suspension electrode (flow rate of 25 mL/min) were used in our FCDI system working under batch mode. The secondary concentration of NaCl solution was measured after 7 h and 30 min, which showed 64% salt removal (14 mg NaCl/g_{AC}). After this stage, a reverse-voltage (–1.2 V) was applied to the system until the NaCl concentration of water reached its initial value. In desorption stage, the water returned to its initial concentration in 75 min with a slope significantly higher than that of desalination (ion adsorption stage; Fig. 15). In this step, the salt content of the solution and flowable suspension was re-evaluated.
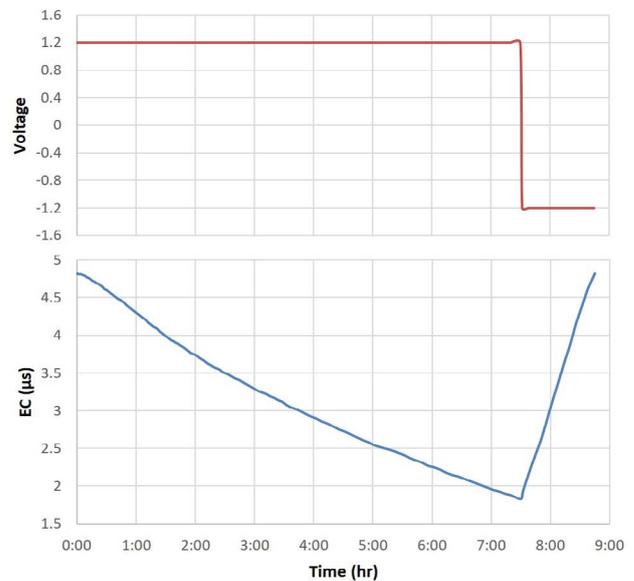

Fig. 16. Adsorption and desorption stages (voltage–time and conductivity–time profile).

Comparing with the initially measured values, we concluded that mass balance holds for the salt. This shows that the salt ions were only electrostatically adsorbed or desorbed and they were not transformed into another compound. Therefore, our experiments did not involve Faradaic reactions such as hydrolysis.

Fig. 16 shows the voltage and conductivity profile of this experiment for adsorption and desorption stages.

6. Conclusion

This paper was aimed to present a brief review on the electrochemical desalination process of FCDI. In addition to express the history of this process, the components and the parameters applied in the assembling of an FCDI system were separately introduced. The assembly of the system and its performance were also addressed by preparing an FCDI pilot at the laboratory scale. Four experiments were conducted on this FCDI system working under batch mode. In these experiments, water and flow-electrodes worked under closed-cycles. These experiments indicated that using 5 wt.% suspension electrode with the flow rate of 25 mL/min, it is possible to desalinate 100 mL feed water with an initial concentration of 500 mg NaCl/L and flow rate of 10 mL/min by 90% in about 7 h. The desalination ability of this system was also investigated on the solution with higher initial concentration (3,000 mg NaCl/L). The result revealed SAC value of 14 mg NaCl/g_{AC} at this concentration. Finally, a reverse-voltage was applied to the stainless steel current collector plates, which confirmed negligible Faradaic reactions as well as the reversibility of the FCDI process.

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