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REVIEW

Review on carbon-based electrode materials for application in capacitive deionization process

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Abstract Most of the electrochemical studies related to porous carbon electrodes are those which can be used for either electrostatic energy storage or for energy conversion [using electrical double layer capacitor (EDLC)]. The techniques, such as electrodialysis, membrane filtration, advanced oxidation process, thermal evaporation, can be used now-a-days to treat salty water. Among which, capacitive deionization (CDI) has emerged as a novel cost effective and environment friendly desalination technology. CDI process involves the removal of inorganic ions from the salty water by applying an electrical potential between two porous carbon electrodes. Because of the passage of electrical potentials in the system, the unwanted ions present in the water sample will be adsorbed on the electrode surfaces. Hence, the electrodes which are having high surface area can exhibit higher desalination capacity. In this article, the application of various carbon-based composite electrode materials such as activated carbon and PVDF composite, carbon–metal oxide composite, carbon–CNT composite, carbon–polymer composite and carbon sheet (carbon aerogel, activated carbon cloth) in CDI process is systematically reviewed and presented. CDI process is being developed now-a-days especially toward commercialization in treating the brackish water.

Keywords Carbon-based electrode materials · Capacitive deionization · Desalination

Introduction

Desalination of brackish groundwater and seawater has already emerged as an important technology in many parts of the world. With increasing human population and continuous growth of per capita water consumption in emerging economies like India, the need for competitive desalination processes would only increase in future. At present, reverse osmosis (RO) is the dominant desalination technology shown in Fig. 1 for desalination (Almarzooqi et al. 2014). Detailed comparisons of various desalination technologies are provided in Table 1.

Thermal processes are quiet energy intensive. Substantial improvements in the development of thin film composite (TFC) membranes have made the RO process highly competitive. Electrodialysis (ED), which employs Faradaic processes at higher cell voltages of 2–3 V is now considered to be energy efficient to treat the dilute salt solutions. Specific energy consumption data collected for RO and ED processes, for different salt concentrations (Oren 2008; Zhao et al. 2013a, b, c) are presented in Fig. 2.

The capacitive deionization is a promising new energy efficient technology for electrochemical desalination of wastewater. CDI is an electrosorption process that uses a low electrical potential (0.6–2.0 V DC) to remove ions from solution by adsorbing them onto the electrical double layer (EDL) of two porous carbon electrodes. The negatively charged cathode can adsorb cations like calcium

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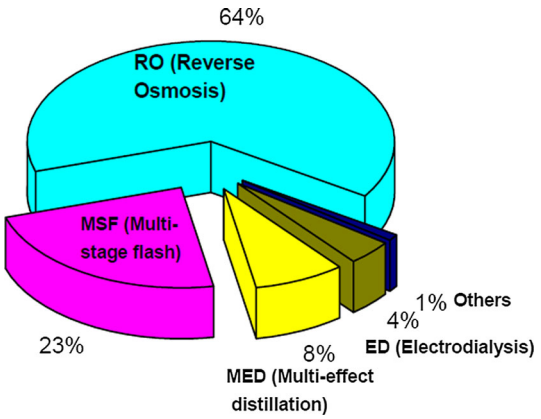

Fig. 1 Global desalination technologies share by capacity (AlMarzooqi et al. 2014)

(Ca^{2+}), (Mg^{2+}) and heavy metal ions such as chromium (Cr^{3+}), lead (Pb^{2+}) and cadmium (Cd^{2+}), while the positively charged anode can absorb anions such as nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-) and arsenate (AsO_4^{3-}), which may result in water deionization and purification. CDI is a simple non-faradaic process which depends on the electrosorption of cations and anions on charged carbon surfaces (Bill et al. 1961). CDI technology is cost effective and eco-friendly compared with membrane filtration process such as reverse osmosis (RO) at low TDS concentration range (<10 mg/L), which can be especially beneficial for saline groundwater treatment especially for rural or remote communities.

The anodic and cathodic reactions occur during the charging process for the carbon electrodes dipped in NaCl are shown in Eqs. (1) and (2) (Oren 2008).

$$C + Na^+ + e \rightleftharpoons C^-Na^+ \quad [\text{Reduction}] \tag{1}$$

$$A + Cl^- \rightleftharpoons A^+Cl^- + e^- \quad [\text{Oxidation}] \tag{2}$$

A solid non-consumable electrode material (cathode, i.e., C) in the reduced state may form a bond (usually ionic bond) with the cations present in the solution. Similarly, a non-consumable anion-responsive electrode material (anode, i.e., A) can form an effective bond with the anions (in the oxidized state) present in the solution. It is noted that reduced cathode and oxidized anode can be of good ion exchangers. Coupling these electrodes (i.e., A and C) in a suitable cell and passing a current at appropriate applied potential may be used to remove the salinity from aqueous salt solution.

Caudle et al. investigated the removal of salts by this process by passing the solution through a porous electrode, which is made of activated carbon powder (Caudle et al. 1966). The CDI actually works through a parametric pumping process involving alternative charging and discharging steps (Johnson and Newman 1971) as shown in Fig. 3. In the charging step (Fig. 3a), the salt is removed from the feed solution by separate cationic and anionic electrosorption on cathodes and anodes, respectively. In the second discharging step (Fig. 3b), the salt is collected in a separate brine solution. This alternative pumping process for purifying the feed was investigated by (Johnson and Newman 1971). This was followed by further investigation by Oren and Soffer (1978, 1983). The electrodes used in CDI process require very high surface area and should operate over long periods without material contamination. The electrodes used in early studies could not meet such stringent requirements. In 1996, J. Palmer and co-workers from Lawrence Livermore Laboratory, California published a series of papers on CDI using high surface area aerogel electrodes (Farmer et al. 1996a, b, c; Farmer et al. 1997). This laboratory also introduced a prototype desalination unit. Published papers include studies on synthetic salt solutions containing NaCl, $NaNO_3$ (Farmer et al. 1996b) and NH_4ClO_4 (Farmer et al. 1996c). This may actually be termed as a second stage in CDI process development. Aerogel electrodes met most of the specification requirements for a CDI unit.

The cost of this electrode, however, still remains quite high. Porada et al. (2013) in their review work published in 2013 have provided a year wise sketch on the historic developments in CDI processes. An abridged version containing electrode and electrode modifications introduced in CDI process is provided in Table 2. Activated carbon-based electrodes still remain the main focus of research. But many modified composites including TiO_2 (Ryoo and Seo 2003), multiwalled carbon nanotubes (Dai et al. 2005), carbon nanofibers (Wang et al. 2012a, b, c, d) and graphene oxide (Li et al. 2012) are some of the important developments. Surface modification for ion selectivity in place of membrane capacitive deionization (MCDI) units is yet another recent innovation (Biesheuvel et al. 2011).

Since 1996, CDI has indeed received considerable attention. The subject has also been reviewed quite recently at regular intervals. Some interesting reviews published in 2008 (Oren 2008; Anderson et al. 2010; Porada et al. 2012, 2013; Almarzooqi et al. 2014) provide extensive useful information on the historic perspective as well as recent developments. The theory of capacitive deionization has also been significantly extended in recent times to include the effect of dynamic adsorption–desorption processes (Biesheuvel et al. 2009), pore diffusion (Zhao et al. 2010), pore space (Biesheuvel et al. 2011), electrode thickness (Porada et al. 2012) and surface treatment (Cohen et al. 2011).

Table 1 Energy comparison of desalination technology

Desalination technology	Thermal	MFE	MED-MVR	MED-TVR	ED	RO	CDI
Basic mechanism	Steam is salt-free, condenses to form pure water	Steam is salt-free, condenses to form pure water	Steam is salt-free, condenses to form pure water	Steam is salt-free, condenses to form pure water	Ions move through anions and cation membrane	Ions move through anions and cation membrane	Ions adsorb and/desorb on electrode due to DC voltage
Feed water	Seawater	Seawater	Seawater	Seawater	Brackish water only	Seawater and brackish water	Brackish water only
Total capital cost	High	High	High	High	Medium–high	Low	Low
Status	Major application	Major application	Major application	Major application	Significant for low salt feeds	Major application	Developmental
Energy requirement	–	6.6 kWh/m^3 ($\sim$125 Wh/gal)-seawater	7.9–10.8 kWh/m^3 (30–41 Wh/gal)-seawater	56.8–83.2 kWh/m^3 (215–315 Wh/gal)-seawater	2.03 kWh/m^3 (7.7 Wh/gal)-brackish water	6.6–9.3 kWh/m^3 (25–35 Wh/gal)-seawater	$\sim$4.2–8.5 kWh/m^3 (16–32 Wh/gal)-seawater 0.05–0.1 kWh/m^3 (0.2–0.4 Wh/gal)-brackish water
Strengths	Well established	Well established	Well established	Well established	Well established	Established, lower energy demand	Removes minor ions, energy recovery
Weakness	Energy demand	Energy demand	Energy demand	Energy demand	Seawater desalination is a topic	Energetic efficiency is low	Seawater desalination is difficult
Challenge analysis	Better scale control, materials, hybrid optimization	Better scale control, materials	Better scale control, materials	Better scale control, materials	Lower cost, membranes and ED optimization	Better membranes and module design; high-performance membrane from nanotechnology	Practical modules and scale-up; novel nano-structures electrodes with high energy recovery

Brackish water TDS: 800–3200 mg/L, seawater TDS: 35,000 mg/L

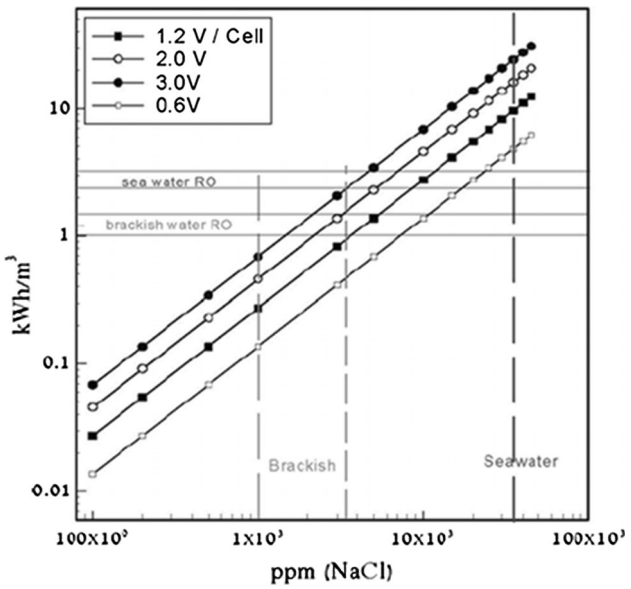

Fig. 2 Specific energy consumption for CDI as a function of NaCl concentration and for different voltages, as compared with brackish and seawater RO desalination (Oren 2008)

The present literature survey mainly focuses on the electrode materials and electrode surface modifications for CDI. The research publications which appeared during the past decade are mainly covered in this survey. For earlier developments one may refer the recent reviews (Table 2) cited above.

Carbon particle-based electrodes for CDI

As discussed above, aerogel sheet electrodes were initially employed for the successful development of high surface area electrodes. To achieve cost effectiveness, current efforts mainly focus on carbon particle-based electrodes. Activated carbon powders mixed with polymerizing materials like polyvinyl alcohol (PVA) or poly vinylidine fluoride (PVDF) and conductivity-enhancing materials like carbon black are mixed and compacted at different experimental conditions to obtain highly porous active electrode materials. These electrode developments were initially focused on super capacitors. Parallel developments are now taking place in the area of CDI and super capacitors.

The structure of some of the carbon allotropes employed in carbon electrodes is presented in Fig. 4 (Noked et al. 2011). Amorphous carbons possess least localized structures but provide high surface area (Fig. 4a). Diamond is highly structured but provides minimum surface area and electronic conductivity (Fig. 4b). Graphite electrodes provide high conductivity but their electrosorption capacity is quite low (Fig. 4c). Fullerenes (Fig. 4d), carbon nanotubes (Fig. 4e) and graphenes (Fig. 4f) are the high surface area materials that are finding place in novel electrodes for supercapacitors as well as CDI (Noked et al. 2011).

The surface modified carbon cloth material (treated with KOH) having TiO_2 nanoparticles in the surface has increased electrosorption capacity (5–10 %) than with untreated activated carbon electrodes (Zou et al. 2008a, b). Detailed studies on KOH chemical treatment on the activated carbon electrodes in CDI for removal of NaCl have been reported (Villar et al. 2010). MnO_2-based carbon nanocomposites have also been developed recently. Salt removal efficiency for the MnO_2/nanoporous carbon was 16.9 μmol/g, which was higher than commercially available activated carbon (Yang et al. 2011). Low surface area carbon electrodes can be coated with nanoporous thin films of Al_2O_3 or SiO_2 to achieve higher efficiency in CDI (Lado et al.2013 and Han et al. 2013). The mechanistic insights on capacitive enhancement are also available (Han et al. 2013).

Many operational parameters can indeed influence the overall performance efficiency of three-dimensional electrode packs. A simple two carbon electrode flow cell may be conveniently used to study the performance efficiencies of these electrodes (Avraham et al. 2009). The charging potential can influence the oxidation and reduction processes on carbon surface leading to irreversible surface modifications (Lee et al. 2010). Even nonzero discharge potential has been shown to improve charge efficiency (Avraham et al. 2009). Continuous charging of the carbon surface with the same polarity has been shown to exhibit some interesting inversions in electrode behavior (Bouhadana et al. 2011).

The pore structure of three-dimensional electrodes can indeed be quite different. As a generalization two different pore regions, namely inter-particle pore region and intra-particle pore region, are assumed in the ion-transfer calculations (Wen et al. 2012). The structural and performance aspects of such electrodes have also been investigated (Brogioli et al. 2012).

The charging step indicated in Fig. 3a requires energy input. Naturally, one should also get electrical energy and release during the discharge step (Fig. 3b). Since in this step, the electric charge stored in the electrodes (which behave as supercapacitors) is released. This is similar to electrodialysis reversal. This aspect is receiving considerable attention in recent times (Brogioli et al. 2012; Dermentzis and Ouzounis 2008).

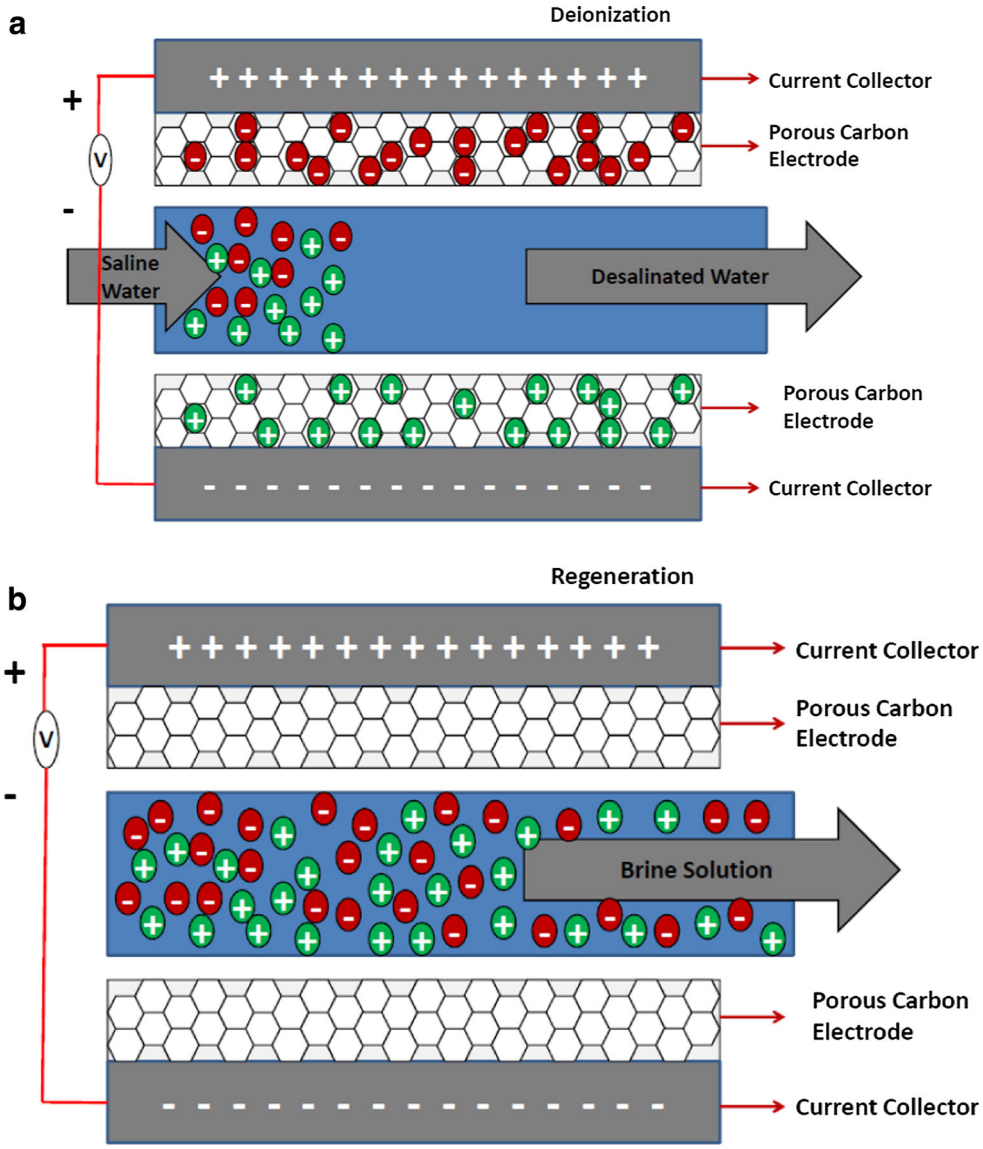

Fig. 3 Schematic representation of the capacitive deionization **a** purification and **b** regeneration processes

The applied electrode potential between the electrodes, the salt concentration, and nature of the cationic and anionic species present in the solution, the flow parameters and the charge–discharge delay times can also influence the overall CDI performance. Response surface methodology has been used for optimizing such operational parameters. In CDI, the optimum level of performance has shown with a cell voltage of 1.57 V, initial NaCl concentration of 1000 mg/L and flow rate of 25 mL/min. Under these conditions, the maximum electrosorption capacity obtained was 10.67 mg/g (Zhao et al. 2014). Electrosorption selectivity of different ionic species has been compared in another recent study using activated carbon cloth electrodes. Using CDI, the ions such as Na^+ (132.4 μmol/g), Mg^{2+} (62.12 μmol/g), Ca^{2+} (33.91 μmol/g) and K^+ (3.38 μmol/g) have been removed. The salt removal efficiency was found by 57.9 % for Ca^{2+}, 47.2 % for Mg^{2+} and 25.2 % for Na^+ and 26.2 % for K^+ (26.2 %), respectively, using CDI (Hou and Huang 2013; Hou et al. 2013 and Huyskens and Helsen 2013). Specific studies relating to boron removal (30 %) (Avraham et al. 2011), water recovery from brackish water containing oil contaminants (Kim et al. 2010) and reverse osmosis reject (Lee et al. 2009) has also been reported. Sol–gel approach for the preparation of electrodes was found to improve the desalination efficiency (Kim et al. 2014).

Graphene oxide composite electrodes

Graphene and graphene oxide-based nanoparticles are currently receiving attention in many areas of electrochemistry as well as nanotechnology. A few recent studies

Table 2 Timeline of electrode developments and electrode modifications for CDI, indicating milestones since the inception of CDI in 1960

Developments	References
Electrode material development	Blair and Murphy (1960)
Application of carbon aerogel	Farmer et al. (1996a)
Electrodes with addition of TiO_2 composite	Porada et al. (2013)
Application of MWCNT	Ryoo and Seo (2003)
Membrane capacitive deionization	Li et al. (2012)
Application of CNT/CNF	Wang et al. (2006)
Mechanism of salt removal based on faradaic reaction followed by ion exchange resin	Choi and Choi (2010)
Application of GO based electrodes	Wang et al. (2012a, b, c, d)
Efficiency increased by surface treated electrode	Cohen et al. (2011)
Selective removal of nitrate	Kim et al. (2012)
Ion selective CNT (SO_3^-)	Yang et al. (2013)
Carbon modified electrodes	Almarzooqi et al. (2014)
Metal–organic composite	Liu et al. (2015)

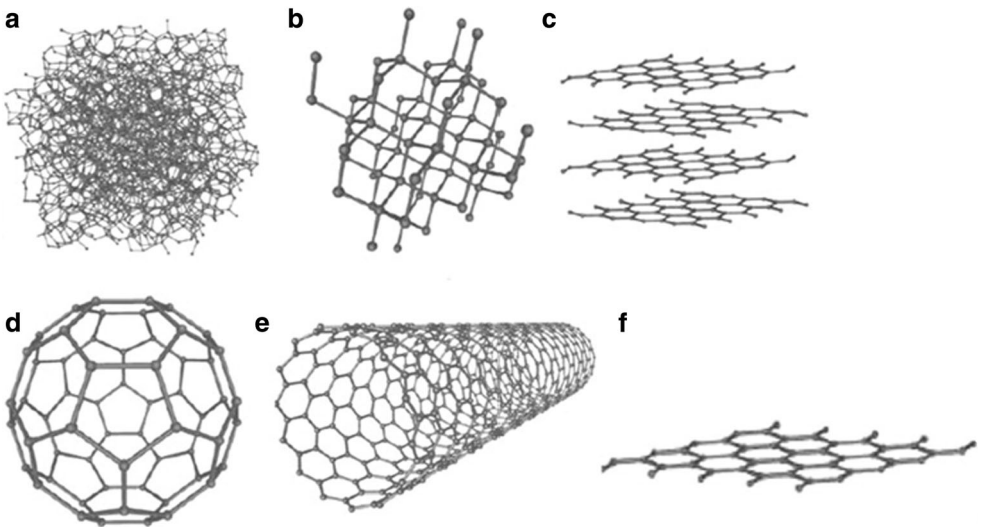

Fig. 4 Some of the structures of various carbon allotropes. **a** Amorphous carbon, **b** diamond, **c** graphite, **d** fullerene, **e** CNT, **f** graphene

have shown the potential use of such composite in CDI for water recovery. The effect of wettability of graphene nanoparticles on the CDI performance was reported. The salt removal efficiency of 83.4 % and the specific electrosorptive capacity of 8.6 mg/g using graphene oxide-based materials in CDI process reported recently (Jia and Zou 2012). Graphene-like nanofibers (GNFs) have also shown improved CDI performance. The specific electrosorptive capacity using GNFs was found to be 23.18 μmol/g for removing sodium ions (Na^+). However, the GNFs and the activated carbon (AC) composite have shown the electrosorption capacity of 73.47 μmol/g for the removal of Na^+ ions. Comparison of electrosorptive performance by employing GNFs and AC is shown in Fig. 5a. The surface area of GNF was found to be 989.54 m^2/g and for activated carbon was 222.01 m^2/g. Because of this, GNF has shown better electrosorption capacity (23.18 μmol/g) than activated carbon material (13.73 μmol/g. The principle of CDI and the mechanism of electrosorption of ions onto AC and GNFs electrodes are shown in Fig. 5b. TEM and SEM images of AC and GNFs are shown in Fig. 5c, d (Li et al. 2010). Fictionalization and surface modification of graphene nanocomposite for CDI have also been described (Wang et al. 2012a, b, c, d). A novel approach for the preparation of graphene warped MnO_2 nanocomposite is reported (Wang et al.

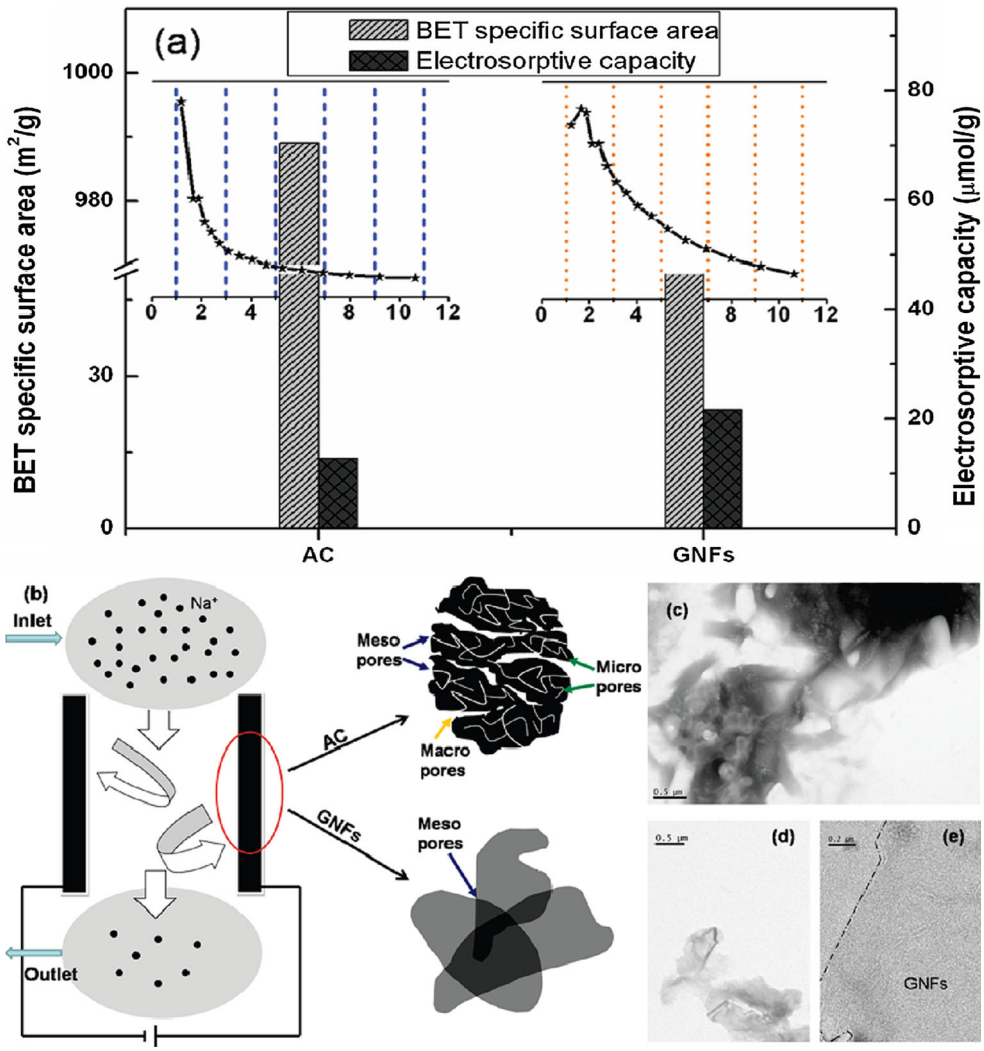

Fig. 5 **a** Comparison of electrosorptive performance by employing GNFs and AC at the same experimental condition, the pictures at *top-left* and *top-right* depict the pore size distribution of AC and GNFs below 10 nm, respectively. **b** Mechanism of CDI employing AC and GNFs electrode. TEM observation images of AC (**c**) and GNFs involve (**d**) and high (**e**) magnification, respectively (Li et al. 2010)

2012a, b, c, d). This process involves the conversion of graphite into graphene and intercalating the same with nano MnO_2. CDI using the above electrode resulted in improved specific capacitance (292 F/g), electrosorption capacitance (5.01 mg/g) and salt removal efficiency (~93 %) (EI-Deen et al. 2014).

Carbon nanotube composite electrodes

Carbon nanotubes also exhibit high surface area with ionic adsorption properties. However, the preparation of CNT-based composite electrodes is also new area of research with significant future potential.

CNT prepared in the form of sponge has been studied in NaCl solution. This has shown a maximum desalination capacity of 40 mg/g (Wang et al. 2011). Electrophoretic deposition is another approach for the preparation of CNT-coated film electrodes. This exhibited mesoporous network structure and which may be beneficial for the enhanced electrosorption capacity (Nie et al. 2012a, b). Different types of carbon nanoparticles have also combined for the preparation of composite electrodes. For example, graphene/CNT composite exhibited excellent desalination behavior when compared with graphene (GR) and commercial activated carbon (AC). The electrosorptive capacity of the GR/CNT, GR and AC was found to be 1.41, 1.10 and 0.99 mg/g, respectively (Zhang et al. 2012). It was reported that ordered mesoporous carbon (OMC)/CNT composite electrodes exhibited excellent desalination efficiency. The desalination capacity for OMC/CNT, OMC and AC was found to be 10.74, 9.19 and 3.69 μmol/g (Peng et al. 2012). In another study, the performance of CNT and

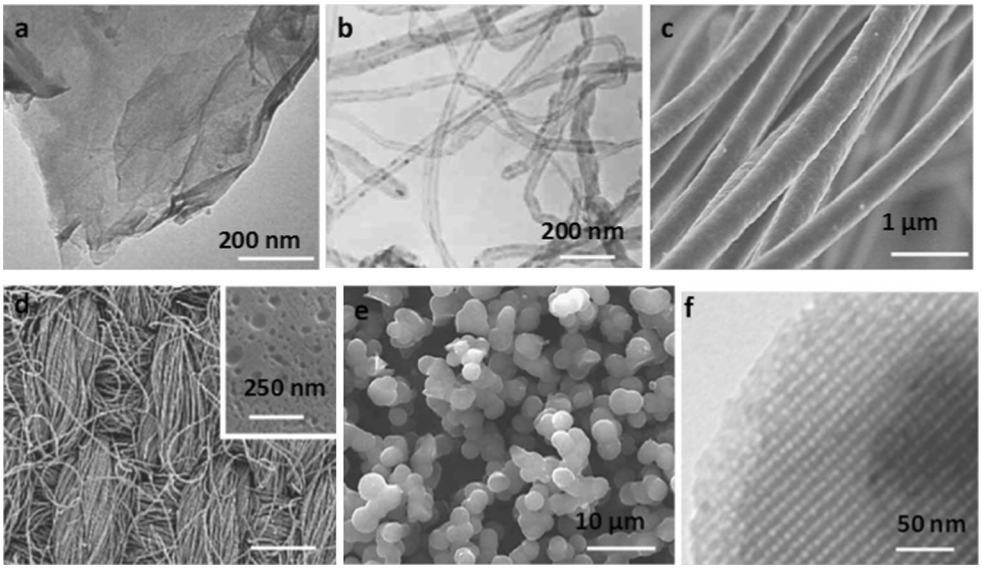

Fig. 6 Section of carbon materials used for CDI. Graphene-like carbon flake (**a**), multiwalled carbon nanotubes (**b**), electrospun fibers (**c**), activated carbon cloth (**d**), carbon aerogels (**e**) and ordered mesoporous carbon (**f**) (Noked et al. 2011)

reduced graphene oxide (RGO) is compared with specific capacitance of CNTs (202 F/g), RGO (293 F/g) and CNTs/RGO composite (311.1 F/g) at 10 mV/s in 1 M NaCl solution (Li et al. 2013). The SEM images of different carbon materials used in CDI cells are also provided in Fig. 6 (Porada et al. 2013).

Mesoporous carbon electrodes

Conventional carbon black used in activated carbon composites for improving electronic conductivity is porous in nature. The microporosity of carbon black has been studied recently (Stoeckli et al. 2002). The positive influence of such mesoporous conducting carbon black on the performance of activated carbon electrodes in CDI is now well established (Nadakatti et al. 2011).

Many ordered mesoporous carbon materials are now synthesized and characterized for potential use in capacitive deionization. Sol–gel process still remains a simple approach for this electrode preparation and resulted in excellent electrode material for CDI (Li et al. 2009). Synthesis of hierarchical ordered mesoporous carbon from phloroglucinol–glyoxal has been described (Mayes et al. 2010). Electrospinning technique is used for the synthesis of carbon nanofiber (CNFs) by facile method. This nanocarobonaceous material is composed of polyacrylonitrile (PAN) and poly(methyl methacrylate) (PMMA). It was reported that CNFs have shown the salt removal efficiency of ~90 % and a specific capacitance of 237 F/g (Wang et al. 2012a, b, c, d; El-Deen et al. 2013).

Mesoporous carbon materials (Zou et al. 2008a, b) and hollow carbon nanofibers (El-Deen et al. 2014) have been investigated for the desalination of brackish water. Mesocarbon materials prepared by self-assembly have also been tested for desalination of saline water. These electrodes have shown better specific capacitance and higher removal efficiency than activated carbon materials (AC) and ordered mesoporous carbon materials (OMC). The specific capacitance of activated carbon (AC) and ordered mesoporous carbon (OMC) materials was reported to be 133 and 107 F/g, respectively, and their salt removal efficiency was reported to be 11.6 and 4.3 µmol/g, respectively (Tsouris et al. 2011).

Polymer composite electrodes

The wettability of activated carbon can be enhanced by preparing a polymer composite with polyvinyl alcohol. Such polymeric composite prepared using glutaric acid for cross-linking was found to enhance the performance of activated carbon electrodes (Park et al. 2011). Carbon nanofibers for CDI have been synthesized from materials like polyacrylonitrile using electrospinning method (Barakat et al. 2014). Modification in the preparation technique can significantly modify the performance of such carbon nanofiber-based electrodes (Li et al. 2014).

Table 3 Composition of carbon aerogel–silica gel composite electrodes and comparison of coulombs during ten cycles

S. no.	Type	Composition of carbon aerogel–silica gel	Average charging coulombs, (A min)	Average discharging coulombs, (A min)	Average specific discharging coulombs, (A min)/g	Average CDI efficiency (%)
1	A	100 wt% carbon aerogel + 0 wt% silica gel	0.354	0.136	0.680	38.4
2	B	75 wt% carbon aerogel + 25 wt% silica gel	0.374	0.140	0.824	37.4
3	C	50 wt% carbon aerogel + 50 wt% silica gel	0.364	0.146	0.973	40.1
4	D	25 wt% carbon aerogel + 75 wt% silica gel	0.322	0.102	0.785	31.6

Conducting polymer-based carbon electrodes can enhance the adsorption capacity as well as electronic conductivity of the electrode material. No conductivity additives would be required for such electrodes. Polypyrrole/graphite (PPy/G) composite electrode was recently evaluated for CDI process. Specific adsorption capacity of PPy/G electrodes varies with the type of dopants (Liu et al. 2012). Activated carbon electrodes, modified with polyaniline were also found to be effective for this application. The salt removal capacity using PANI/AC composite electrodes in CDI process was found to be 3.15 mg/g which was much higher than that of AC (1.98 mg/g (Yan et al. 2014). As well as PANI/AC has shown superior conductivity as AC. Development of single-walled carbon nanotube/polyaniline composite electrodes exhibited a better salt removal efficiency (12 %) compared to that of the SWCNT (Yan et al. 2012).

Carbon sheet electrodes

Electrodes in the form of ultrathin porous sheets would be much more convenient for preparing high surface area electrode packs for CDI. This is one of the reasons for the initial success of CDI unit development with aerogel electrodes (Table 2). Development activities in aerogel electrodes are still going on.

Carbon aerogel electrodes

Aerogel-based electrodes Pekala et al. 1992; Moreno-Castilla and Maldonado-Hodar 2005) are developed now-a-days for novel applications. The ionic adsorption studies related to CDI using aerogel electrodes are also being reported from time to time. The electrical double layer model for the porous aerogel electrodes has been extended for the study in ionic adsorption from aqueous solutions (Yang et al. 2001). A new aerogel and silica gel composite electrode has also been developed for this purpose. These composite electrodes have been evaluated by electrochemical parameters and are presented in Table 3 (Yang et al. 2005). It was found that resorcinol formaldehyde (RF) organic aerogel-based electrodes have shown high electrical conductivity (~13.2 S/cm), specific capacitance (~220 F/g) and salt removal efficiency 97.6 % at 1.7 V (Jung et al. 2007).

The nanostructured aerogel electrodes can be easily contaminated by the impurities in the brackish water selected for deionization. This stability aspect has been investigated recently (Haro et al. 2011; Xu et al. 2008). The influence of operating parameters of the CDI unit on their overall performance in brackish waters has also been investigated (Xu et al. 2008).

Activated carbon cloth electrodes

Activated carbon cloths are now-a-days prepared commercially by a handful of manufactures globally. These cloths are also highly porous. These materials are now finding application in organic adsorption in water purification (Cukierman 2013). These materials, however, are hydrophobic, and their conductivity is also low (Huidobro et al. 2001). However, activated carbon cloth can be chemically activated using (NH_4Cl, $AlCl_3$, $ZnCl_2$, $FeCl_3$, H_3PO_4 or Na_2HPO_4) (Huidobro et al. 2001) and

electrochemically (Berenguer et al. 2012) activated for application as electrode materials in CDI process. These materials are now being evaluated for application in the area of supercapacitors (Xu et al. 2007).

Recently activated carbon cloth electrodes have also been evaluated for CDI process. These electrodes can now be operated in monopolar and bipolar modes in CDI flow reactors (Lee et al. 2012; Lee and Choi 2012). The effect of surface modification and electrode performance is an active area of research at present. Nitric acid modification was found to improve CDI efficiency. The efficiencies of untreated carbon cloth, KOH-treated carbon cloth and HNO_3-treated carbon cloth are reported to be 53, 58 and 67 %, respectively (Oh et al. 2006). The influence of chemical activation time can also influence the surface properties for CDI application (Ahn et al. 2007).

Divalent cations can be selectively adsorbed on activated carbon cloth. The possibility of using activated carbon cloth electrode for hardness removal based on this property has been studied recently (Seo et al. 2010). Surface modification of carbon cloth electrode by zinc oxide nanorods was found to improve the hydrophilicity and desalination behavior significantly (Myint and Dutta 2012).

Membrane capacitive deionization

During the charging process in CDI, ideally the cations alone should move into the porous cathode material and anions alone should move into the positively charged anode material. During the discharge process, these ions should move out. However, in real experiments, the coions will also move into the anode and cathode surfaces. This would lead to loss of efficiency of deionization. To overcome this problem, ion-selective membranes are fixed closer to the electrode surface. Cation exchange membrane near the cathode will allow cations to selectively move in (charging) and out (discharging). Anion exchange membrane will function similarly near the anode allowing selective anion movement. This modification is termed as membrane capacitive deionization (MCDI) shown in Fig. 7.

Research work has progressed quite swiftly in the field of MCDI. Excellent recent reviews cover the subject quite extensively. The salt removal efficiency of MCDI cell was enhanced by 32.8–55.9 % compared to CDI cell, and current efficiency of 83.9–91.3 % was higher for the MCDI compared to 35.5–43.1 % for the CDI. Single-walled carbon nanotube (SWCNT) was used together with cation and anion exchange membrane to achieve salt removal efficiency of 97 %. This efficiency was much higher than corresponding CDI salt removal efficiency of 60 % (Kim et al. 2010; Kim and Choi 2010a; Li and Zou 2011 and Biesheuvel and Van der wal 2010). Many new ion exchange membranes have been developed and evaluated for MCDI application (Kwak et al. 2012). Optimizations of experimental conditions for efficient salt adsorption and removal have been reported (Zhao et al. 2013a, b, c). MCDI units have also been operated at constant current conditions instead of the conventional constant cell voltage operation (Zhao et al. 2012). The energy efficiency of MCDI is found to be comparable to RO processes under constant current operation (Zhao et al. 2013a, b, c).

MCDI units are ideal for treating low-level salt contamination. This approach is found to be suitable for the production of ultra pure water (Lee et al. 2012). Some studies have also evaluated the performance efficiency of MCDI for the removal of acetic acid (76.97 %) and sulfuric acid (98.08 %) from biomass (Kim et al. 2012; Kim and Choi 2012). MCDI can be effectively utilized to remove $ZnCl_2$ (Jung et al. 2012). MCDI has also been reported to save water up to 28 % and chemicals up to 85 % in cooling tower operations (Limpt and Van der wal 2014). MCDI can also be useful in treating the wastewater in thermal power plants. MCDI has shown maximum salt removal efficiency (92 %) and energy consumption (1.96 Wh/L) than CDI in treating the water sample (Lee et al. 2006).

Conceptually, MCDI is certainly an improvement over CDI. However, the ion exchange membranes certainly may increase the cost of production of CDI unit. During the past few years, selective coating of carbon electrodes with ion exchange resins is found to be an effective alternative approach than using separate membranes. Polyvinyl alcohol and sulfosuccininc acid (SSA) coating can serve as an effective cation exchange membrane. The SSA was effectively introduced as a cross-linking agent in PVA/SSA polymer. The specific capacitance of the PVA/SSA-coated carbon electrodes was higher by 14.8–30.9 % compared with uncoated electrode (Kim et al. 2010; Kim and Choi 2010b, c). Alternatively, new approach based on advance membrane capacitive deionization (A-MCDI) has been developed recently. The coated polymer layer on carbon electrode can be sulfonated or aminated to obtain cation or anion exchange surface. The thin layer reduces contact resistance between the ion exchanger and electrode of a MCDI. A-MCDI was expected to exhibit high removal efficiency and a low current consumption compared to a conventional MCDI. To compare CDI, MCDI and A-MCDI, salt removal efficiency of 79.1, 9.23 and 83.4 % and power consumption of 212.3, 2.318 and 23.07 mWh,

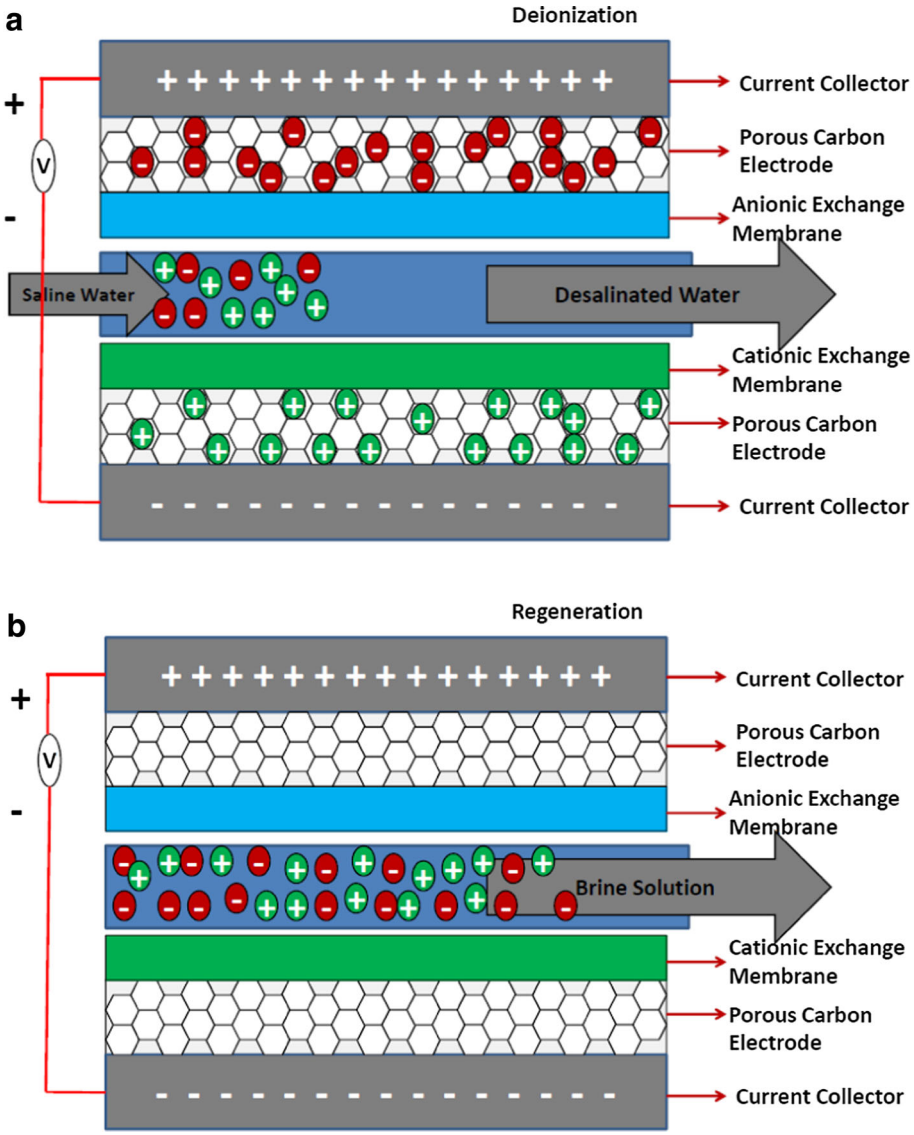

Fig. 7 Schematic representation of the membrane capacitive deionization **a** purification and **b** regeneration process

respectively, have been reported (Lee et al. 2011). Electrophoretic deposition of CNT and poly acrylic acid composite can also exhibit cation selectivity due to the presence of carboxylate group (Nie et al. 2012).

Studies on actual CDI units

Most of the basic investigations on CDI have been carried out in a single parallel plate flow cells with two identical electrodes. However, a few laboratories have also described laboratory modules which can deliver pure water at the rate of 75 L/day. Typical schematic representation of laboratory module CDI cell unit is provided in Fig. 8a (Welgemoed and Schutte 2005). The actual cell module with feed and drain water connections is shown in Fig. 8b.

The first such laboratory module was described by Joseph Palmer and co-workers in the USA (Johnson and Newman 1971). Since then improved laboratory modules have been developed in South Africa (Broseus et al. 2009) Canada (Mossad et al. 2012; Mossad and Zou 2012) and Australia (Mossad et al. 2012; Mossad and Zou 2013). EST water & technologies (People's Republic of China) has developed a CDI process in large-scale for desalination of wastewater in industries, such as petrochemical industry, steel mills,

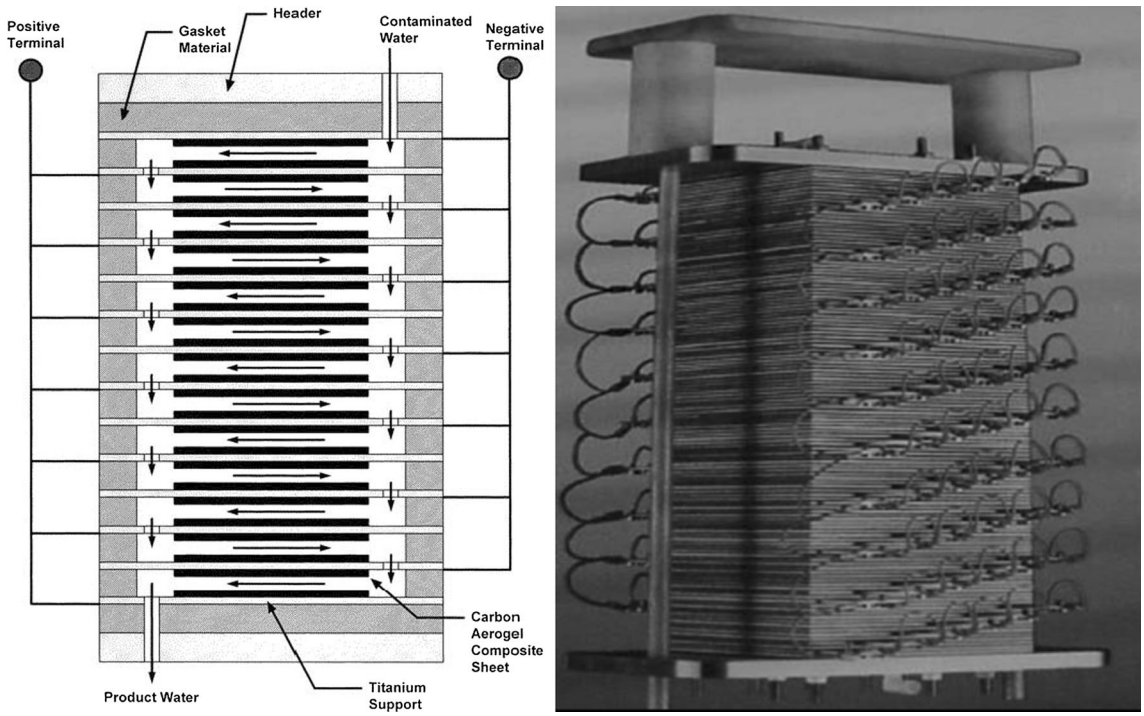

Fig. 8 Schematic representation of an electrochemical adsorption-regeneration cell (Welgemoed and Schutte 2005)

thermoelectric power plants, coal chemical manufacturing, paper mills. As on now more than 30 industrial systems are installed in China, where most of the facilities are for industrial/municipal wastewater recovery/reuse with treatment capacities ranging from 100 to 2000 m^3 h^{-1}. In terms of energy consumption, EST modules are attractive in comparison to RO modules, with values of energy consumption around 1.0 kWh m^{-3} for EST CDI and 1.5 kWh m^{-3} for RO (Suss et al. 2015). The influence of feed composition and other operating parameters has also been described in these studies. Commercial CDI units are also entering the market in recent times. It appears that commercialization of CDI technology has still a long way to go before becoming a technology in common use.

Conclusion

The review presented here suggests that CDI technology is at an interesting and challenging phase of development today. The technological feasibility has now been clearly established. Further studies to improve cost effectiveness, energy efficiency and system stability for handling different feed compositions are in progress. Fabrication of cost-effective electrodes for CDI units is under development. Replacement of ion exchange membranes with selective polymer coating will certainly find a place in the CDI units of future. Optimizing the system for constant current operation would certainly improve the energy efficiency. The influence of multivalent ions and organic impurities during long-term operation of CDI units is definitely a serious challenge to be tackled in the future.

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