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공학석사 학위논문

The Effect of Organic Fouling Formed by Humic Acid to the
Desalination Performance in Capacitive Deionization

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Abstract

Capacitive deionization (CDI) technology has served as an energy efficient technique of salt removal to produced fresh water for supporting water scarcity. The presence of humic acid in water sources contributed to the concern of its effect to the CDI system. This study has experienced in effect of organic fouling to CDI by investigating in deposition of humic acid on carbon electrode surface and long-term stability operation with the presence of humic acid in the feed solution. With the deposition of humic acid on the carbon electrode surface, the severe decrease in salt removal performance and electrode electrochemical property was observed due to the active surface area of the carbon electrode was covered by humic acid particle (increasing in hydrophilicity). To observe the long-term operating effect of humic acid to the CDI, feed contaminated with 3.6 mg/L of humic acid was used as the influent feed. After 20 hr of desalination, the salt removal efficiency of the system fed with solution contained humic acid was approximately 26% decreased. In water containing humic acid, the characteristic peak in concentration profile of CDI treated effluent indicating the degradation of electrode surface was observed much earlier (3 hr) in comparison with control system (12 hr). Moreover, the anode was significantly affected by humic acid than the cathode as could be observed by the anode wettability seriously changed to hydrophilic and the specific capacitance decreased. These declines in salt removal performance and electrode electrochemical property could be recovered by applying cleaning method after operation. DI water and NaOH solution was used as cleaning agent. High cleaning efficiency was reached within short period of time with high concentration of NaOH and also increasing in flow rate. Therefore, pre-treatment steps to remove humic acid from water streams must be required to reduce its effects to the CDI performance and carbon

electrodes. Chemical cleaning with alkaline solution were able to effectively restore the recovery of the CDI performance after suffering with humic acid accumulation.

Keywords: Capacitive Deionization, Humic acid, Long-term stability, Chemical cleaning

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Chapter 1. Introduction

Water scarcity is becoming a serious problem as the world population growth. Figure 1 shows the inverse relationship between world population growth and water availability. According to the graph, the water availability will be less than 5,000 m³ while the human population will become more than 10 billion indicating the great worldwide water shortage. Therefore, preventing water scarcity is one of the major research areas in engineering and science fields. Moreover, accessible freshwater resources including river, lake and ground water occupy only a tiny fraction of 0.26% of the total freshwater storage (Shiklomanov, 2000). As a consequence, providing clean fresh water in a safe, inexpensive and energy-efficient manner is amongst the most important technological challenges in the coming decades for preventing of the water scarcity (Semiat, 2008; Schiermeier, 2008). Desalination is a definition of such an approach that fresh water can be produced by removal salts from the water passing through the process. Currently, most of the widely used desalination technologies include membrane separation process: reverse osmosis (RO), electrodialysis (ED) and thermal distillations are energy and cost intensive and can cause secondary pollution (Shannon, 2008).

Capacitive deionization (CDI) technology can be one of energy efficient process for desalination process. It is a promising ion removal technology using electro ad/desorption by applying an electrical potential difference over two porous electrodes to gain significant amount of purity water and then the potential would be uncharged from the system resulting in energy releasing. Anions are removed from the water and are stored in the positively polarized electrode. Likewise, cations are stored in the cathode, which is the negatively polarized electrode without

charge transfer reactions in the electrical double layer (EDL), which is generated oppositely positioned electrode. CDI is operated by applied potential as electrodialysis to drive charged species (ions) to the electrodes. However, CDI only requires electrode, while electrodialysis requires ion-exchange membranes that costs more than electrodes. Also, CDI process does not require high applied pressure as RO, which can be operated with low cost. (Anderson, Cudero & Palma, 2010). The production cost of CDI is about three times lower than that of the low-pressure RO process (Welgemoed & Schutte, 2005). Other advantages of using CDI such as simple design, low cost, environmentally friendly, and operation at ambient conditions have also captured attentions over all existing conventional desalination technology (Yan, Zou & Short, 2014; Xu, Drewes, Heil & Wang, 2008; Kim & Choi, 2010).

For electrodes of CDI process, activated carbon (AC) is the most common material found in water treatment systems. AC has several advantages as working electrode material such as high porosity and low cost (Oren, 2008; Ying, Yang, Yiaccumi & Tsouris, 2002; Ryoo & Seo, 2003; Kinoshita, 1988). Several research reported the AC as an electrode material in CDI since 1960 by Caudle and Murphy introduced the technique of making porous carbon electrodes from AC in a flow-through mode desalination system (Zou, Morris & Qi, 2008). Moreover, AC has also been used as an adsorbent to remove organic contaminants from water due to its exceptional adsorption capability (Freeman, 1990; Velten, Knappe, Traber, Kaiser, Gunten, Boller & Meylan, 2011). In major water source including seawater and brackish water, humic acid is a significant portion of the dissolved organic matter, which is 40 to 90 percent (Godini, Khorramabady & Mirhosseini, 2011). Therefore, the accumulation of humic acid on the electrode fabricated from AC should be considered as an affecting factor to the CDI performance. Humic acid is also

known as a model compound to form organic fouling layers on membrane surface in previous desalination and filtration studies (Tang, Kwon & Leckie, 2007; Schafer, Pihlajamaki, Fane, Waite & Nystrom, 2004; Seidel & Elimelech, 2002). In spite of the importance of humic acid fouling in CDI process, the research of adverse implication of effect of CDI organic fouling is still limited (Oren, 2008). When carbon electrode surface is covered with organic substances, the cleaning process must be applied before the reuse of carbon electrode. In previous studies, chemical cleaning method was applied for organic fouling control in various filtration system (Wenhui, Guocheng, Jie, Limei & Libing, 2012; Martin & Ng, 1984; Tragardh, 1989; Qilin & Elimelech, 2004). The objective of this study is to investigate the effect of organic fouling by humic acid in CDI process.

In this study, humic acid fouling experiment was conducted in lab-scale CDI system. The organic fouling experiments were conducted in two parts. In the first part of experiment, humic acid deposited electrodes were used in CDI system. To investigate the organic fouling effect in real CDI system, humic acid contaminated feed water was used with virgin carbon electrodes from CDI process in the second part of experiment. For controlling the effect of humic acid to the CDI performance, cleaning method was applied. DI water and NaOH solution was used as cleaning reagents. To achieve high recovery efficiency within a short period of time, high concentration NaOH solution was applied to the system with increasing in the flow rate.

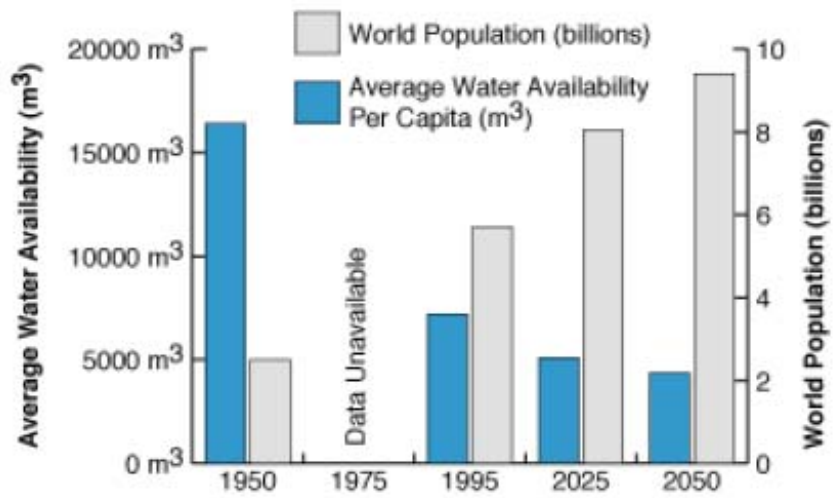


Figure 1. Chart of correlation between population growth average water availability

Chapter 2. Literature Review

2.1 Desalination

Desalination is a separation technology used to reduce the dissolved salt content of saline water (brackish or seawater) to a usable level. With improvements in technology, desalination processes are becoming cost-competitive with other methods of producing usable water for the growing needs. The desalination process essentially separates saline water into two parts. One is the treated water or product water which has a low concentration of salt, and the other is the concentrated brine water which has much higher concentration than the original feed water.

2.1.1 Worldwide used desalination technologies

The two major types of technologies that are used around the world for desalination can be broadly classified as either thermal or membrane process. A visual summary of all these processes and their impact on the desalination market is presented in Figure 2 and 3.

2.1.1.1 Membrane process

There are two types of membrane process used for desalination: reverse osmosis (RO) and electrodialysis (ED). Among membrane based plant, 86% belong to RO plants while ED represents only 14%, according to the review of Chaudhry (S. Chaudhry, 2003). In the RO process, water from a pressurized saline solution is separated from the dissolved salts by flowing through a water-permeable membrane. The major energy requirement is for the initial pressurization of the feed water. For seawater desalination, the feed pressure commonly ranges

from 60-80 bars (Avlonitis, S.A., K. Kouroumbas & N. Vlachakis, 2003), while for brackish water, the figure is much lower (~20 bar) (Arras, W., N. Ghaffour & A. Hamou, 2009).

Electrodialysis (ED) is like reverse osmosis which it is also membrane based desalination means. However, instead of the usage of semi-permeable membrane, ion-exchange membranes are used. An electrical potential is used to move salts through a membrane, leaving fresh water behind as product water. ED was commercially introduced in the 1960s, about 10 years before reverse osmosis (RO). Although ED was originally conceived as a seawater desalination process, and it has generally been used for brackish water desalination.

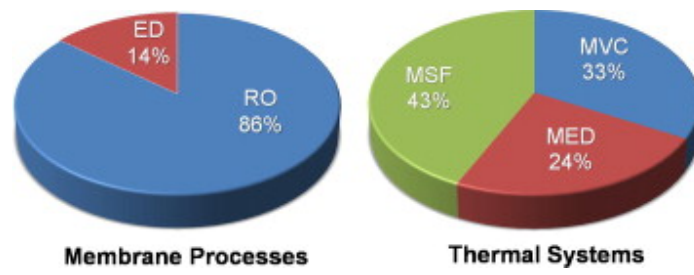


Figure 2. Percentage of membrane and thermal desalination plants worldwide (Anderson, Cudero & Palma, 2010).

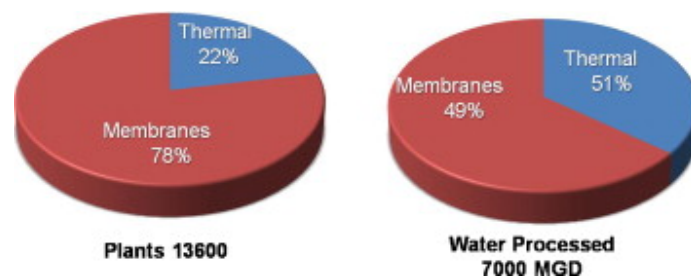


Figure 3. Percentage of membrane and thermal desalination plants worldwide and water processed by these plants. MGD: million gallons per day (Anderson, Cudero, & Palma, 2010).

2.1.1.1 Thermal process

Thermal technologies, as the name implies, involve the heating of saline water and collecting the condensed vapor (distillate) to produce pure water. The process occurs on the basis of phase change of water, which requires a significant amount of energy input under ambient conditions (water boiling point=100 °C at 1 bar). This technology has rarely been used for brackish water desalination, because of the high costs involved. They have however been used for seawater desalination and can be sub-divided into three groups: Multi-Stage Flash Distillation (MSF), Multi-Effect Distillation (MED), and Vapor Compression Distillation (VCD). In MSF, feed water evaporates in a series of flashing chambers (countercurrent heat exchangers) with decreasing temperature and pressure heated by a steam, which results in the production of large amount of vapour that is then re-condensed on the external surface of a tube bundle. In MED, evaporation occurs on the external surface of a tube bundle which is heated by motive steam condensing inside the tubes (Zhao, 2013). In VCD process, sea water is preheated in a tubular heat exchanger by the outgoing fresh and salt water streams. The sea water is then boiled in the tubes of the still. The vapors are compressed and led back to the still to condense on the outside of the tubes.

2.2 Capacitive Deionization (CDI)

CDI technology can be one of energy efficient process for desalination process. It has been served as a competitive energy efficient technique for salt removal from water.

2.2.1 Principle of CDI process

CDI uses pairs of oppositely placed porous carbon electrodes which store ions upon applying an electrical voltage difference, see Figure 4. The ions are harvested from the water flowing through a spacer channel in between the two electrodes and are immobilized in the pores inside the carbon material. This process is based on the formation of electrical double layers (EDL) inside the intraparticle pores. The EDL can be defined as the region between two different phases has a complex distribution of charge which form at the solution interface in the micropores of the porous electrodes, namely cations are stored in the negatively charged electrode (cathode) and anions are stored in the positively charged electrode (anode) (Zhao, 2013). The first model of EDL was proposed by Helmholtz in 1883 (Elimelech, 1995), and describes the distribution of charges at the double layer as in the case of a capacitor: surface accumulates charge of one sign while at the solution side the opposite sign charges are accumulated as shown in Figure 5. A second model developed by Guoy–Chapman in 1913 already took into account the gradient of electron density at a charged interface, the so-called Thomas–Fermi screening distance, and its variation with distance from the surface. The consequence of this screening is that there exists a distribution of electric charge in the double layer region depending on the potential at the surface. In this model, other factors such as the Boltzmann distribution due to thermal effects (ions are not static) were also included. However, this model described ions as point charges. As a result, it predicted unrealistic high capacitance values due to extremely short distances. Lastly in 1924, Stern completed the model by assuming that the double layer can be divided in an “inner” region where ion distribution followed Langmuir's adsorption isotherm, while the region further from the surface could be roughly described with the Gouy–Chapman model. Thus, the total

capacitance can be calculated like a series union of both, inner double layer (or Helmholtz's) and diffuse layer.

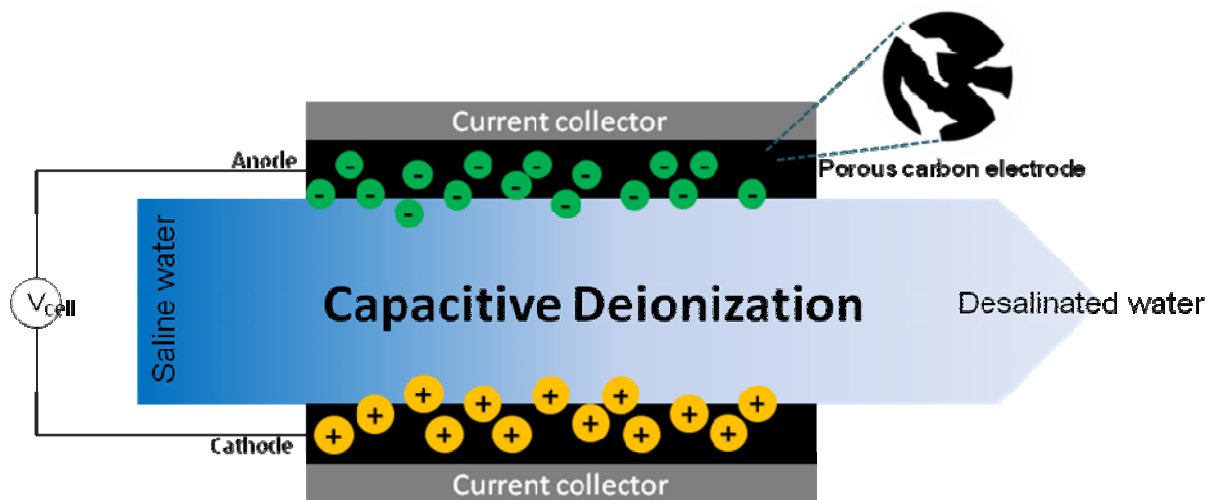


Figure 4. Schematic design of a cell for capacitive deionization, CDI. Upon applying a voltage difference between two porous carbon electrodes, ions are attached into the electrode, cations into the negative electrode (cathode, bottom), anions into the positive electrode (anode, on top).

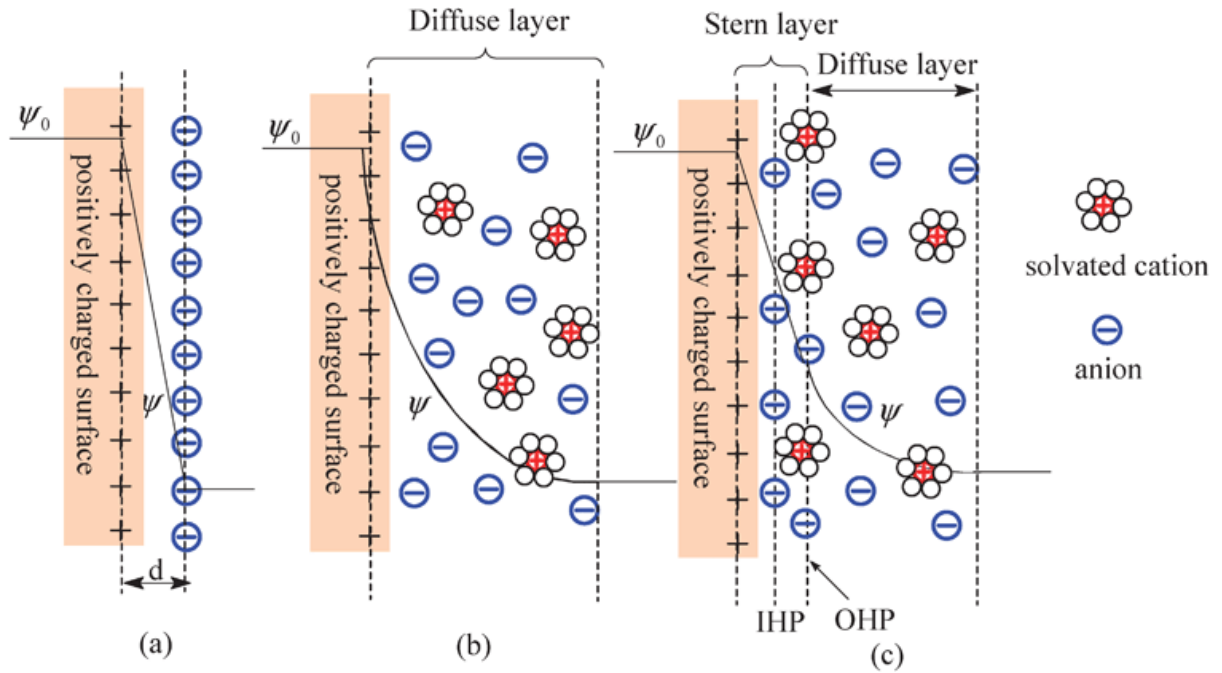


Figure 5. Models of the electrical double layer at a positively charged surface: (a) the Helmholtz model, (b) the Gouy–Chapman model, and (c) the Stern model, showing the inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). The IHP refers to the distance of closest approach of specifically adsorbed ions (generally anions) and OHP refers to that of the non-specifically adsorbed ions. The OHP is also the plane where the diffuse layer begins. d is the double layer distance described by the Helmholtz model. ψ_0 and ψ are the potentials at the electrode surface and the electrode/electrolyte interface, respectively (Zhang & Zhao, 2009).

In order to measure the actual water desalination by CDI, the change of ion concentration over time has to be measured and interpreted. The method can be done by collecting water samples and analyzing the ion composition. Only if a single salt solution is used, simple on-line measurement of water conductivity is enough. Several options are available for the layout of a CDI experiment and in particular for the location of the conductivity probe, i.e., where the conductivity is actually measured. The main aspect for ion concentration test is invented by feeding water from a storage vessel and the conductivity of the water leaving the cell is measured directly at the exit of the cell. In this case the measured effluent conductivity will start to drop soon after applying the cell voltage. Later on, the effluent conductivity rises again to the inlet value (Figure 6), because the electrodes have reached their adsorption capacity. The total amount of removed salt molecules can be calculated from numeric integration of the effluent concentration versus time data.

Electrochemically, the capacitance of a CDI system can be evaluated by means of cyclic voltammetry. The potential window is constrained by the water redox potential values, typical operation values being 1.2-1.5V. In absence of faradaic contributions, capacitance can be obtained directly from the voltamogram and sweep rate:

$$C = \int \frac{dq}{dV} = I \int \frac{dt}{dV} = \frac{I}{v} \quad (1)$$

Where q = charge in Coulombs, V = potential difference in V, t = time in s, I = intensity (in Amperes), and v = sweep rate in Vs⁻¹.

The behavior of new electrode materials towards electro-adsorption could be directly obtained from resulting voltamogram. The more featureless and rectangular the curve the better, meaning that only capacitive processes take place without any contribution of faradaic (redox) reaction.

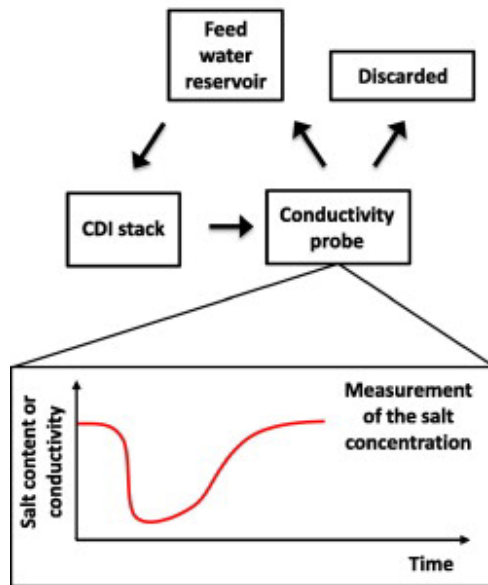


Figure 6. Schematic of main design for CDI experiment: The water conductivity is measured at the exit of the stack, or cell, and the outflow is discarded afterwards, or recycled to the large feed water reservoir. (Porada, Zhao, van der Wal, Presser & Biesheuvel, 2013)

2.2.2 Historical Background

CDI dates back to the pioneering electrochemical demineralization work of the Caudle and Johnson groups in the late 1960s and early 1970s (Anderson, Cudero, & Palma, 2010). However, a renewed interest in the CDI concept came in the mid-1990s when Farmer et al. (Farmer, 1996) at Lawrence Livermore National Labs (LLNL), working on high surface area conducting carbon aerogels, developed their own version of a CDI device. The crucial aspect of these new materials was their large increase in surface area. Capacitance scales with surface area (Eq. (2)); thus high surface area carbon materials used as electrodes improve capacitance and have better performance with respect to electro-sorption. These high surface area materials have been essential in the development of both CDI devices and also electrical double layer (EDL) capacitors.

$$C = \epsilon_r \epsilon_0 \frac{A}{D} \quad (2)$$

where C , is the capacitance in farads F ; A is the area of each plate in a traditional capacitor (usually metal) in square meters; ϵ_r is the relative static permittivity (sometimes called the dielectric constant) of the material between the plates, (vacuum =1 F/m), ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m) and D is the separation between the plates, in meters.

2.2.3 Feedwater Composition

The feed water used in CDI experiments can have very different compositions, ranging from analytical grade water with specified amounts of ions, to the complex compositions of brackish natural water or industrial process or waste water. In general, real water (diluted sea water, tap water, ground water, waste or process water from agriculture or industrial sources) will contain

many different ions, monovalent as well as divalent, and with some ions being amphoteric (i.e., their charge dependent on pH, such as HCO_3^- or HPO_4^{2-}). It will also contain colloidal matter, such as humic acids.

2.2.4 Electrode Materials

The electrode plays an important role in the CDI process because it is the place where ions are stored during operation. The use of activated carbon particles as an electrode material in CDI dates back to the early 1960s when Caudle (Caudle, 1966) and Murphy (Murphy & Cooper, 1969) first introduced the technique of making porous carbon electrode from activated carbon particles in a flow-through mode desalination system, and more recently by Zou et al. (Zoe, Morris and Qi, 2008). However, the selection of electrode materials is normally based on the cost, tunability of porosity, the specific surface area as well as the availability of these materials (Zhao, 2013). Recently, novel carbon material such as mesoporous carbon, carbon nanotubes, grapheme and composite of ordered mesoporous carbon and carbon nanotubes, composite of graphene and carbon nanotube, carbon nanotube/activated carbon particles composite as well as graphene/activated carbon particles composite were proved to be promising CDI electrode material (Yan, Zou & Short, 2014). Figure 7 provides a selection of images of various carbons used for CDI applications.

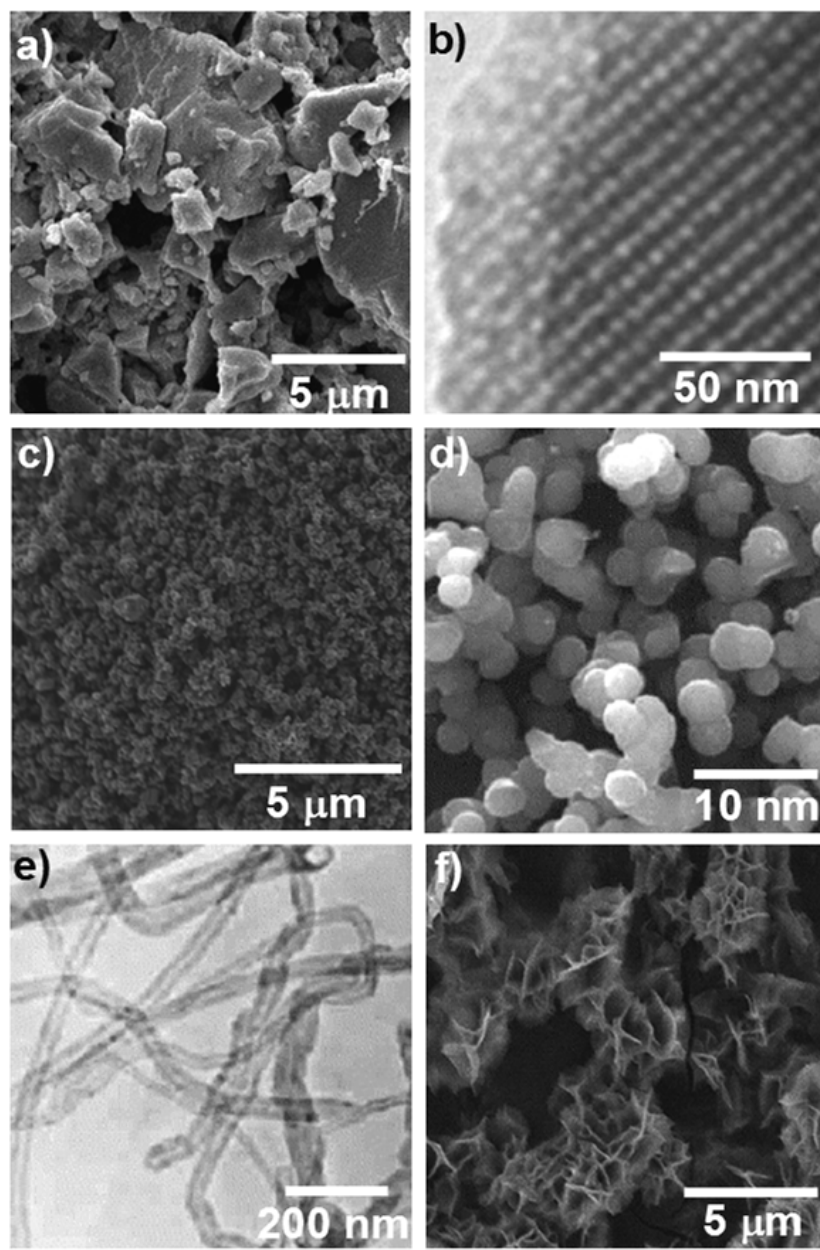


Figure 7. Selection of carbon materials used for CDI. a) activated carbon (Norit DLC Super 30, Norit Nederland B.V., the Netherlands), b) ordered mesoporous carbon (Peng, 2011), c) carbide-derived carbon (Arulepp, 2006), d) carbon aerogels (Li, 2006), e) multi-wall carbon nanotubes (Zhang, 2006), f) graphene (Li, 2009).

2.2.5 Organic fouling in CDI

Previous study in organic fouling effect to the CDI performance was reported by Mossad and Zou (Mossad & Zou, 2013). Fouling of the CDI with activated carbon electrodes was systematically investigated. Electrode fouling caused by dissolved organic matter using sodium salt of humic acid as a model foulant (measured by total organic carbon concentration, TOC) in The CDI feed solutions was investigated in a series of controlled fouling experiments. The severe decline in salt removal performance was observed after long-term conducting with water contaminated with humic acid salt, contributed to the system high energy consumption. The higher organic concentration in the CDI feed solution, the more reduction of salt removal efficiency. Moreover, organic matter accumulated in the pores of the activated carbon electrodes of the CDI cells did not respond to the desorption by reversing the applied voltage during the regeneration cycle.

2.2.5 Long-term stability of CDI

The study in long-term stability of the CDI system was reported (Cohen, Avraham, Bouhadana, Soffer & Aurbach, 2011). The study states the initial fully symmetric behavior of carbon electrode may lose when the system is operated for a long time, presented in the gradual decrease in CDI electro-sorption performance and the occurrence of the inversion (desorption of ions during charging step) as shown in Figure 8. The inversion effect could be observed from the appearance of ion-desorption peaks in the beginning of charging step of the charge-discharge cycle, shown as a peak in the expanded scale section in Figure 8. Intuitively, this would mean that the charge consumed at the beginning of the charging step is used for desorption rather than

adsorption of salt indicating that the electrode stores a significant amount of salt at the end of each discharging cycle implying to the loss of symmetric behavior of carbon electrode due to the surface degradation. The most probable reason of the loss of electrode symmetric behavior is the presence of trace oxygen in the aqueous solution, which can be easily reduced on the negative electrodes. The reduction reactions on the surface of a cathode through two pathways, as shown below (Kinoshita, 1988):

(1) Direct four-electron pathway:



(2) Peroxide pathway:



followed by the reduction of peroxide:



This situation automatically pushed the positive electrode to the higher potential and gradually oxidized, then contributed to the damage of its pore systems. The possible oxidation reactions on the anode surface are as follow (Lee, Bae & Choi, 2010):



followed by the disproportionation of chlorine:



And the oxidation of the carbon electrode itself:



In practice, anode potentials of 0.7 to 0.9 V (vs. NHE) are required to oxidize carbon (Kinoshita, 1988)

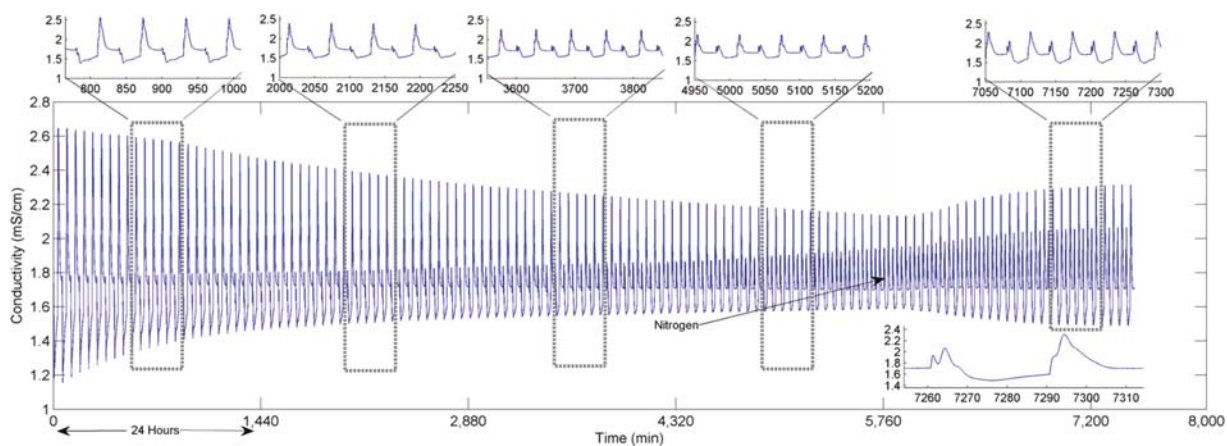


Figure 8. Conductivity/time profile of the solution measured at the outlet of the cell in a CDI experiment during 5 days. Each charging or discharging step lasted 60 min, whereas the voltage applied to the cell fluctuated between 900 and 0 mV (Aurbach, 2011).

Chapter 3. Materials and Methods

3.1 Fabrication of carbon electrodes

A carbon electrode used in both parts of experiment was fabricated using activated carbon powder (YP50, Power Carbon Technology, Korea) and carbon black (super P, TIMCAL Graphite & Carbon, SWISS). Carbon black was mixed into activated carbon to increase its conductivity (Kim, Kim, Chino, Suezaki & Endo, 2006) although high loading of carbon black in activated carbon would induce a deterioration of the total capacitance due to the small surface area of the CB. The activated carbon powder and carbon black was blend by stirring using a rotator at least for 12 hr to have homogeneous phase. Polytetrafluoroethylene (PTFE, Aldrich Co., USA) was added to the mixture of activated carbon powder and carbon black as a binder. Approximately 4 to 5 ml of ethanol was also concurrently added as a solvent to form slurry. The electrode was constructed according to the ratio of 86:7:7 %wt activated carbon, carbon black and PTFE. After the slurry was mixed for 30 min to prepare paste, it was rolled for making sheet type carbon electrode of 300 μm thickness, see Figure 9. After fabrication, the electrode was cut into an appropriated shape fitting for employing in CDI cell (50 mm of diameter, 3 mm of thickness).

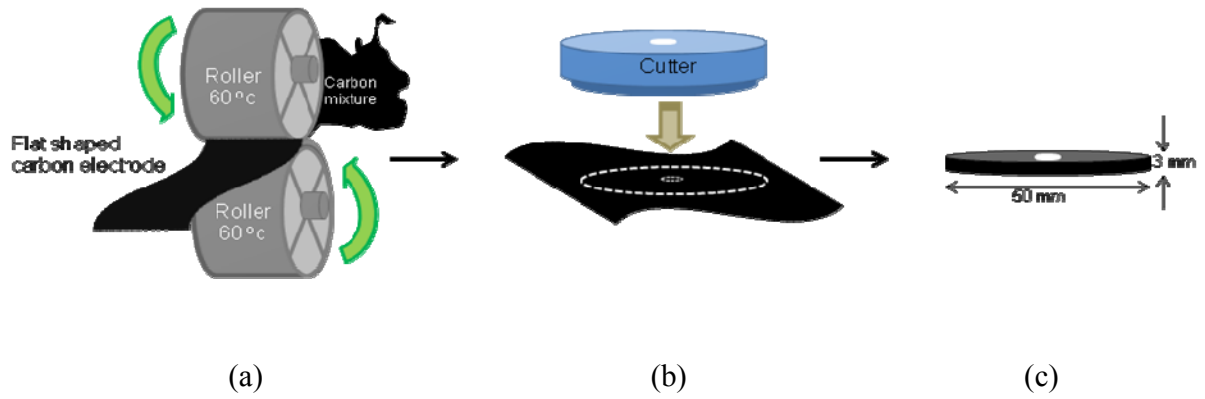


Figure 9. Electrode fabrication diagram: (a) Pressing of slurry carbon mixture in rolling press method; (b) Electrode cutting and (c) Flat shape of carbon electrode with 50 mm of diameter and 3 mm of thickness.

3.2 Characterization of Electrodes

The contact angles (for wettability evaluation) of the electrodes were obtained by contact angle analyzer (DSA 100, KRUSS, Hamburg, Germany). In order to examine the electrochemical property of the electrodes, cyclic voltammetry (CV) measurements were conducted in a conventional three electrode system using a computer-controlled potentiostat/ galvanostat (PARSTAT 2273A, Princeton Applied Research, USA) in 1 M NaCl as base electrolyte. The carbon electrodes were used as working/counter electrode ($d = 1.8$ cm) and Ag/AgCl (saturated KCl) as reference electrode. The potential values in this study were quoted with reference to Ag/AgCl (saturated KCl). The current in cyclic voltammograms was express as specific current based on weight of activated carbon powder. The values of specific capacitance of the electrode was calculated by Eq. (1) with cyclic voltammograms (Gileadi, 1993).

3.3 Humic acid stock solution preparation

In this work, humic acid stock solution was prepared referring to reported method in organic fouling study of membrane technology (Mi & Elimelech, 2008). Briefly, Aldrich Humic Acid (AHA) powder (Sigma-Aldrich, St. Louis, MO) was dissolve in DI water. The pH of the AHA solution was adjusted to approximately 1 by addition of 1 M HCl. Then, precipitation of AHA took place for 10 min. The AHA solution was then centrifuged at 4000 rpm for 10 min. After centrifugation, the supernatant was discarded and the precipitate was resuspended in 1 M HCl solution. The above cleaning procedure was repeated five times. Finally, 1 M of NaOH was added and the final pH of AHA solution was set to 9. The concentration of the AHA stock

solution was obtained by measurement mass of the sample after drying for overnight, and the concentration of the stock solution was 5,420 mg/L.

3.4 CDI test

CDI desalination performance was examined in CDI unit cell using flow type system, as shown in Figure 10. The CDI unit cell was employed to examine desalination efficiency of carbon electrode. In the CDI cell, water-permeable non-conductive nylon cloths were used as separators between two parallel electrode sheets to prevent short circuit. The thickness of nylon cloth was about 200 μm . Graphite sheets were installed on back side of the electrodes as current collectors. The holes ($d = 4 \text{ mm}$) were provided on lower compartment electrode and current collector to create flow channel.

During an ion adsorption test cycle, a feed solution was supplied to CDI unit cell by peristaltic pump with 10 mL/min of volumetric flow rate. A potential of the CDI unit cell was controlled by an automatic battery cycler (WBC S3000, WonA Tech Corp. Korea). Before the ion removal test, the system was always pretreated for 18 min. The ion removal test was initiated from the charging step which intends to achieve an adsorption by charging the cell with a potential of 1.2 V for 5 min to allow the formation of an electrical double layer on the surface of electrodes, resulting in the ion removal of the solution. After that, the discharging step for desorbing ions was immediately performed by change potential to zero for 5 min.

The desalination efficiency was evaluated from conductivity change of the effluent during the CDI operation (charging/discharging). The conductivity of effluent was measured by conductivity meter (F-54 BW, HORIBA, Japan) and automatically recorded at 6.0 s intervals by

HORIBA data Navi system. The accumulated ion removal amount was shown as an ion mass per weight of activated carbon powder (mg/g carbon) removed during charging step, which was selected at the last cycle. The ion mass converted from conductivity measured during desalination experiment.

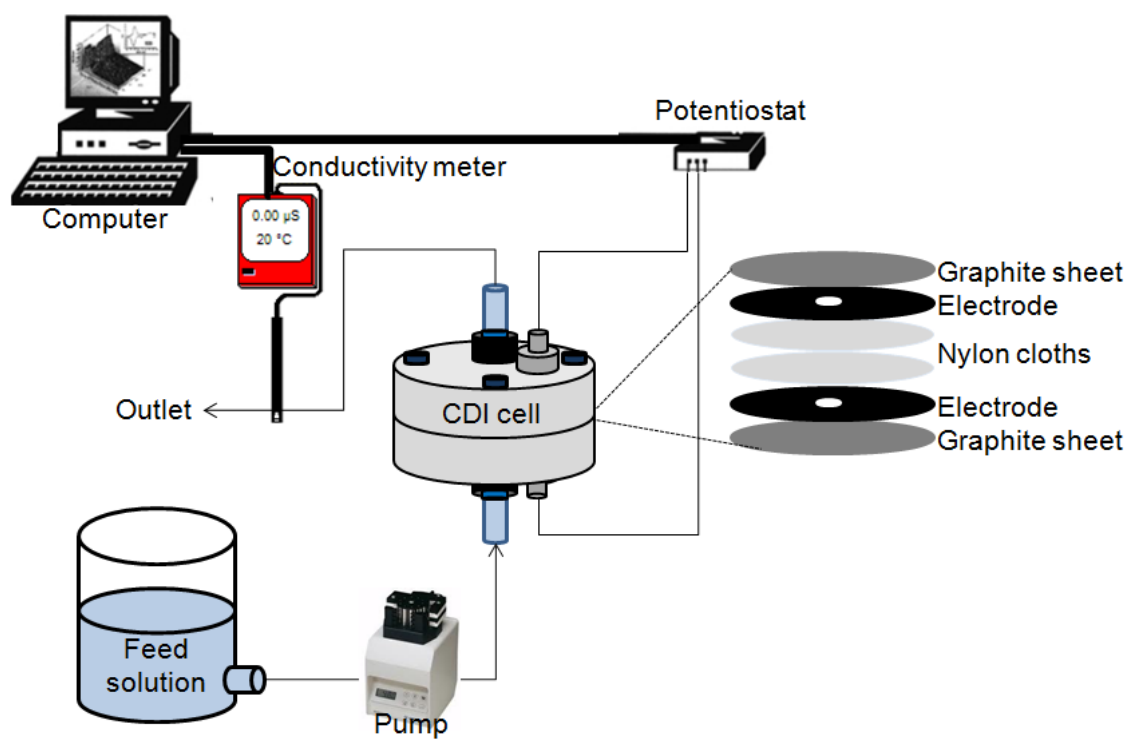


Figure 10. A schematic view of laboratory-scale CDI system.

3.5 Experiment methods

3.5.1 Effect of humic acid deposition on carbon electrodes

In this part, the fabricated carbon electrodes were immersed in humic acid solution diluted from stock to form the deposition of humic acid on the electrode surface. The concentration of 30 mg/L of humic acid was prepared and the carbon electrodes were immersed at a fixed loading of 20 ml in 90x15 mm petri dishes. The samples were conducted in an orbital-shaker at 100 rpm and shaken for 18 hr at 28°C to reach the adsorption equilibrium (Godini, Khorramabady & Mirhosseini, 2011). Then, the humic acid deposited carbon electrodes were assembled in the CDI cell to operate CDI test in section 3.4 with 10 mM of NaCl was used as a feed solution. The system was performed for 5 cycles (1 cycle comprised of 5 min charging and 5 min discharging step) and was compared with the system operated with virgin carbon electrode.

3.5.2 Continuous long-term operating with feed containing humic acid

In this part, the feed solution containing humic acid was synthesized by adding humic acid stock solution into 10 mM of NaCl. Final concentration was measured by total organic carbon (TOC) analysis and this was up to 3.6 mg/L. Large amount of the feed was prepared to support 20 hr of the CDI operation. The synthesized feed was used as an inlet to the CDI test in section 3.4 and the system would be compared with the system operated with the feed without humic acid (only NaCl in feed).

3.5.3 Cleaning Method

The regeneration procedure of exhausted carbon electrode was as follows. After 20 hr long-term operation of CDI with the feed containing humic acid, the system was cleaned by feeding DI water with higher flow rate of 22 mL/min and 100 mM of NaOH (pH of 11) solution. Each cleaning (with DI water and NaOH) was operated for 5 min. After cleaning, CDI test would be performed again to observe the salt removal performance recovery. The regeneration efficiency is judged on the extent that it recover the desalination capacity of the carbon electrode. The following method of calculation was employed to quantify the recovery rate. The original desalination capacity (D_0) was deemed to be that the quantify of ions removed from solution by per unit weight of activated carbon powder. The desalination capacity of the regenerated carbon electrode (D_r) was deemed to be that quantify of the same ions removed from solution per unit weight of regenerated activated carbon powder.

$$RE \% = (D_r/D_0) \times 100\% \quad (9)$$

Chapter 4. Results & Discussion

4.1 Effect of humic acid deposition on carbon electrodes

The wettability of both Humic acid deposited carbon electrode and virgin electrode was obtained from the contact angle measurement as shown in Figure 11. The contact angle of HA fouled carbon electrode was 24° (Figure 11 (b)) smaller than the virgin carbon electrode which was 115° (Figure 11 (a)). Smaller contact angle of humic acid deposited electrode exhibited higher hydrophilicity property where with the carbon surface of electrode was covered with humic acid which the major characteristic is hydrophilic attributed to the presence of polar groups with hetero elements such as oxygen, nitrogen and sulfur.

Figure 12 shows the capacitance profile of humic acid deposited electrode and virgin carbon electrode, which smaller rectangle aspect was observed in the carbon electrode that was covered with humic acid. The specific capacitance of each electrode was calculated by mentioned above equation. It was found that the specific capacitance was decreased from 105 F/g carbon (virgin carbon electrode) to 42 F/g carbon (HA fouled carbon electrode), indicating that accumulation of organic foulant on the carbon electrode surface could severely degrade the charge storage capability. The decrease of specific capacitance implies that the active surface area of working electrode was reduced contributed to depreciation in ion accumulation of during charging and ion regenerating during discharging. Moreover, it could be observed that the cyclic voltammogram curve of virgin electrode appears to be nearly rectangular shape while it is distorted to slim, leaf like shape for fouled electrode, due to ions being able to only arrive at shallow within pores and the increasing diffusion resistance.

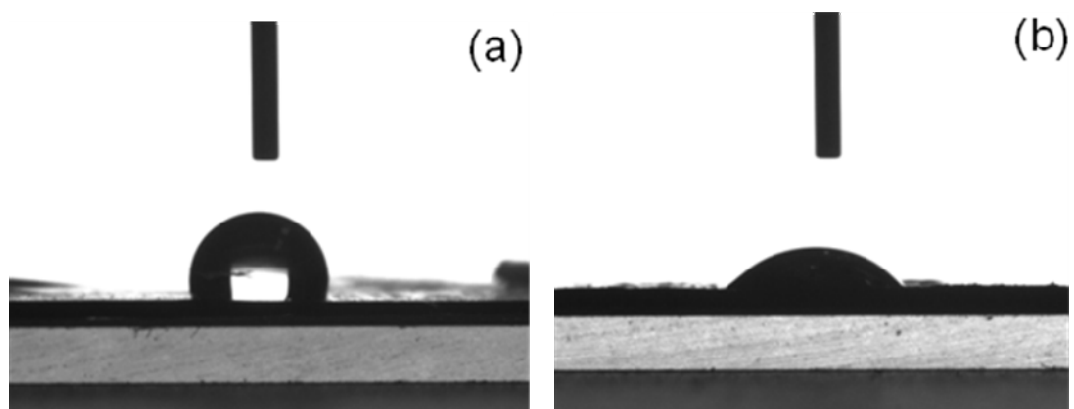


Figure 11. Surface wetting property of (a) Virgin carbon electrode and (b) Humic acid deposited carbon electrode. The contact angle of virgin carbon electrode and humic acid deposited carbon electrode are 117° and 24° respectively.

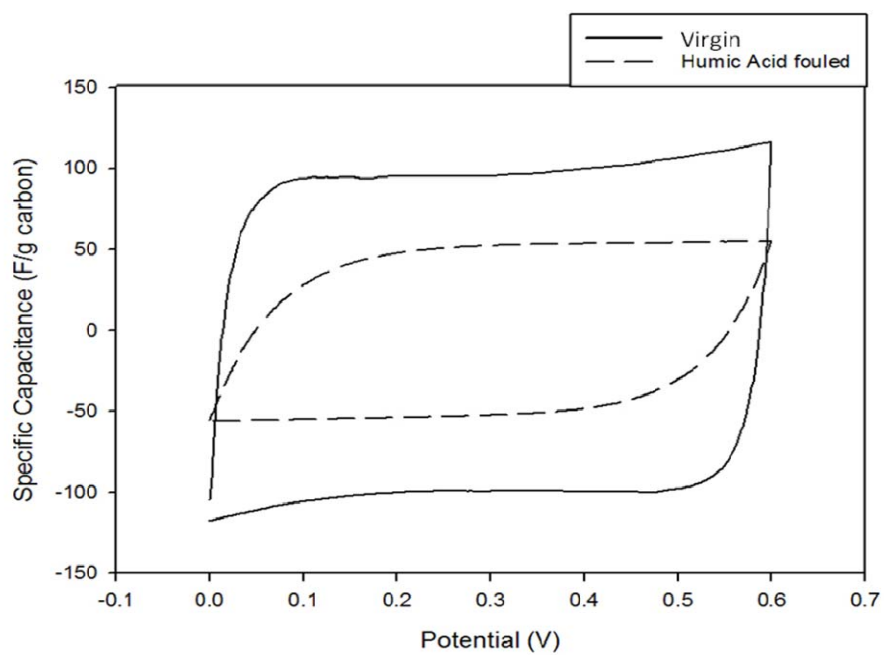


Figure 12. Cyclic voltammograms (scan rate = 2 mV/s) of humic acid deposited carbon electrode (dashed line) and virgin carbon electrode (solid line) with 1 M of NaCl

The desalination performances of two systems using humic acid deposited carbon electrode and virgin carbon electrode were shown in Figure 13. Figure 13 (a) shows the aspect of NaCl effluent concentration during 5 desalination cycles which one cycle consists of 5 min charging and 5 min discharging. It is very obvious that NaCl concentration profile of charging and discharging steps of the system using humic acid deposited electrode has much shrink than the system with virgin carbon electrode due to the electrochemical properties change of electrode. With this phenomenon, it could be considered that the fouled electrode has less ability to remove the ions in charging step and release the ions in discharging step. The amount of ions accumulated during charging step was interpreted from the area under the curve of charging step as exhibited in Figure 13 (b). During charging step of the system using virgin carbon electrode, the salt ions could be approximately removed to 11 mg/g carbon, while only 2.5 mg/g carbon of the salt ions was removed when the carbon electrode was covered with humic acid. These decreases in desalination performance of the system using humic acid fouled carbon electrode could be accounted by the change of electrode electrochemical properties after the fouling of humic acid. The concentrated ions from the solution could only access to the carbon electrode surface in the very shallow level because of the humic accumulation.

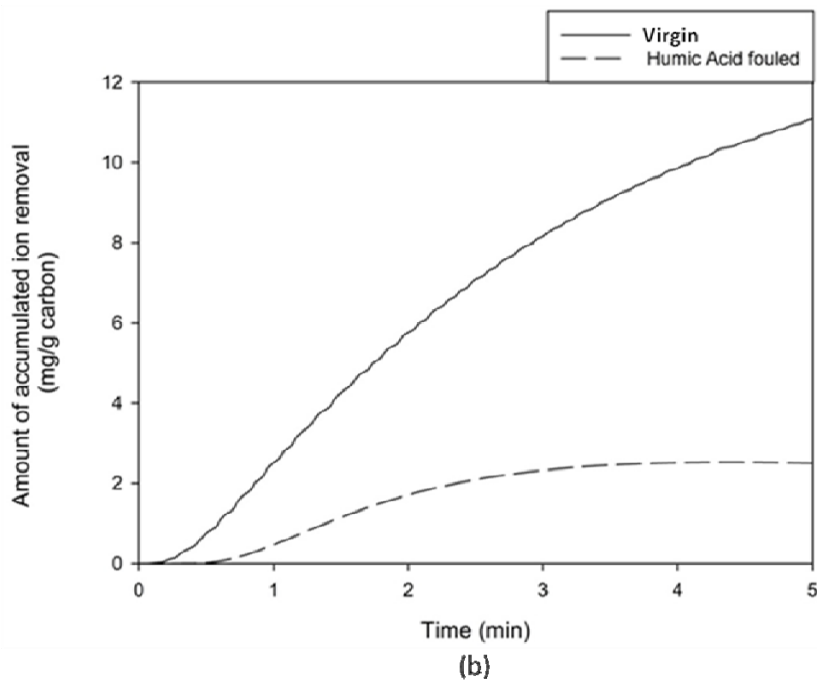
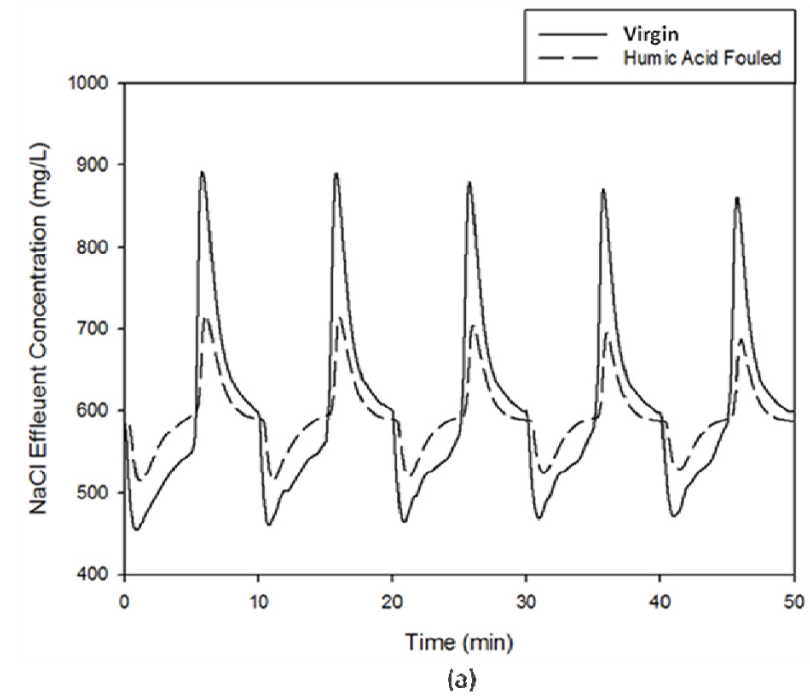


Figure 13. Desalination performance of humic acid deposited carbon electrode (dashed line) and virgin carbon electrode (solid line), volumetric flow rate = 10 mL/min, cell

potential of 1.2 V for 5 min during charging step, and of zero potential for 5 min during discharging step): (a) ion removal aspect; (b) amount of accumulated ion removal during charging step (The charging step was selected at fifth cycle.)

4.2 Continuous long-term operating with feed containing Humic acid

The desalination performances of two systems with prolong cycling using two different feed solutions is shown in Figure 14, which are 10 mM of NaCl and 10 mM of NaCl contained 3.6 mg/L of humic acid. 120 cycles of 5 min charging and 5 min discharging profile of each system is displayed in Figure 14 (a). Black solid line indicates the desalination performance of the system using only NaCl as a feed solution and the red solid line shows the desalination performance of feed containing humic acid. Both systems show gradual decrease in ions adsorption and desorption capability in each cycle with elapsed operating time due to the dissolved oxygen effect that has stated in section 2.2.5. However, the system which was contained humic acid indicated much severe desalination performance decline. After 20 hr of cycling, the amount of ions removal of the last cycle of each system was interpreted from concentration profile. It was observed that only 4.6 mg/g carbon of salt could be removed when the system contained humic acid, while 6.8 mg/g carbon of salt was eliminated when the system was not contaminated (Figure 14 (c)). Moreover, the inversion effect which would be observed from the appearance of the small peaks at the beginning of charging step due to the electrode deterioration was also investigated in this study. These unique peaks were clearly revealed after 700 min (approximately 12 hr) of CDI operation with only NaCl solution as a feed (Figure 15 (a)) while they could be remarked since the early operation with only 200 min (approximately 3 hr) when the system was fed with humic acid contained solution (Figure 15 (b)). This may imply that humic acid affected to the desalination performance of the CDI system by accelerating the loss of symmetric behavior and the deterioration of carbon electrode.

An interesting phenomenon can be seen in Figure 16. This Figure shows the capacitance profile obtained from cyclic voltamogram of electrodes used from both systems of only NaCl in feed and the feed containing humic acid. The electrodes were sorted out into anodes and cathodes and compared with the controlled (pristine electrode). After prolong cycling with only NaCl solution, the capacitance of the anode was significantly increased to 155 F/g carbon, while the capacitance of the cathode and the controlled electrode was 110 and 105 F/g carbon, respectively. This increase in ions storage capability of anode while of the cathode still unchanged may be considered of the anode surface deterioration due to the oxidation reaction at the anode after prolong cycling. In the system fed with humic acid contained solution, 127 F/g carbon was obtained from the anode and 100 F/g carbon from the cathode. The capacitances of each electrode in both systems were compared. After the anode was used to operate with humic acid contained solution for 20 hr, the capacitance then decrease from 155 to 127 F/g carbon while there was only small change in the cathode capacitance (from 105 to 100 F/g carbon). This decrease in capacitance of carbon electrode is similar to the study of effect of humic acid deposition on carbon electrode that was shown previously. The capacitance significantly decreases when the humic acid is deposited on carbon electrode surface. As this result, it may determine that the humic acid has a great effect to the anode than the cathode by decreasing in the capacitance.

Another observation of the humic acid has much influence to the anode is shown in Figure 17. The wettability was obtained from the contact angle measurement. The contact angle of the controlled electrode was 117° while the anode and the cathode after NaCl prolong cycling was 87° and 97° , respectively. The anode after long-term operation with feed contaminated with

humic acid shows the smallest contact angle (45°) indicating hydrophilicity increase due to the cover of humic acid on the anode surface while the cathode is covered with only small amount of humic acid which was shown in small decrease in contact angle from 97° to 93° .

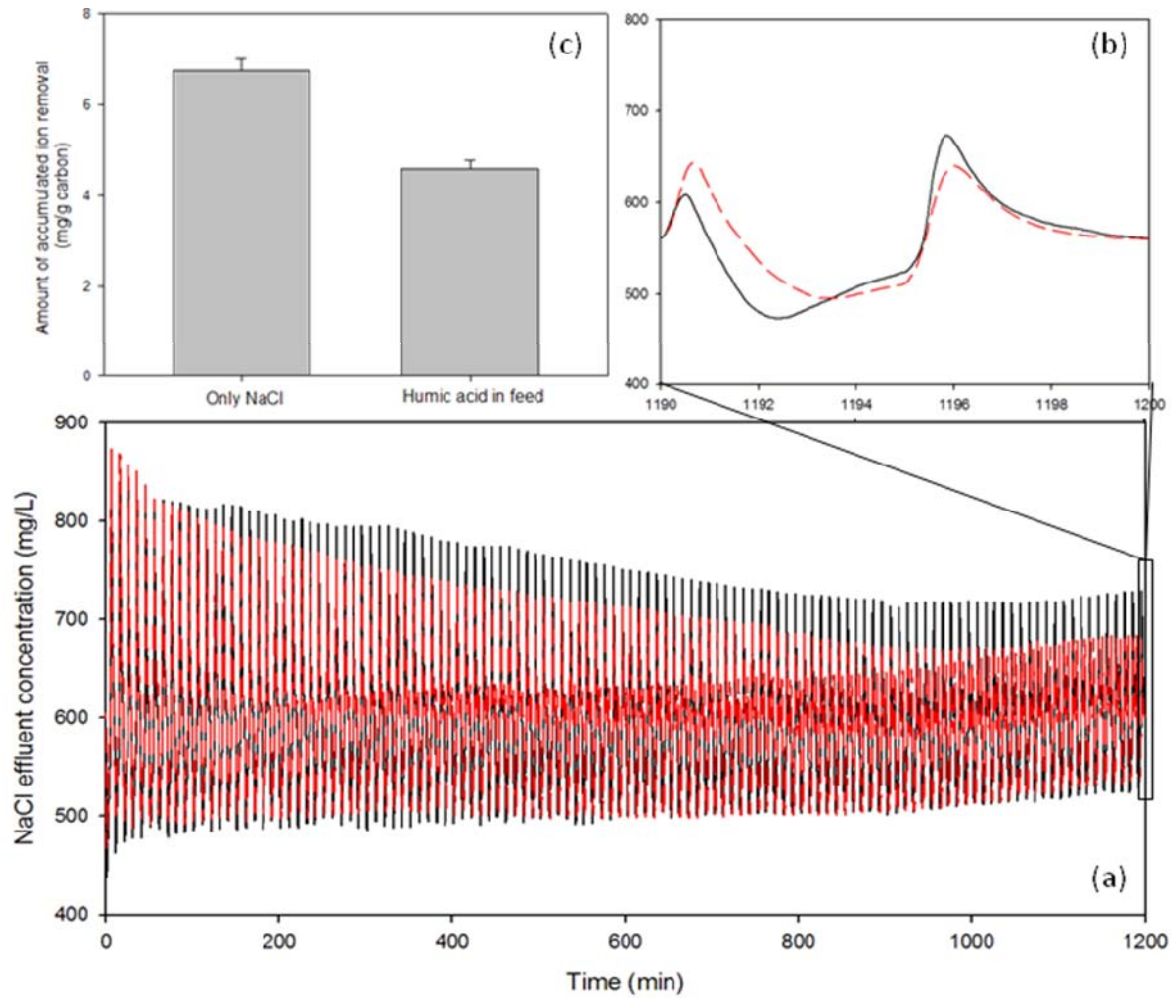


Figure 14. Desalination performance profile of two systems with prolong cycling using two different feed solutions, 10 mM of NaCl (black solid line) and 3.6 mg/L of humic acid in 10 mM of NaCl (red solid line). Each charging or discharging step lasted 5 min with 120 cycles operation: (a) Expanded aspect of the last cycle; (b) amount of accumulated ion removal during charging step of the last cycle interpreted from (a).

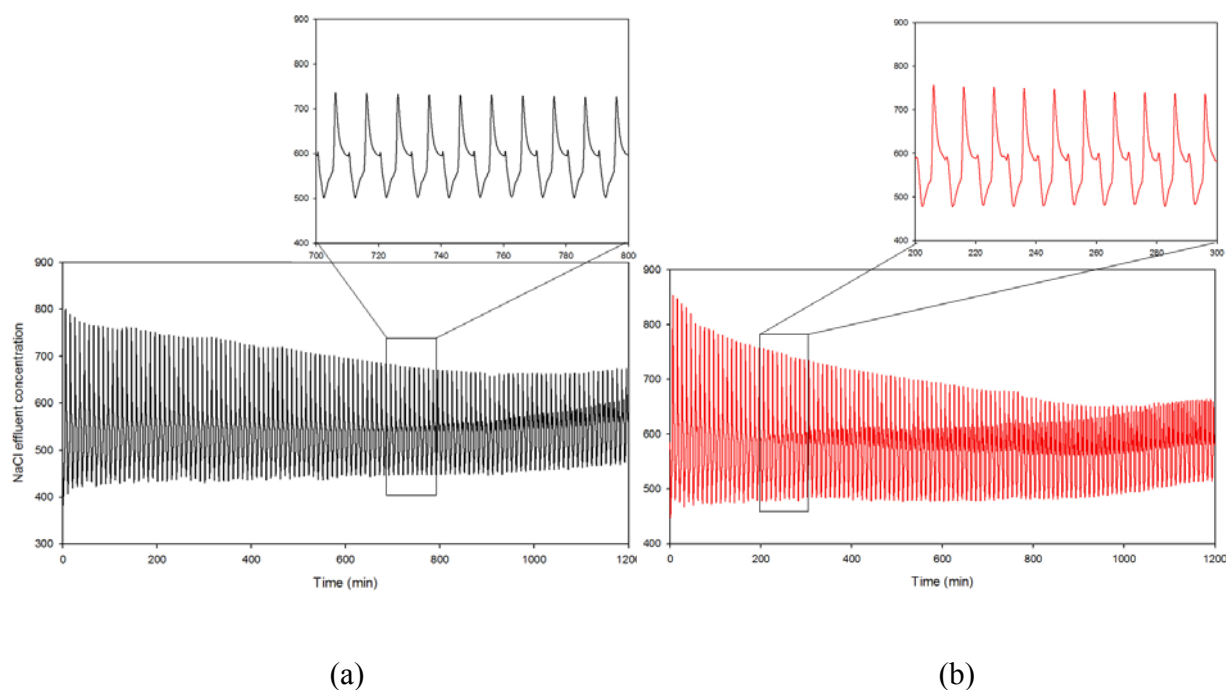


Figure 15. Split concentration/time profile clearly revealing in inversion effect (ions desorption peaks at the beginning of charging step): (a) System fed with NaCl, the peak starts occurring at 700 min (approximately 12 hr); (b) System fed with humic acid contained solution, the peak starts occurring at 200 min (approximately 3 hr).

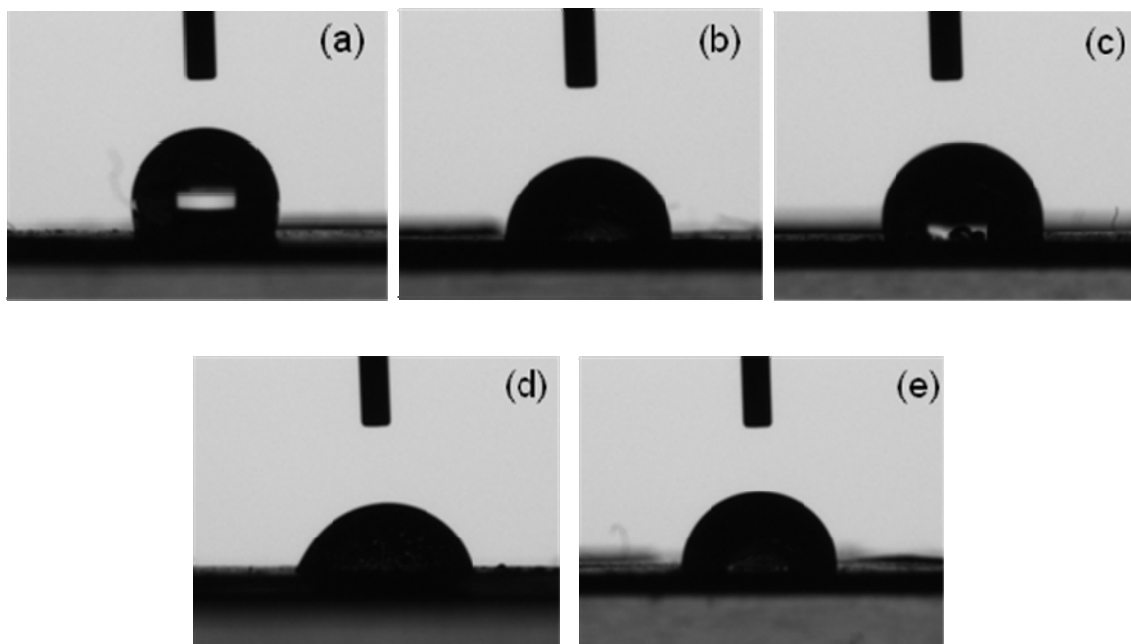


Figure 16. Surface wettability of (a) Controlled (pristine electrode) (b) Anode after NaCl prolong cycling (c) Cathode after NaCl prolong cycling (d) Anode after humic acid + NaCl prolong cycling and (e) Cathode after humic acid + NaCl prolong cycling. The contact angle of (a), (b), (c), (d) and (e) are 117° , 87° , 97° , 45° and 93° respectively.

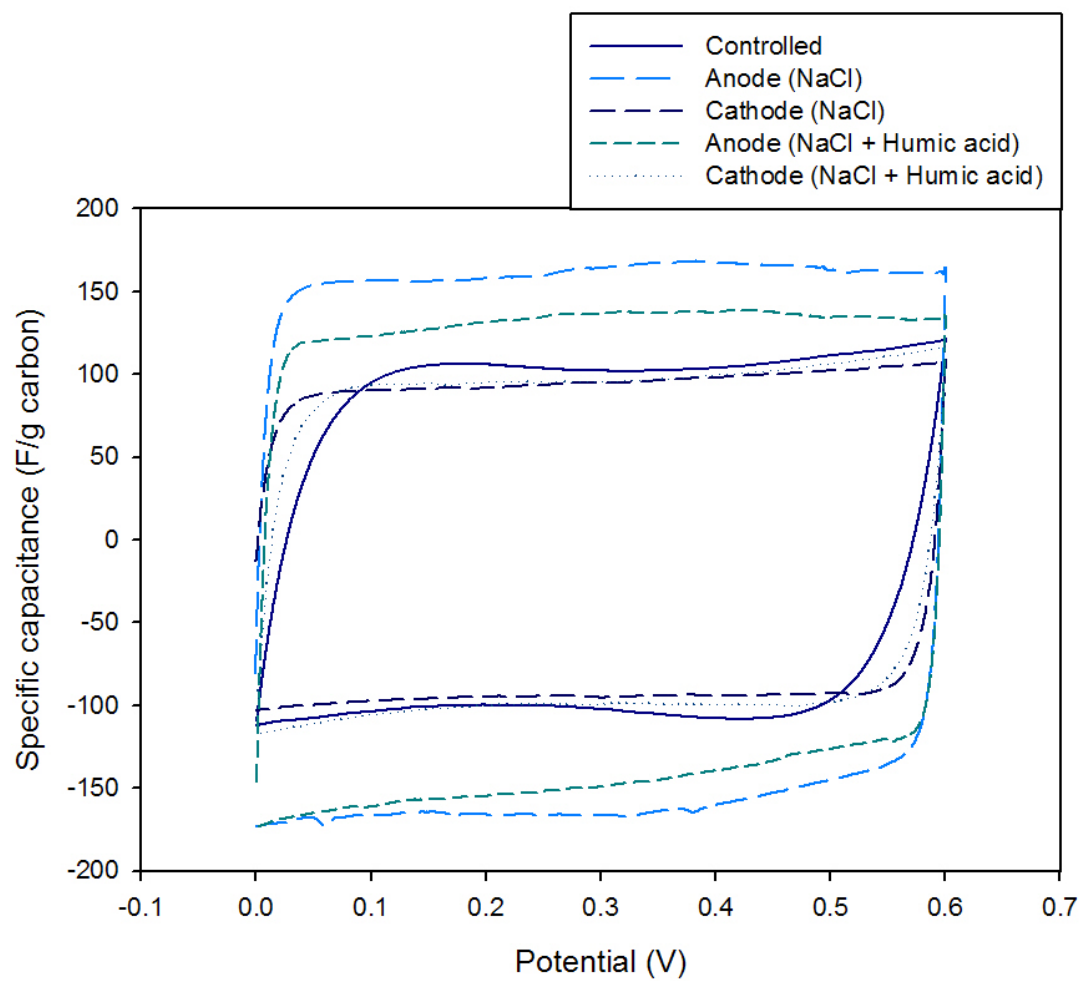


Figure 17. Cyclic voltammograms (scan rate = 2 mV/s) of the controlled (pristine electrode) and the anodes and cathodes from different feed system.

4.3 CDI performance recovery after cleaning

After 20 hr long-term operation of CDI with the feed containing humic acid, the system was cleaned by feeding DI water with higher flow rate of 22 mL/min and 100 mM of NaOH solution (pH of 11). Figure 18 displays the salt removal capability after each cleaning. As stated above, salt ions could be removed approximately 6.8 mg/g carbon at the last cycle of the system with NaCl and was decreased to 4.6 mg/g carbon in case of humic acid contained in the feed. Cleaning with DI water and increasing in flow rate can recover the salt removal performance from 4.6 mg/g carbon to 5 mg/g carbon. The salt removal could be highly recovered up to 6.6 mg/g carbon with using NaOH as a cleaning agent. The specific capacitances and the contact angles of the anode and cathode which was cycled with humic acid contained solution were measured after cleaning with NaOH solution. The recovery in specific capacitance is shown in Figure 19. The specific capacitances of both anode and cathode were analyzed respectively to 153 and 109 F/g carbon as almost the same with the system without humic acid. An alike recovery was also in sight of the contact angle as shown in Figure 20. The anode's contact angle was recovered from 45° to 85° and from 93° to 95° in case of cathode. Therefore, with using a high concentration of NaOH as a chemical cleaning, the desalination performance, electrochemical (specific capacitance) and physical (wettability) property of carbon electrode can be effectively recovered.

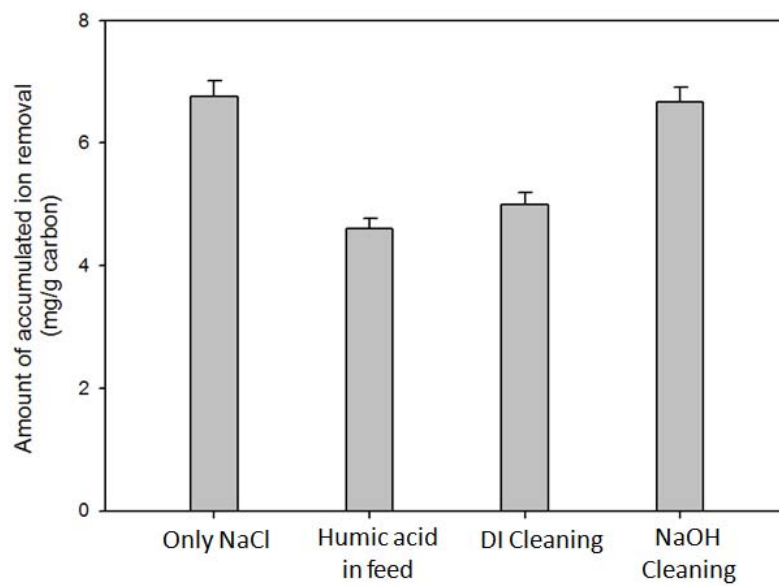


Figure 18. The salt removal capability after cleaning with DI water and 100 mM of NaOH solution with increasing flow rate (22 mL/min)

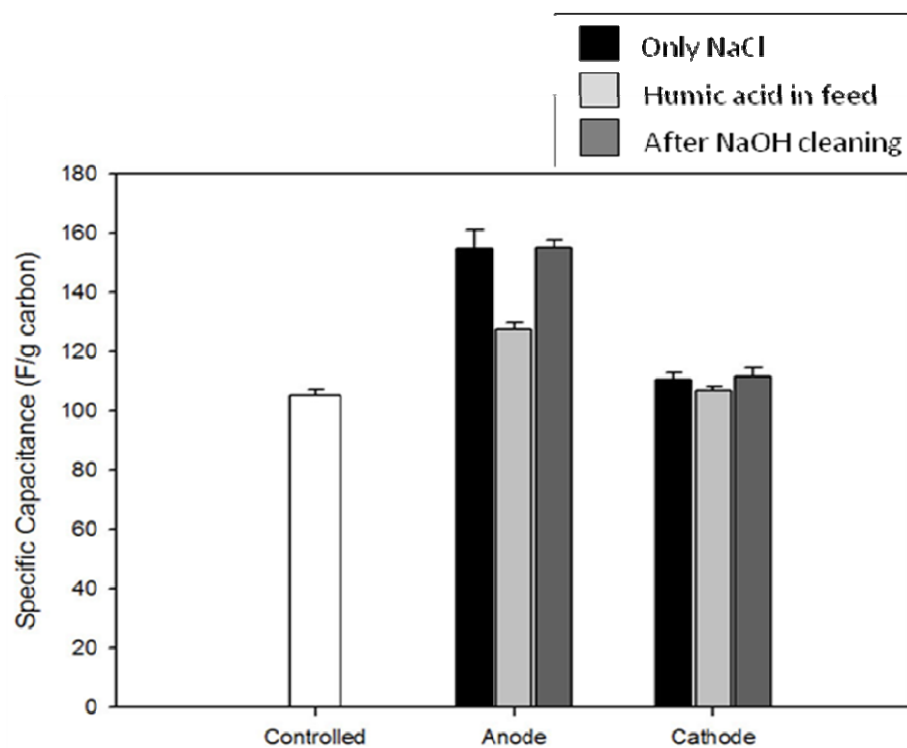


Figure 19. The specific capacitance recovery after NaOH cleaning

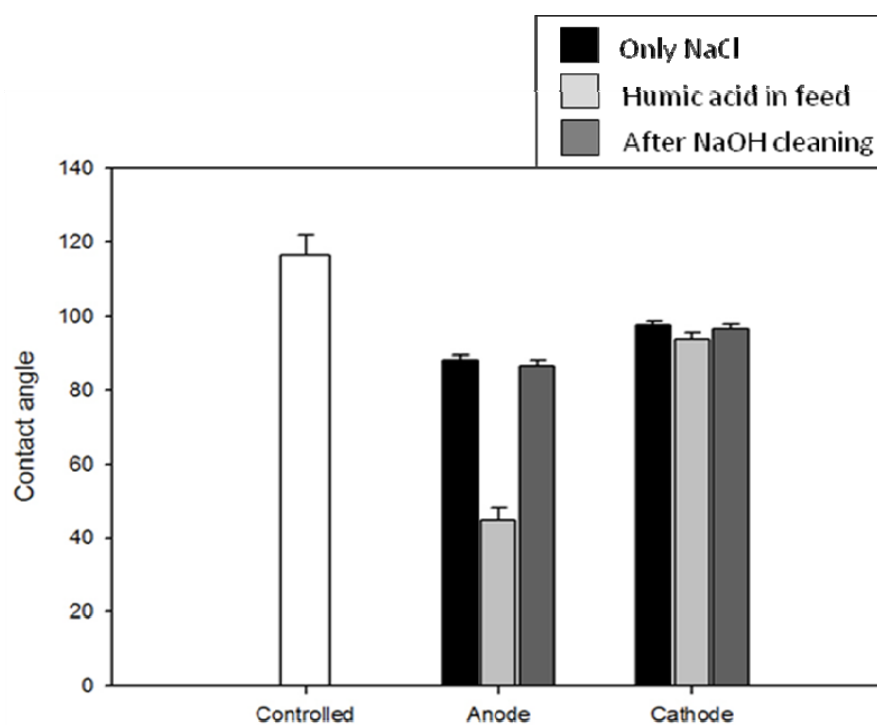


Figure 20. Wettability recovery after NaOH cleaning

Chapter 5. Conclusion

In this study, effect of organic fouling formed by humic acid experiment was conducted in a lab-scale CDI system. In the first part of this study, humic acid deposited carbon electrodes were used in CDI process. By using humic acid deposited carbon electrodes, severe decrease in salt removal performance and specific capacitance of the electrode were observed since the active surface area was decreased by humic acid fouling. Second part, long-term operation of the CDI test was performed by using feed solution contaminated with humic acid. With 3.6 mg/L of humic acid was contained in 10mM NaCl solution, an ion removal performance was decreased from 6.8 to 4.6 mg/g carbon after 120 cycling (20 hr). Moreover, rapid inversion effect was shown due to the humic acid existence in feed solution, which showed only after 300 min of operation. The anode was investigated to be significantly affected by humic acid than the cathode as could be observed by the anode wettability changed to hydrophilic indicating humic acid particle deposition on its surface and the declination of the specific capacitance. The desalination performance after prolong operation with humic acid was investigated to be recovered by applying cleaning method with DI water and 100 mM of NaOH solution simultaneously with flow rate of 22 ml/s. As a result, with using a high concentration of NaOH as a cleaning agent, the desalination performance, electrochemical (specific capacitance) and physical (wettability) properties of carbon electrode was effectively recovered. Therefore, pre-treatment steps to remove humic acid from water streams must be required to reduce its effects to the CDI performance and carbon electrodes. Chemical cleaning with alkaline solution were able to recover the CDI performance.

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