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Review

Capacitive deionization: Processes, materials and state of the technology

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ABSTRACT

Capacitive deionization (CDI) is a novel technology that has been successfully utilized for many water treatment/purification applications. In many cases, the CDI technology has shown increased efficiency compared to the other contemporary technologies. There have been some recent developments in this field that have enhanced the overall adsorption capacity and thus performance of CDI. Different types of carbon electrodes, such as conventional and latest forms of porous-carbon and graphene based electrodes have been used in the CDI technology. This has facilitated mass transfer in the form of adsorption of salt ions onto modified electrodes and increased the effectiveness of CDI operations. This paper aims to assess the overall state of the CDI technology and review basic concepts, saturation-regeneration of CDI electrodes, and various types of materials used for electrodes. In addition, this article reviews the recent progress made in electrode surface modifications by metals or metal oxides, membrane, polymer, organics and other compounds that have resulted in increased efficiency of ion extraction from the water. The evaluation of past and present published research on use of low-cost carbon forms as CDI electrodes to reduce the overall cost and eliminate the need of regeneration of saturated electrodes is also a part of the article.

1. Introduction

The demand for more quantity of potable water has always been there. The researchers are exploring all possible ways to meet this demand. Seawater is one of the sources that have been focus of recent research in potable water as it is available in huge quantities throughout the world. Besides, brackish water problem is very common in coastal areas. Countries with desert lands and lack of fresh water resources are seeking more cost effective and innovative approaches for desalination of water. Requirement of huge amount of energy, cost of production, fine tuning of design aspects etc. have made it difficult for existing desalination technologies such as; multi-effect desalination (MED), reverse osmosis (RO), multistage flash (MSF) etc. to become sustainable solution option [1,2]. Capacitive deionization (CDI) has emerged as a better suited alternative for these existing technologies in terms of energy efficiency, environmental friendliness and the ion removal efficiency [3]. In a typical CDI cell operation, porous carbon is used as electrodes, a low DC voltage (about 1.2 V) is applied across these electrodes and saline water is pumped into the cell. The oppositely charged electrodes extract the salt ions from water flowing between the electrodes that are separated by small distance of few millimeters. The prolong use of a CDI cell for removal of charged ions (called adsorption phase) usually results in saturation of electrodes and thus lower removal efficiency.

Saturated electrodes that are a result of adsorption phase either can be replaced with a new set of electrodes or regenerated. The regeneration of saturated electrodes can be achieved by desorbing the ions either by applying reverse voltage or short-circuiting the electrodes [1,2,4–8]. There is no need for application of any external pressure to extract ions as required in membrane filtration and some other desalination processes as extraction of ions is aided by the electrostatic force. In case of brackish water, where salt ions are fewer with respect to huge amount of water in which they are dissolved, it is more energy efficient to remove these ions rather than extracting the water as in reverse osmosis. Therefore, CDI is more efficient than RO for water with low salt concentration. However, optimization of operating parameters is still required for large scale applications and same is true for seawater CDI desalination. As there is a desorption stage associated in CDI operations, there is a possibility of energy recovery and it has attracted attention of many researchers. The latest research approaches in CDI are therefore focused on solving the issues such as need for optimization of operational parameters, improvement of co-ion adsorption, and enhancement of surface area and porosity of CDI electrodes.

Modification of surface area of activated carbon, carbon aerogel, graphene, carbon nanotube, carbon nanofoam and other carbon-based electrodes is one alternative for increasing the efficiency of CDI processes. Studies have shown that greater surface area and appropriate pore size distribution (based on the size of the target ions) play a very

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important role in removal efficiency of CDI cells. Usually two same types of electrodes were used in a classical CDI cell which is termed as “symmetric” operation of CDI in various literatures. Modifying each electrode with different metal oxides and consequently shifting the potential zero charge (PZC) location increased the removal efficiency of preferred ions to a significant extent [6]. This is termed as “asymmetric” operation of CDI in literatures, because of the electrochemical dissimilarity of the electrodes. The focus of some studies was on selective ion removal from a solution of mixed ions. For example, fabrication of nitrate selective carbon electrode using resins has shown significant improvement in nitrate removal in one of these studies [7]. High surface area and high electrical conductivity are the most important requirements of CDI electrodes. Synthesis method and activation process are also crucial factors in controlling properties of the surfaces in carbon based electrodes. Resorcinol-formaldehyde method allows a good control in synthesizing carbon aerogel (CA) with desired surface area by varying the mixing ratio and pyrolysis temperature. Thermal activation by CO₂ of CA electrodes in CDI operations made them immensely successful in removing ions such as nitrates and phosphates [9]. Carbon aerogel/fiber paper electrodes washed with acetone and nitric acid also exhibited higher removal capacity in CDI process [10].

Another alternative to improve the efficiency of CDI operations is introduction of ion exchange membranes between the electrodes and spacer channel (the space between two electrodes), and is termed as membrane capacitive deionization (MCDI). These membranes restricts co-ions (ions which have the same charge with respect to an electrode in the removal stage and which becomes oppositely charged in regeneration stage) adsorption during the regeneration process, thus improving the adsorption capacity of electrodes after regeneration [11]. Recent approaches in this research aimed to make MCDI a better alternative for RO in desalination of seawater. MCDI can be more energy efficient than RO for salinity concentrations < 60 mM [4]. Overall energy consumption in MCDI cells has gone down with possible energy recovery during regeneration stage [11]. In one of the modified MCDI methods, electrodes are coated with ion exchange polymers which improve the contact adhesion between the electrodes and ion exchange membranes, resulting in a lower contact resistance and lower bulk resistivity. Consequently energy consumption got lowered compared to conventional MCDI operation [12]. A model is also developed that can successfully helped to predict steady state in CDI operation [13]. The model describes the CDI operation in terms of different operational parameters i.e., flow rate, water quantity, CDI capacitance, resistance, spacer volume, applied potential, and initial concentration etc.

The concept of charge efficiency, defined as a ratio of charge equivalent of total ions adsorbed at equilibrium over charge supplied to an electrode, was developed to give more accurate understanding of the CDI process [14]. There are recent electrode modification studies that aimed to increase the charge efficiency of CDI cells by surface treatment of electrodes with metal oxides. One of these studies, used surface treated electrodes and a “third” electrode of activated carbon fiber to increase the charge efficiency [15].

Statistical models such as Box-Behnken and ANOVA were used in couple of studies to optimize the operational parameters such as initial concentration, flow rate and cell voltage to maximize the electro-sorption of ions in CDI cell [2,16]. The Box-Behnken statistical model was used to predict removal percentage of arsenic in solar panel based CDI setup with activated carbon electrodes. The method predicted the removal to be 84.2% and 100% at different experimental conditions, while actual values were observed to be 82.6% and 98% respectively [16].

This paper reviews the latest modification of CDI processes, recent trends of electrode development using a combination of materials and the current state of the technology. It provides comparative analysis of results achieved in recent research studies in this field. There are some recent publications that reviewed the technology and presented some

interesting information [3,17–23]. However, this paper presents in-depth discussion involving broader range of key parameters and accounts for latest progress in this field. It will help in developing a better understanding of CDI technology and its operational parameters.

2. Process of capacitive deionization

2.1. Basic operation

A capacitive deionization cell includes two electrodes supported on their respective base plates (usually glass/plexiglass) and put together face to face in a parallel configuration with very little separation. The space between electrodes is kept either as open channel [10] or a spacer material is used. Spacer material can be a woven/non-woven fabric [24] or a polymeric mesh [25] or any other mesh like material which is made of electrically insulated, chemically inert and anti-corrosive material [26]. The spacer should allow the solution and ions to flow through to reach the electrical double layer region. In some cases, ion exchange membranes [4] are used in between the electrode and spacer/open channel. Anion exchange membranes only allow anions to go through and cation exchange membrane does the vice versa. A schematic diagram of the typical batch mode CDI experiment is shown in the Fig. 1.

A current collector is also used to provide required charges to electrodes from an external power supplier. Typically, graphite current collectors are used to ensure inertness and corrosion free environment. The use of copper wire as current collector resulted in corrosive reactions in one of the studies [27]. A CDI cell is analogous to a capacitor. The electrodes in a CDI cell are arranged just like capacitor plates and a DC voltage is applied across these electrodes. In CDI cells, aqueous solution with ions to be removed can flow between electrodes. The ions from the solution are attracted, under applied electrical field, on to oppositely charged electrodes as shown in Fig. 2. Water exiting a CDI cell is relatively deionized as compared to water entering the CDI cell. The CDI cell could be fed with water in a single-pass configuration (water travels between electrodes of the cell just once before exiting the cell) or cyclic configuration (water exiting the CDI cell is again directed back to the same CDI cell for multiple times). The single-pass configuration is used with multiple CDI cells arranged in a series while the cyclic rotation is used in case of a single cell (lesser number of cells) where the solution from a reservoir is cyclically pumped through the electrodes using a peristaltic pump. The conductivity (Fig. 1) of the reservoir is observed in real time to measure concentration of ions. Equilibrium condition is achieved when the electrodes can no longer adsorb ions because all adsorption sites are taken by the adsorbed ions and conductivity of the solution no longer changes.

After the adsorption process the saturated electrodes can undergo regeneration/desorption process. This regenerated electrode can be used for adsorption process again, as needed. The process of regeneration is opposite of the adsorption process in case of CDI cells as shown in the Fig. 3.

In this process, the electrodes are either shorted or polarity of the electrodes is reversed. It helps adsorbed ions dislodge and come out into bulk liquid between electrodes before they are flushed out of the CDI cell. A deionized water or salt solution (typically with lower concentration than that of preceding adsorption) stream is pumped through the system to wash out these ions resulting in an ion-saturated stream.

During this regeneration process there is a possibility for dislodged ions to get reabsorbed at the oppositely charged electrode. This is not ideal for regeneration and can be avoided by applying lower voltage for a brief period of time. Alternately, electrodes are simply short circuited and wash-water is pumped at a higher flow rate. To overcome this challenge of re-adsorption some researchers came up with the idea of membrane capacitive deionization where an ion exchange membrane is used in between the electrode and the spacer/open channel. These membranes allow ions that are dislodged from an electrode a one-way

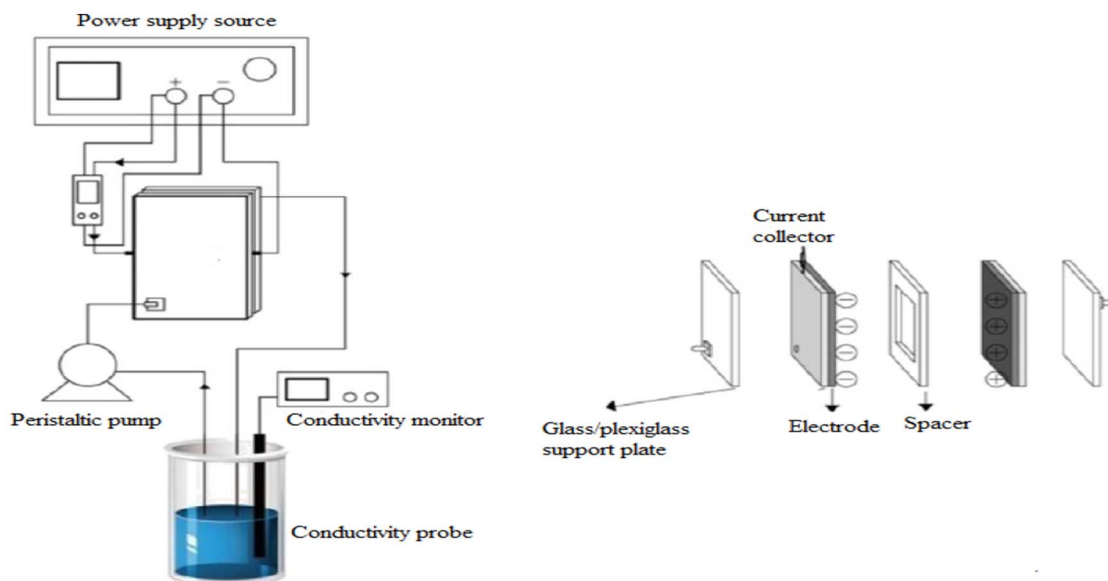


Fig. 1. Process of batch mode CDI experiments - reprinted from [2], Copyright (2013), with permission from Elsevier.

passage to pass through into the bulk solution and prevent the re-absorption on the other electrode (as membrane on the other side would not allow this ion to pass through). This membrane also helps in increasing charge efficiency [14] of the system by allowing counter ion adsorption and co-ion exclusion (details discussed in membrane and charge efficiency sections). The typical process of MCDI is shown in Fig. 4.

2.2. Electrode materials

The most widely used electrodes in CDI applications are carbon based electrodes. Many of these electrodes have high electrical conductivity, low contact resistance (a voltage drop from electrode to the current collector), appropriate wetting behavior, low cost, good process-ability, desirable bio-inertness and needed chemical stability [3]. Various forms of carbon, including its allotropes and composites are used in CDI applications such as – activated carbon [28], carbon cloth [29], carbon aerogel [10], carbon nanotube [30], carbide derived carbons [31], and graphene [32] etc. These materials are chosen due to their high specific surface areas (SSA) and porous structures, which ensures plenty of available area for electro-sorption. In case of graphene its selection is based of ease of regeneration of saturated electrodes. Many metal oxides and carbon composites are used by some researchers due to their enhanced electrochemical performance [33]. Examples of electrode materials used in CDI applications can be seen in Tables 1 to 4a, 4b.

3. Digging deeper into the science of capacitive deionization

3.1. Effect of porosity of electrodes

The porosity of the electrode material plays a vital role in adsorption and electro-sorption performance. The relationship between pore openings and hydrated radius of different ions are discussed in many recent articles. Previous studies [34–37] based on traditional electrical double layer (EDL) suggested that most of the electro-sorption happens in mesopores. However, according to at least one study, the amount of electro-sorption happening in micro-pores could be significant as well [24]. It was explained using modern EDL theories which consider ion hydration and water-water interaction phenomena instead of classical EDL theories. In such models, ions are expected to form a single layer in the middle of the pore, where classical model suggests that there may be no electro-sorption at all in these micropores because of diffuse layer overlapping. Also, it was found that electro-sorption capacity increased with increase in applied potential and ionic strength as diffuse layer in the EDL shrinks (Fig. 5). In one study, three mesoporous carbons with 2D-hexagonal, 3D-cubic and 3D-bicontinuous pore openings were used as electrodes [36]. The average pore openings of these materials were 7.57 nm, 3.42 nm and 3.25 nm respectively. This study suggested that electrode with 2D-hexagonal structure favors monovalent ions to get adsorbed in the pore walls. The electrode with 3D-cubic space favored monovalent and trivalent ions. The third one, with 3D-bicontinuous

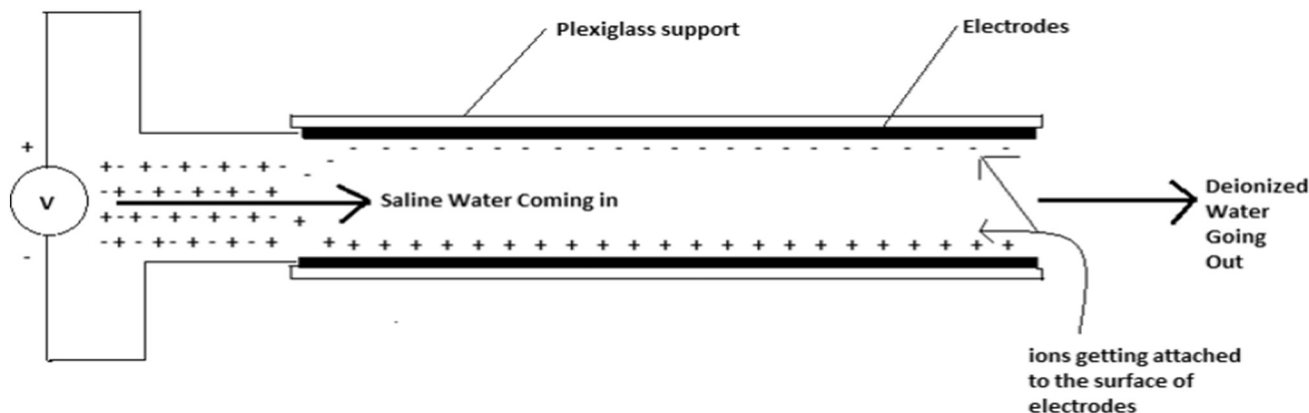


Fig. 2. Basic idea of adsorption in CDI process.

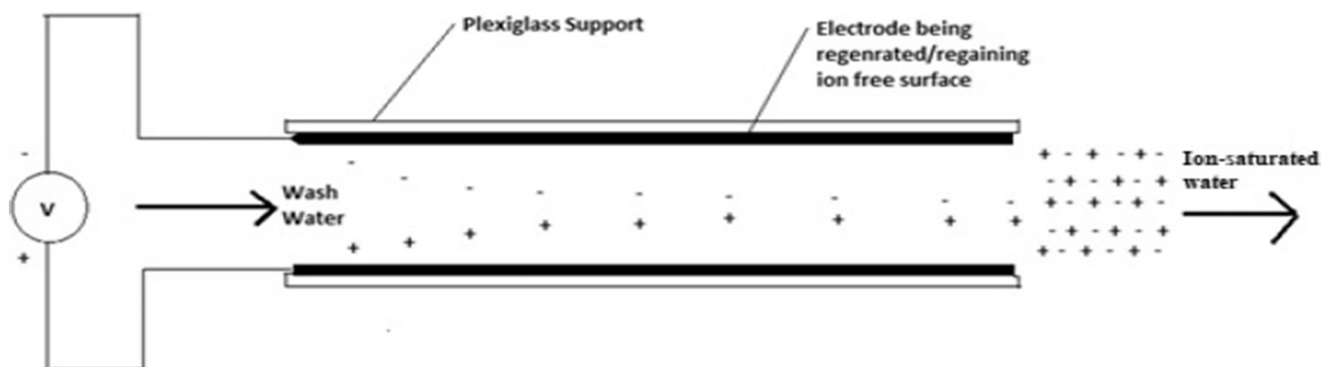


Fig. 3. Regeneration of electrodes in CDI process.

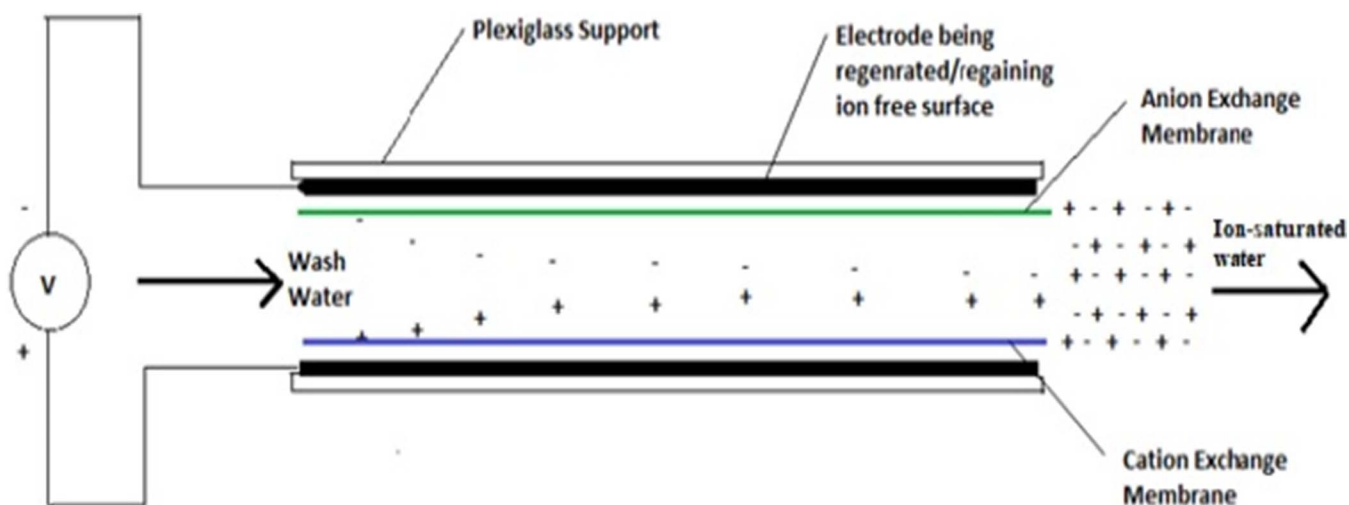


Fig. 4. Process of membrane capacitive deionization during desorption.

Table 1
Removal by different electrodes with different specific surface area (SSA) and pore opening.

Reference	Electrode materials	Removal in % or mg/g	SSA (m ² /g)	Average pore size (nm)
[28]	Pure activated carbon (parent)	50%	932.4	4.2
	Activated carbon treated with KOH	55%	889.1	4.19
	Activated carbon treated with CO ₂	60%	851.3	4.07
[38]	Reduced graphene oxide and activated carbon fiber composite (RGO/ACF-10)	7.2 mg/g	621	2.2
	RGO/ACF-1	–	584	2
	RGO/ACF-5	–	612	2.2
	RGO/ACF-15	–	456	2.2
	RGO	–	53	15.3
	ACF (parent)	4.7 mg/g	630	1.9
[39]	OMC-S (nickel sulfate based ordered mesoporous Carbon)	0.93 mg/g	1491	3.7
	OMC-N (nickel nitrate based)	0.54 mg/g	1594	3.3
	OMC-W (without nickel salt)	0.602 mg/g	950	4
	Activated carbon (AC)	0.275 mg/g	845	–
[30]	Multiwalled carbon nanotube	13.07 mg/g	208	13.7
	AC	6.03 mg/g	964	2.1

pore opening, did not show significant electro-sorption compared to the performances of first two electrodes. The probable reason is its bi-continuous path in pore structure (Fig. 6).

Resorcinol based mesoporous carbon graphite (RMCG) electrodes and phloroglucinol based mesoporous carbon graphite electrodes (PMCG) electrodes were synthesized and their performances were compared to carbon aerogel electrodes [37]. The pores of the PMCG electrodes have narrower distribution as compared to RMCG electrodes. At around, 5000 ppm salt concentration carbon aerogel electrodes exhibited lower removal rate than that of PMCG and RMCG electrodes in CDI experiments (Fig. 7).

The performance comparison of some electrode materials with different specific surface areas and pore openings is presented in Table 1. It is evident from this comparison that it is not just only pore sizes and high surface areas that contribute to higher removal capacity. The pore structures and pore size distributions also have to be taken into consideration along with other variables.

3.2. Effect of charge efficiency of electrical double layer

Concept of charge efficiency was first defined as the ratio of equilibrium salt adsorption and total electrode charge [14]. In ideal

Table 2

Key parameters and their significance in selection of CDI electrodes selection based on physical, chemical and other characteristics.

Parameter	Significance
Specific surface area (SSA)	Needed to provide space for ions to be adsorbed onto the electrode surface. Essential for obtaining higher specific capacitance.
Pore size distribution	Pore sizes and their distribution is important for removal of ions with a certain radius and to overcome electrical double layer overlapping. Pore smaller than target ions will contribute in overall surface area but would not be effective in removal of target ions.
Conductivity	Higher conductivity or lower resistance values lead to faster charge transfer and hence faster ion adsorption-desorption.
Electroactive surface	The more ion accessible surface an electrode has the more it would be efficient in ion removal. Higher SSA increases possibility of more accessible surface, but doesn't guarantee the material highly efficient as electrode. Pore openings, physical arrangement of pore paths etc. also affects the availability of active or accessible surface.
Stability	An electrode must be stable at applied voltage ranges and its surrounding chemical environment.
Cost	Constraints of cost and corresponding efficiency of electrodes must be considered

Table 3a

Capacitance of different electrodes under different specific current.

Reference	Electrode materials	Capacitance (F/g) at specific current (A/g)	
		0.05 A/g	1 A/g
[38]	Reduced graphene-oxide and activated carbon fiber composite (RGO/ACF-10)	256	193
	RGO	135	98
	ACF	214	148
[44]	Graphene-oxide & porous carbon nanofiber composite (GO-PCNF)	151.6	–
	PCNF	105.9	–

conditions, it is expected that for supply of one unit of charge to the electrode, one oppositely charged ion with same unit charge would be adsorbed. Therefore, the charge efficiency value will be equal to 1. But this is not the case in double layer phenomena. The idea of charge efficiency arose from the fact that in the electrical double layer, formed near electrode surface, inclusion of not only counter ions takes place but also exclusion of co-ions occurs. This reduces the overall efficiency < 1 for the system. Later, based on this concept, it was demonstrated that electro-sorption capacity of the electrodes can be increased by improving the charge efficiency as well [40]. The electrode (denoted by A15 in the work and Fig. 8) with highest BET surface area showed the lowest electro-sorption capacity in their CDI experiments.

The reason behind the lowest electro-sorption, was attributed to the

lower charge efficiency showed by A15 compared to other electrodes. The lower charge efficiency value of A15 electrodes may have been caused by higher pore volume and lesser graphitized structure (as reported by analyzing FTIR spectra). It is evident, from Fig. 9, that A15 showed highest physical adsorption capacity as expected due to its higher surface area. But when it came to electrosorption performance, the trend was same as charge efficiency.

3.3. Constant voltage and constant current methods

Constant voltage (CV) and constant current (CC) modes are both widely used in CDI operation [3]. Sometimes these modes can be used simultaneously in different parts of a CDI system to ensure optimized performance by each part [41]. The pros and cons of both CV mode and CC mode under same operating conditions were discussed [42]. The Fig. 10 shows effluent concentration at CV and CC mode.

As current density varies in CV mode, the effluent concentration also gradually decreases (adsorption) and gradually increases (desorption). The final concentration is dependent on applied voltage. As voltage increases the final concentration decreases in adsorption process (Fig. 10a). Since, CC mode is operated at a predetermined current density, the effluent concentration remains constant depending on this applied current density throughout adsorption process (Fig. 10b).

Therefore, CC mode is a better fit in situations where a desired concentration of effluent is required. On the other hand, if maximum removal of ions is required for a process, CV mode is suggested to be used as it can deliver higher adsorption rate at the same operating

Table 3b

Capacitance of different electrodes under different scan rates.

Reference	Electrode materials	Capacitance (F/g) for given scan rate (mV/s)					
		1 mV/s	3 mV/s	5 mV/s	10 mV/s	20 mV/s	50 mV/s
[45]	Activated carbon cloth (ACC) grafted with ZnO nanorod	95	70	–	–	–	30
	ACC grafted with ZnO microsheet	74	63	–	–	–	24
	ACC grafted with ZnO nanoparticle	75	55	–	–	–	21
	ACC grafted with ZnO microsphere	73	62	–	–	–	20
[39]	OMC-S (nickel sulfate based ordered mesoporous carbon)	192	–	150	125	–	–
	OMC-N (OMC based on Nickel Nitrate)	174	–	135	110	–	–
	OMC-W (OMC without Nickel salt)	140	–	133	95	–	–
	OMC-S (nickel sulfate based ordered mesoporous carbon)	108	–	82	40	–	–
[46]	Carbon nanofiber (CNF-based on Phenolic resin) -600	–	–	–	1.6	1.1	0.7
	CNF-800	–	–	–	41.8	37.7	30.5
	CNF-1000	–	–	–	52.1	48.8	41.4
[47]	ACC	100	–	–	70	–	40
	ACC-ZnO nanorod	80	–	–	60	–	50
[33]	Graphene and MnO ₂ nanorod composite	–	–	–	292	–	–
	Graphene and MnO ₂ nanoparticle composite	–	–	–	180	–	–
	Pristine graphene	–	–	–	144	–	–
	Activated carbon (AC)	–	–	–	205	–	–
	GO-PCNF	–	–	–	151.6	–	–
[30]	PCNF	–	–	–	105.9	–	–
	Multiwalled carbon nanotube (MWCNT)	–	–	47.4	–	–	–
	AC	–	–	72.5	–	–	–

Table 4a
Removal per electrode mass by different electrodes under variable conditions.

Reference	Operating conditions	Electrode type	Removal (mg/g)
[45]	Solution: 100 mg/L NaCl; applied voltage: 1.2 V; flow rate: 2 mL/min; electrode area: 8.4 cm ² ; temp: N/R	Activated carbon cloth (ACC)	5.8
		ACC grafted with ZnO nanorod	8.5
		ACC grafted with ZnO microsheet	8.5
		ACC grafted with ZnO nanoparticle	1
		ACC grafted with ZnO microsphere	2.5
[6]	Solution: 500 mL 233 mg/L NaCl; applied voltage: 1.2 V; temp: N/R; electrode mass: 0.75 g; spacer: 3 mm; flow rate: 8.4 mL/min; electrode area: 40 cm ²	Carbon xerogel (CX)	1.9
		CX-SiO ₂ as cathode & CX as anode	3
		CX-COOH (oxidized CX) as cathode & CX as anode	3.8
		Carbon aerogel	5.8
[37]	Solution: 100 mL 5000 mg/L NaCl; applied voltage: 1.2 V; temp: 25 °C; electrode mass: N/R; spacer: 6 mm; flow rate: 30 mL/min; electrode area: 110 cm ²	Resorcinol based mesoporous carbon on graphite	13.8
		Phloroglucinol based mesoporous carbon on graphite	12.4
		Activated carbon	0.8
[32]	Solution: 25 mg/L NaCl; applied voltage: 2 V; temp: N/R; electrode mass: N/R; spacer: N/R; flow rate: 25 mL/min; electrode area: 98 cm ²	Graphene like nanoflakes (GNFs)	1.35
		Graphene oxide-porous carbon nanofiber	7.8
[44]	Solution: 100 mg/L NaCl; applied voltage: 1.2 V; temp: N/R; electrode mass: N/R; spacer: N/R; flow rate: 6 mL/min; electrode area: N/R	PCNF	5.9
		Activated carbon (AC)	2.5
[46]	Solution: 2000 mg/L; applied voltage: 1.2 V; temp: 25 °C; electrode mass: N/R; spacer: N/R; flow rate: 6 mL/min; electrode area: 9 cm ²	Carbon nanofiber (CNF-based on phenolic resin) -600	20.1
		CNF-800	35.9
		CNF-1000	50.1
[47]	Solution: 1000 mg/L NaCl; applied voltage: 1.6 V; temp: N/R; electrode mass: N/R; spacer: N/R; flow rate: 3 mL/min; electrode area: 8.4 cm ²	ACC	1.92
		ACC-ZnO nanorod	3.6
[49]	Solution: 5 mg/L 200 mL NaCl; applied voltage: 450 mV; temp: 20 °C; electrode mass: N/R; spacer: 3 mm; flow rate: 4 mL/min; electrode area: 60 cm ²	Carbon nanotube (CNT)	1.36
		Air plasma treated CNT	2.4

Table 4b
Percentage of salt removal by different electrodes under variable conditions.

Reference	Operating conditions	Electrode	Removal (%)
[25]	Solution: 40 mL 220 mg/L CaCl ₂ ; applied voltage: 1.5 V; temp: N/R; electrode mass: N/R; spacer: 0.1 mm (mesh); flow rate: 0 (stagnant); electrode area: 25.8 cm ²	Carbon fiber sheet (as cathode & anode)	19
		CF-SiO ₂ as cathode and CF-Al ₂ O ₃ as anode	75
[33]	Solution: 50 mL 45 mg/L NaCl; applied voltage: 1.2 V; temp: room; electrode mass: N/R; spacer: N/R; flow rate: N/R; electrode area: N/R	Graphene and MnO ₂ nanorod composite	93
		Graphene and MnO ₂ nanoparticle composite	75.3
		Pristine graphene	67.5
		Activated carbon	38.1

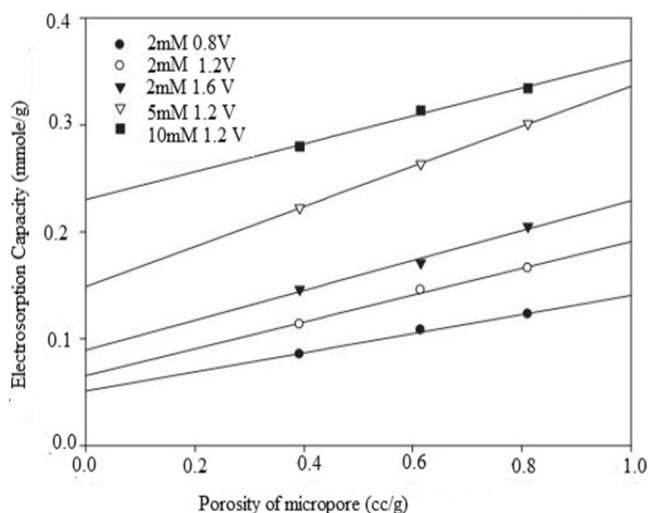


Fig. 5. Electro-sorption capacity vs micro-porosity at various applied voltages and ionic strength – reprinted from [24], Copyright (2014), with permission from Elsevier.

condition (Fig. 11a). Charge efficiency values are higher for CV mode than that of CC mode in voltage range < 0.8 V and lower in voltage range > 0.8 V. For both modes, charge efficiency gradually decreases at higher voltage range (Fig. 11b). Though, adsorption efficiency is greater for CV at same operating conditions, it comes at a cost of higher energy consumption. Fig. 11c shows the energy requirement per ion removal at different cell potential for both CV and CC modes. A MCDI system was much more energy efficient when it was operated in CC mode [4].

4. Electrode and other development approaches in capacitive deionization process

Development and improvement of electrodes and their characteristics have been the most focused research area in CDI literature. Oftentimes electrode material choice in CDI is influenced by the performance of electrodes in supercapacitor literature. Table 2 provides a summary of selection criteria for electrodes in CDI based on some key performance parameters and their significance for CDI electrodes selection.

Carbon based electrodes have been the most popular choice in supercapacitor as well as CDI applications because of their shared desirable traits of low cost, corrosion resistivity, high surface area, good

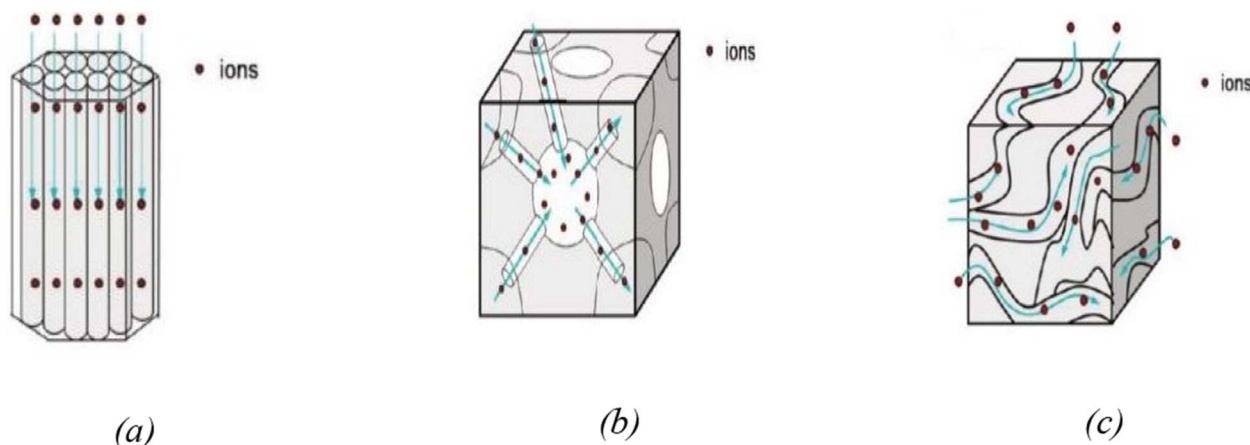


Fig. 6. Possible ion-diffusion path in three different pore structures (a) 2D-hexagonal (b) 3D symmetry cube (c) 3D-bicontinuous-Reprinted (adapted) with permission from [36]. Copyright 2011 American Chemical Society.

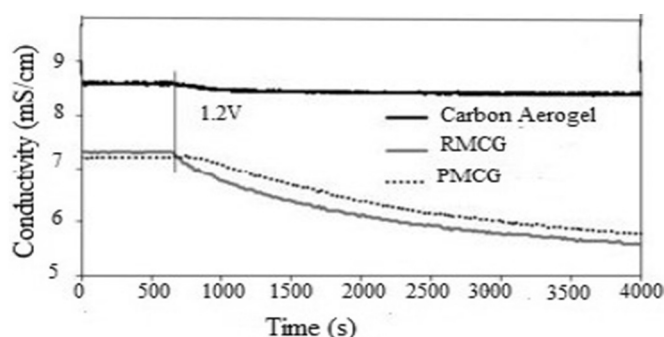


Fig. 7. Comparison of removal rate by carbon aerogel electrode with PMCG and RMCG – reprinted (adapted) with permission from [37]. Copyright 2011 American Chemical Society.

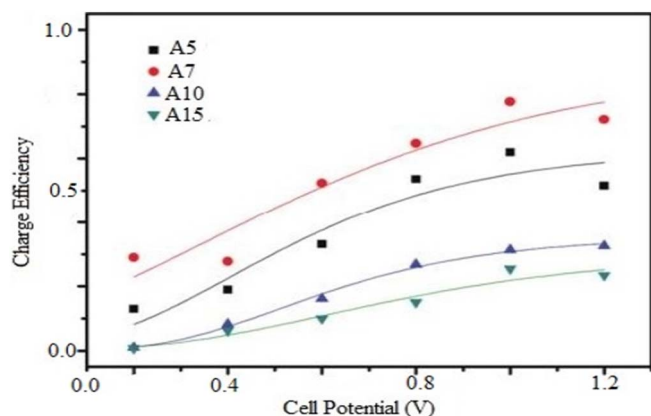


Fig. 8. Charge efficiency of electrodes- Reprinted (adapted) with permission from [40]. Copyright 2012 American Chemical Society.

electrical conductivity and good stability. Many forms of carbon from activated carbon to carbon nanotube have been used as carbon cloth electrodes. Also, carbon allotropes like carbon aerogel, carbon nanofiber, and graphene etc. have been used as electrodes for CDI operations. Recent research efforts are focused on minimizing the cost of production, enhancing efficiency and regeneration of these materials.

4.1. Electrode preference and surface modification

One of the efforts in surface modification is to coat the carbon substrate with a metal oxide to improve the electrode's specific

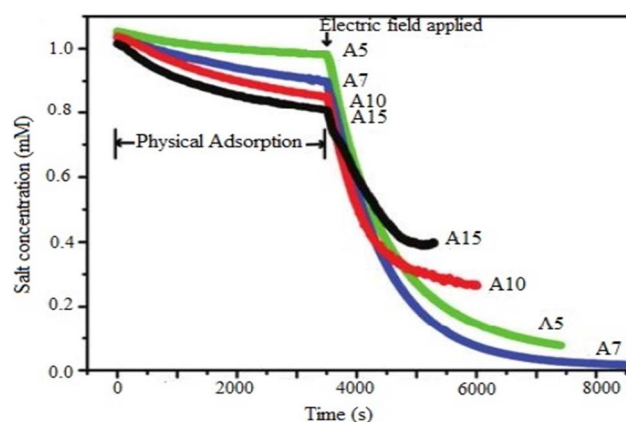


Fig. 9. Physical adsorption and electro-sorption performance of the electrode - reprinted (adapted) with permission from [40]. Copyright 2012 American Chemical Society.

capacitance which in turn increases ion removal efficiency. However, the maximum capacitance of carbon-based electrodes is limited to 150 F/g, which is also evident in the literature data provided in Tables 3a and 3b. Generally, oxides of transition metals, such as RuO_2 , MnO_2 , NiO , SnO_2 , ZnO , TiO_2 , V_2O_5 , CuO , and Fe_2O_3 , are used to fabricate composite electrodes of carbon substrates [43]. Specific capacitance of metal oxides is much higher compared to a carbon counterpart. Therefore, when incorporated with carbon substrates the composites show better specific capacitance (Tables 3a & 3b) and show higher percent removal and mass removed per unit mass efficiency (Tables 4a and 4b) compared to the parent carbon substrate.

A few issues regarding metal oxide deposition on carbon substrates leaves room for more research and improvement of electrodes such as; high resistivity of metal oxides which increases the sheet resistance and lowers charge transfer rate; cracking of electrodes due to strains in metal oxides caused by charge-discharge and poor control over SSA and pore size distribution during fabrication process. Recently, researchers have started exploring metal coatings for CDI electrodes. In one such study the electrode surface was coated with silver and showed some promising results [48].

Other approaches to improve electro-sorption performance of electrodes include activation of surfaces through chemical treatment or oxidation with acids or other reagents. Some approaches focused on synthesis methods to have better control on key parameters for improved efficiency. Coal tar pitch (CTP) based activated carbon and its modified form was used as a low cost alternative for most promising electrode material carbon aerogel [8]. Commercial CTP was used to prepare the electrode which was activated using KOH with KOH/

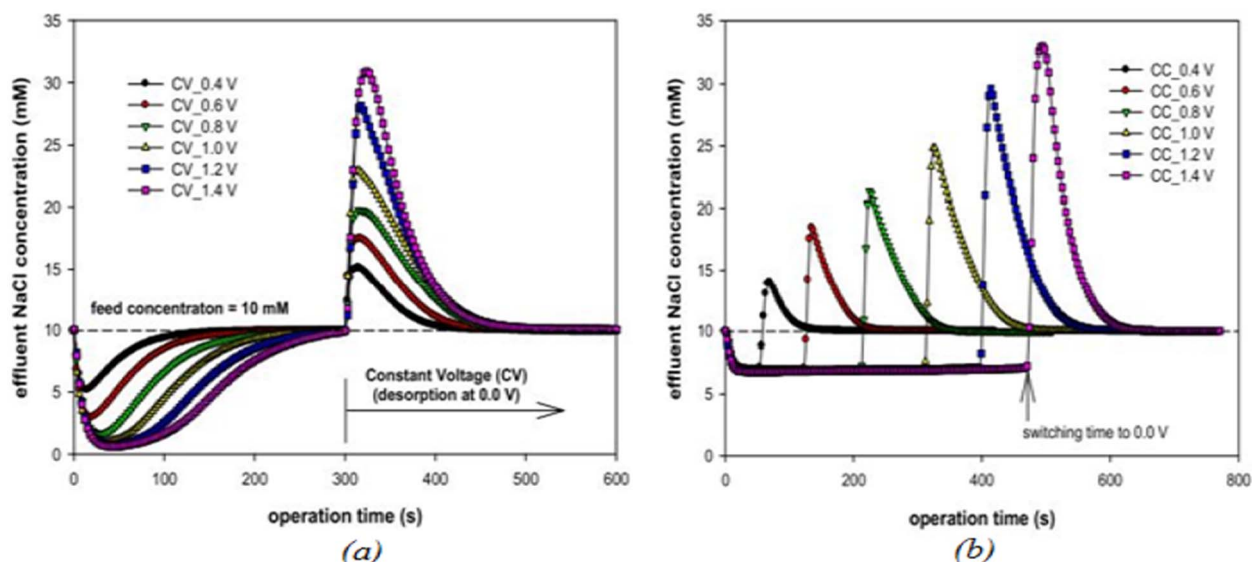


Fig. 10. Effluent concentration in (a) CV and (b) CC mode – reprinted from [42].

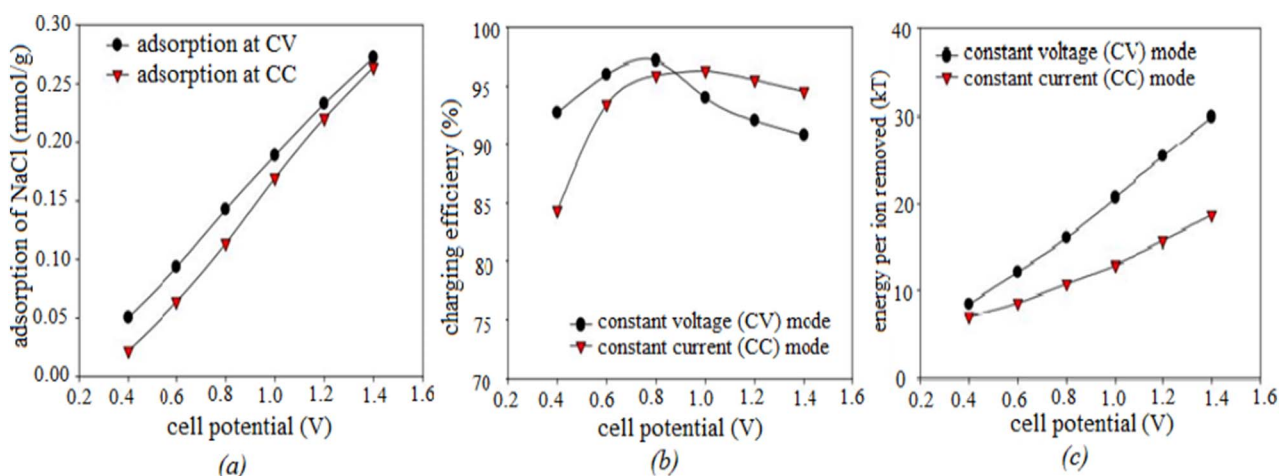


Fig. 11. Adsorption efficiency (a), charge efficiency (b) and energy consumption (c) at different cell potential for CV and CC mode – reprinted from [42].

carbon ratio at 5:1 proportion. The activated carbon was then modified in following three ways: (i) thermal treatment at 600 °C and 1000 °C under nitrogen flow, (ii) thermal treatment using H₂ and (iii) thermal treatment using CO₂. The removal efficiency was 55% when parent activated carbon was used as electrode. This efficiency was reduced when the electrodes were treated thermally at 600 °C and 1000 °C (30% and 20% respectively). This low efficiency was attributed to the resulting lower surface area in these treated forms. Activated carbon modified by treatment with CO₂ also showed a lower efficiency than parent activated carbon, though it has got higher surface area and larger pore sizes. This low efficiency was due to the removal of oxygenated groups in this treated form. The best removal efficiency was observed in case of activated carbon treated thermally using H₂, which was about 60%. This form of activated carbon showed high charge capacity with high surface area and large quantity of oxygenated groups.

Conventional activated carbon and its KOH and TiO₂ activated forms were also compared as CDI electrodes [28]. It was observed that there was no notable change in surface area (from 932 m²/g to 889 m²/g) and porosity when activated with KOH, but a significant decrease to 851 m²/g in surface area when activated with TiO₂ (Table 2b). In both cases it was found that activated electrodes performed higher as compared to original form of electrodes. This improvement was attributed

to the more hydrophilic nature of materials when activated. However, these traditional methods of producing activated carbon do not offer good control on the pore size distribution.

Two carbide derived carbon (CDC) electrodes (TiC or SiC) with a control over porosity in sub-angstrom range (depending on synthesis conditions and parent metal carbide) were used and compared with two types of activated carbon as CDI electrodes [31]. This control is important for measuring and controlling the salt adsorption rate in CDI operations. These electrodes were named as AC-1, AC-2, CDC-1 and CDC-2 and tested as CDI electrodes for voltage range of 1.2–1.4 V and initial salt concentration of 5 mM. Based on salt adsorption rate, it was found that CDC-2 had 15% and 33% higher efficiency than AC-1 and AC-2 respectively at cell voltage being 1.2 V, which became even higher (18% and 35%) when cell voltage was increased to 1.4 V. On the other hand, CDC-1 had 28% and 44% higher efficiency than AC-1 and AC-2 respectively at the entire voltage range (1.2–1.4 V). These results suggest that CDC-1 was the most efficient electrode in the experimental conditions and salt used. It was observed that difference in the structure of the material had only minor effects on the charge storage capacity. This leads to a hypothesis that material which is suitable for high charge storage in super-capacitor applications, may also be suitable for efficient CDI application. However, the charge efficiency was found to be 0.8, a value closer to unity which is important for charge efficient

CDI operation. The charge storage capacity was found to be highest for CDC-1 and lowest for AC-2 and followed a trend as shown here: CDC-1 > CDC-2 > AC-1 > AC-2, which is exactly same order as salt removal capacity. The contradiction of experimental data with the general view of classical EDL theory was that salt removal capacity would be proportional to BET surface area. In this experiment, it was found AC-1 and AC-2 had larger BET surface area and larger total pore volume than the CDCs. However, the salt adsorption capacity was much higher in the case of CDCs.

Measurement of the electro-sorption capacitance of environmentally concerning chlorides, nitrates and phosphate ions using a carbon aerogel electrode synthesized by resorcinol formaldehyde was also done [9]. Carbon aerogel activated by thermal treatment with CO₂ and chemical activation by KOH. This thermal activation with CO₂ yielded a material with high surface area with large pore volumes. It was observed that there was a close relationship between ionic radii and capacitance values. These values were 75.8 F/g and 78.3 F/g for smaller chloride and nitrate ions respectively and 61.2 F/g for larger phosphate ion. The resulted increase in the surface area due to activation also increased capacitance values which were recorded as 120.3, 100.5 and 86.9 F/g for chloride, nitrate and phosphate ions respectively. The theoretical hypothesis that larger ions are hard to be adsorbed in the pores with lesser diameter was confirmed by the fact of lower capacitance rate in case of larger phosphate ions.

The examples of various electrode materials and their corresponding specific surface areas are provided in Table 5. The table shows a wide range of SSAs ranging from a very low value of 1.88 m²/g for carbon fiber sheet to 1300 m²/g for activated carbon cloth electrodes.

Though activated carbon (AC) has larger surface areas than many other composites forms, its electrosorptive capacity was much lower. This low capacity may be attributed to smaller micropores that are inaccessible to some ions but contribute towards high surface area.

Many research publications were focused on development of novel and low-cost methods of synthesizing carbon based porous electrodes for CDI. In one study, calcinated watermelon peels were used as carbon source and were activated with KHCO₃ followed by washing in HCl [50]. The resulting materials showed very high specific surface area (2360 m²/g) and electrosorption capacity (17.38 mg/g). A three-dimensional foam like carbon (3DFCN) with a simple photochemical

method was developed. It showed electrosorption capacity of 20.0 mg/g. Nitrogen doped hollow carbon spheres (N-PHCS) prepared by mixing polystyrene and dopamine hydrochloride (as carbon and nitrogen source) showed very high specific capacitance (152 F/g at 5 mV/s scan rate) with a good electrosorption capacity (12.95 mg/g) [51]. Ordered mesoporous carbon and carbon nanotube (OMC/CNT) electrodes showed higher electrosorption capacity (10.74 μmol/g) than that of OMC (9.19 μmol/g) and activated carbon (3.69 μmol/g) [52]. KOH-activated OMC/CNT in a later work by the same group showed better electrosorption performance (11.83 μmol/g) than that of pristine OMC/CNT [53]. Table 6 lists some other approaches by different research groups to develop carbon based electrodes for CDI.

Most recently metal oxide framework derived carbon electrodes have been used in some studies for supercapacitor [60] and capacitive deionization applications [61–65]. This method of electrode fabrication gives much better control over many parameters like pore size, specific surface area, framework structure of the electrode etc. Porous carbon polyhedrons (PCPS) derived from zeolitic imidazolate framework-8 showed electrosorption capacity of 13.86 mg/g [65]. This performance of PCP was further improved (up to 20.05 mg/g) by fabricating composite with hierarchical porous carbon nanotube (hCNT) [62]. Zinc to carbon ratio in metal framework has shown to be a dictating factor of electrosorption capacity in one work, where electrodes with Zn/C ratio of 0.68, 0.9 and 1.35 showed electrosorption performance of 3.7 mg/g, 6.3 mg/g and 8.1 mg/g [63]. Porous carbon derived from Al-based metal organic gels showed ultrahigh performance of 25.16 mg/g [66]. Other ultrahigh performing electrodes are usually low-density foam like electrodes such as – 3D foam like carbon nanoarchitecture showing electrosorption performance of 20.9 mg/g [67].

4.2. Graphene based electrodes

In recent years many graphene based electrodes have been developed for CDI applications. Graphene, a carbon-based material with excellent conductivity, inertness, low density and high surface area, is an ideal material for being used as a host for composite electrode materials [17,68,69]. One of the first attempts to used Graphene synthesized by modified Hummers method showed decent electrosorption capacity of 1.85 mg/g [70]. A novel method of graphene production via dispersion of graphene oxide and ethanol in pyridine was described. The resulting material showed electrosorption capacity of 0.88 mg/g [71]. Three dimensional macroporous graphene architectures (3DMGA) have been synthesized and used as CDI electrodes [72]. These 3DMGA electrodes showed better capacitance (58.4 F/g) then traditional graphene electrodes (35/3 F/g) at 5 mV/s scan rate. 3DMGA consequently showed better electrosorption capacity (3.9 mg/g) than that of traditional 3D graphene (2.5 mg/g) and activated carbon (2.9 mg/g). Another study [73] synthesized 3D graphene based hierarchically porous carbon structure and showed improvement of specific capacitance (from 101.5 F/g to 151.7 F/g) as well as electrosorption capacity (6.2 mg/g to 14.7 mg/g) when compared to pristine 3D graphene as electrode in CDI. Porous graphene framework (PGF) developed through UV-assisted polymerization with high specific capacitance (190 F/g) showed better electrosorption capacity (19.1 mg/g) when compared to mesoporous carbon nanofiber (15.2 mg/g) [74]. PGF calcinated at low temperature showed better electrosorption capacity (17.1 mg/g) than that of PGF calcinated at high temperature (12.7 mg/g). Graphene carbon nanostructure (GCNS) was synthesized from glucose (as carbon precursors), Fe(NO₃)₃·9H₂O (as graphitization precursor) and NH₄Cl (as a blowing agent) [75]. The resulting material showed electrosorption capacity of 38.63 μmol/g and specific capacitance of 54.68 F/g. Graphene-mesoporous carbon nanosphere grafted (GN/MCS) electrodes showed higher capacitance (211 F/g) compared to graphene (73 F/g) and mesoporous Carbon (164 F/g) [76]. These GN/MCS developed for supercapacitors can also be used as electrodes in CDI cell in future research. Carbon aerogel-reduced graphene oxide (CA-RGO) composite

Table 5
Specific surface area (SSA) of different electrodes.

References	Electrode materials	SSA (m ² /g)
[45]	Activated carbon cloth (ACC)	1200
	ACC grafted with ZnO nanorod	700
	ACC grafted with ZnO microsheet	1300
	ACC grafted with ZnO nanoparticle	300
	ACC grafted with ZnO microsphere	500
[6]	Carbon xerogel (CX)	196.2
	CX-SiO ₂ as cathode & CX as anode	218.3
	CX-COOH (oxidized CX) as cathode & CX as anode	196.9
[25]	Carbon fiber sheet	1.88
	CF-SiO ₂ as cathode and CF-Al ₂ O ₃ as anode	25.6 & 18
[37]	Carbon aerogel	289
	Resorcinol based mesoporous carbon on graphite	488
[32]	Phloroglucinol based mesoporous carbon on graphite	610
	Activated carbon	989.54
[44]	Graphene like nanoflakes (GNFs)	222.01
	Graphene oxide-porous carbon nanofiber (GO-PCNF)	474
	PCNF	583
[46]	AC	1047
	Carbon nanofiber (CNF-based on phenolic resin) -600	481
	CNF-800	579
[47]	CNF-1000	617
	Activated carbon cloth (ACC)	1228
[49]	ACC-ZnO nanorod	587
	Carbon nanotube (CNT)	95
	Air plasma treated CNT	106

Table 6

Other methods of carbon based electrode development and corresponding changes.

References	Electrodes compared for performance	Adsorption capacity (mg/g)	Capacitance (F/g)
[54]	N, P doped meso/microporous carbon	20.78	207 at 1 mV/s
	KHCO ₃ treated meso/microporous carbon	16.63	150 at 1 mV/s
	NH ₄ H ₂ PO ₄ treated meso/microporous carbon	15.2	115 at 1 mV/s
	Calcinated meso/microporous carbon	9.95	109 at 1 mV/s
[55]	N-doped bimetallic zeolite imidazolate framework	12.25	
	Zeolite imidazolate framework –8	6.12	
	Zeolite imidazolate framework- 67	11.38	
[56]	Dodecahedron-like carbon framework derived from metal organic frameworks	20.05	
	ZIF-8	13.01	
[57]	3D hierarchical carbon architectures (3DHCA)	17.83	142 at 5 mV/s
	Calcinated carbon	6.88	64 at 5 mV/s
[58]	3D hierarchical porous carbon with a bimodal pore arrangement	2.16	60 (No scan rate mentioned)
	Ordered mesoporous carbon (OMC)	1.94	40 (No scan rate mentioned)
[59]	N-doped hollow multi yolk shell carbon (N doped-HMYSC)	16.1	204 at 1 mV/s
	Hollow carbon	12.7	150 at 1 mV/s

Table 7

Graphene based electrode and their modified forms.

References	Modified form of graphene used	Performance by different electrodes				
		Type of electrode	Adsorption capacity	Capacitance (F/g)	SSA (m ² /g)	Pore size (nm)
[84]	Graphene-mesoporous carbon (GE/MC) composite	MC	590 µg/g	36 at 5 mV/s	685.2	3.16
		GE/5%MC	731 µg/g	57.5 at 5 mV/s	567.7	2.5
[85]	Graphene and carbon nanotube composite (GR/CNT)	GR	1.10 mg/g	30 at 10 mV/s	479.5	–
		GR/10%CNT	1.41 mg/g	70 at 10 mV/s	342.9	–
[86]	3D graphene and hierarchically porous carbon composite (3DGHPC)	3DG	4.41 mg/g	–	250.3	–
		3DGHPC	6.18 mg/g	–	384.4	–
[87]	Graphene coated with hollow mesoporous Carbon Structure (GHMCS)	GHMCS	2.3 mg/g	43.33 at 1 mV/s	–	–
		Compact Graphene	1 mg/g	23.33 at 1 mV/s	–	–
		HMCS	2 mg/g	32.39 at 1 mV/s	–	–
[88]	Reduced graphene oxide-activated carbon composite	20% RGO-AC	0.83 mg/g	181 at 1 mV/s	779	–
		RGO	–	140 at 1 mV/s	407	–
		AC	0.41 mg/g	67 at 1 mV/s	963	–

electrodes showed better removal efficiency (59%) than that of unmodified carbon aerogel (46.9%) [77]. Nitrogen doping on graphene electrodes has resulted in high performing electrode materials in some research. Nitrogen doped graphene (NG) showed electrosorption capacity of 4.81 mg/g while pristine graphene showed 3.85 mg/g [78], whereas in case of nitrogen doped electrospun reduced graphene oxide-carbon nanofiber composites (NG-CNF) the capacity was 3.91 mg/g [79]. Nitrogen doped graphene sponge (NGS) electrodes showed ultrahigh performance of 21.0 mg/g [80]. Recently, many graphene based electrodes have been reported to show ultrahigh performance such as – 3D graphene architecture interconnected with in-plane nanopores (NP-3DG) with electrosorption capacity of 17.1 mg/g [22], carbon nanotube-graphene hybrid sponge (CNT-GNS) with 18.7 mg/g [81] and 3D graphene framework and macroporous carbon spheres (CDGF-MCS) with 19.8 mg/g [82]. Table 7 lists modified forms of graphene and their performance as CDI electrodes.

Sulfonic functional group grafted graphene (3DSGR) and amine functional group grafted graphene (3DNGR) electrodes were developed and compared in CDI cell for different cathode-anode configuration (asymmetric electrode configuration) in conjunction with 3D graphene (3DGR) electrodes. Electrosorption capacity by different configurations of electrodes are shown in Table 8. Removal of heavy metal lead (Pb) was also studied in one study [83] using, ethylenediamine (EDTA) and 3-aminopropyltriethoxysilane grafted 3D graphene. The resulting performance at the pH value of 6 was 99.9% Pb²⁺ removal and 98.7% Na⁺ removal. The concept of the work was to adsorb lead ions by EDTA through chelation reaction and sodium ions through electrosorption.

Table 8

3D graphene-based electrode's performance at asymmetric electrode systems.

References	Applied conditions	Cathode-anode	Electrosorption capacity (mg/g)
[89]	1.4 V, 40 mL/min 50 mg/L NaCl	3DGR-3DGR	2.91
		3DNGR-3DGR	3.82
		3DSGR-3DGR	5.33
	1.4 V, 40 mL/min 500 mg/L NaCl	3DNGR-	13.72
		3DSGR	
		3DGR-3DGR	9.48

4.3. Inclusion of membrane, polymer, resins, ion selective materials etc.

In membrane capacitive deionization (MCDI), the ion exchange membranes are placed in front of the electrodes to block the co-ions from getting re-adsorbed by the other electrode in the regeneration phase when the applied voltage is reversed. Experimental and theoretical results for desalination capacity and rates in both constant voltage and constant current methods were reported as functions of adsorption/desorption time, salt concentration in the feed, electrical current and cell voltage in one of the studies [2]. It was observed that the duration of desalination cycles depends on influent salt concentration. For lower influent salt concentration, this duration got lower i.e., the cell voltage reached the final voltage level quickly. On the other hand, adsorption capacity decreased if desorption time is decreased. It resulted in incomplete regeneration which decreased the ion removal efficiency of next adsorption phase. In another work [90] it was showed that by varying water flow rate the effluent salt concentration could be controlled and fine tuned to a desired level. All these observations led them

to introduce a new performance indicator in CDI operation, which was named average salt adsorption rate (ASAR). ASAR is the salt adsorption per cycle, per gram of total mass of electrode. It can be maximized by keeping influent salt concentration around 20 mM, adsorption current of 1 A, water flow rate higher than 40 mL/min and desorption time of 50 s.

The more advanced MCDI system is also going through further development and a recent improvement in this system is the introduction of ion exchange polymers. In one study [12], polyethyleneimine (PEI) was used as cation exchange polymer and dimethyl diallyl ammonium chloride (DMAAC) as anion exchange polymers, which were casted into the electrodes. The resulted removal efficiency was 93% for NaCl solution which was much higher compared to traditional MCDI system with efficiency 74% and conventional CDI system with efficiency of 25% at same experimental conditions.

Much of the recent work is focused on developing the CDI technique by using inexpensive activated carbon fiber which was once thought to yield less desalination rate and charge efficiency compared to novel carbonaceous materials with high surface area, porosity and favorable pore structures. Incorporation of ion exchange polymers, membrane, resins etc. are showing a new avenue for the development of this low-cost electrode material. Three CDI cells with electrode system that was modified with ion exchange felt (IEF), ion exchange membranes (IEM) and ion exchange resins (IER) was tested as electrodes [91]. They used low-cost activated carbon fiber as electrodes in all three systems dealing with NaCl solution with initial concentration of 1000 mg/L and applied voltage of 1.2 V. The regeneration phase included both short circuiting and discharge desorption. The removal rate and efficiency was found to follow order as shown here: CDI-IER (670 ± 20 mg/Lh and $90 \pm 1\%$ /h) > CDI-IEM (440 ± 15 mg/Lh and $60 \pm 2\%$ /h). The removal rate of 24% by CDI-IEF was poor compared to CDI-IER and CDI-IEM's performances. The desalination rate and efficiency both increased significantly (270 to 670 mg/Lh and 83% to 90%/h) in CDI-IER with increasing applied voltage and decreased slightly with decrease in effluent flow rate.

A hybrid system comprising of reverse osmosis (RO) and CDI to produce ultrapure water (UPW) from seawater was also developed [92]. RO-constant current CDI hybrid system was found to be superior over RO-constant voltage CDI system in terms of quality and quantity of UPW produced while both systems consumed same amount of energy at similar operational conditions. Another study [93] used the asymmetric model of CDI in case of MCDI operation. This study reported the best performance of MCDI cell at conditions where cathode was configured at 0.5 V PZC and anode at -0.1 V PZC.

The Box-Behnken design based on response surface methodology (RSM), a statistical tool to optimize the operational parameters in physical processes was used in one study [2]. The experiments were conducted with CDI cell at applied voltage range of 1.2–1.6 V, initial concentration of NaCl solution 200–1000 mg/L and flow rate 10–40 mL/min and used activated carbon-based electrodes which has good range of mesopores for overcoming the electrical double layer effect. The polynomial statistical fit presented in the publication, predicted optimal value of electrosorption capacity to be 10.67 mg/g with $R^2 = 0.9945$ and p -value < 0.0001. Experimental values showed maximum electro-sorption of 10.53 ± 2.1 mg/g at cell voltage, initial concentration and flow rate of 1.57 V, 1000 mg/L and 25 mL/min. Four activated carbon fibers (ACF) electrodes with different BET surface areas were used in one study [40]. Though physical adsorption rate increases with increasing BET surface area, but electro-sorption performance in CDI cell did not follow the same pattern. Because the CDI capacity also depends on the charge efficiency of electrical double layers as discussed in Section 3.2 of this article. Polypyrrole-coated multiwalled carbon nanotube doped with nitrogen as electrodes was used in a CDI cell and showed high specific capacitance (103.1 F/g), high energy density (161 mWh/g) and power density (14.4 W/g) [94]. The material exhibited high energy storage in super-capacitor applications as well as high electro-sorption capacity of 0.5 M Na_2SO_4 electrolyte.

4.4. Energy recovery and development of energy efficient electrodes

Quantifying the amount of energy that can be recovered in MCDI operation was focused in one study [11]. This energy recovery makes charge efficiency, which is the ratio between ionic charge removed and electrical charge supplied, close to unity. This value is far below unity for other conventional CDI systems. There are different forms of energy that are consumed during MCDI operation. One of them is the thermodynamic energy which is needed to separate feed water stream into diluted and concentrated streams. This energy cannot be recovered as it is the minimal energy required for desalination of water stream. The energy that can be recovered was determined in their study by charging and discharging of electrodes. There was a combined resistance caused by graphite current collector used in the experiment, electrodes, membranes and spacer compartments which caused an initial jump in the cell voltage. This jump was higher when the electrodes were charged at high currents. Part of this energy was stored in the electrical double layers that could be recovered, but other part was used to overcome an internal resistance which was not recoverable. There were other energy losses due to redistribution of ions in the pores and Faradaic reactions. The experimental data suggested that by charging electrodes at lower current not only required less energy but also increased the potential of more energy recovery during the regeneration step. On the other hand, higher initial salt concentration lowered the initial resistance which implied that in this case recoverable energy should have even higher. In their study, 25% of energy was recovered at 12 A and salt concentration of 8.6 mM which increased higher up to 63% with the salt concentration 273 mM while the current remained the same. Again, this energy recovery went up to 73% when charging was done at 2 A and discharging at 12 A. The estimated recoverable energy by extrapolating the values of charging and discharging currents was found to be $84\% \pm 1\%$, which was not dependent on the salt concentration of water. These observations led to an estimation of energy consumption of 0.26 kW-h/m^3 of produced water which was much lower than energy consumed by reverse osmosis for brackish water. Another group [4] aimed at quantifying the energy efficiency in terms of influent concentration, flow rate and water recovery. They observed that MCDI energy consumption should be $< 1 \text{ kWh/m}^3$ of fresh water produced for it to be a better alternative to reverse osmosis. Experimental data showed that MCDI is more energy efficient at salinity level lower than 60 mM.

Most of electrode development research efforts have focused on energy efficient electrodes that have less resistivity and thus good ion and charge transport capability in the deionization process. Energy density and power density values have increased in many for the electrodes after some form of modification (Table 9).

One study [96] focused on TDS removal from one on-site pilot scale CDI unit for groundwater treatment found that the energy requirement of the system used went down with the flow rate. The energy consumption dropped to 1.52 kWh/m^3 at 9 L/min from 10.5 kWh/m^3 at 1 L/min.

4.5. Suspended electrodes (FCDI systems) and inverted CDI (i-CDI systems)

Suspended type or flow-able CDI (FCDI) electrode is a fairly new concept in supercapacitor applications [97]. Same concept was applied in CDI applications by mixing anisometric activated carbon powder (capacitance of 92 F/g as revealed by cyclic voltammetry and specific surface area of $1800 \text{ m}^2/\text{g}$) and an acetylene black (AB) as conductive additive along with NaCl electrolyte solution [1]. The basic advantage of suspended electrodes is that the electrode material can be replenished with fresh sorbent material without interrupting the system, while in traditional CDI processes it must undergo a regeneration process once the electrodes are saturated with ions or electrodes must be replaced with new set of electrodes. Other advantages include overcoming the challenge of scaling up the CDI system for real world

Table 9
Energy and power density by different carbon-based electrodes.

References	Electrode	Energy density (Wh/Kg)	Power density (W/Kg)
[84]	Mesoporous carbon	1.31	67.37
	Graphene-mesoporous carbon composite	1.97	70.9
[85]	Graphene	4.07	
	Graphene-carbon nanotube composite	5.49	
[72]	Traditional graphene		42.42
	3D macroporous graphene architecture		45.34
[52]	Carbon nanotube (CNT)		54.88
	Ordered mesoporous carbon-CNT composite		56.81
[95]	Co ₃ O ₄ nanosheet, Ag dot grown on 3D graphene	26.7	600

applications, ability to separate clean and ion saturated stream and energy efficient recovery etc. Electrochemical impedance study revealed an ohmic resistance around $1.6\ \Omega$ which is fairly comparable with traditional electrodes. A removal electrosorption efficiency of 68% was achieved. The results indicate that if the total system is developed by using much more efficient materials, it could desalinate seawater in one charging period. The Fig. 12 shows the schematic diagram of a suspended electrode in a CDI application.

In typical constant voltage operations with carbon based electrodes, after long (50–500) hours of adsorption-desorption cycles the CDI cell shows a loss in performance due to oxidation reaction at the surface of the electrodes [99]. This oxidation leads to formation of $-\text{COO}^-$ groups resulting in a net negative charge at the electrode surface. Concept of inverted CDI (i-CDI) is developed to utilize this phenomenon. In i-CDI systems, electrodes were modified chemically, cathode (with NH_3^+) to have net positive charge and anode (with COO^-) to have net negative charge [99,100]. These innate surface charges on electrode surfaces help in adsorption and desorption of ions (desorbed when connected to oppositely charged DC power terminals and adsorbed when the electrodes are shorted. This behavior of i-CDI units is completely opposite of conventional CDI system, but it demonstrated that salt separation was well maintained in 600-hour long operation. Further studies are required to develop in-depth understanding and large-scale applications of i-CDI based operations.

4.6. Targeted removal

Targeted or selective ion removal is also being investigated by some research groups. This approach helps in removing a specific ion when there are competing ions in the system. This method has come handy in developing novel techniques for water softening [101] or metal ion removal [6]. Chemical vapor deposition method was successfully used to increase selectivity of monovalent ions over divalent ions following adsorption/electro-sorption [34]. They focused on adjusting pore openings between the sizes of monovalent and divalent ions so that only monovalent ions can get adsorbed into the pores. Another study [7] aimed at removing only nitrate ions from solution which they termed as “selective” removal. In that study, BHP55 resin was used to coat CDI carbon electrodes. The BHP55 resin was selected as a coating material based on the understanding from literature and adsorption tests. The publication lists the adsorption performance of removal of the ions in the following order: nitrate > sulphate > chloride. These coated materials were used as electrodes in a CC CDI operation and effluent was a mixture of NaCl, NaNO₃ and Na₂SO₄. The same test was repeated under same experimental conditions using uncoated carbon electrodes. In case of nitrate selective electrodes as compared to the uncoated electrodes, the total adsorption was 34% higher and nitrate removal was 100% higher. The results of this study indicate the potential of removal of other ions selectively; for example; chelating resin coated electrodes may be able to remove selectively Ca^{2+} or other metal ions. Another study [102] used activated carbon for selective removal of copper ions. The electro-sorption was in limited extent at low voltages, but removal was still happening due to electrostatic forces. The higher the initial concentration and applied voltage were, the higher was the removal rate and electro-sorption capacity. At 0.8 V they found the electro-sorption capacity to be 24.57 mg/g and electro-sorption constant rate $0.038\ \text{min}^{-1}$ based on Langmuir model. Both values are much higher compared to formerly reported values for copper ion.

4.7. Pilot scale studies

Some pilot scale studies are also done for application of CDI in real world conditions. In one such case, CDI technology was applied for removal of total dissolved solid (TDS) from groundwater in an on-site unit [96]. The study found water recovery rate to be 75–80% and was able to significantly remove nitrate, fluoride, arsenic along with calcium, magnesium and sodium ions. The usual fouling issues that are part of any on-site water treatment were also observed in pilot scale CDI studies. One pilot scale study [103] conducted in Australia at sites of Wilora and Mawson Lakes found that TDS removal efficiency of CDI

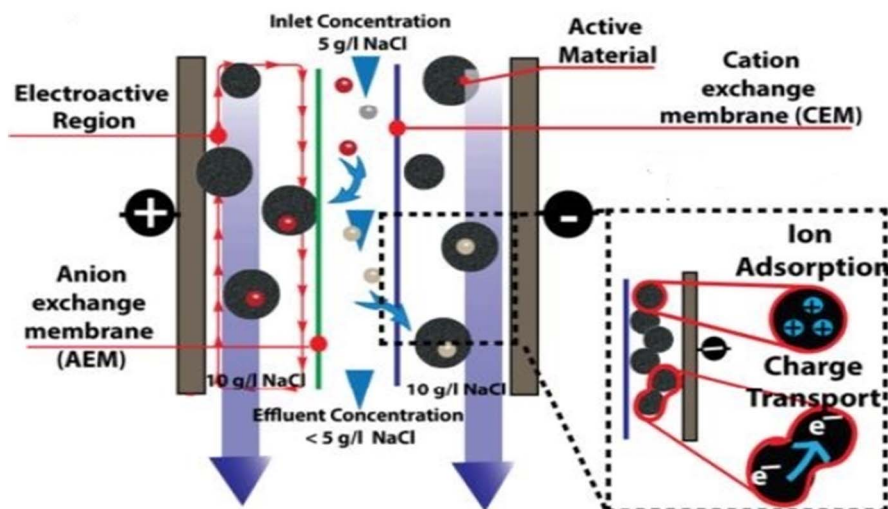


Fig. 12. Diagram of suspension electrodes in capacitive deionization (used with permission) [98].

electrodes decreased with time due to fouling issues. The decrease in removal efficiency was much worse (from 86% to 55% in 15 days) for Mawson Lake than that of Wilora Lake (82% to 75% in 15 days). This decrease was attributed to high organic contents present in Mawson Lake. Mild cleansing solution of 0.01 M citric acid was found to be effective for removal of calcium and magnesium scaling. While, 0.01 M sodium hydroxide helped to minimize organic fouling. These solutions were able to restore the actual capacity of the CDI unit. In another study [104], TiO₂ coated reduced graphene oxide (TiO₂-RGO) electrodes were developed that demonstrated an ability to minimize fouling by humic-acid through photocatalytic process. These studies provide a good base of knowledge but more such studies are needed for greater understanding of issues related to fouling under various conditions with electrodes of different materials in a large-scale CDI based water treatment plants.

5. Conclusion

Various technologies such as reverse osmosis (RO), membrane filtration, and multistage flash and many other are commonly used for water desalination. The CDI technology based water desalination has shown increased efficiency compared to these contemporary technologies. This process is theoretically less energy consuming compared to reverse osmosis for many reasons such as CDI is operated at low voltages and current, with low pressure pumps while RO uses high pressure pumps to overcome resistance to membranes. Most of the efforts have been focused to improve electrode characteristics and optimizing operational conditions to increase the efficiency of CDI operations.

Different forms and composites of carbon have shown remarkable efficiency ranging from as low as 0.275 mg/g (for activated carbon) to 50.1 mg/g (phenolic resin based carbon nanofiber), which is > 180 times the capacity of activated carbon. Inclusion of membranes, polymers and resin has shown to improve the ion removal capacity of the electrodes. Yet, the research on CDI is on-going and there are areas that still need a greater focus on many important issues in the near future. Some of the issues and unanswered questions are listed below.

- In most of the adsorption and desorption CDI studies the electrodes were studied in a solution of one or two sample salts. A comprehensive study with more complex solutions with competing ions is needed for full understanding of CDI electrodes' behavior.
- There is not much secondary pollution in case of CDI. However, there is a production of wastewater saturated with salt ions that are removed from CDI systems during regeneration. There is no significant study that focused on characterizing and analyzing the salt ions saturated wastewater stream. Very little, if any, work has been done in minimizing this wastewater stream and maximizing the production of net treated water.
- While high surface area is required for effective adsorption, still some materials with inherent high surface area showed lower removal capacity. Selection of electrodes with desired pore size distribution for more efficient adsorption of ions is also a critical issue in upcoming CDI related research.
- The cost associated with materials, manpower, capital investment, maintenance and operation would depend on various factors such as source water quality, location of sites, quality of the treated water and other relevant factors. Even though, CDI operates at a low voltage range with low current, safety issues related to large scale plant have not been addressed. It is expected that next thrust of the CDI research would be in this direction that would cover instrumentation and automation of the technology for the utility systems of the future smart cities.
- Large scale application of CDI based surface water treatment for industrial as well as municipal purposes would require additional pre and post processing. As carbon electrodes can host many organic and inorganic materials through physical adsorption, there remains

a chance of fouling issues which is common issue in regular water treatment plants. Pre-filtering or other options are needed to be explored so that water is free of unwanted substances in the CDI influent stream.

- Carbon electrodes also store energy (like supercapacitors) along with ions. This aspect of the CDI technology has not been investigated much. A good understanding of this area would help in recovering this energy which in turn will reduce the cost and energy requirements of a CDI systems.

There has been a significant progress in terms of various types of materials used as CDI electrodes and configurations of electrodes for better yield. The knowledge base has been created and the effectiveness of the technology has been demonstrated in many studies directed for specific cases. The CDI technology is paving a path for this technology to be an alternative option for deionization/desalination in the future world where cost and energy savings would be vital issues and sources of freshwater would be scarce.

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