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Removal of ammonium ions by capacitive deionization and membrane capacitive deionization units

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ABSTRACT

In this study, capacitive deionization (CDI) and membrane capacitive deionization (MCDI) unit cells were used to remove NH_4^+ ions. The influences of operating parameters such as the applied voltage, the initial ammonium concentration and the flow rate on the effectiveness of ammonium removals were investigated. In addition, the effects of different membrane types on MCDI performances were also studied. The results showed that, the electrosorption performances of CDI and MCDI increased by increasing the initial concentration, flow rate and the applied potential. It was observed that the adsorption capacity of MCDI unit was much higher than that of CDI due to the presence of ion-exchange membranes. MCDI technology may provide better advantages on ammonium removal.

Keywords: Capacitive deionization; Electrosorption; Ammonium removal

1. Introduction

Ammoniacal nitrogen in wastewater is a major environmental concern since it may cause eutrophication in receiving water bodies. Hence, the removal of ammonium nitrogen has gained great importance [1,2]. There are various conventional methods for ammonium removal including chemical precipitation [3], membrane processes [4–8], ion exchange/adsorption [9–11], biological treatment [12] and air stripping [13]. However, each process has various disadvantages. Biological nitrogen removal is problematic due to its sensitive operating conditions and its need for additional chemicals. Chemical precipitation in the form of struvite may also be used; however, higher magnesium is required at high ammonia and phosphorous concentrations causing higher operating costs [7]. Applications of membrane processes are limited by considering the necessity of high transmembrane pressures resulting in higher operational cost due to energy expense. Furthermore, it requires additional treatment steps before discharge in addition to the fouling problems [14]. The fouling problems of membranes process have been minimized by using reverse electrodialysis process. However, the process need large membrane area due to the restriction of limiting current density which increases the investment costs [14]. In recent years, researchers have investigated the ammonium removal either by capacitive deionization (CDI) or membrane capacitive deionization (MCDI) processes [15,16]. Farmer et al. [17] investigated the electrosorption of NH_4 ions by carbon aerogel electrodes and reported 52% removal efficiency at 50 mg/L initial concentration by a CDI cell consisted of 48 pairs of electrodes. A recent report has demonstrated that the electrosorption of ammonium with graphene laminated electrodes from synthetic solution containing 400 mg/L NH_4Cl reached

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to 98% NH_4–N removal efficiency [16]. A pilot scale study has also been reported in the literature. The activated carbon electrodes of the CDI stacks with a total surface area of 40 m^2 were used to investigate the electrosorption performance of ammonium ions (1,000 mg/L). 88.1% of NH_4 removal efficiency was observed [15].

CDI is an attractive deionization technology without any chemical usage and low energy consumption [16,18]. In CDI process, the charged particles are removed from a solution that flows through between two porous carbon electrodes. The ions are stored within the electrical double layer (EDL) that developed at the interface of the electrolyte and electrodes [19]. In CDI process, the ion separation mechanism is electrostatic adsorption process which is achieved under low direct voltages (<2 V) [19–21]. By the application of electrical field to CDI cell, carbon-based electrodes charged positive and negative as anode and cathode, respectively. During the absorption step, ions consistently move towards the electrode surface [22]. The amount of adsorbed ions gradually decreases along the adsorption process due to the limited ion adsorption capacity of the electrodes [23]. When the electrodes reach their saturation capacity, regeneration process is started. The regeneration period is aimed to release the adsorbed ions from the electrodes by reversing the charge of applied electrical potential. Consequently, the adsorbed particles at the oppositely charged electrodes start to desorb [21]. The adsorption capacity is limited with the capacity of the diffuse layer in CDI. In order to enhance the sorption capacity and to overcome the problems associated with desorption step, ion selective membranes have been used in CDI units, which is known as MCDI process. Ion-exchange membranes are assisted to separate positive and negative charged ions at MCDI unit. During the adsorption process the cations pass through the cation-exchange membrane and hold onto the cathode as the anions transfer through the anion-exchange membrane and adsorb onto the anode. Besides, the desorbed ions are blocked by the ion-exchange membranes and retained in the bulk solution [21]. This ion separation mechanism of the ion-exchange membranes also ensures the prevention of co-ion adsorption during the regeneration process. The adsorption capacity of CDI and MCDI processes are closely dependent on the properties of carbon electrode and the applied voltage. Electric potential is the key factor effecting the electrosorption capacity of the electrodes and adsorption–desorption characteristics [19,24].

Most CDI and MCDI studies deal with the removal of indifferent ions mostly sodium and chloride. As outlined above, studies related to ammonium is relatively recent. When ammonium is removed from the solution, the pH also changes, which may affect the ion transport. Furthermore, the studies related to the effect of membrane types on the ion transport and comparative energy consumptions have been very limited. Therefore, in this study, it was aimed to investigate the removal of ammonium ions using both CDI and MCDI processes. First, the influences of various operational parameters including applied voltage, flow rate, initial solution concentration on the process efficiency were studied. Change of NH_4–N, pH and conductivity with time were observed. Then, the influence of ion-exchange membrane types on NH_4–N removal was investigated. Finally, the energy requirement per mass of NH_4–N removals for both CDI and MCDI were determined.

2. Experimental setup

2.1. Fabrication of activated carbon electrodes

Method developed by Hou et al. [20] was used to prepare carbon electrodes. First, the polymer polyvinylidene fluoride (molecular weight: 530,000, Aldrich, Germany), which was used as a binder agent, was dissolved in dimethylacetamide (Aldrich). Then, the activated carbon powder with surface area of 1,500 m^2/g (Darco 100 mesh powder, Sigma-Aldrich) was added to the mixture as a conductive material. The mass ratio of polymer, solvent and activated carbon mixture was 5:1:0.1. The mixture was stirred for 24 h to obtain the homogeneity. After that, the slurry was cast onto the electrically conductive graphite sheets (0.5 mm in thickness) using a casting knife. The casted electrodes were then dried in an oven at 120°C for 2 h to remove the solvent from the pores of the activated carbon. The total dry carbon mass on the electrodes used in CDI unit was 10.66 g. The activated carbon mass used in MCDI units with Ionsep MC, Ionsep HC and Ionsep AM membranes were 1.90, 2.38 and 2.26 g, respectively.

2.2. Configuration of CDI and MCDI cells

The area of each carbon electrode used in both CDI and MCDI cells was 8 × 8 cm^2. In CDI cell, the anode and the cathode were separated by a nylon net spacer as a turbulent promoter and to prevent the short circuit. The thickness of the spacer was 0.5 mm. After proper arrangement of electrode layers, they were placed in between a polypropylene frame.

For MCDI cell, each layer had an anode, an anion-exchange membrane, a cation-exchange membrane and a cathode. Electrodes and membranes were separated with spacer and silicon gaskets. Then, the arranged layers were framed by a polypropylene cell. Ion-exchange membranes were installed in parallel between the electrodes. The characteristics of the ion-exchange membranes (Hangzhou Iontech Environmental Technology Co., Ltd.) are listed in Table 1. The distance between the two electrodes was 1 mm for CDI and 2 mm for MCDI due to the presence of ion-exchange membrane layers. The CDI unit consisted of 7 cells with 14 electrodes that were connected hydraulically in series and electrically in parallel. As for MCDI unit, four electrodes and four membranes were placed in the system to create two identical cells. The electrodes were connected to a direct current power supply (GW Instek PST-3202). During the adsorption and desorption processes, voltage and current values were recorded at 30 s intervals.

Both systems were operated in a continuously recirculated flow mode. The solution was fed to the bottom of the reactors and the effluent water was taken from the top of the opposite end. The total volume of the recirculated water was 100 mL and the solution was stirred with a magnetic stirrer throughout the experiments. A schematic view of CDI/MCDI unit is given in Fig. 1, NH_4Cl (Sigma-Aldrich) solution was provided to the units by a peristaltic pump (Cole Parmer, Masterflex 77521-57) at constant flow rate. For each feed concentration (100, 300, 600, 900 mg/L) the CDI and MCDI units were operated at different flow rates (10, 20, 30 mL/min) and various potentials (0.8, 1, 1.2 V). Between each experiment, to remove the residual ion concentration on the electrodes, the systems were flushed with deionized water for 30 min at 10 mL/min. The experiments were continued until the steady state conditions reached (the conductivity variation was approached to zero).

Table 1
Main characteristics of the ion-exchange membranes

Membrane type	Thickness (mm)	Ion-exchange capacity (mol/kg)	Water permeation period (min)	Diffusion coefficient ($\times10^{-3}$ mmol NaCl/ (cm^2 h mol/L))	Permselectivity (%)	Resistance of surface (Ω cm^2)
Cation-exchange membranes						
Ionsep MC	0.42	2.4	30	4.7	91	6–10
Ionsep HC	0.42	2.2	45	3.2	92	10–12
Ionsep AM	0.42	2.2	120	2.8	93	10–13
Anion-exchange membranes						
Ionsep MC	0.42	2.2	75	4.3	90	8–10
Ionsep HC	0.42	2	90	3.7	92	10–13
Ionsep AM	0.42	2	140	3	93	11–14

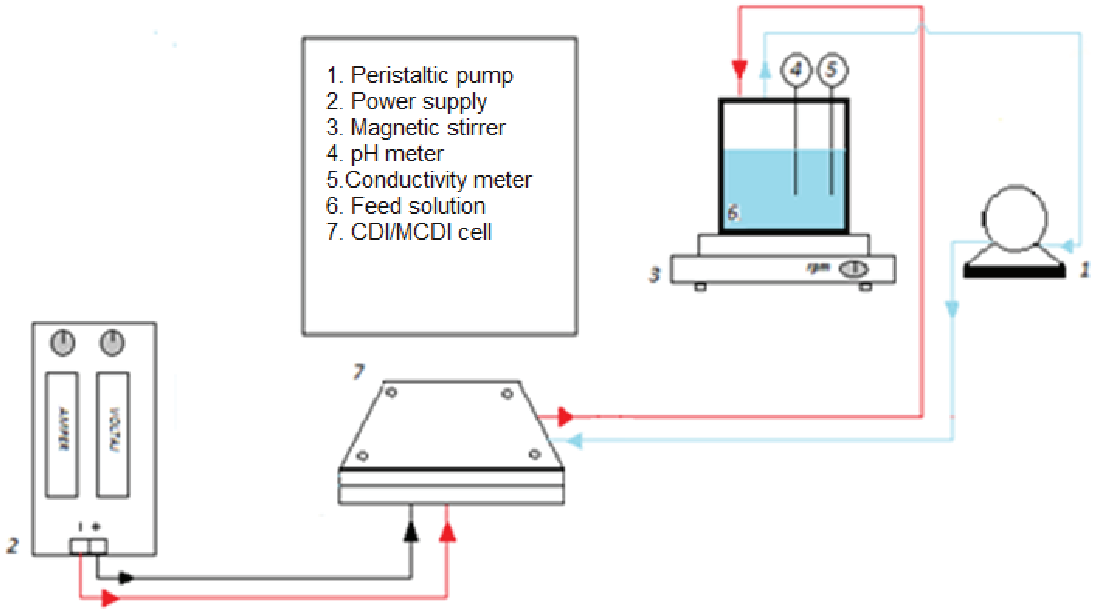

Fig. 1. Schematic diagram of CDI and MCDI unit cells.

The cycle durations (sorption or desorption) for CDI and MCDI were 30 and 20 min, respectively. During the desorption step of the CDI unit, the voltage was reversed for 30 s then adjusted to 0 V for 30 min. On the other hand, the applied potential was reversed for the same period for the regeneration process (desorption) of MCDI. The reversed voltage was applied along the desorption process for 20 min to increase the ion releasing performance. Duplicate experiments were conducted to verify the reproducibility of the results.

The electrosorption performance (q_e) was evaluated by calculating the adsorbed NH_4–N amount on the activated carbon pores as follow [25]:

$$q_e = \frac{(C_o - C)V}{M} \quad (1)$$

where C_o and C (mg/L) refer to the initial and final concentrations of the NH_4–N, M (g) is amount of activated carbon on the anode and V (L) is the volume of the feed solution recirculated throughout the reactor.

2.3. Analytical methods

The chemicals used in the experiments were analytical grade and were used without any purification. The concentration NH_4–N was continuously measured by Hach Lange ISENH4181 ammonium probe. Solution pH was determined by a pH probe (Hach Lange PHC101), and conductivity measurements were performed by a conductivity meter (Hach Lange CDC401). The conductivity, ammonium and pH were automatically recorded at 10 s intervals.

3. Results and discussion

3.1. Comparison of electrosorption performances of CDI and MCDI

The CDI and MCDI cells were operated in three consecutive cycles and the variations of the electrical current, pH and conductivity during adsorption and desorption periods were observed. The results are presented in Fig. 2. It was seen that the electrosorption processes were reversible. The identical adsorption and desorption cycles were the proof of an ideal operation without any electrode reactions. The amount of charge flowing through the cell during the adsorption cycle was equal to the charge flowing in desorption [26]. During the adsorption period the conductivity of the solution started to decrease and reached to a minimum value. As the voltage was applied to CDI and MCDI cells the ammonium concentration of the solution started to decrease and an equilibrium was achieved between the electrodes and the solution. The adsorption and desorption processes concurrently occurred in the cells [22]. This known phenomenon causes several problems such as incomplete regeneration of the electrodes, depletion of the active sides at electrodes, requirement of longer regeneration times and blocking off ions that will adsorb/desorb on the following period [21]. In order to prevent those negative effects, the voltage was applied intermittently at the desorption period of CDI unit. At the beginning of the regeneration step, 45 s of reverse potential was applied. Then, in order to block the attractive forces upon the counter ions, the electrical potential was set at 0 V for the rest of desorption process. As seen in Fig. 2, for CDI unit co-ion effect was prevented and similar deionization trends were achieved as in MCDI. The final conductivity of desorption period was higher than the initial conductivity level of the first cycle of CDI. Because at the regeneration step of the negatively charged electrode, the cations in the EDL started to move towards the solution to maintain the electroneutrality. Because of the electrostatic forces, anions could migrate towards the electrode surface and some deep-seated portion of the cations was trapped at the EDL. Then at the following adsorption period, the cations in the EDL were easily adsorbed onto the electrode surface when anions were expelled from negatively charged electrode. Kim and Choi [27] reported that this phenomenon might be the reason for the gradual increase of the effluent concentration at the early stages of adsorption period [25]. As seen in Fig. 2, the desorption periods were successfully completed in this study.

The flow of current through the cell implies the effective adsorption or desorption of ions in the system [28]. During the adsorption process, due to the decreased ion concentration in the feed channel, the electrical current decreased to 0 V from 0.48 to 0.2 A in CDI and MCDI, respectively. At the

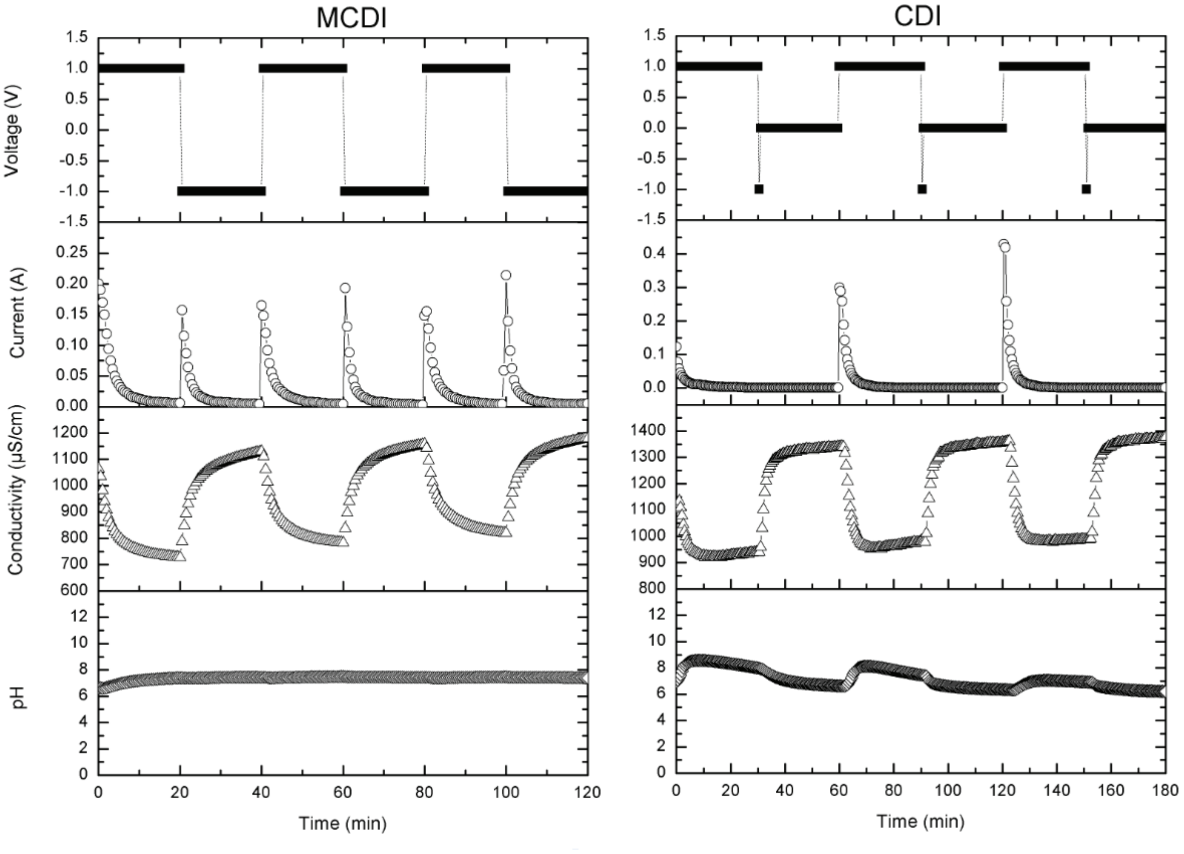

Fig. 2. The conductivity, pH, voltage and current trends of CDI and MCDI units at 1 V, initial NH_4–N concentration of 100 mg/L and flow rate of 10 mL/min.

desorption period, the migration of ions back to the solution leads to an increased electrical conductivity and the current rose back to its initial level. Besides, the change of current was not significant during the adsorption period. As seen in Fig. 2, the current trends of CDI and MCDI cells were dissimilar because of the different regeneration method. By the initiation of the shock wave of reversed voltage, the current of CDI unit was instantly decreased to zero.

For a better evaluation of the process effectiveness, the current efficiencies (η_c) were calculated. The term is defined as the ratio of the total charge of the adsorbed ions to the charge passed through the cell and calculated by the following equation [29]:

$$\eta_c = \frac{\left(C_o - C\right)VF}{\int I \mathrm{d}t} \tag{2}$$

where C_o and C are the initial and final molar concentrations of NH_4–N during an adsorption period (mol/L), V is the total volume of the solution (L), F is the Faraday constant (96,500 C/mol) and I is the current that passed through the cells (A).

The current efficiencies were used to compare the performances of CDI and MCDI processes. The current efficiencies were calculated as 16% and 59.3% for CDI and MCDI, respectively. Lower current efficiency values indicated that the current flowed through the CDI cell enabled to adsorb the counter ions in the meantime rejected the co-ions [29]. Huyskens et al. [30] verified that the reason of the lower current efficiencies was the occurrence of Faradaic reactions and concentration polarization phenomena at the spacer side of the CDI cell [30]. The higher current efficiency value of MCDI indicates that the effective separation of co-ions/counterions was achieved through the system.

The pH of the effluent was measured at 10 s intervals to understand if there was any Faradaic reaction at the electrodes. The pH variations of the MCDI system were consistent as seen in Fig. 2. The pH values of the CDI system remained stable in between 6 and 8. Depending upon these pH values, the NH_4^+ ions were remained ionized form throughout the experiment. The reason of the slight pH fluctuations of the CDI system may because of the difference in ion mobilities of hydrogen ion and ammonium ion in the solution [31].

3.2. *Effect of voltage on electrosorption*

The influence of the cell potential to the ammonium removal of CDI and MCDI was shown in Fig. 3 at 0.8, 1 and 1.2 V applied potentials. The flow rate of the system was fixed at 10 mL/min and the initial NH_4–N concentration was 100 mg/L for CDI and 600 mg/L for MCDI. The maximum voltage value applied to the electrodes was 1.2 V to prevent water decomposition [23,32].

The removal efficiency of ammonium increased with increasing applied potential due to stronger electrostatic interaction between the electrodes and charged particles. For CDI unit the amount of adsorbed ammonium was 0.62 and 0.84 mg/g at 0.8 and 1 V, respectively (Fig. 3). And for MCDI unit 4.89 and 5.34 mg/g ammonium was adsorbed at 0.8 and 1.0 V, respectively. The maximum adsorption capacity was recorded at 1.2 V. Electrosorption of CDI reached to 1.04 mg/g, which was significantly lower than 6.8 mg/g of the maximum adsorption value of MCDI. MCDI unit showed 6–7 times better performance comparing with CDI unit. This is not due to the difference in the initial concentrations of NH_4–N as discussed below. It was apparent that the presence of membranes allowed ions to be trapped not only in the double layer but also in the electrode region. Furthermore, membranes prevented or retarded back diffusion of adsorbed ions towards the bulk solution.

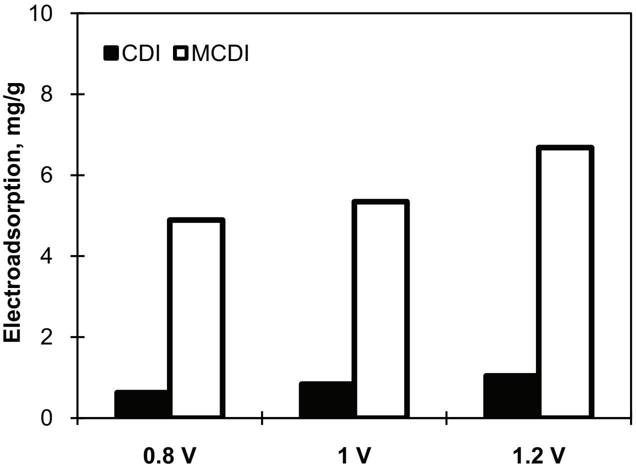

Fig. 3. Effect of voltage on NH_4–N sorption capacity.

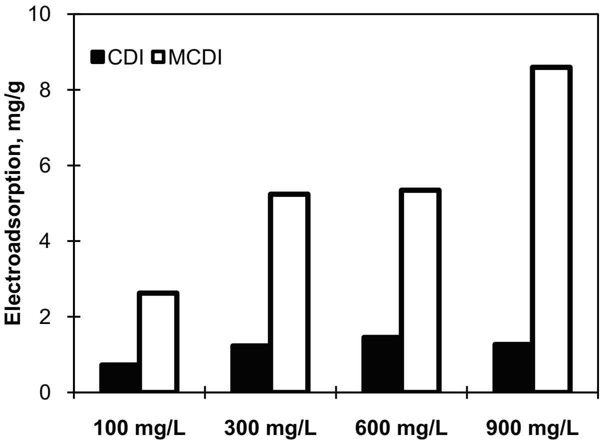

Fig. 4. Effect of initial NH_4–N on electrosorption.

3.3. *Effect of initial concentration of NH_4–N on electrosorption*

To study the effect of initial NH_4–N concentration on its removal, four different concentrations (100, 300, 600, 900 mg/L) of NH_4–N were studied at 1.0 V and 10 mL/min. The results are presented in Fig. 4. The capacity of the EDL depends on the concentration. Higher ion concentration indicates lower ohmic losses of the solution resulting higher effective voltage between the electrodes, hence the adsorption capacity of the cells increase [29]. With respect to Fig. 4, in CDI cell, the adsorbed NH_4–N was 0.72, 1.23, 1.45 and 1.26 mg/g at 100, 300, 600 and 900 mg/L of feed concentration, respectively.

When the initial concentration of the cells increased, the electrosorption also increased gradually to a certain extent. Similar results were obtained by other researchers. Mossad and Zou [33] have reported that higher initial concentration lead to increased electrosorption performance. As the initial NH_4–N concentration reached to 900 mg/L, lower electrosorption performance was achieved compared with that at 600 mg/L of inlet concentration, which showed that the electrosorption capacity of the carbon electrodes reached to their saturation level. However, at 900 mg/L initial concentration, electrosorption performance of MCDI unit continued to increase due to the assistance of ion-exchange membranes. The electrosorption values were recorded as 2.62, 5.24, 5.34 and 8.59 at 100, 300, 600 and 900 mg/L initial concentrations, respectively.

These results proved that the desalination performance of MCDI process was about 4 times higher than CDI process. Besides, MCDI unit enabled to treat higher concentrations without any performance decline. Higher desalination was achieved at higher feed concentrations but the initial concentration and the energy consumption were need to be evaluated to determine the treatment capacity of unit cells.

3.4. Effect of flow rate on electrosorption

Effect of flow rate on electrosorption performance was investigated at three different flow rates (10, 20, 30 mL/min). The results are presented in Fig. 5. The applied voltage was kept constant at 1 V and the initial NH_4–N concentration was fixed at 100 mg/L (for CDI) and 600 mg/L (for MCDI). The deionization performance was slightly affected by flow rates for both unit cells. When the flow rate was decreased from 30 to 10 mL/min, the adsorption performance enhanced slightly. It was seen that as the flow rate increased from 10 to 30 mL/min the electrosorption of ammonium decreased from 0.67 to 0.58 mg/g in CDI unit. Deionization efficiency of MCDI unit was about eight times better and the adsorbed ammonium was of 5 and 5.4 mg/g at 30 and 10 mL/min, respectively. The deionization performance was nearly the same at all flow rates; however, at 10 mL/min of flow rate both units showed better performance. At lower flow rates, the ions have longer residence time through the cell. Thus, the lower flow rates enable the required contact time of the solution with the activated carbon pores to penetrate, hold and adsorb. Therefore, at lower flow rates the ions have much time to diffuse from bulk solution to the carbon electrodes.

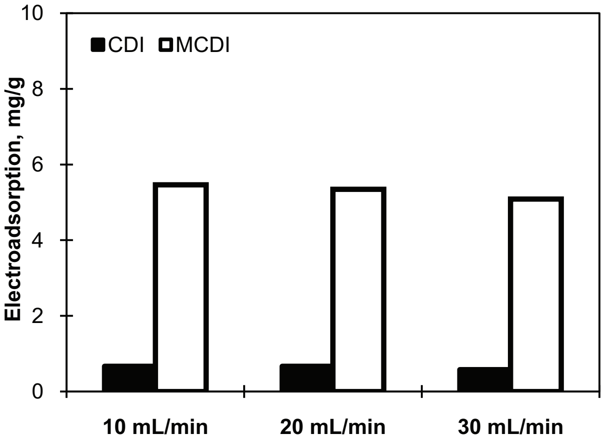

Fig. 5. Effect of flow rate on electrosorption.

3.5. Effect of membrane type on MCDI

Based on the previous experiments the optimum operation parameters were determined and the ammonium removal performances of three different membrane types were evaluated. The results at 1.0 V of potential, 10 mL/min of flow rate and 1,000 mg/L of initial NH_4–N concentration were shown in Fig. 6. Ionsep MC membrane showed better performance compare with Ionsep HC and AM membranes. As seen in Table 1, Ionsep MC membrane has higher ion-exchange capacity (2.4 mol/kg) and diffusion coefficient (4.7×10^{-3} mmol NaCl/cm^{2}h mol/L). For 10 mL/min flow rate experiment the adsorption capacity of Ionsep MC membrane was 14% and 25% better than Ionsep HC and AM membranes, respectively. The resulting electrosorption capacities at 1.0 V for the Ionsep MC, HC and AM ion-exchange membranes were 8, 5.7, 4.4 mg/g, respectively. Depending on the enhanced adsorption capacity of the Ionsep MC membrane the desorption processes were also efficient.

Energy consumptions for each mg of NH_4–N adsorbed or desorbed are presented in Table 2. For MCDI process, energy consumption was not significantly affected by the membrane type. There were some variations; however, there was no marked difference. On the other hand, as the applied voltage decreased, energy consumption per mg of ion removal decreased as well. Energy consumption was in between 4.4–5.5 J/mg NH_4–N at 0.8 V, 5–6.5 J/mg NH_4–N at 1.0 V and 6.6–7.9 J/mg NH_4–N at 1.2 V. The values in the first adsorption were slightly off than the other data set. This is likely a result of incomplete removal of ions from the previous experimental run. Energy consumption values for CDI did not show an apparent trend. However, the consumption per mg of NH_4–N removal was much greater than MCDI process ranging from 7 to 37 J/mg NH_4–N.

4. Conclusion

In this study, removals of NH_4^+ ions by CDI and MCDI cells were investigated. The CDI and MCDI reactors were operated in three consecutive cycles and the variations of the electrical current, pH and conductivity with time were observed. It was observed that MCDI showed better electrosorption

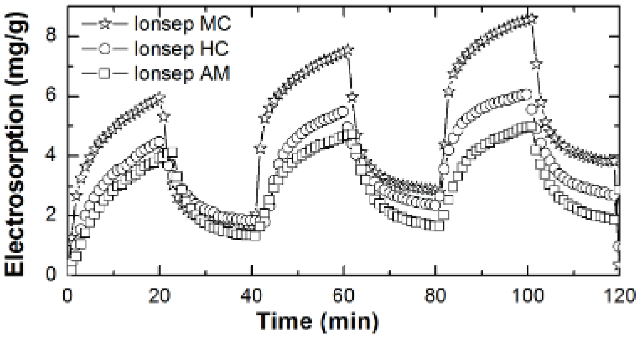

Fig. 6. Effect of membrane type on electrosorption.

Table 2
Energy consumptions for NH_4–N removal by CDI and MCDI processes

	Voltage (V)	Energy (J/mg NH_4–N [adsorbed/desorbed])					
		1.		2.		3.	
		Adsorbed	Desorbed	Adsorbed	Desorbed	Adsorbed	Desorbed
MCDI							
Ionsep MC	0.8	1.3	5.8	5.1	5.5	5.1	5.5
	1	4.5	6.9	6.2	6.5	6.2	6.3
	1.2	5.5	7.8	7.2	7.9	7.2	7.9
Ionsep HC	0.8	4.0	5.1	4.5	4.9	4.7	5.0
	1	5.4	6.3	5.8	6.2	5.9	5.9
	1.2	5.4	7.6	5.9	7.5	7.3	7.1
Ionsep AM	0.8	3.5	5.4	4.4	4.7	4.5	4.5
	1	4.2	5.1	4.8	4.8	4.9	4.9
	1.2	6.0	6.7	6.6	6.6	6.7	6.7
CDI							
	0.8	37.2	–	18.4	–	31.1	–
	1	7.2	–	11.6	–	21.3	–
	1.2	15.2	–	17.3	–	30.6	–

performance than CDI. The electrosorption performance of both CDI and MCDI was increased with increasing voltage values. The maximum adsorption capacity for NH_4–N was recorded at 1.2 V reaching 1.04 and 6.8 mg/g for CDI and MCDI, respectively. As the initial NH_4–N concentration increased, the electrosorption capacities of both CDI and MCDI also increased. The sorption capacities for CDI at 100, 300, 600 and 900 mg/L of NH_4–N were 0.72, 1.23, 1.45 and 1.26 mg/g, respectively. On the other hand, the observed efficiencies for MCDI were 2.62, 5.24, 5.34 and 8.59 mg/g, respectively. The effect of flow rate on the process efficiency was negligible. The deionization performance was nearly the same at all flow rates; however, at 10 mL/min flow rate both units showed slightly better performance. When the flow rate increased from 10 to 30 mL/min, the electrosorption of ammonium decreased from 0.67 to 0.58 mg/g in CDI and the electrosorption of ammonium in MCDI were 5.4 and 5.0 mg/g at 10 and 30 mL/min, respectively. Energy consumption per NH_4–N removals was in the range of 4–8 J/mg NH_4–N for MCDI and 7–37 J/mg NH_4–N for CDI process. The low cost and environmental friendly MCDI process was found to be a promising alternative compared with conventional ammonium removal methods.

Acknowledgement

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References

[1] A. Thornton, P. Pearce, S.A. Parsons, Ammonium removal from solution using ion exchange on to MesoLite, an equilibrium study, J. Hazard. Mater., 147 (2007) 883–889.

[2] A.G. El-Deen, J.H. Choi, K.A. Khalil, A.A. Almajidc, N.A.M. Barakat, A TiO_2 nanofiber/activated carbon composite as a novel effective electrode material for capacitive deionization of brackish water, RSC Adv., 4 (2014) 64634–64642.

[3] M. Turker, I. Celen, Removal of ammonia as struvite from anaerobic digester effluents and recycling of magnesium and phosphate, Bioresour. Technol., 98 (2007) 1529–1534.

[4] K. Hayrynen, E. Pongracz, V. Vaisanen, N. Pap, M. Manttari, J. Langwaldt, R.L. Keiski, Concentration of ammonium and nitrate from mine water by reverse osmosis and nanofiltration, Desalination, 240 (2009) 280–289.

[5] N. Yin, G. Yang, Z. Zhong, W. Xing, Separation of ammonium salts from coking wastewater with nanofiltration combined with diafiltration, Desalination, 268 (2011) 233–237.

[6] J. Zhang, Q. She, V.W.C. Chang, C.Y. Tang, R.D. Webster, Mining nutrients (N, K, P) from urban source-separated urine by forward osmosis dewatering, Environ. Sci. Technol., 48 (2014) 3386–3394.

[7] W.T. You, Z.L. Xu, Z.Q. Dong, Y.J. Zhao, Separated performances of ammonium sulphate and ammonium chloride solutions treated by vacuum membrane distillation, Can. J. Chem. Eng., 92 (2014) 1306–1313.

[8] D. Ippersiel, M. Mondor, F. Lamarche, F. Tremblay, J. Dubreuil, L. Masse, Nitrogen potential recovery and concentration of ammonia from swine manure using electrodialysis coupled with air stripping, J. Environ. Manage., 95 (2012) S165–S169.

[9] A. Malovanyy, H. Sakalova, Y. Yatchyshyn, E. Plaza, M. Malovanyy, Concentration of ammonium from municipal wastewater using ion exchange process, Desalination, 329 (2013) 93–102.

[10] N. Widiastuti, H. Wu, H.M. Ang, D. Zhang, Removal of ammonium from greywater using natural zeolite, Desalination, 277 (2011) 15–23.

[11] M. Zhang, H. Zhang, D. Xu, L. Han, D. Niu, L. Zhang, W. Wu, B. Tian, Ammonium removal from aqueous solution by zeolites synthesized from low-calcium and high-calcium fly ashes, Desalination, 277 (2011) 46–53.

[12] P. Kuntke, M. Geleji, H. Bruning, G. Zeeman, H.V.M. Hamelers, C.J.N. Buisman, Effects of ammonium concentration and charge exchange on ammonium recovery from high strength wastewater using a microbial fuel cell, Bioresour. Technol., 102 (2011) 4376–4382.

[13] X.H. Lei, N. Sugiura, C.P. Feng, T. Maekawa, Pretreatment of anaerobic digestion effluent with ammonia stripping and biogas purification, J. Hazard. Mater., 145 (2007) 391–397.

[14] W.T. Mook, M.H. Chakrabarti, M.K. Aroua, G.M.A. Khan, B.S. Ali, M.S. Islam, M.A. Abu Hassan, Removal of total ammonia nitrogen (TAN), nitrate and total organic carbon (TOC) from aquaculture wastewater using electrochemical technology: a review, Desalination, 285 (2012) 1–13.

[15] R. Broseus, J. Cigana, B. Barbeau, C. Daines-Martinez, H. Suty, Removal of total dissolved solids, nitrates and ammonium ions from drinking water using charge-barrier capacitive deionisation, Desalination, 249 (2009) 217–223.
[16] Y. Wimalasiri, M. Mossad, L. Zou, Thermodynamics and kinetics of adsorption of ammonium ions by graphene laminate electrodes in capacitive deionization, Desalination, 357 (2015) 178–188.
[17] J.C. Farmer, D.V. Fix, G.V. Mack, R.W. Pekala, J.F. Poco, Capacitive deionization of NH_4ClO_4 solutions with carbon aerogel electrodes, J. Appl. Electrochem. 26 (1996) 1007–1018.
[18] H. Li, L. Zou, Ion-exchange membrane capacitive deionization: a new strategy for brackish water desalination, Desalination, 275 (2011) 62–66.
[19] R. Niu, H. Li, Y. Ma, L. He, J. Li, An insight into the improved capacitive deionization performance of activated carbon treated by sulfuric acid, Electrochim. Acta, 176 (2015) 755–762.
[20] C.H. Hou, C.Y. Huang, A comparative study of electrosorption selectivity of ions by activated carbon electrodes in capacitive deionization, Desalination, 314 (2013) 124–129.
[21] F.A. AlMarzooqi, A.A. Al Ghaferi, I. Saadat, N. Hilal, Application of capacitive deionisation in water desalination: a review, Desalination, 342 (2014) 3–15.
[22] J.B. Lee, K.K. Park, H.M. Eum, C.W. Lee, Desalination of a thermal power plant wastewater by membrane capacitive deionization, Desalination, 196 (2006) 125–134.
[23] C.H. Hou, C.Y. Huang, C.Y. Hu, Application of capacitive deionization technology to the removal of sodium chloride from aqueous solutions, Int. J. Environ. Sci. Technol., 10 (2013) 753–760.
[24] K.H. Park, D.H. Kwak, Electrosorption and electrochemical properties of activated-carbon sheet electrode for capacitive deionization, J. Electroanal. Chem., 732 (2014) 66–73.
[25] I. Cohen, E. Avraham, Y. Bouhadana, A. Soffer, D. Aurbach, Long term stability of capacitive de-ionization processes for water desalination: the challenge of positive electrodes corrosion, Electrochim. Acta, 106 (2013) 91–100.
[26] L. Jae-Hun, B. Wi-Sup, C. Jae-Hwan, Electrode reactions and adsorption/desorption performance related to the applied potential in a capacitive deionization process, Desalination, 258 (2010) 159–163.
[27] Y.J. Kim, J.H. Choi, Enhanced desalination efficiency in capacitive deionization with an ion-selective membrane, Sep. Purif. Technol., 71 (2010) 70–75.
[28] Y.J. Kim, J. Hur, W. Bae, J.H. Choi, Desalination of brackish water containing oil compound by capacitive deionization process, Desalination, 253 (2010) 119–123.
[29] Y. Zhao, Y. Wang, R. Wang, Y. Wu, S. Xu, J. Wang, Performance comparison and energy consumption analysis of capacitive deionization and membrane capacitive deionization processes, Desalination, 324 (2013) 127–133.
[30] C. Huyskens, J. Helsen, A.B. de Haan, Capacitive deionization for water treatment: screening of key performance parameters and comparison of performance for different ions, Desalination, 328 (2013) 8–16.
[31] S. Porada, R. Zhao, A. van der Wal, V. Presser, P.M. Biesheuvel, Review on the science and technology of water desalination by capacitive deionization, Prog. Mater Sci., 58 (2013) 1388–1442.
[32] S.M. Jung, J.H. Choi, J.H. Kim, Application of capacitive deionization (CDI) technology to insulin purification process, Sep. Purif. Technol., 98 (2012) 31–35.
[33] M. Mossad, L. Zou, A study of the capacitive deionisation performance under various operational conditions, J. Hazard. Mater., 213–214 (2012) 491–497.