Desalination of brackish water using capacitive deionization (CDI) technology

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ABSTRACT

Capacitive deionization (CDI) is a desalination technology utilizing electrosorption and desorption of ionic salts. Carbon materials are the main components of electrodes in CDI, while addition of organic and inorganic materials with carbon materials enhances the desalination performance. In this study, powdered activated carbon (PAC) as well as PAC combined with titanium dioxide (TiO_2) electrodes was prepared. The deionization performance was evaluated using three CDI systems. Feed solution having concentration of 2,000 mg/L was used in small- and lab-scale CDI systems. $PAC + TiO_2$ electrodes showed 28% more salt removal as compared to PAC electrodes in the small-scale CDI system using one pair of electrodes. Laboratory-scale CDI system using six pairs of $PAC + TiO_2$ electrodes showed adsorption capacities of 2.64, 4.30, and 6.67 mg NaCl/g-adsorbent at 1.3, 1.6, and 1.8 volts, respectively. Pilot scale CDI system using 20 pairs of $PAC + TiO_2$ electrodes at 1.8 volts showed maximum salt removal of 84, 82, and 71% for the feed NaCl concentrations of 2,000, 2,500, and 3,000 mg/L with adsorption capacities of 7.7, 10.4, and 11.2 mg NaCl/g-adsorbent, respectively. As the amount of salt ions to adsorbent increases, the exchangeable sites on the adsorbent structure become saturated, which results in decrease of salt removal efficiency, while the adsorption capacities increased with increase in concentration due to elevated mass transfer rate of salt ions inside the pores.

Keywords: Capacitive deionization; Desalination; Powdered activated carbon; Titanium dioxide; Salt concentration; Electrosorption

1. Introduction

Capacitive deionization (CDI) is cost-effective, performance efficient and environmentally friendly desalination technology in which ionic salts are removed electrochemically from brackish water [1]. CDI involves application of very low electric field between two electrodes which forces the ionic species to adsorb on oppositely charged electrodes. These ions

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make electrical double layer (EDL) near the surface of electrodes, get held, and thus acts like energy stored in super capacitors [2]. Ions desorb from the surface of electrodes by eliminating the electric field and washing with deionized (DI) water results in the regeneration of electrodes [3].

Conventional desalination technologies such as reverse osmosis (RO), ion exchange, and electrodialysis (ED) are mostly adopted to separate salts from water [4,5]. These technologies have various pros and cons, such as the energy cost for these processes is very high, although the processes are simple and provide high quality freshwater. In RO and ED technologies, there are problems of scaling as well as maintenance of specific permeates flux. In the ion exchange process, resins are costly, require regular regeneration, and produces brine [4,6–8]. The advantages such as low pressure and non-membrane process make CDI technology a competent and an alternate technology for desalination [9,10].

For CDI, electrodes have high surface area, good electrical conductivity for effective charge holding, and suitable pore size for effective desalination [11]. A number of carbon materials such as activated carbon [6,12], carbon aerogels [8–11], activated carbon cloth [13], carbon black [14], carbon nanotubes and nanofibers [15], etc. have been reported as electrode materials for CDI. In addition, titanium dioxide (TiO$_2$) modifications with various electrode materials for CDI were also reported in order to evaluate the effect of TiO$_2$ on desalination. Kim et al. [16] reported that the TiO$_2$-coated carbon electrodes have two times greater desalination efficiency then carbon electrodes and the enhanced desalination efficiency was due to high wettability of TiO$_2$-coated carbon electrode. Lee et al. [17] used ion-selective composite carbon electrode with 10 wt.% of TiO$_2$ in CDI desalination experiments and reported that the desalination efficiency was enhanced by about 30% as compared to that of the uncoated carbon electrode. Ryoo et al. [18] reported that the incorporation of TiO$_2$ in activated carbon cloth increased electrosorption and decreased physical adsorption which notably enhanced the ion removal capacity.

The objectives of this study were to compare the desalination performance of powdered activated carbon (PAC) vs. PAC + TiO$_2$ electrodes at the small-scale CDI system, to compare the voltages for maximum salt removal efficiency at the laboratory-scale CDI system, and to investigate treated water produced at the pilot-scale CDI system by varying salt concentrations. The electrode characterization for understanding the system performance was evaluated by cyclic voltammetry (CV) and scanning electron microscopy (SEM).

2. Material and methods

2.1. Preparation of electrodes

The electrode slurry was prepared by mixing PAC (Acros, USA) having BET surface area of 540 m^2/g and polyvinylidene fluoride (International laboratory, USA), as polymer binder, in an organic solvent, *N,N*-Dimethylacetamide solution (>99%, Merck, USA). Furthermore, TiO$_2$ was added into the slurry which was obtained by reacting titanium (IV)-butoxide (>97%, Sigma–Aldrich, USA) and absolute ethanol (99.8%, labscan, Poland) according to the method given by Velasco et al. [19] with a slight modification i.e. absolute ethanol was used instead of *n*-butanol. The slurry was made homogeneous by blending the mixture vigorously using magnetic stirrer for 7 h. Electrodes were oven dried at 120°C for 2 h to evaporate the organic solvent after the electrode slurry was casted onto a graphite sheet (Asia-Pacific Sealing Technologies, Pakistan). Polymer binder and TiO$_2$ content in the fabricated electrode were 10 and 12 wt.% of PAC, respectively. Similar procedure was adopted for the preparation of PAC electrode without addition of TiO$_2$. The details of CDI systems and electrodes are reported in Table 1.

2.2. Scanning electron microscopy

The surface morphology analysis of the PAC + TiO$_2$ electrode was carried out with scanning electron microscope, expanded to an analytical SEM by the addition of optional EDS (JSM-6490, JEOL, Japan). The images were recorded at a magnification of 5,000.

2.3. Cyclic voltammetry

To examine the electrochemical properties of the prepared electrodes, cyclic voltammetric measurements were performed using a potentiostat (DY2113, Digi-Ivy, Inc., USA) with three-electrode system. The reference electrode was an Ag/AgCl electrode, while the counter electrode was made up of a thin platinum wire, and working electrodes were PAC and PAC + TiO$_2$. CV was performed at room temperature using 0.5 M NaCl solution. The potential range was −0.6– +0.6 at the scanning rate of 50 mV/s.

2.4. Desalination performance by CDI systems

Initial desalination performance experiments were conducted on a small-scale CDI system. Desalting efficiencies of PAC vs. PAC + TiO$_2$ electrodes were compared using NaCl feed solution concentration of

Table 1
Electrodes specifications for CDI systems

CDI system type	Electrode type	Electrode dimensions (mm)	No. of electrodes	Mass of adsorbent (gm)
Small scale	PAC	$203.2 \times 76.2 \times 1.5$	2	11.8
	PAC + TiO$_2$	$203.2 \times 76.2 \times 1.5$	2	11.8
Laboratory scale	PAC + TiO$_2$	$203.2 \times 76.2 \times 1.5$	12	71
Pilot scale	PAC + TiO$_2$	$304.8 \times 152.4 \times 1.5$	40	336

approximately 2,000 mg/L at 1.3 V and flow rate of 25 mL/min was maintained. The only difference between the small- and laboratory-scale CDI systems was that in the small-scale CDI system, experiments were evaluated by running a single cell unit with one pair of electrode, whereas for laboratory scale, three cell units, each cell having two pairs of PAC + TiO$_2$ electrodes, were connected in series with each other using a pump flow system as shown in Fig. 1. The electrodes were stacked over each other and provided with holes to create flow channel. The pair of electrodes was separated by a separator made of nonconductive thin rubber gasket material to avoid short circuiting. Space of approximately 2 mm was kept between the electrodes by a putting a nonconductive rubber spacer and individually connected with a digital DC power supply. Acrylic sheets were attached onto the back of the electrodes in the CDI cells assembly. NaCl feed solution concentration of approximately 2,000 mg/L was supplied to the laboratory-scale CDI system by peristaltic pump (Masterflex, USA) at 25 mL/min. The salt removal tests were conducted by charging the electrodes with a potential of 1.3 V until there was no significant change observed in the concentration of the effluent. Once electrode sites were saturated, the desorption of ions was performed by changing the potential to 0 V and washing the electrodes with DI water. Same procedure was repeated with potentials of 1.6 and 1.8 V and salt removal percentage was studied at each voltage, respectively. The conductivity and total dissolved solids (TDS) concentration changes in the effluent were measured using conductivity meter (CON 110, Oakton, USA) at different time intervals.

Pilot-scale CDI performance for desalination (adsorption) was evaluated by running an electrode unit assembly consisting of 20 pairs of electrodes using a pump flow system as shown in Fig. 2. The configuration of electrodes was same as described earlier in laboratory-scale CDI system. The NaCl feed solution concentrations were 3,000, 2,500, and 2,000 mg/L while keeping pumping rate kept constant at 25 mL/min. The salt removal tests were performed at 1.8 V, while the regeneration was achieved within 20 min at 0 V and DI water flow rate was maintained as 25 mL/min. All the experiments were performed in triplicate in order to report representative results. The adsorption capacities were calculated by the change in the concentration during the charging/discharging step of the CDI cells assembly. The adsorption capacity (Q) (mg-NaCl/g-adsorbent) was calculated as [20]:
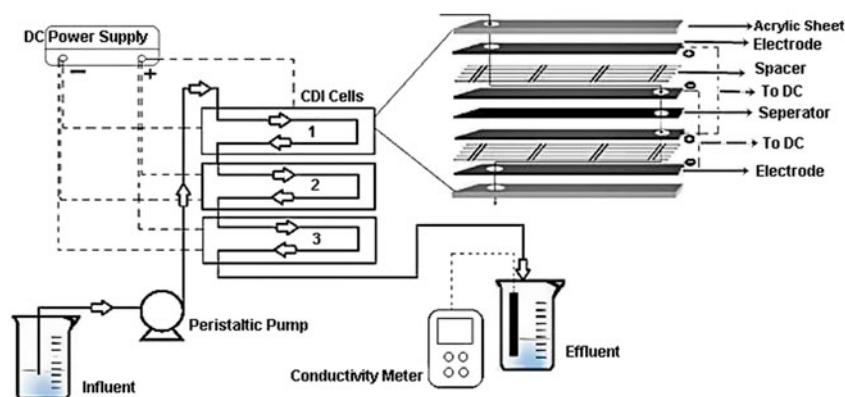

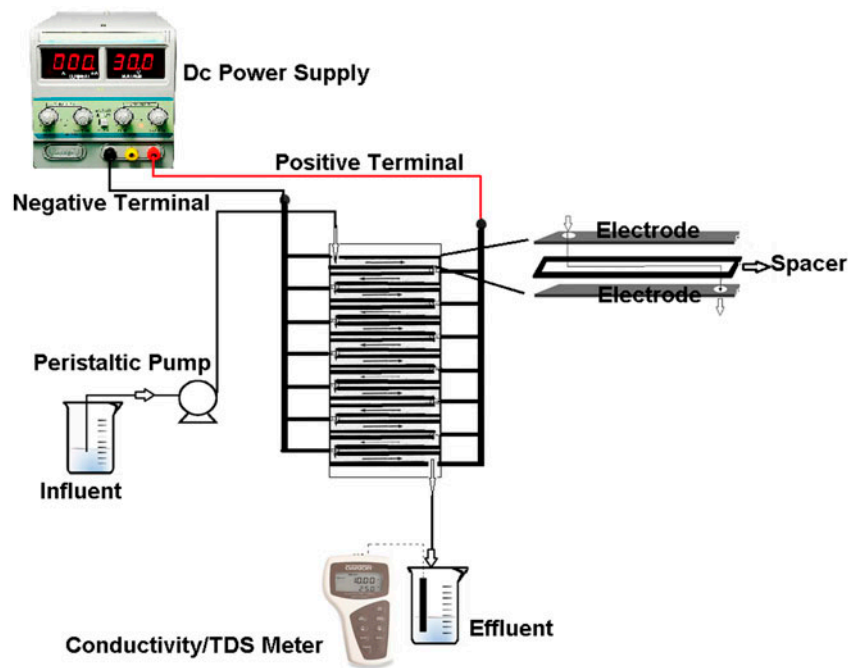Fig. 1. Process flow diagram of the laboratory-scale CDI system.

Fig. 2. Process flow diagram of the pilot-scale CDI system.

$$Q = \frac{(C_i - C_e)}{M} \times V \tag{1}$$

where C_i (mg/L) is the influent concentration and C_e (mg/L) is the effluent concentration during adsorption. V (L) is the volume of the product during the adsorption process and M (g) is the mass of the adsorbent.

For the comparison of performance under different applied voltages, the desalted product was expressed as the salt removal rate [21]:

$$\text{Salt removal } (\%) = \frac{C_f - C_p}{C_f} \times 100 \tag{2}$$

where C_f (mg/L) represents the feed concentration and C_p (mg/L) represents the lowest product concentration during adsorption.

3. Results and discussion

3.1. Surface morphology of the electrode

Fig. 3(a) shows the SEM image of TiO$_2$-modified PAC electrode. It can be observed from the image that there is continuous irregular network with presence of PAC, binder, and TiO$_2$ particles. Fig. 3(b) shows the surface structures of the electrode with different pore sizes, mainly mesopores. Electrosorption capacity is greatly dependent on the pore size distribution of the electrode. The significant number of macropores (>50 nm) leads to low surface area and low electrosorption capacity, while mesopores (2–50 nm) are very suitable for electrosorption due their pore size [15].

3.2. CDI performance of the electrodes

Fig. 4 shows effluent concentration variations for the small-scale CDI system. Once the voltage of 1.3 V was applied, the concentration of the effluent decreased sharply to 1,916 mg/L for PAC and 1,883 mg/L for PAC + TiO$_2$ electrodes after 5 min of adsorption operation. The ions were electrosorbed onto the electrodes' surface and the concentration was decreased until there was no significant change noted in the effluent concentration over time. PAC + TiO$_2$ electrodes showed 28% more salt removal as compared to PAC electrodes. This increase in salt removal can be attributed to the addition of TiO$_2$ in electrodes that enhances salt removal efficiency by decreasing physical adsorption, while promoting electrosorption and high wettability of electrodes [16,18].
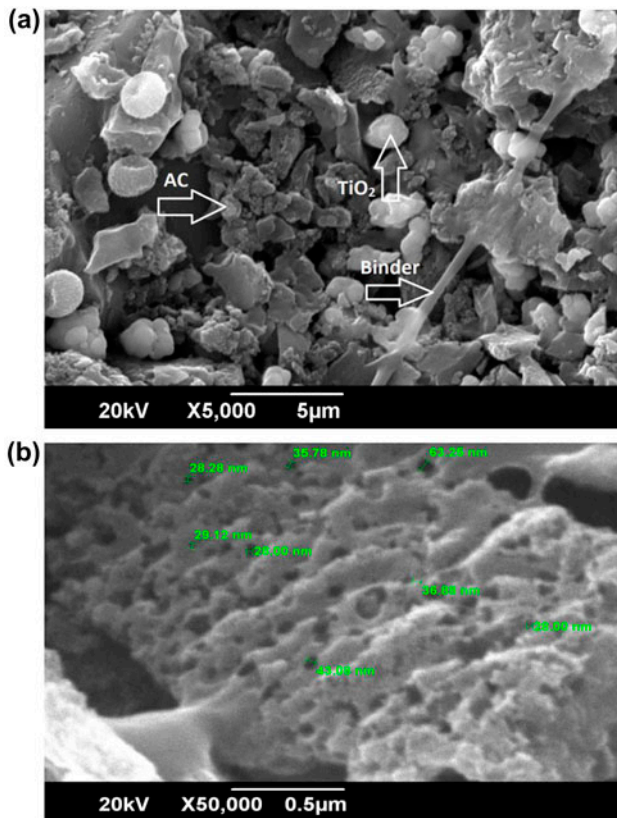
Fig. 3. (a) SEM image (magnification 5,000×) of the PAC + TiO$_2$ electrode and (b) SEM image (magnification 50,000×) of the PAC + TiO$_2$ electrode.
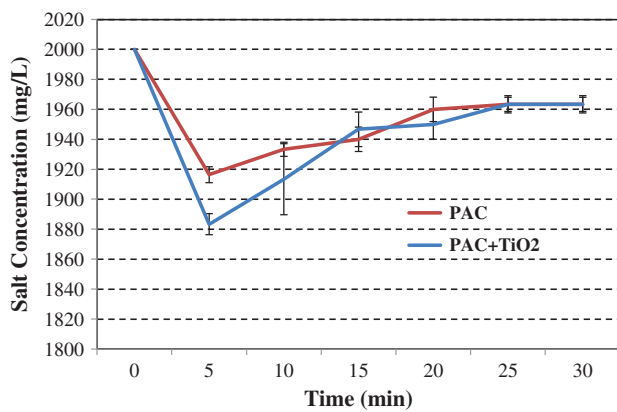

Fig. 4. Concentration variations of the small-scale CDI system at 1.3 V using PAC vs. PAC + TiO$_2$ electrodes.

Further experiments were conducted on the laboratory-scale CDI system using PAC + TiO$_2$ electrodes. Fig. 5 shows effluent concentration variations at different applied voltages. It was observed that a rapid reduction in the effluent concentration appeared for
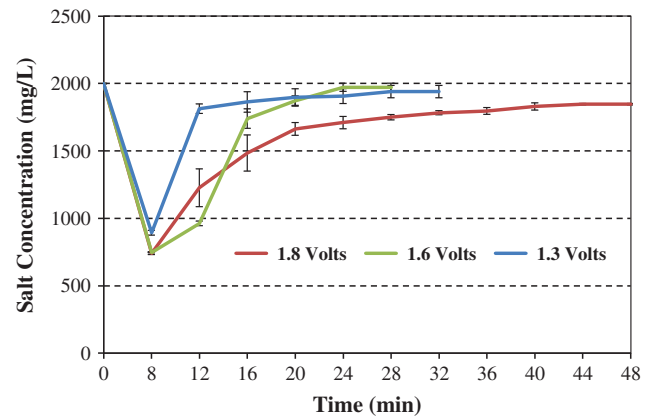

Fig. 5. Concentration variations of the laboratory-scale CDI system at different applied voltages using PAC + TiO$_2$ electrode.

all the voltages within 8–12 min of adsorption operation, meanwhile the concentration tends to get closer to the influent concentration after 20–32 min for 1.3 and 1.6 V but at 1.8 V, the concentration reached 1,846 mg/L after 44 min of operation. This depicts that greater the electrode potential, greater will be the saturation time and greater will be the salt removal. Higher voltages exert stronger electrostatic forces and thicker EDL, consequently the electrosorption capacity increases with the enhancement of the cell voltage [22,23].

The salt removal efficiencies and adsorption capacities increased with the increase in voltage from 1.3 to 1.8 V as presented in Table 2. NaCl concentration dropped to 882 mg/L at 1.3 V, 744 mg/L at 1.6 V, and 731 mg/L at 1.8 V from the feed concentration of 2,000 mg/L. The CDI performance at 1.8 V was found to be the optimum because of maximum salt removal efficiency of 64% and adsorption capacity of 6.67 mg-NaCl/g-adsorbent. No visible gas bubbles were observed during experiments, which indicate that no electrolysis reaction occurred at lower applied potentials (1–2 V) [24,25].

Fig. 6 shows effluent concentration variations for the pilot-scale CDI system operated at 1.8 V with variable feed concentrations of NaCl solutions using PAC + TiO$_2$ electrodes. Maximum salt removal of 84, 82, and 71% was observed for NaCl concentrations of 2,000, 2,500, and 3,000 mg/L with adsorption capacities of 7.7, 10.4, and 11.2 mg-NaCl/g-adsorbent, respectively. The amount of treated water under 1,000 mg-TDS/L was 1.5, 1.1, and 0.6 liters for 2,000, 2,500, and 3,000 mg/L, respectively. The reason for a decrease in salt removal efficiency with increase in concentration is that as the amount of salt to

Table 2
Salt removal efficiencies and adsorption capacities for the laboratory-scale CDI system

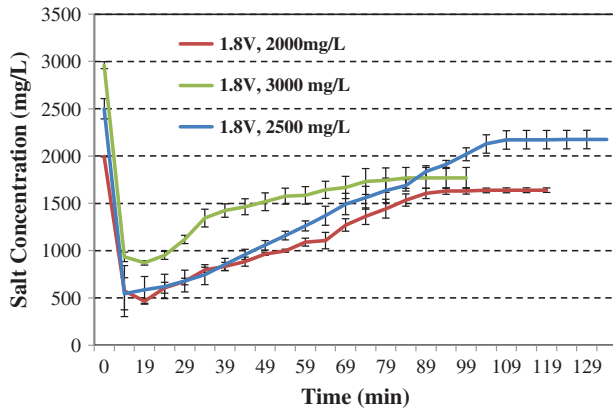| Voltage (V)	Volumetric flow rate (mL/min)	Salt removal (%)	Adsorption capacity (Q) (mg-NaCl/g-adsorbent)
1.3	25	56	2.64
1.6	25	62	4.30
1.8	25	64	6.67

Fig. 6. Concentration variations of the pilot-scale CDI system at 1.8 V using PAC + TiO$_2$ electrode for different feed concentrations.

adsorbent increases, the exchangeable sites on the adsorbent structure become saturated, which results in the decrease of the salt removal over time. In this study, the salt adsorption capacity increased with increase in concentration, which is due to elevated mass transfer rate of salt ions inside the pores and reduction in the overlapping effect by greater concentrations [26].
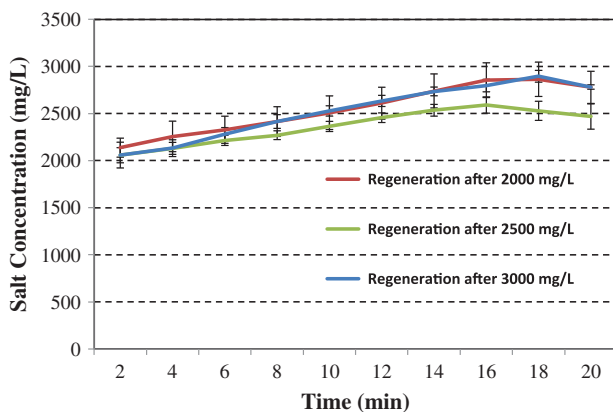
Fig. 7 shows that the regeneration of electrodes of the pilot-scale CDI system. Once the voltage was removed from the electrodes and washed with DI water during regeneration of electrodes, the effluent concentration increased as compared to the influent concentration because the adsorbed salt ions were washed off from the surface of the electrodes and the regeneration of the electrodes was accomplished within approximately 20 min.

3.3. Electrochemical properties of the electrodes

CV was performed to study the electrochemical properties of the electrodes. Fig. 8 shows cyclic voltagrams acquired in the electrosorption and desorption of NaCl on the PAC and PAC + TiO$_2$ electrodes. There was no major evidence of oxidation/reduction reactions on both types of electrodes, as balance growth and drop in current with electric potential were noticed. The CV results showed that the main contribution of the salt ions removal from the solution was electrical double layer (EDL) on the surface of the electrode under the charged potential and there were no major Faradic or electrochemical reactions [27,28]. In CDI cell, the loops correspond to sweeping area in cyclic voltagrams, which actually demonstrate the
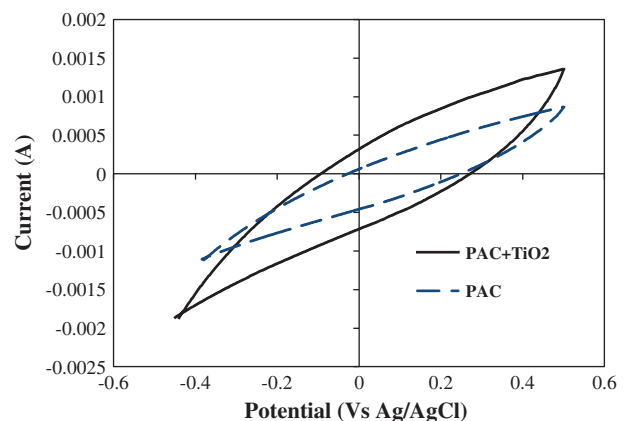

Fig. 7. Regeneration concentration variations of the pilot-scale CDI system.

Fig. 8. Cyclic voltagrams of the PAC vs. PAC + TiO$_2$ electrodes.

adsorbed amount of salt ions on the surface of the electrode. The sweeping area of PAC + TiO$_2$ electrode was greater than the PAC electrode, which exhibits an increase in the electrosorption of salt ions by the addition of TiO$_2$ with PAC.

4. Conclusions

In this study, initial experiments were conducted using PAC and PAC + TiO$_2$ electrodes to access the salt removal efficiencies of both electrodes. PAC + TiO$_2$ electrodes showed 28% more salt removal as compared to PAC electrodes. Further experiments were conducted using PAC + TiO$_2$ electrodes in laboratory- and pilot-scale CDI setups. In the laboratory-scale CDI system, the adsorption capacities were found to be 2.64, 4.30, and 6.67 mg-NaCl/g-adsorbent and salt removals were 56, 62, and 64% for 1.3, 1.6, and 1.8 volts, respectively. Higher voltages exerted stronger electrostatic forces resulting in higher electrosorption capacities. Moreover, pilot-scale CDI system using 20 pairs of PAC + TiO$_2$ electrodes exhibited maximum salt removal efficiency of 84, 82, and 71% and adsorption capacities of 7.7, 10.4, and 11.2 mg NaCl/g-adsorbent for the feed NaCl concentrations of 2,000, 2,500, and 3,000 mg/L, respectively. The salt adsorption capacity increased with increase in salt concentration, which was due to elevated mass transfer rate of the salt ions inside the pores. The results indicate the potential application of PAC–TiO$_2$ electrodes for desalination of brackish water using CDI technology.

Competing interests

Authors declare no competing interests.

Acknowledgments

List of symbols

Q	—	adsorption capacity (mg-NaCl/g-adsorbent
C_i	—	influent concentration (mg/L)
C_e	—	effluent concentration (mg/L)
C_f	—	feed concentration (mg/L)
C_P	—	lowest product concentration (mg/L)
V	—	volume of effective product (L)
M	—	mass of adsorbent (g)

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