

Selective abatement and recovery of nutrients from wastewaters using electrochemical technologies

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# Selective Abatement and Recovery of Nutrients from Wastewaters using Electrochemical Technologies

by

# **Changyong Zhang**

A thesis submitted in fulfilment of the requirements for the degree

of Doctor of Philosophy



School of Civil and Environmental Engineering

Faculty of Engineering

The University of New South Wales

March, 2019

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Abstract

Enormous amounts of freshwater and high-quality fertilizers are required to expand agricultural activity in support of the growing global population and required improvement in living standards. Wastewater contains a large amount of nutrients which, if discharged to rivers and lakes, may result in severe eutrophication with this phenomenon leading to the depletion of dissolved oxygen, deterioration of water quality and acute/ chronic death of aquatic creatures. Therefore, removal and recovery of these nutrients from wastewater will bring significant economic and environmental benefits. Electrochemical technologies such as flow-electrode capacitive deionization (FCDI) and electrochemical advanced oxidation processes (EAOPs) have been adopted for removal/recovery nutrients from wastewaters in view of their advantages over other alternatives (e.g., minimal requirement for auxiliary chemicals, amenability to automation, versatility and potential to be powered by renewable energy from wind and solar sources).

The first section of this thesis focuses on investigation of the electrochemical processes (involving both Faradaic and non-Faradaic reactions) in typical electrochemical systems with particular attention given to processes operating in capacitive deionisation (CDI) cells. We provide a detailed insight into both the positive and negative effects of these processes. Guidelines and strategies that could be used to reduce or eliminate the negative side effects of Faradaic reactions are presented and approaches to best utilizing Faradaic reactions in a positive manner (e.g., nutrients removal/recovery) are described. The latter section of this thesis focusses on the application of these electrochemical processes to selectively sequester/recover nutrients. Using an EAOP cell, ammonia can be efficiently converted into harmless nitrogen gas with concentrations of by-products (i.e., chlorate, nitrate and chloramine) well below WHO guidelines, with the assistance of *in situ* electro-generated active chlorine whereas nitrate can be abated using an FCDI cell, with non-electrostatic adsorption of nitrate to the carbon particles initially playing a vital role. An innovative capacitive membrane ammonia stripping (CapAmm) system, which is composed of a FCDI cell and a membrane contactor (hollow-fibre and flat-sheet), has been developed and found to be a promising alternative for ammonia removal/recovery from both dilute and high-strength wastewaters. As for the recovery end-products, further studies described in this thesis reveal that the transformation of ammonia into ammonia solution is the optimal choose in view of its high market value. Of particular interest is the low voltage used in CapAmm system for nutrients recovery, rendering its suitability for integration with photovoltaic power supply technology that can significantly reduce energy cost.

One major limitation of these approaches is the poor electrical conductivity of the carbon flow electrodes (several orders of magnitude lower than conventional static electrodes) with this restricting the nutrient removal/recovery efficiency, increasing the internal resistance and, ultimately, resulting in higher energy consumption. In addition, pumping of the flow carbon particles consumes energy, which must be taken into account in the overall energy budget of the technology. Scale-up from small bench size units to full-sized modules will also obviously be required. It is envisaged that CapAmm cells could be stacked together to provide the required throughput but challenges will need to be overcome, particularly with regard to optimizing flow electrode composition (i.e., electrolyte, carbon loading and active electrode materials), flow cell design (i.e., channel geometry and current collector materials) and operating strategy (i.e., slurry flow rate, charging/discharging time control).

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# Abstract

Enormous amounts of freshwater and high-quality fertilizers are required to expand agricultural activity in support of the growing global population and required improvement in living standards. Wastewater contains a large amount of nutrients which, if discharged to rivers and lakes, may result in severe eutrophication with this phenomenon leading to the depletion of dissolved oxygen, deterioration of water quality and acute/ chronic death of aquatic creatures. Therefore, removal and recovery of these nutrients from wastewater will bring significant economic and environmental benefits. Electrochemical technologies such as flow-electrode capacitive deionization (FCDI) and electrochemical advanced oxidation processes (EAOPs) have been adopted for removal/recovery nutrients from wastewaters in view of their advantages over other alternatives (e.g., minimal requirement for auxiliary chemicals, amenability to automation, versatility and potential to be powered by renewable energy from wind and solar sources).

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*规格严格,功夫到家 自强不息,厚德载物* Never Stand Still

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# **Chapter 1. Introduction**

It is estimated that global population will reach 9.8 billion in 2050 with this population boom as well as an improvement in living standards expected to lead to great pressure on food production. Enormous amounts of freshwater and high-quality fertilizers will be required to increase agricultural activity to the levels required. Nitrogen and phosphorus are essential constituents of agricultural fertilizers and, as such, will be required in large amounts. Current fertilizer production, however, heavily depends on the consumption of non-renewable energy (*i.e.*, coal, petroleum and natural gas) and finite mineral resources. For instance, ammonia nitrogen - a basic chemical that is needed to produce a variety of nitrogen fertilizers (*i.e.*, urea, ammonium nitrate and ammonium sulfate) and industrial products (i.e., nylon, plastics and melamine), is chiefly synthesised by combining atmospheric nitrogen gas with hydrogen gas through the classical Haber-Bosch process (Galloway et al., 2008, Gruber and Galloway 2008). This is an energy-intensive process that requires an elevated temperature (~500 °C) and pressures (200-300 atm) with the assistance of catalyst (iron) and currently accounts for  $\sim 2\%$  of the global total energy use and produces  $\sim 1.6\%$  of total world CO<sub>2</sub> emissions (Zhou et al., 2017a). Therefore, it is highly desirable to find effective and sustainable alternatives for enabling availability of fertilizer and guaranteeing food security.

At odds with the cost of producing N and P for fertilizer production, wastewater contains a large amount of nutrients. It is reported that some 30% of the nitrogen and 20% of the phosphorus in fertilizers ultimately go to wastewaters (Verstraete et al., 2009). Discharging wastewaters to natural surface water bodies (*i.e.*, lakes, rivers and estuaries) without proper removal of excessive nutrients will result in severe eutrophication, with this phenomenon leading to the depletion of dissolved oxygen, deterioration of water quality and acute/ chronic death of aquatic creatures. Given the harmful influences of excessive nutrients inputs, more and more stringent regulations have been established in both developed and developing countries.

It should be recognized that nutrients present in wastewaters are recoverable and valuable resources, with significant economic and environmental benefits. For example, nitrogen in wastewaters can be sequenced and/or recovered through diverse technologies including biological processes, breakpoint chlorination, air stripping, chemical precipitation, ion exchange, membrane separation and electrochemical processes. Traditional wastewater treatment plants (WWTPs) take advantage of the classical biological nitrification/denitrification processes to effectively convert reactive nitrogen compounds into nitrogen gas. However, this practice requires extensive tankage, appropriate C:N ratio, temperature maintenance and pH control, with potent greenhouse gases (particularly N<sub>2</sub>O) emitted during the wastewater treatment. Breakpoint chlorination provides another physical-chemical means to progressively decompose ammonia nitrogen with the assistance of active chlorine however formation of toxic by-products such as chloramines, trihalomethanes and haloacetic acids make this technique less attractive (Charrois and Hrudey 2007). Ammonia stripping requires consumption of extra alkali and heating to transform ammonium ions into deprotonated form (volatile NH<sub>3</sub>) as well as aeration to strip it from the liquid phase with these processes consuming much energy (Bonmati and Flotats 2003, Zhang et al., 2012). Chemical precipitation is another popular technique, which can simultaneously capture ammonia nitrogen and phosphorus as struvite, a slow-release fertilizer applied in agriculture and horticulture. This process, however, strongly relies on pH, ambient temperature, ion molar ratios, liquid turbulence and requires a supply of magnesium (El Diwani et al., 2007, Hovelmann and Putnis 2016).

Electrochemical technologies have been extensively applied for wastewater treatment and resource recovery since the latter half of the 20<sup>th</sup> century. Electrochemical systems offer a variety of advantages over established water treatment technologies, such as minimal requirement for auxiliary chemicals and production of secondary waste, amenability to automation, versatility and safety and can be potentially powered by renewable energy from wind and solar sources. In addition, electrochemical technologies can be easily incorporated with other technologies making them attractive for achieving multiple functions (Radjenovic and Sedlak 2015). Particular attention is given to two electrochemical technologies in this thesis: electrochemical advanced oxidation processes (EAOPs) and capacitive deionization (CDI) with these technologies utilized for the purpose of selective nutrient sequestration and recovery.

### **1.1 Capacitive deionization**

Capacitive deionization is a cost-effective, energy-efficient and environmentally friendly electrochemical technology that has been actively applied in brackish water desalination, water softening, resource recovery, wastewater remediation and energy recovery (Anderson et al., 2010). In the last two decades, the CDI field has experienced exponential development with exciting innovations in cell configuration, electrode and membrane design, experimental methods, fundamental modelling and a broadening of applications. As evidence of this growing interest, a remarkable number of peerreviewed journal papers have been published in this area since the year 2000 (**Figure 1-1**).



**Figure 1-1.** (a) Evolution of the number of publications in the CDI field in the past two decades. The inserted graph presents the percentage of publications regarding different

cell configurations since 2016. Data source: Web of Science. (b) Timeline illustrating the years when different CDI cell configurations were developed and the corresponding seminal works published (Tang et al., 2018).

# 1.1.1 Background

A typical CDI cell is composed of two oppositely placed porous carbon electrodes for ion electro-adsorption with a spacer channel enabling the feedwater to flow between these electrodes. When applying a constant voltage or current, the charged species in the spacer channel will be transported toward the oppositely charged electrodes and be adsorbed in the electric double layers (EDLs) formed at the electrode solution interface thereby generating a stream of freshwater (charging/adsorption step). Once the electrodes reached adsorption saturation, the system can be regenerated through short-circuiting of the two electrodes or reversing the cell polarity resulting in the stored species being released back into the bulk solution and producing a brine stream (discharging/desorption step). With periodic charging and discharging operation, CDI can generate freshwater and brine intermittently.

### **1.1.2 Cell configuration**

Over the past few decades, more than a dozen CDI configurations have been invented. The earliest and most-investigated configuration is "flow-by" or "flowbetween" CDI in which water flows in parallel with the two electrode pair. This classical module is easy to assemble and seal. In comparison, in "flow-through" configuration, feedwater flows straight through one electrode to another and parallel to the electric field with this configuration recognised to prolong the feedwater-electrode contact time and enhance mass transfer. Another significant advance over the traditional CDI configuration has been the incorporation of ion exchange membranes (IEMs) between the carbon electrodes. This so-called "membrane capacitive deionization" (MCDI) approach improves the desalination performance as well as suppressing undesired Faradaic reactions. More recently, inverted CDI (iCDI), hydrid CDI (HCDI), desalination battery and flow-electrode CDI (FCDI) configurations have emerged with these various options broadening the functionality of CDI. Among these configurations, FCDI is the most attractive with the promise of achieving continuous operation and high-salinity water desalination due to the capability of *ex-situ* regeneration of the flow electrodes (that are typically made up of flowing carbon particles).



Figure 1-2. Typical CDI configurations (Tang et al., 2018).

### **1.1.3 Electrochemical processes in CDI**

Upon electrolysis, a variety of electrochemical processes will occur at the carbon electrode and electrolyte interface with these processes classified into two categories: non-Faradaic reactions and Faradaic reactions. Both processes are critical for CDI performance and determine the salt removal efficiency, energy consumption, byproducts generation and system stability. Non-Faradaic processes including capacitive ion storage, ion transport effects and chemical surface charge are at the heart of the CDI desalination process (Liu et al., 2015, Porada et al., 2013c). These reactions are described briefly below.

- (i) Capacitive ion storage takes advantage of the formation of EDLs (i.e., Stern layer and diffuse layer) at the electrode/electrolyte interface. In order to improve the capacitive ion storage, significant research effort has focused on developing new electrode materials with high specific surface area, appropriate pore distribution and superior electrical conductivity.
- (ii) Ion transport effects relate to the impact of differences in ion mobility on ELD formation and ion removal. During practical operation, various ions (e.g., sodium, potassium, calcium, chloride, sulfate, nitrate, protons and hydroxyl ions) co-exist in the feedwater and their adsorption rates will vary significantly when transported from spacer channel via macropores to micropores, thus leading to the possibility for selective ion separation and pH fluctuations in treated water.
- (iii) Surface chemical charge refers the presence of charged groups (*e.g.*, carboxylic, amine and sulfonic) at the carbon/electrolyte interface, with these functional groups leading to variation of point of zero charge. One possible benefit of these functional groups is to suppress the parasitic co-ion expulsion from the micropore during the charging period thereby improving the salt storage capacity and energy efficiency of the water desalination process.

Faradaic processes including anode oxidation reactions (such as carbon oxidation, chloride oxidation and water oxidation), cathode reduction reactions (such as

dissolved oxygen reduction) have attracted more recent attention, with these processes leading to a number of negative effects including desalination performance decline, effluent pH fluctuation and undesirable energy consumption. However, considerable scope exists for development of approaches to either suppress or benefit from these Faradaic processes.



Figure 1-3. Overview of the key electrochemical processes in CDI system (Porada et al., 2013c).

# **1.2 Electrochemical oxidation processes (EAOPs)**

Electrochemical advanced oxidation processes (EAOPs) are used in a variety of well established technologies and have been practiced for more than 50 years. Given the intensive investigations that have occurred in the enhancement of electrocatalytic activity and electrode materials stability and optimisation of cell architecture in recent years, EAOPs have reached an advanced stage of development with these technologies effectively commercialized for treatment of wastewater containing a broad-range of contaminants including phenols, dyes, pesticides, drugs, arsenic, ammonia and nitrate. In an EAOP cell, contaminants can be abated by (i) direct oxidation and (ii) indirect oxidation, mainly depending on the applied potentials, nature and structure of the electrode materials, target compounds properties and electrolyte pH (Bergmann et al., 2014, Martinez-Huitle et al., 2015).

### 1.2.1 Direct oxidation

Electrochemical oxidation can occur at the anode through direct electron transfer between the anode and the target contaminants. During electrolysis, contaminants are first adsorbed onto the anode surface, where they can be gradually degraded into a variety of intermediate or end products without the need for involvement of other substances. The oxidation products will be released into the bulk solution or remain at the active sites of the anode where they may undergo further degradation. Direct oxidation plays an important role for the abatement of some refractory pollutants, as it is actually the first step to their removal in most cases. The nature of the anode materials is reported to strongly influence both the selectivity and efficiency of the direct oxidation processes (Chaplin et al., 2009). Transition metal oxides (SnO<sub>2</sub>, RuO<sub>2</sub>, IrO<sub>2</sub>, PbO<sub>2</sub> and Ti<sub>4</sub>O<sub>7</sub>), boron-doped diamond (BDD) and carbon materials (carbon fiber and carbon cloth) are widely used anode materials.

### **1.2.2 Indirect oxidation**

Indirect oxidation occurs via the in situ electro-generation of powerful oxidants at the anode, such as hydroxyl radicals, active chlorine species, peroxodisulfate, peroxodiphosphate and peroxodicarbonate, with these entities capable of either selectively or non-selectively degrading target compounds at the anode surface. The anodic production of OH can be express as follows (Martinez-Huitle et al., 2015):

$$H_2O \rightarrow OH^+H^+ + e^- E^0 = 1.23 \text{ V/SHE} (1-1)$$

When chloride ions are present in the electrolyte, anodic oxidation of chloride will occur, with the production of active chlorine species (Martinez-Huitle et al., 2015):

$$2C1^{-} \rightarrow C1_2 + 2e^{-}$$
  $E^0 = 1.36 \text{ V/SHE} (1-2)$ 

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^-$$
(1-3)

$$\mathrm{HClO} \to \mathrm{H}^{+} + \mathrm{ClO}^{-} \tag{1-4}$$

At the cathode, dissolved oxygen can be reduced via a two-electron reaction resulting in the production of hydrogen peroxide, which can be then activated by adding, for example, iron(II) to the system (Foller and Bombard 1995, Gligorovski et al., 2015):

$$O_2 + H^+ + 2e^- \rightarrow H_2O_2$$
  $E^0 = 0.69 \text{ V/SHE}$  (1-5)

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + OH$$
 (1-6)

### **1.3 Layout of this thesis**

This thesis is composed of ten chapters. The overall goal is use electrochemical technologies (e.g., EAOPs and CDI) for the selective abatement and/or recovery nutrients (e.g., ammonia and nitrate) from water/wastewater in an energy-efficient and economic-efficient manner. More specifically, the objectives pursued in this thesis are summarised below.

The first objective is to comprehensively investigate the Faradaic reactions occurring in electrochemical systems. The types (*e.g.*, anodic oxidation of carbon electrodes, cathodic reduction of oxygen and Faradaic ion storage) and mechanisms of Faradaic reactions in various CDI systems (*e.g.*, flow-by CDI, flow-through CDI, membrane CDI and flow-electrode CDI) are introduced in Chapters 2 and 3 and their potential negative and positive influence on CDI performances identified. Guidelines and strategies that may be used to supress the negative side effects of these reactions are presented and approaches to best utilizing Faradaic reactions in a positive manner (e.g., nutrients removal/recovery) addressed.

The second objective is to evaluate the nutrient removal performance using electrochemical technologies. Active chlorine mediated ammonia oxidation in an EAOP cell is revisited in Chapter 4 with the objectives to (i) determine the effects of operating parameters on the rate and extent of ammonia removal, and (ii) development of a detailed mechanistically-based kinetic model of the complex interactions that occur during electrochemically-mediated ammonia oxidation processes (with these insights expected to assist in optimising implementation of the technology). Nitrate sequestration using innovative FCDI operated in single-pass mode is investigated in Chapter 5. The influences of current density and hydraulic retention time (HRT) on the process performance are investigated with special consideration given to the nitrate adsorption mechanisms. Based on the resulting conclusions, viable strategies are proposed for the continuous operation of FCDI.

The third objective is to apply the techniques investigated for nutrient recovery. In Chapter 6-8, an innovative process called capacitive membrane stripping for ammonia recovery (CapAmm) is developed. During operation, ammonia is transported across a cation exchange membrane and selectively accumulates in the cathode chamber of a flow electrode. This step is followed by transformation to dissolved NH3 with subsequent stripping via a hydrophobic gas membrane (hollow-fiber or flat-sheet) and recovery as nitrogen fertilizer. A number of operational parameters associated with ammonia recovery performance are investigated and optimized. An overall analysis of the operational cost and economic benefits of the resource recovered highlights the opportunities and challenges of CapAmm in sustainable water, resource and energy management. The overarching goal of Chapter 9 is to present a proof-of-concept of a FCDI-based approach that enables production of high-value ammonia-rich products from wastewaters by a chemical-free method. All major chapters in this thesis are based on published or submitted articles, as detailed below.

Chapter 2: **Zhang**, C., He, D., Ma, J.; Tang, W., Waite, T.D., Faradaic reactions in capacitive deionization (CDI) - problems and possibilities: A review. Water Res. **2018**, 128, 314-330.

Chapter 3: Zhang, C., He, D., Ma, J., Tang, W., Waite, T. D., Comparison of faradaic reactions in flow-through and flow-by capacitive deionization (CDI) systems. Electrochim. Acta **2019**, 299, 727-735.

Chapter 4: Zhang, C., He, D., Ma, J., Waite, T.D., Active chlorine mediated ammonia oxidation revisited: Reaction mechanism, kinetic modelling and implications. Water Res. 2018, 145, 220-230.

Chapter 5: Song, J., Ma, J., Zhang, C., He, C.; Waite, D., Implication of nonelectrostatic contribution to deionization in flow-electrode CDI: case study of nitrate removal from contaminated source waters. Front. Chem. **2019**, *7*, 146.

Chapter 6: Zhang, C., Ma, J., He, D., Waite, T.D., Capacitive membrane stripping for ammonia recovery (CapAmm) from dilute wastewaters. Environ. Sci. Technol. Lett. **2017**, 5(1), 43-49.

Chapter 7: Zhang, C., Ma, J., Song, J., He, C., Waite, T.D., Continuous ammonia recovery from wastewaters using an integrated capacitive flow electrode membrane stripping system. Environ. Sci. Technol. **2018**, 52(24), 14275-14285.

Chapter 8: Zhang, C., Ma, J., Waite, T. D., The roles of acid types on ammonia recovery performance of the capacitive membrane stripping system (**Under review**)

Chapter 9: Zhang, C., Ma, J., Waite, T. D., Ammonia-rich solution production from wastewaters using chemical-free flow-electrode capacitive deionization. ACS Sustain. Chem. Eng. **2019**. DOI: 10.1021/acssuschemeng.9b00314.

# Chapter 2. Faradaic reactions in capacitive deionization (CDI) – problems and possibilities

# 2.1 Introduction

With the increasing population growth and rapid industry development, the demand for freshwater has become one of the most global challenges of the 21<sup>st</sup> century (Elimelech and Phillip 2011, Porada et al., 2013b, Shannon et al., 2008). The United Nations Educational, Scientific and Cultural Organization (UNESCO) estimates that nearly one third of the world's population is now living in water-stressed regions with this number expected to double by the year (UNESCO 2009). To satisfy this demand, various water desalination technologies have been developed to produce freshwater from seawater and brackish water given that nearly 98% of the total water available falls into these categories (where "brackish water" is classified as water containing salt concentrations in the range of 1,000-10,000 mg/L) (Elimelech and Phillip 2011, Georgopoulou et al., 2001, Humplik et al., 2011). Of the various water desalination technologies available (e.g. reverse osmosis and electrodialysis), capacitive deionization (CDI) is considered to be one of the most promising alternatives for desalination of brackish waters with low to medium salinity due to its high energy efficiency, cost effectiveness and, if managed effectively, low maintenance requirement (Porada et al., 2013c, Subramani and Jacangelo 2015, Suss et al., 2015b). The study of CDI dates back to the late 1960s and early 1970s (Caudle 1966, Johnson and Newman 1971, Murphy and Caudle 1967), followed by a gap in the development of this technology between the late 1970s and mid 1990s (Porada et al., 2013c). Over the last twenty years however,

breakthroughs in electrode materials and preparation (Huang et al., 2017, Liu et al., 2015), cell configurations (Gao et al., 2015b, Jeon et al., 2013a, Lee et al., 2006, Lee et al., 2014, Suss et al., 2012), operational modes (Garcia-Quismondo et al., 2016, Zhao et al., 2012b), and process modelling (Dykstra et al., 2016b, Porada et al., 2013a, Tang et al., 2016a) have generated renewed interest in CDI technology from both water treatment and energy recovery perspectives. As evidence of this renewed interest, the number of papers published in the CDI field has increased enormously since 2000 (**Figure 2-1**).



**Figure 2-1.** The number of peer-reviewed papers published in the CDI field since the year 2000, and the comparison of the number of CDI papers in several countries in year 2006 and 2016 (inserted table).

In a typical CDI cell (**Figure 2-2**), when applying a voltage difference across the two electrodes, cations are attracted to the cathode and anions to the anode, resulting in the salt ions being removed from solution. Following ion electrosorption, the electrodes can be regenerated by short-circulating the anode and cathode or executing polarity reversal, with the trapped ions released back into the brine stream (Huang et al., 2013, Suss et al., 2015b, Zhao et al., 2013). There are two main mechanisms for ion storage during CDI desalination processes, i.e., non-Faradaic ion storage and Faradaic ion
storage (Biesheuvel et al., 2017, Su and Hatton 2016), with non-Faradaic capacitive ion storage the most important electrochemical process for salt removal. This process is based on the formation of an electrical double layer (EDL) at the carbon electrode where, upon applying a potential difference, ions are captured electrostatically and stored capacitively in the diffusive layer and Stern layer formed inside the carbon electrode intraparticle pores (Porada et al., 2013c). In order to enhance the non-Faradaic capacitive ion storage, considerable efforts have been invested in fabricating electrode materials with high adsorption capacity and sustainable use. These properties are usually associated with materials that possess high surface area, appropriate pore distribution, excellent electrical conductivity and good chemical stability (Liu et al., 2015).



Figure 2-2. Overview of CDI operation and non-Faradaic capacitive processes in CDI.

Faradaic processes, although assumed by early investigators to facilitate ion removal from water (Johnson et al., 1970, Porada et al., 2013c), have not been extensively examined until recently. Whilst non-Faradaic processes are at the heart of the CDI phenomenon, it is now recognized that Faradaic reactions (**Figure 2-3**) also

play important roles in the CDI process. Various types of Faradaic reactions exist in CDI systems, some of which need to be considered seriously as they may lead to (i) a decrease in electrode performance, energy efficiency and/or electrode lifespan and/or (ii) the formation of chemical by-products and/or pH fluctuations of the product water (Cohen et al., 2013,2015, He et al., 2016b, Lee et al., 2014) while others can be employed to improve desalination performance through pseudocapacitive/intercalation effects and formation of charged species. In this study, three types of Faradaic reactions are categorized as described below.

Type I are oxidation reactions that occur at the anode including carbon electrode oxidation, chloride oxidation, water oxidation, and other particular contaminant oxidation reactions such as oxidation of inorganic ions and organic matter. Of these reactions, the carbon oxidation reactions have attracted the most attention given the deleterious effects that may accrue such as pore structure impairment and mass loss with subsequent decrease in carbon electrode longevity and deterioration of CDI performance (Cohen et al., 2013, Wouters et al., 2013).

Type II are reduction reactions that take place at the cathode with oxygen reduction being the most common. While it has been reported that the oxygen reduction reaction leads to the asymmetric distribution of potential of the anode and cathode with subsequent acceleration of the anodic carbon oxidation reactions (He et al., 2016b), the in-situ generation of by-products such as H<sub>2</sub>O<sub>2</sub> as a result of oxygen reduction might be constructively used for water disinfection (possibly via combination with UV irradiation) and/or degradation of organic contaminants provided that H<sub>2</sub>O<sub>2</sub> can be effectively activated to produce more powerful oxidants. In addition, cathodic reduction reactions may contribute to the removal of heavy metals from water as a result of the possible deposition of the metals at the electrodes.

Type III are Faradaic ion storage processes in which pseudocapacitive/intercalation effects are used to store ions through reversible redox reactions instead of electrostatic storage in the EDLs at the electrode/electrolyte interfaces Chen et al. (2017a), Lee et al. (2014), Smith (2017), Su and Hatton (2016). Due to the superior ion electrosorption capacity of intercalation electrodes compared to traditional carbon electrodes, Faradaic ion storage processes have received considerable attention recently (Lee et al., 2014).

Some of the most commonly investigated intercalation electrode materials are sodium transition metal oxides (NaT<sub>M</sub>O, T<sub>M</sub> = Mn, Ti, Fe, Ni, Co, etc., see **Figure 2-3b**), sodium iron pyrophosphate, prussian blue analogues, for the capture of cations and conductive polymers (polypyrrole or polyaniline, see **Figure 2-3c**), Ag/ACl, BiOCl, for the bonding of anions (Han et al., 2015, Palomares et al., 2012, Porada et al., 2016, Su et al., 2016).



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**Figure 2-3.** Schematic presentation of three types of Faradaic processes (anodic oxidation, cathodic reduction and Faradaic ion storage processes).

In the current review, we provide a comprehensive description of the possible Faradaic reactions that could occur in CDI desalination processes. We also provide insight into both the positive and negative effects of these reactions. Guidelines and strategies that may be used to reduce or eliminate the negative side effects of Faradaic reactions are presented and approaches to best utilizing Faradaic reactions in a positive manner are described.

### **2.2 Types of Faradaic reactions**

Three major types of Faradaic reactions are addressed in this review article include (I) anodic reactions associated with oxidation of the carbon electrode, chloride and water, (II) cathodic reactions, particularly those involving oxygen reduction, and (III) Faradaic ion storage occurring on particular redox-active electrodes.

## 2.2.1 Anodic oxidation reactions

### 2.2.1.1 Carbon oxidation

Of all the anodic Faradaic reactions in the CDI system, those involving carbon electrode oxidation are of most importance given their potential negative impact on the performance and longevity of the system. The standard electrode potential for carbon oxidation is  $0.7 \sim 0.9$  V (vs. SHE) (Kinoshita 1988), which is likely to be within the CDI potential window when the CDI cell is operated at 1.2 V or higher. As such, during the CDI desalination process, the carbon anode might not only electrochemically store anions but may also sacrificially take part in the oxidation process with the carbon electrode initially incorporating oxygen containing groups and, eventually, being converted into CO<sub>2</sub>, which consequently leads to carbon mass loss and deterioration in CDI performance. These oxidation processes may be a consequence of both direct oxidation when the anode is polarized according to Eqs 2-1 to 2-3 (Ayranci and Conway 2001, Bayram and Ayranci 2011, Lee et al., 2010, Maass et al., 2008, Oh et al., 2008) and indirect oxidation as a result of the anodic generation of oxidants such as chlorine and hydroxyl radicals (HO<sup>•</sup>).

$$C + H_2O \rightarrow C = O + 2H^+ + 2e^-$$
 (2-1)

$$C + H_2 O \rightarrow C - OH + H^+ + e^-$$
(2-2)

$$C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^ E^0 = 0.207 \text{ V/SHE}$$
 (2-3)

Strategies to evaluate the oxidation of the CDI electrodes are based on monitoring the changes in the functional groups of electrodes using methods such as Xray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) mapping, Fourier transform infrared spectroscopy (FTIR), acid-base titration and cyclic voltammetry (Bouhadana et al., 2011b, Chen et al., 2013, Cohen et al., 2013,2015). The changes in the XPS oxygen (O 1s) and carbon (C 1s) response to the charging and discharging cycling of the carbon anode and cathode were also demonstrated (Cohen et al., 2013). It was found that the intensity of the O 1s spectrum increased while the C 1s intensity decreased in the carbon anode after longterm operation, indicating that the anode acquired more oxygen containing groups during the desalination process (Cohen et al., 2013). A similar work based on XPS analyses observed that various new oxygen-containing species were formed on the carbon electrode surface after prolonged operation although the types of these oxygen species were not fully identified (Bouhadana et al., 2011b). Cohen et al. 2015 also reported that the oxygen composition in the anode increased from 3.77 to 8.52 wt % following long-term CDI operation (20 days) based on SEM-EDX results. By performing cyclic voltammetry measurements, Haro et al. (2011) evealed that the intensity of the cathodic/anodic peaks assigned to quinone/hydroquinone groups on the

carbon anode increased following several cycles of CDI operation, confirming the gradual oxidation of the carbon to oxygen-containing groups. In addition, thermal analysis of these anodes suggest that the appearance of high temperature desorption bands, generally identified as CO-evolving groups, could be attributed to the incorporation of carbonyl-type groups on the carbon electrodes. These observations agree with the acid-base titration results reported by Chen et al. (2013) who found that the amount of –COOH groups present in a carbon electrode increased from 0.027 to  $0.391 \text{ mmol g}^{-1}$  following use.

Increase in resistivity, decrease in surface area and pore volume and positive shift in potential of zero charge (PZC) during the prolonged charging-discharging cycles have also been associated with the anodic oxidation of carbon electrodes (Cohen et al., 2015, Duan et al., 2015a, Gao et al., 2014, Haro et al., 2011, Omosebi et al., 2014). Recent results also demonstrated that oxidation of the carbon anode induced changes in pore structure with a decrease in the volume of the micropores (Bayram and Ayranci 2011, Chen et al., 2013), the parameter recognised to contribute most strongly to ion electrosorption capacity (Porada et al., 2013a). As such, the prolonged anodic oxidation of carbon electrodes can be expected to lead to the deterioration of electrode structural properties with resultant desalination performance decline (Gao et al., 2014, Omosebi et al., 2014). Therefore, approaches to the reduction and/or the elimination of this Faradaic side reaction are critically required.

## 2.2.1.2 Chloride and water oxidation

Anodic oxidation of  $Cl^-$  and water may occur during the CDI electrochemical treatment of brackish waters. The mechanisms involving the anodic oxidation of  $Cl^-$  are as follows: (i) the direct oxidation of  $Cl^-$  at the anode yields free chlorine (i.e.  $Cl_2$ ) (Eq 2-4), (ii)  $Cl_2$  is rapidly hydrolyzed and disproportionates to form hypochlorous acid

(HClO) (Eq 2-5) and (iii) HClO and its deprotonated form ClO<sup>-</sup> (Eq 2-6) can be further oxidized to chlorate (ClO<sub>3</sub><sup>-</sup>) anodically (Eq 2-7). Additionally, the direct oxidation of Cl<sup>-</sup> to ClO<sub>3</sub><sup>-</sup> may occur at the anode (Eq 2-8) (Comninellis and Nerini 1995, Jung et al., 2010a, Martínez-Huitle and Brillas 2009, Martinez-Huitle et al., 2015, Szpyrkowicz et al., 1994):

$$2\text{Cl}^- \to \text{Cl}_2 + 2\text{e}^ E^0 = 1.36 \text{ V/SHE}$$
 (2-4)

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^-$$
 (2-5)

$$\mathrm{HClO} \to \mathrm{H}^{+} + \mathrm{ClO}^{-} \tag{2-6}$$

$$6\text{HClO} + 3\text{H}_2\text{O} \rightarrow 2\text{ClO}_3^- + 4\text{Cl}^- + 12\text{Cl}^- + 3/2\text{O}_2 + 6\text{e}^- \quad E^0 = 0.46 \text{ V/SHE} \quad (2-7)$$

$$Cl^{-} + 3H_2O \rightarrow ClO_3^{-} + 6H^{+} + 6e^{-}$$
  $E^0 = 1.45 \text{ V/SHE}$  (2-8)

The formation of ClO<sub>3</sub><sup>-</sup> during CDI operation has been confirmed by Lado et al. (2013) and Wouters et al. (2013), who showed that a minimal amount of ClO<sub>3</sub><sup>-</sup> accumulated during the first 5 min whilst rapid removal of Cl<sup>-</sup> occurred over this same time period. With Cl<sup>-</sup> concentration approaching steady state following 10 min of charging, the production rate of ClO<sub>3</sub><sup>-</sup> increased significantly. It was also found that the more Cl<sup>-</sup> that was removed from solution, the more extensive was the generation of ClO<sub>3</sub><sup>-</sup> in the CDI system (Wouters et al., 2013). This result suggests that Cl<sup>-</sup> associated with the anode surface rather than free Cl<sup>-</sup> in solution was the main contributor to the generation of ClO<sub>3</sub><sup>-</sup>. It should be noted that while a (relatively low) cathode potential of -1.74 V (vs. SHE) was reported in the above work, neither the anode potential nor charging voltage were provided. As such, quantification of ClO<sub>3</sub><sup>-</sup> generated under more typical CDI operating conditions with well-defined anode potential is required to properly interpret these results.

As noted earlier, the anodic oxidation of water (Eqs 2-9 and 2-10) may also occur (Barrera-Díaz et al., 2014, Martinez-Huitle et al., 2015, Moreira et al., 2017, Sires et al., 2014):

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^ E^0 = 1.23 \text{ V/SHE}$$
 (2-9)

$$H_2O \rightarrow HO + H^+ + e^ E^0 = 2.80 \text{ V/SHE}$$
 (2-10)

Although the oxygen evolution reaction (Eq 2-9) exhibits a relatively lower standard redox potential than that for the chloride oxidation reaction (Eq 2-4), the oxidation of  $Cl^-$  is likely to occur preferentially in the CDI system in view of its lower overpotential and the abundance of  $Cl^-$  in the vicinity of the anode during the electrosorption process (Abdel-Aal et al., 1993, Balaji et al., 2009, Bennett 1980, Hlushkou et al., 2016, Knust et al., 2013).

To limit the extent of current leakage due to the occurrence of water electrolysis, the CDI process is typically operated at charging voltages below the limit of 1.23 V (Porada et al., 2013c). It is critical however that the anode potential be monitored over the duration of CDI operation since it is likely that (i) an asymmetric distribution of potentials of the electrodes will occur with a positive shift in potential of the anode, and (ii) significant pH fluctuations in the vicinity of the anode will occur.

## **2.2.2 Cathodic Reduction reactions**

#### 2.2.2.1 Dissolved oxygen reduction

Dissolved oxygen (DO) is ubiquitous in feed waters to CDI units. As a result, Faradaic oxygen reduction reactions occur at the cathode with the possible oxygen reduction reactions shown in Eqs 2-12 to 2-14. Dissolved oxygen can be reduced either via two-electron transfer to hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (Eq 2-12) with  $E^0 = 0.69$  V/SHE or four-electron reduction to water via Eq 2-14 with  $E^0 = 1.23$  V/SHE (Shapira et al., 2016). In view of the evidence for the presence of H<sub>2</sub>O<sub>2</sub> in CDI systems (He et al., 2016b), the cathodic reduction of oxygen most likely occurs via the two-electron transfer pathway according to Eq 2-12.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
  $E^0 = 0.69 \text{ V/SHE}$  (2-12)

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$$
  $E^0 = 1.78 \text{ V/SHE}$  (2-13)

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$
  $E^0 = 1.23 \text{ V/SHE}$  (2-14)

It has been reported that the CDI cathode potential is typically in the range -0.3 to -0.6 V (vs. SHE) suggesting that cathodic oxygen reduction is inevitable. Recent batch-mode CDI studies have revealed that decrease in DO concentration is accompanied by formation of  $H_2O_2$  (He et al., 2016b). The reduction of DO concentration follows pseudo-first-order kinetics; i.e.,

$$-\frac{\mathrm{d}[\mathrm{O}_2]}{\mathrm{d}t} = k[\mathrm{O}_2] \tag{2-15}$$

where *k* represents the pseudo-first-order rate constant for DO decrease. As reported by He et al. (2016), the *k* values increased from  $5.4 \times 10^{-5}$  to  $2.7 \times 10^{-3}$  s<sup>-1</sup> with increase in charging voltage from 0.5 to 1.5 V. The steady-state concentration of H<sub>2</sub>O<sub>2</sub> varied significantly with the charging voltage with H<sub>2</sub>O<sub>2</sub> concentration reaching as high as 60  $\mu$ M when the charging voltage was 1.2 V, as shown in **Figure 2-4**.

Kim et al. (2016) also reported the cathodic generation of  $H_2O_2$  on operation of a CDI unit in single-pass mode. It was found that approximately 0.1 mg of  $H_2O_2$  was produced over 50 operation cycles at a charging voltage of 1.2 V. Electrochemical analysis confirmed that cathodic oxygen reduction was thermodynamically favourable even at very low charging voltages (e.g., 0.6 V).



**Figure 2-4.** (a) Decay of  $O_2$  during charging at different charging voltages, and (b) variation of steady-state concentration of  $H_2O_2$  generated during charging at different charging voltages followed by discharging at 0 V. Adapted with permission from ref <sup>45</sup>. Copyright 2016 American Chemical Society.

### 2.2.2.2 Carbon reduction

Carbon electrodes not only undergo anodic oxidation but also experience cathodic reduction or hydrogenation (Eq 2-16) resulting in the introduction of additional "C–H" groups to the carbon electrodes (Soffer and Folman 1972). Although several research groups have mentioned the possibility of occurrence of carbon reduction in their CDI systems (Chen et al., 2013, Lado et al., 2014), there has been no conclusive evidence presented to date to confirm the occurrence of this reaction.

$$C + H_2O + e^- \rightarrow C - H + OH^-$$
(2-16)

The range of redox potentials over which the main Faradaic reactions occur on the CDI anodes and cathodes and typical electrode working potentials as a function of cell voltage are shown in **Figure 2-5** Holubowitch et al. (2017). The potential map provides a very useful practical guide for optimization of cell voltage such that side Faradaic reactions are minimized.



**Figure 2-5**. Potential map of the possible electrode processes with increased cell voltages. Adapted with permission from Holubowitch et al. (2017).

### 2.2.3 Faradaic ion storage

Faradaic ion storage processes involve the application of intercalation electrodes (mainly transition metal containing material or conductive polymer) for ion harvesting from saline waters. The ion storage mechanisms involve the trapping of ions into the crystallographic sites of the intercalation materials via redox reactions with this process fundamentally different from the EDL charging process occurring within conventional carbon electrodes. Due to the exemplary salt electro-adsorption capacity and potential ion selectivity of these electrodes, Faradaic ion storage processes are attracting increasing attention.

Interest in Faradaic desalination has been inspired by sodium and lithium ion battery systems (Chen et al., 2017a, Huang et al., 2015, Kim et al., 2016a, Lee et al., 2014, Lee et al., 2017). Transition metal-containing materials have been most commonly used for cathode construction while preparation with sodium manganese oxide (Na<sub>0.44</sub>MnO<sub>2</sub>, Na<sub>2</sub>Mn<sub>5</sub>O<sub>10</sub>), lithium manganese oxide (Li<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub>), sodium iron pyrophosphate (Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub>), sodium nickel hexacyanoferrate (NaNiHCF) and sodium iron hexacyanoferrate (NaFeHCF) are of most interest in view of their capacity to trap alkali metal ions such as  $Na^+$  and  $Li^+$  but lower preference for ions such as  $Mg^{2+}$  and  $Ca^{2+}$ . Examples of reactions occurring at these cathodes are provided in Eqs (2-20), (2-21)):

$$Na_{0.44-x}MnO_2 + xNa^+ + xe^- Na_{0.44}MnO_2$$
 (2-20)

$$xLi^{+} + Li_{1-x}Mn_{1-x}^{III}Mn^{IV}O_{2} + xe^{-} LiMn^{IV}Mn^{III}O_{4}$$
 (2-21)

There appears to be much less choice for the anode. Silver, conductive polymers or BiOCl have been reported to be effective for the capture of chloride ions, the most common anions in the saline water. Examples of reactions taking place at the anodes are shown in Eqs (2-22), (2-23), (2-24):

$$Ag + Cl^{-} \leftrightarrow AgCl + e^{-}$$
 (2-22)

$$xCl^{-} + xPP^{0} \qquad x[PP^{+}Cl^{-}] + xe^{-}$$
 (2-23)

$$Bi + Bi_2O_3 + 3Cl^ 3BiOCl + 3e^-$$
 (2-24)

Detailed discussion of the applications and desalination performances of Faradaic electrodes is presented in Section 5.1.

# 2.3 Negative effects of Faradaic reactions

As mentioned earlier, the aging of carbon electrodes, due particularly to anodic oxidation of electrode materials over long-term CDI operation, results in numerous side effects such as desalination performance decline, water quality fluctuations and undesirable energy consumption.

## 2.3.1 Desalination performance decline

CDI cells are usually (depending on the design) initially symmetrical with the potentials of the anodes and cathodes identical assuming they possess the same surface area and pore distribution (Bouhadana et al., 2011a, Cohen et al., 2015, Cohen et al., 2011). After a number of cycles of charging and discharging operation, the distribution

of potential between the anodes and cathodes ceases to be symmetrical due to the occurrence of Faradaic side reactions (e.g. the reduction of oxygen that inevitably occurs at the cathode) with a positive shift in potential of the anodes. Consequently, the anode potential may exceed its potential limit of stability, leading to the occurrence of anodic carbon electrodes oxidation. In turn, changes in the structure of the electrodes due to anodic oxidation may further drive the CDI cell away from symmetric behaviour with the occurrence of  $CI^-$  and water oxidation (see more details in Section 2), finally resulting in decline in the charge efficiency and the desalination performance.

There have been several studies showing the decline in desalination capacity and charge efficiency during prolonged CDI operation (Bouhadana et al., 2011a, Cohen et al., 2013, Gao et al., 2015b, Lu et al., 2017). Gao et al. (2015b) conducted a detailed investigation with CDI cells equipped with 16 pairs of pristine carbon xerogel electrodes at charging/discharging voltages of 1.2/0 and 0.8/0 V. As shown in Figure 2-6a and b, both the electrosorption capacity and charge efficiency declined significantly with an increase in the cycle number during the prolonged cycling tests. A more rapid decline in the desalination performance was observed on increase in the charging voltage from 0.8 to 1.2 V. Another recent study also reported that the charge efficiency dropped sharply (from 92% to 69.5%) and was accompanied by a dramatic increase in cell voltage (from 0.6 to 4.8 V) due to the occurrence of inevitable Faradaic reactions. Despite these changes, the rate of ion adsorption increased significantly (by around 7 times) (Liang et al., 2017). An indicator of CDI performance decline after prolonged charge-discharge cycles relates to the occurrence of a so-called "inversion effect", which was reflected by the occurrence of ion desorption (i.e. a rise in effluent conductivity) during charging. In turn, ions are adsorbed and trapped in the electrodes (i.e. effluent conductivity decreases) on cell discharge (Bouhadana et al., 2011a).



**Figure 2-6.** Plots of electrosorption capacity ( $\Gamma$ ), and charge efficiency ( $\Lambda$ ) as a function of time for a CDI cell operated at charging/discharging voltages of (a) 1.2/0 V and (b) 0.8/0 V. Adapted with permission from Gao et al. (2015b). Copyright 2015 Royal Society of Chemistry. (c) Variation of pH as a function of time for a CDI cell operated at charging/discharging voltages of 0.7/0V and 0.9/0V, respectively. Adapted with permission from ref Cohen et al. (2013). Copyright 2013 Elsevier.

# 2.3.2 Water quality fluctuations

As mentioned above, the occurrence of Faradaic reactions at the CDI electrodes may lead to pH fluctuations and the formation of chemical byproducts, leading to severe fluctuations in the effluent water quality.

He et al. (2016) reported that the effluent pH varied significantly with different charging voltages in a batch-mode CDI cell. Upon applying a charging voltage of 0.9 V, the pH rapidly climbed to ~10 and then reached steady state while the effluent pH increased slightly and then decreased rapidly at charging voltages higher than 1.2 V, which was in agreement with other studies (Lado et al., 2014, Lee et al., 2010). Cohen et al. (2013) also reported that over long-term CDI operation (13 days), the pH shifted to more acidic conditions with pH fluctuations particularly severe during charging at 0.9

V, while the pH fuluctuations were insignificant and within the pH range of 6–7 when the CDI cell was charged at a lower voltage of 0.7 V. Interestingly, the pH in the vicinity of the electrodes showed a big difference to the bulk solution. A highly inhomongenous pH environment appeared during the water desalination processes, with the near-anode and near-cathode pH reached to 2.4 and 10.3 under a typical operation voltage of 1.2 V, respectively (Holubowitch et al., 2017). An earlier work used the litmus-paper to roughly mearsure the near-electrode pH values and also observed that the pH close to anode can decrease to as low as 2-3 while the pH at cathode can climb higher than 10 (Choi 2014). In FCDI, similar results were with an anodic pH of 1.5 and cathodic pH of 12.5 (Nativ et al., 2017).

According to Eqs 12 and 14, the oxygen reduction reactions at the cathode consume H<sup>+</sup> with these reactions the dominant Faradaic processes ocurring when the voltage is relatively low (e.g. < 1.0 V), resulting in pH increase (Lee et al., 2010). With an increase in the charging voltage, carbon electrode oxidation reactions start to occur (Eq 3) with the release of H<sup>+</sup> into solution. As the charging voltage further increases, Cl<sup>-</sup> and water oxidation could take place at the anode (Eqs 2-4 to 2-8). Most of these oxidation reactions are capable of generating H<sup>+</sup>, resulting in a decrease in the pH of the treated stream. Other interpretations of observed pH variations on operation of CDI systems are possible and could be attributed to the difference in ion mobility of H<sup>+</sup>, OH<sup>-</sup> and other ions and/or the non-Faradaic preferable electrosorption of these ions (Andres and Yoshihara 2016, Han et al., 2013b, Porada et al., 2013c). Interestingly, Dykstra et al. (2017) presented a model to predict the pH changes in the MCDI cell. They found that although the different mobilities of various ions contributed to the pH fluctuation of the effluent, Faradaic reactions played a more important role for the pH changes during the CDI operation. Bouhadana et al. (2011) reported that the pH fluctuation was

dramatically reduced when replacing dissolved air with nitrogen by bubbling nitrogen gas into the solution, suggesting that the pH fluctuation depend strongly on the Faradaic reactions involving oxygen at the electrodes.

While it has been reported that change of pH exerted an insignificant influence on salt removal during CDI operation (Porada et al., 2012a), significant effluent pH fluctuations remain problematic. For example, when cations such as  $Ca^{2+}$  and  $Mg^{2+}$  are present in the feed water, scale formation on the surface of the cathodes is likely to be a problem, particularly at higher pHs where carbonate minerals containing these cations readily form (Choi and Kang 2016). It is also worthwhile mentioning that the stability of some of the redox-active electrodes (such as those made from transition metal oxides/carbon composite) is likely to depend strongly on pH. A rapid decrease of pH in the vicinity of the anodes could lead to the undesirable leakage of metal ions from the metal oxide composites, potentially posing significant health risks to consumers.

In addition to pH fluctuations, Faradaic reactions may also generate undesired byproducts during charging and discharging cycles. One example is the production of  $ClO_3^-$ , which, as described earlier, could be generated upon the oxidation of  $Cl^-$  at the anode (Wouters et al., 2013). The presence of high dosages of  $ClO_3^-$  in effluents will cause serious health risks for both humans and animals (Srinivasan and Sorial 2009), including oxidative damage to erythrocytes and mutagenic activities in mammalian cells (Jung et al., 2010a, Richardson et al., 2007). Due to these toxic effects, the WHO has proposed a threshold limt for  $ClO_3^-$  in drinking waters of <0.7 mg L<sup>-1</sup> (Edition 2011). As such, effecitive strategies must be implemented to prevent the generation of  $ClO_3^-$  and its derivative by-products if CDI is applied to drinking water purification.

## 2.3.3 Energy loss

Faradaic reactions (also referred to as "parasitic electrochemical charge transfer"), leakage currents and ohmic losses are the main reasons that the energy efficiency declines, possibly by 20-30%, over months of operation (Farmer et al., 1996). Recent studies of the energy loss mechanism in CDI units under constant current (CC) operation found that resistive and parasitic losses, primarily due to leakage currents associated with Faradaic reactions at the electrodes, were the two major sources of energy loss (Hemmatifar et al., 2016). It is demonstrated that resistive energy loss was dominant under high current conditions as it increases approximately linearly with current for fixed charge transfer. On the other hand, parasitic loss dominated in low current cases as the electrode is held at higher voltages for a longer period of time (Qu et al., 2016).

### **2.4.** Strategies to reduce/eliminate Faradaic side effects

Faradaic reactions may cause a range of negative side effects over prolonged CDI operation including desalination performance decline, water quality fluctuations and undesirable energy consumption. A variety of strategies may be envisaged to reduce/eliminate these Faradaic side effects including optimization of the CDI configuration, modification of CDI operation mode and fabrication of novel CDI electrodes.

## **2.4.1** Alternative CDI configurations

### 2.4.1.1 Membrane Capacitive Deionization

Membrane capacitive deionization (MCDI) is a significant improvement over conventional CDI and involves the incorporation of ion-exchange membranes (IEMs) in front of the CDI electrodes thereby enabling more selective ion adsorption and desorption (Li et al., 2008). Incorporation of IEMs in CDI is also recognized to be an effective method to alleviate particular Faradaic reactions including the cathodic reduction of oxygen and anodic oxidation of carbon (Omosebi et al., 2014).

Tang et al. (2017a) compared the Faradaic reactions occurring in CDI and MCDI cells equipped with carbon cloth electrodes through investigation of H<sub>2</sub>O<sub>2</sub> production and DO decay. During charging, H<sub>2</sub>O<sub>2</sub> was generated with a steady-state concentration of up to 60  $\mu$ M in the CDI cell due to DO reduction at the cathode (Eq 2-12) while less than 2  $\mu$ M H<sub>2</sub>O<sub>2</sub> was observed in the MCDI cell. This was consistent with the observation that DO decreased rapidly to <1 mg L<sup>-1</sup> in the CDI cell while insignificant decay of DO was observed in the MCDI cell. As reported previously, the oxygen diffusivity in Neosepta and Nafion membranes is two orders of magnitude smaller than that in water (Ogumi et al., 1984). Consequently, IEMs incorporated in CDI units could act as efficient barriers to transport of DO to the cathode, thereby inhibiting oxygen reduction could contribute to the alleviation of the positive shift of potential distribution to the anode over long-term CDI operation (Bouhadana et al., 2011b, Cohen et al., 2013).

More interestingly, some researchers presented the effects of Faradaic reactions on the long-term performance of CDI and MCDI units equipped with carbon xerogel electrodes (Omosebi et al., 2014). Unlike CDI which was found to experience severe desalination performance decline in a short period of time, MCDI exhibited stable performance over the 50 h of operation. Post-testing evaluation of the used CDI anode showed a positive shift of  $E_{PZC}$  by 0.5 V after 50 h operation, while the voltage increase of the anode  $E_{PZC}$  was only 0.2 V in the MCDI cell. These results clearly demonstrated that the carbon oxidation reactions were suppressed by the incorporation of IEMs into the CDI unit (more details in Section 3.1).

#### 2.4.1.2 Inverted Capacitive Deionization

Gao et al. (2015b) proposed a new CDI configuration, called inverted capacitive deionization (i-CDI) with the aim to diminish side effects of Faradaic reactions and achieve a stable and efficient desalination performance. The i-CDI system involves the use of an anode with net negative surface charge and a cathode with net positive surface charge. Interestingly, salt removal in this novel i-CDI system was achieved in a manner completely opposite to traditional CDI systems with cell charging leading to ion desorption from the EDLs of the electrodes while cell discharging by short-circuiting the anode and cathode led to ion adsorption (Figure 2-7a and b). Most importantly, desalination performance was shown to be maintained for over 600 h; an improvement in lifetime of the system by 530% compared to that of a conventional CDI system operated under similar conditions. In more recent work, Gao et al. (2015b) developed an amine-treated anode (with  $-NH_3^+$  groups providing positive surface charge) and acidtreated carbon cathode (with COO<sup>-</sup> groups providing negative surface charge) and achieved a desalination capacity of 5.3 mg  $g^{-1}$  at charging/discharging voltages of 0/1.1 V with this performance representing a significant improvement with regard to both salt removal capacity and working voltage window compared to the first-generation of i-CDI systems. Wu et al. (2016) further fabricated an i-CDI system equipped with an activated carbon cathode modified by poly (4-vinylpyridine) and a carbon anode treated with nitric acid, and achieved a remarkably high salt removal capacity of 20.6 mg  $g^{-1}$ .

In i-CDI systems, the oxidation of the anode is not regarded as an adverse effect as is the case in conventional CDI systems. Indeed, oxygen-containing functional groups formed during the carbon oxidation process increase the net negative surface charge thereby further expanding the available internal working voltage window for salt separation performance (**Figure 2-7c**). As a consequence, the formation of oxide thinlayers at the anode could contribute to a significant improvement in CDI desalination stability in long-term operation, paving a new way for high performance CDI.



**Figure 2-7.** Schematic of (a) capacitive deionization, (b) inverted capacitive deionization, (c) the working voltage window for the i-CDI. Adapted with permission from Gao et al. (2015b). Copyright 2015 Royal Society of Chemistry.

### 2.4.1.3 Flow-electrode capacitive deionization

Flow-electrode capacitive deionization (FCDI) is an innovative MCDI method using suspended carbon slurry that flow in the flow channels carved on the current collectors. FCDI exhibits a number of distinctive benefits for water desalination, i.e., continuous desalination behavior, and potentially energy and resource recovery if designed and operated appropriately (Hatzell et al., 2015b, Jeon et al., 2013a). It has been reported recently that the anode pH could decrease to 1.5 while cathode pH increased to 12.5, when the FCDI was operated in a separated flow electrode mode (anode and cathode slurry flowing separately) (Nativ et al., 2017). However, when using the combined flow-electrode (the anode and cathode flow electrodes mixing outside the FCDI cell), the Faradaic reaction could be partly supressed with the combined flowelectrode pH stabilized at around 7 and the energy consumption much lower compared to the separated flow-electrode CDI.

### 2.4.1.4 Flow-by Capacitive Deionization

Flow-by and flow-through modes are two types of common CDI configurations (Guyes et al., 2017, Suss et al., 2012). Using flow-by configuration was believed to increase the stability of CDI system, with the lifetime of CDI cell enhanced 360% compared to that of the flow-through configuration (Cohen et al., 2015). As such, flow-by CDI is considered to be a better configuration than flow-through CDI, mainly due to the presence of a hydrodynamic diffuse boundary layer which prevents rapid transport of dissolved oxygen to the surface of the cathode. The limitation of oxygen reduction on the cathode results in the reduction of an asymmetric distribution of potentials in flow-by cells.

### 2.4.2 Operational approaches

#### 2.4.2.1 Optimization of the voltage window

As reported by Lu et al. (2017), CDI underwent significant performance decline even when operated at a voltage as low as 1.2 V. To mitigate the performance decline, they tested a number of different charging and discharging voltages, and finally obtained the optimal operation voltage window to be charging at 0.8 V and discharging at -0.4 V. The CDI system exhibited a slightly lower desalination capacity (6.3 mg g<sup>-1</sup>) under this voltage window compared to that of the 1.2/0 V experiment (7.3 mg g<sup>-1</sup>). Nevertheless, it is an important finding that carbon oxidation was inhibited in this optimal voltage window with negligible performance degradation observed, even after more than 70 operation cycles.

#### 2.4.2.2 Constant current operation

To reduce Faradaic reactions, one straightforward and effective method is to apply a lower charging voltage to the CDI cells. Indeed, there always exists a conflict between mitigation of anodic oxidation of carbon electrodes and enhancement of desalination performance. Based on the Gouy-Chapman-Stern model, higher charging voltage applied to the CDI cell results in improvement of ion electrosorption capacity while the higher voltage could lead to increased anodic oxidation of the carbon electrodes over prolonged CDI operation (Zhao et al., 2009). As such, CC mode is more favorable than CV mode since electrodes undergo less time at higher voltages with lower resistive and parasitic losses during CC operation (Qu et al., 2016).

### 2.4.2.3 Periodic electrode polarity reversal

It has been found that the decline of the CDI electrosorption capacity on aging of the carbon electrodes can be recovered to a large extent by periodically reversing the cell polarity (Cohen et al., 2015, Farmer et al., 1996). Cohen et al. (2015) have examined this possibility and found that when the CDI unit was operated periodically according to the following four steps: (i) 0.9 V, (ii) 0 V, (iii) -0.9 V, (iv) 0 V, with each step lasting for 30 minutes, the desalination performance showed no obvious decline even after running for 34 days while control experiments with the charging/discharging cycle of 0.9 V/0 V achieved only 5 days of stable operation. The pH fluctuations were only in the range of 5.8 to 7, indicating reasonable stability of the cell. Unlike the regular behavior of the conventional CDI with one electrode serving as the anode and the other as the cathode during charging, in periodic polarity reversing mode each electrode periodically serves as anode or cathode. This operation provides an identical working condition for both electrodes in long-term operation, thereby avoiding the asymmetric shifting of the  $E_{pzc}$  between two electrodes and thus suppressing the Faradaic reactions, especially reducing the rate and extent of the oxidation of the electrodes (Cohen et al., 2015).

Similarly, Gao et al. (2017) reported desalination performance of the CDI stack equipped with carbon xerogel electrodes by alternating polarization of  $\pm 1.2/0$  V. Longterm operation suggested that this operation mode could eliminate the formation of inversion peaks thereby effectively extending the cycling stability for salt ion removal. The surface charge of both carbon electrodes gradually shifted from "positively charged" to "negatively charged" due to the inevitable and irreversible Faradaic reactions as each electrode alternately served as CDI anode during this alternating polarization process. These studies also demonstrated for the first time that the highest salt adsorption capacity was attained after 200-hour of operation when the positively and negatively charged surface sites on the electrodes became nearly equal.

#### 2.4.2.4 Deoxygenation cell

As demonstrated previously, the presence of dissolved oxygen results in undesirable oxygen reduction reactions at the cathode even under a low operating voltage. Use of a low-cost deoxygenation cell to remove dissolved oxygen before the water enters the CDI cell results in inhibition of the oxygen reduction reaction and suppresses its competition with the cation capacitive adsorption, thereby resulting in an enhanced salt adsorption capacity and reduced energy consumption (Holubowitch et al., 2017).

### 2.4.3 Novel CDI electrode fabrication

Recent studies have demonstrated that the impregnation of certain types of polymers could effectively suppress the Faradaic effects. Choi et al. (2010) fabricated carbon electrodes by mixing the activated carbon powder with polyvinylidene fluoride (PVDF) binder and showed that the Faradaic current decreased significantly with increase in the PVDF content of the carbon electrodes. Further investigations suggested that the polymer binder could reduce the redox activity of the functional groups (i.e., carbonyl- or quinone-type oxygen functional groups) on the carbon surface (Hsieh and Teng 2002). In addition, a novel polymer-impregnated carbon anode involving coating the Type I strong base anion resin, N-methyl-2pyrrolidone (NMP) and PVDF mixture onto carbon cloth was fabricated by Gao et al. (2010) The experimental results showed that stable desalination performance and higher charge efficiency were achieved with much less significant effluent pH fluctuations obtained using this novel anode. Meanwhile, the  $E_{PZC}$  of the pristine anode shifted positively by ~0.26 V whereas the polymer-coated anode showed minimal obvious  $E_{PZC}$  shift after prolonged operation, demonstrating that the coverage of anion-exchange polymer layers could effectively mitigate the anodic oxidation of carbon electrodes.

Srimuk et al. (2016) chemically modified activated carbon (AC) electrodes with titania, which could provide additional catalytic activity for oxygen-reduction reactions at the cathode and prevented the oxidization of carbon electrode. The study revealed that titania coated AC electrodes exhibited higher desalination capacity and better long-time stability than pure AC electrodes in oxygen saturated NaCl solution. After 15 operating cycles, the AC-titania hybrid electrode presented a comparable high salt removal capacity of 8 mg g<sup>-1</sup>, whereas CDI with the pure AC electrodes almost lost all the desalination capacity. It was demonstrated that pure AC electrodes exhibited the oxygen reduction reaction in a two-electron transfer and produced H<sub>2</sub>O<sub>2</sub>, which was then used to attack the carbon electrodes, resulting in a decline in desalination performance. In contrast, AC-titania electrodes consumed the oxygen via a three-electron transfer reaction that suppressed the formation of H<sub>2</sub>O<sub>2</sub>, preventing the carbon

electrode from being oxidized, and partially reducing the deterioration of the CDI desalination performance.

### **2.5.** Potential positive applications of Faradaic reactions

Although Faradaic reactions are generally recognized to cause serious problems including electrode deterioration and associated desalination performance decline, water quality fluctuations and undesirable energy loss, some Faradaic reactions may contribute to the enhancement of desalination performance and/or may contribute to the achievement of CDI multifunctionality (such as simultaneous desalination and disinfection/micropollutant degradation). These possibilities are discussed briefly below.

# 2.5.1 Desalination performance enhancement

### **2.5.1.1** Faradaic ion storage

Over the past few years, researchers have been focusing on optimization of traditional CDI systems equipped with static porous carbon electrodes and have achieved salt adsorption capacities approaching ~15 mg g<sup>-1</sup>. For flow carbon electrode system, a slightly higher salt adsorption capacity of ~20 mg g<sup>-1</sup> is expected. Due to the low intrinsic charge storage capacitance of porous carbon electrodes, however, a CDI device based on the mechanism of non-Faradaic capacitive adsorption (ion storage in the EDLs of carbon micropores) suffers from the limitation of improvement of salt adsorption capacity. As mentioned in section 2.3, an alternative means of enhancing ion storage is to employ innovative pseudocapactive electrodes which extract ions through reversible Faradaic reactions that occur on intercalation of highly concentrated saline water and in the selective harvest of particular ions. The comparison of desalination performance among electrodes based on EDL and Faradaic ion storage mechanisms are summarized in **Table 2-1**.

Following the pioneering attempts at using pure Faradaic-based CDI cells in which sodium-manganese oxide ( $Na_2Mn_5O_{10}$ ) was employed as the cathode for sodium capture while silver served as the anode for chloride capture (Pasta et al., 2012), a modified hybrid CDI cell was proposed by Lee et al. (2014). This hybrid CDI cell was composed of a Faradaic type cathode (sodium-manganese oxide materials, Na4Mn9O18) and a non-Faradaic type anode (porous carbon materials), leading to a desalination capacity of 31.2 mg  $g^{-1}$ , twice as high as that for pure carbon capacitive electrodes. In their following work (Kim et al., 2016a), sodium iron pyrophosphate (Na<sub>2</sub>FeP<sub>2</sub>O<sub>7</sub>) electrodes (which served as the Faradaic cathode) were developed with this hybrid CDI system achieving a reasonably high electrosorption capacity (30.2 mg  $g^{-1}$ ). Porada et al. (2016) prepared a novel porous electrode which contained redox-active nickel hexacyanoferrate (NiHCF) nanoparticles and used them for electrochemical water desalination. When applying a current density of 2.8 A m<sup>-2</sup>, a high electrosorption capacity (34 mg  $g^{-1}$ ) was achieved, 1.5 times higher than that of the CDI with carbon electrodes (12.5 mg g<sup>-1</sup>). Meanwhile, the current efficiency reached  $80\% \sim 95\%$ , and the energy costs of desalination can be significantly reduced. Chen et al. (2017a) reported a similar Faradaic capacitive deionization cell based on Na<sub>0.44</sub>MnO<sub>2</sub> cathode and AgCl anode for chemical intercalation and deintercalation of sodium and chloride ions, which earned a stable and reversible desalination capacity of 57.4 mg  $g^{-1}$  after 100 cycles operation with an excellent charge efficiency of 97.9%/95.6% during charging/discharging process. More recently, anther novel Faradaic capacitive-based desalination system was developed with sodium nickel hexacyanoferrate (NaNiHCF) and sodium iron HCF (NaFeHCF) as the electrodes (Lee et al., 2017). One interesting phenomenon is that desalination took place not only during the charging step but also the discharging step. It was demonstrated that this desalination cell exhibited a high

desalination capacity (59.9 mg g<sup>-1</sup>) and efficient energy consumption (5-10 Wh mol<sup>-1</sup>). Following this work, Kim et al. (2017) developed a similar CDI system using identical copper hexacyanoferrate (CuHCF) electrodes to bind sodium and chloride separated via the anion exchange membrane with this cell realizing a desalination capacity of nearly 100 mg g<sup>-1</sup>. Most recently, dual-ion electrochemical desalination systems, using Na<sub>0.44</sub>MnO<sub>2</sub> as the sodium ion Faradaic electrode and BiOC1 as the chloride ion Faradaic electrode have been explored. An extremely high salt capture capacity of 68.5 mg g<sup>-1</sup> and a charge efficiency of 97.7% were achieved (Chen et al., 2017b), with these results suggesting a promising future for highly saline water desalination.

While a variety of electrodes have been fabricated for the selective intercalation of cations, only a few have been developed for the capture of anions. Missoni et al. (2016) developed an alternative  $LiMn_2O_4$ -polypyrrole electrochemical cell to selectively capture lithium chloride from seawater or other natural brine solution. Chloride ions can be successfully extracted by the polypyrrole coated carbon felt anode, while the lithium ions can also be effectively harvested in the  $LiMn_2O_4$  cathode. Upon applying a low potential difference of 0.6-1.1 V, a competitive charge efficiency of 50% and energy consumption of 5-10 Wh mol<sup>-1</sup> was achieved, with an excellent reproducibility of 200 cycles.

In addition to removal salt (cation and anion) from the water, Faradaic ion storage was also applied for the selective separation of charged organic matters from electrolyte solutions containing strong aqueous as well as dilute organic pollutants. Su et al. (2016a) developed carbon electrodes coated with redox material (PVF/CNT), which exhibited an excellent selectivity towards organic anions (carboxylates (–COO–), sulfonates (–SO<sub>3</sub><sup>-</sup>), and phosphonates (–PO<sub>3</sub><sup>-2</sup>)), with a separation factor of more than 140 and 3000 times compared to inorganic anions (PF<sub>6</sub><sup>-</sup> and ClO<sub>4</sub><sup>-</sup>) in aqueous and

organic solutions, respectively. In their following work, similar system with organometallic functionalized redox-cathode and ferrocene-modified redox-anode were used in an asymmetric electrochemical capacitive cell, presenting a remarkable degree of selectivity when binding charged micro-pollutants, i.e., pesticides, endocrine disruptors, and pharmaceutical, with a current density of up to 96%. Their findings provided a promising and energy-efficient pathway for the recovery of value-added products or the separation/isolation of dilute but highly toxic organic pollutants from aqueous or organic systems (Su et al., 2017).

Although Faradaic ion storage is a promising area and one in which there is considerable interest, several problems still remain to be solved.

(i) Most intercalation electrodes are only efficient for capture of particular ions; for example, sodium manganese oxide (NMO) can selectively take up Na<sup>+</sup> while NiHCF shows affinity for K<sup>+</sup>. While attractive for removal of particular ions, this selectivity limits their application with regard to treatment of source waters containing multiple types of ions including Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup> and Mg<sup>2+</sup>;

(ii) There is a lack of materials that can serve as the anion-storage electrodes in aqueous media. Although Ag/AgCl was found to be a highly efficient Cl<sup>-</sup> ion capture electrode, its further application is likely to be limited by commercial constraints. More studies should be focused on the development of cost-effective, efficient and stable intercalation electrodes for anions, such as Cl<sup>-</sup>, F<sup>-</sup>, NO<sub>3</sub><sup>-</sup>,  $SO_4^{2^-}$ , from saline waters;

(iii) Although researchers have claimed that these Faradaic electrodes can be operated for hundreds of cycles without significant decrease in desalination performance, undesired leakage of metal ions from the intercalation materials might occur during prolonged operation, potentially causing risks when used for drinking water desalination (Bouchard et al., 2011, Dion et al., 2016). Meanwhile, the average salt adsorption rate of these intercalation electrodes are generally slow, which would also restrict their practical application.

**Table 2-1.** Comparison of the desalination performance among electrodes based on the

 EDL ion storage mechanism and Faradaic ion storage mechanism.

Electrode materials		Operation voltage/Current density	Initial salt concentration (mM)	Electroadsorption capacity (mg $g^{-1}$ )	Charge efficiency	Ref.
EDL electrode	Cathode/anode: <sup>a</sup> Carbon aerogel	1.2 V	8.5	2.9	n.a.	(Farmer et al., 1996)
	Cathode/anode: Graphene	2.0 V	0.4	1.8	n.a.	(Li et al., 2009)
	Cathode/anode: Activated carbon	1.2 V	3.4	3.5	84%	(Kim and Choi 2010)
	Cathode/anode: Activated carbon	1.2 V	5	6.9	85%	(Porada et al., 2012b)
	Cathode/anode: Carbon aerogel	1.5 V	50	9.6	43%	(Suss et al., 2012)
	Cathode/anode: Graphene sponge	1.2 V	8.5	14.5	50%	(Xu et al., 2015b)
	Cathode/anode: Carbon nanotubes@ graphene	1.2 V	8.5	18.7	55%	(Xu et al., 2015a)
	Cathode/anode: Graphene@Carbon fiber	1.2 V	5.1	9.2	n.a.	(Wang et al., 2016a)
Faradaic electrode	Cathode: Na <sub>4</sub> Mn <sub>9</sub> O <sub>18</sub> Anode: activated carbon	1.2 V	100	31.2	n.a.	(Lee et al., 2014)
	Cathode:Na <sub>2</sub> FeP <sub>2</sub> O <sub>7</sub> Anode: activated carbon	1.2 V	100	30.2	n.a.	(Kim et al., 2016a)
	Cathode/anode: Na <sub>2</sub> NiFe(CN) <sub>6</sub>	2.8 A m <sup>-2</sup>	20	34.0	80%	(Porada et al., 2016)
	Cathode: Na <sub>0.44</sub> MnO <sub>2</sub> Anode: AgCl	$3.0 \text{ A m}^{-2}$	15	57.4	98%	(Chen et al., 2017a)
	Cathode/anode: NaNiHCF/ NaFeHCF	5.0 A m <sup>-2</sup>	500	59.9	83%	(Lee et al., 2017)
	Cathode: Na <sub>0.44</sub> MnO <sub>2</sub> Anode: BiOCl	5.7 A m <sup>-2</sup>	13	68.5	97.7%	(Chen et al., 2017b)
	Cathode/anode: CuHCF	2.8 A m <sup>-2</sup>	50	~100	~80%	(Kim et al., 2017)

<sup>a</sup> Cathode/anode means that the CDI used the asymmetry electrode, with the anode and cathode to be the same material.

## 2.5.1.2 Electron mediators

Another innovative application of Faradaic reactions in desalination enhancement involves the introduction of redox-active electron shuttles (such as quinones) into FCDI systems where aqueous suspensions of activated carbon particles flow through a flow channel carved on the current collector (Ma et al., 2016a). The quinone species in the flow-electrode act as an electron mediator with redox transformation between the reduced hydroquinone  $(H_2Q)$  and oxidized benzoquinone (Q)forms of the quinone occuring at the electrode surface and electrolyte interface (Figure **2-8**). The presence of the  $H_2Q/Q$  couple in the flowing carbon suspension significantly accelerated the charge transfer between the carbon particles and current collectors, thereby enhancing both the salt electrosorption and desorption processes (Figure 2-8). On applying a charging voltage of 1.2 V, the average salt removal rate increased by  $\sim 131\%$  on adding H<sub>2</sub>Q (at a concentration of 14 mM) to a 1 wt% activated carbon suspension, with a similar positive effect observed during the discharging process. This result represents a breakthrough in the development of FCDI with the application of Faradaic reactions providing a highly efficient means for enhancing desalination performance.



**Figure 2-8.** (a)The mechanism of charge transfer in the anode flow-electrode chamber when adding aqueous hydroquinone ( $H_2Q$ ) and benzoquinone (Q) as the electron shuttle,

(b) Temporal variation of the salt concentration in the FCDI cell using blank flowelectrodes (1 wt% dispersion of activated charcoal) or redox-active flow-electrodes containing 14 mM H<sub>2</sub>Q (w/ H<sub>2</sub>Q). Reprinted with permission from ref Ma et al. (2016b). Copyright 2016 American Chemical Society.

#### **2.5.2 Other Faradaic applications**

#### 2.5.2.1 Disinfection

As described previously, active species such as HClO, 'OH, and H<sub>2</sub>O<sub>2</sub> can be generated through the occurrence of Faradaic reactions in a CDI cell with these species potentially of use in water disinfection. Laxman et al. (2015) evaluated the bacterial inactivation properties of a CDI cell with activated carbon cloth electrodes and observed an approximate 3-fold reduction in the number of viable bacterial colonies (from  $3 \times 10^4$  CFU mL<sup>-1</sup> in the feed water) following CDI operation. Another group fabricated a novel electrode by impregnating cationic nanohybrids of graphene oxide grafted quaternized chitosan to activated carbon electrodes (GO-QC/AC) (Wang et al., 2015). A CDI cell equipped with this novel electrode achieved an ultrahigh inactivation rate (i.e., 99.9999% or 6 log reduction) of *Escherichia coli* during water desalination while the CDI with the pristine activated carbon electrodes removed less than 82.8% of the viable bacteria present in feed waters. Although the mode of antimicrobial action by CDI has not yet been clearly elucidated, the active oxidants (e.g. HCIO and HO<sup>•</sup>) generated during the electrochemical process could play an important roles in this process (Jeong et al., 2006).

In addition, the  $H_2O_2$  generated via cathodic oxygen reduction, if combined with UV irradiation or  $O_3$ , would also be expected to result in bacterial inactivation. Indeed, previous studies have demonstrated that low concentrations of  $H_2O_2$  (20–150  $\mu$ M)

combined with UV or  $O_3$  lead to enhancement in bacterial inactivation by 0.5–2.0 log units (Cho et al., 2011, Cho and Yoon 2006, Lanao et al., 2008, Rubio et al., 2013).

### 2.5.2.2 Contaminant sequestration

Organic and inorganic micropollutants (such as endocrine disrupting chemicals, heavy metals and arsenic) are prevalent in many water sources and in treated wastewaters which otherwise might be recycled. CDI, apart from removing inorganic salts by non-Faradaic means, may also contribute to the removal of these pollutants through a combination of Faradaic and non-Faradaic processes.

Consider arsenic which is naturally present in groundwaters at concentrations ranging from less than  $0.5 \ \mu g \ L^{-1}$  to more than 5 mg  $L^{-1}$  (Smedley and Kinniburgh 2002). Groundwaters exhibiting arsenic concentrations well above the World Health Organisation (WHO) guideline value for drinking water of 10  $\mu g \ L^{-1}$  (Edition 2011), have been found in Argentina, Chile, Mexico, China and Hungary and, more recently, in West Bengal (India), Bangladesh and Vietnam (Mandal and Suzuki 2002, Smedley and Kinniburgh 2002). As(III) and As(V) are the predominant arsenic forms in natural water with the former being more toxic than the latter (Pous et al., 2015). As most arsenic sequestration technologies are not very effective in directly removing As(III), pre-oxidation of As(III) to As(V) is commonly used to improve the arsenic removal efficiency (Bissen and Frimmel 2003, Leupin and Hug 2005). CDI is capable of serving as an alternative technique for arsenic removal with the potential for utilization of the combined effects of electro-oxidation and electrosorption (Fan et al., 2016, Garrido et al., 2009, Lee et al., 2016, Zhang et al., 2014).

As reported by Fan et al. (2016) As(III) can be anodically oxidized to As(V) followed by electrosorption of the in-situ formed As(V) onto the surface of the anode. Following charging at 1.2 V for 120 min, the arsenic concentrations decreased from 50,

100 and 200 mg L<sup>-1</sup> to 2.3, 9.6 and 42.3 mg L<sup>-1</sup>, respectively, with arsenic present in the treated water predominantly as As(V). It should be noted that in practical groundwater cases arsenic coexists with other inorganic anions (and associated cations) with the concentrations of these inorganic anions (e.g. Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) several magnitudes higher than arsenic. As such, the impact of the presence of other inorganic salts on removal of arsenic by CDI from solution requires careful attention.

In addition to removal of salt and minor components from groundwaters, consideration has also been given to treatment of municipal wastewater effluents. These wastewaters typically contain a range of organic compounds with the chemical oxygen demand (COD) of these effluents ranging from  $\sim 20$  to  $\sim 100$  mg L<sup>-1</sup> as well as inorganic salts at concentrations ranging from  $\sim 100$  to 1000 mg L<sup>-1</sup> (Kim et al., 2008, Li et al., 2011). Recently, Duan et al. (2015b) employed CDI for the simultaneous removal of phenol and NaCl from a synthetic wastewater. The anodic oxidation of phenol was achieved in the CDI system through (i) the direct oxidation of phenol at the anode, generating benzoquinone and catechol by hydroxylation and/or (ii) the indirect mineralization by active chlorine which was generated through the anodic oxidation of  $Cl^{-}$  (Eq 2-4) with the formation of chlorophenols as intermediate in this pathway. These aromatic intermediates were then oxidized to carboxylic acids and, ultimately, to CO<sub>2</sub>. In a similar manner, Liu et al. (2016) confirmed that CDI was capable of breaking down naturally occurring humic substances via anodic electrochemical oxidation with subsequent electrosorption of oxidized humic substances and their derivatives. This indicated that CDI technology may be of use in the pre-treatment of drinking waters as it can decrease the extent of formation of disinfection by-products by partially removal of natural organic matter precursors.

While several attempts have been made to remove heavy metals including Cu(II) (Huang et al., 2014), Cd(II) (Huang et al., 2016), Pb(II) (Yang et al., 2014), and Fe(III) (Li et al., 2010), from waters by CDI, little mechanistic insight has been obtained with both non-Faradic electrosorption and cathodic reduction of cations expected to be of importance for the fixation of these heavy metals.

Huang et al. (2016) investigated the electro-enhanced removal of Cu(II) from water using a CDI cell equipped with activated carbon electrodes. When a low charging voltage of 0.4 V was applied, Cu(II) appeared to be removed from solution via non-Faradaic processes with no apparent deposition of elemental Cu on the cathode surface. During charging at 0.8 V, particles of  $1\sim2$  µm in size appeared on the electrode surface. On further increase in charging voltage to 1.2 V, large numbers of particles were generated and covered a significant portion of the electrode surface. XPS analysis revealed that these particles were a combination of metallic copper (i.e., Cu(0)) and cuprous oxide (i.e., Cu<sub>2</sub>O), confirming the occurrence of cathodic reduction of Cu (II) at relatively higher charging voltages.

### **2.6.** Perspectives and outlook

Faradaic processes in CDI systems have attracted increasing interest in recent years with investigation of both oxidation and reduction reactions resulting from application of charging potential leading to a firmer understanding of both the benefits and pitfalls of Faradaic effects. Here, we have provided a comprehensive review of Faradaic reactions in CDI with particular attention given to cathodic oxygen reduction, anodic carbon oxidation. One approach to gaining a perspective on the occurrence and impacts of CDI Faradaic reactions is to utilize a flowchart as described in **Figure 2-9** with these reactions potentially playing an important role in (i) mitigation or elimination of the undesired Faradaic reactions in the system, (ii) employment of the particular reactions which may be useful for improving desalination performance or achieving CDI multifunctionality (e.g., disinfection and micropolltant sequestration) and (iii) enhancement of Faradaic reaction-mediated desalination based on pseudocapacitive effects. Charge efficiency in achieving particular water quality and water recovery rate targets is used as the key performance parameter in this analysis.



Figure 2-9. Analysis of Faradaic reactions in the CDI system using a flowchart.

Carbon electrode oxidation caused by Faradaic reactions is one of the most critical issues in CDI long-term operation with these reactions resulting in electrode function deterioration and desalination performance decline. Use of membrane CDI (MCDI) appears to be effective in eliminating cathodic oxygen reduction with an associated positive shift in electrode potential to the anode thereby reducing the rate and extent of carbon anode oxidation with resultant extension of electrode lifetime. Combining ion-exchange polymers with the carbon electrodes may also contribute to mitigation of carbon oxidation as well as alleviating resistance and ion-exchange membrane cost issues that are associated with MCDI. More detailed studies on this issue are required in order to refine the replacement of ion-exchange membranes by carbon-polymer composite electrodes.

There are very few examples showing that anodic chloride oxidation occurs in CDI systems with resultant production of active chlorine species that could be applied to in-situ disinfection or indirect oxidant of organic pollutants. This reaction is likely to occur in hybrid CDI systems equipped with both transition metal containing materials and carbon materials as electrodes, where unequal potential distribution and/or metal catalytic properties favor the oxidation of chloride at the anode. One major concern is that the chloride oxidation process is likely to yield chlorinated byproducts, potentially increasing the health hazards associated with drinking water purification using CDI. In such systems, monitoring the possible formation of chlorine by-products such as chlorate, perchlorate, or organochlorine, as well as oxidative products of the anion exchange membrane is recommended, especially when using higher voltages for drinking water desalination.

Cathodic oxygen reduction, considering that the cathode potential is always expected to be lower than the redox potential of the oxygen reduction reaction, will inevitably occur in CDI systems. Our recent findings have revealed that the dissolved oxygen concentration can serve as a simple and convenient indicator of the rate and extent of oxygen reduction (He et.(He et al., 2016b) A mechanically-based kinetic model of the Faradaic reactions occurring at the cathode has been developed and found to satisfactorily describe the variation of DO consumed and  $H_2O_2$  generated during CDI operation (He et al., 2016b). The presence of  $H_2O_2$  could provide the means of inducing disinfection or micropollutant degradation in the CDI system provided that  $H_2O_2$  can be
effectively activated to more powerful oxidants (by, for example, UV photolysis or  $O_3$  addition).

pH fluctuation is another serious issue in CDI systems as it affects the treated water quality and potentially results in scaling issues at the cathode if large amounts of alkaline earth metal ions such as  $Ca^{2+}$  or  $Mg^{2+}$  are present. Although we have demonstrated previously that Faradaic reactions contribute greatly to the pH fluctuations, non-Faradaic processes such differing transport as the and adsorption/desorption rates of protons and hydroxyl ions may also play non-negligible roles. The contribution of Faradaic and non-Faradaic processes to pH fluctuations should be elucidated as this will assist in developing feasible strategies to mitigate its side effects. Additionally, in-situ measurement (e.g. by use of pH micro electrodes) or modelling of the pH variation at/near the electrode interface is required as this will enable further exploration of the mechanism behind pH fluctuations.

To date, most attention has focused on non-Faradaic processes (i.e., capacitive ion storage in EDLs) in CDI with limited attention given to Faradaic processes despite the importance of these processes to both treated water quality and long term stability and performance of this technology. As such, some urgency exists with regard to improving our mechanistic understanding of Faradaic reactions with the goal of effectively mitigating the negative effects of these processes whilst taking advantage of their positive effects.

It is encouraging to see that Faradaic capacitive electrodes can contribute significantly to the enhancement of desalination performance through intercalation effects. Unlike the traditional carbon electrodes that take advantage of the pure EDLs for ion removal, Faradaic capacitive electrodes can remove ion species through Faradaic reactions with high efficiency and low energy consumption. Most recently, ultra-high salt removal capacity of more than 100 mg g-1 was achieved when using these intercalation electrodes, almost seven times higher than that of traditional static capacitive carbon electrodes. However, the stability of such electrodes (particularly associated with the electrochemical leakage of metal ions) is currently a major concern and an issue to which more attention should be paid. Furthermore, it is necessary to develop cost-effective, stable, and novel intercalation cathodes and anodes to meet the requirement of capturing multiple cations and anions from real saline waters.

## **2.7.** Conclusions

In conclusion, examination of Faradaic reactions in CDI is both challenging and exciting and is an area that requires considerably more work. Many challenges remain in (i) the fundamental understanding of Faradaic processes and the search for effective methods to eliminate undesired side reactions (e.g., anodic carbon oxidation), (ii) employment of Faradaic reaction to enhance desalination performance through pseudocapacitive effects and (iii) development of hybrid CDI systems to fulfill the possibility of simultaneous desalination and disinfection/micropollutant removal.

## Chapter 3. Comparison of Faradaic reactions in flow-through and flow-by Capacitive Deionization (CDI) systems

## **3.1 Introduction**

The requirement for sufficient fresh potable water is generally acknowledged as one of the most critical issues of the 21<sup>st</sup> century (Porada et al., 2013c). Recently, renewed attention has been given to capacitive deionization (CDI) in view of the potential for brackish water desalination with greater energy efficiency and costeffectiveness compared to conventional desalination technologies such as reverse osmosis (RO), electrodialysis (ED) and multistage flash distillation (MSF) (Porada et al., 2013c, Suss et al., 2015b). The basic principle of CDI involves the application of a potential difference to a pair of porous (typically carbon) electrodes such that ions in the solution are removed and immobilized in the electrical double-layer (EDL) of the oppositely charged electrode. When the potential is either removed or reversed, the adsorbed ions are released to bulk solution and the electrodes regenerated (Suss et al., 2015b).

Over the past decade, more than a dozen different CDI cell architectures including flow-by CDI, flow-through CDI, membrane CDI, flow electrode CDI and inverted CDI have been developed with the purpose of optimizing salt adsorption capacity, energy efficiency and electrode regeneration rate (Bian et al., 2016, Bian et al., 2015, Jeon et al., 2013a, Suss et al., 2015b, Tang et al., 2017b, Tang et al., 2018). However, the earliest and most widely-used architecture is flow-by CDI in which water flows adjacent to electrode pairs that are separated from each other by a spacer. While easier to assemble and seal than alternate designs, this classical architecture suffers from several limitations including (i) long spacer-to-electrode diffusion times, (ii) high cell internal resistance and volume due to the need for a relatively thick separator between the electrodes, and (iii) insufficient utilization of the adsorption capacity of the porous carbon electrodes (Bouhadana et al., 2009, Suss et al., 2012). Of the alternatives available, flow-through architecture, in which water flows directly from one electrode to another, has been found to be a promising configuration because of the enhanced contact time and mass transfer. Flow-through technologies have been applied in a number of electrochemical water treatment processes including electrochemical membrane filtration (Gao et al., 2015a, Zaky and Chaplin 2013, Zheng et al., 2018), electrochemical disinfection (Rahaman et al., 2012, Vecitis et al., 2011), energy production using microbial fuel cells (Katuri et al., 2011, Zhang et al., 2015a) and capacitive desalination (Andelman 2011, Suss et al., 2012). Flow-through CDI was first proposed by Newman and Johnson (Johnson and Newman 1971, Johnson et al., 1970) and further developed by Suss et al (Suss et al., 2012). In the configuration used by these investigators, the feed water flows straight through the macropores of the electrodes along the primary electric field direction with this configuration resulting in enhanced mass transfer of ions to the micropores with a higher desalting performance and charge efficiency compared to the typical flow-by configuration (Suss et al., 2012, Wang et al., 2016b).

Both non-Faradaic and Faradaic reactions occur in CDI systems with non-Faradaic reactions involving the storage of ions in the EDL at the carbon/electrolyte interface upon charging recognized to be the primary mechanism of desalination (Porada et al., 2013c, Zhang et al., 2018a). Faradaic reactions however are also recognized to be important to the performance of CDI (Choi 2014, Cohen et al., 2013, He et al., 2016b, Zhang et al., 2018a). At the anode (*i.e.*, the electrode that is positively charged during electrosorption), oxidation reactions including carbon electrode oxidation, water oxidation and, potentially, chloride oxidation (He et al., 2016b, Lee et al., 2010) may occur while reduction reactions such as oxygen reduction take place at the cathode (*i.e.*, the electrode that is negatively charged during electrosorption) (Avraham et al., 2011, He et al., 2016b). On one hand, these reactions lead to a series of unexpected side effects such as deterioration in desalination efficiency, decrease in electrode lifespan, precipitation on membrane surface or pores, increase in energy consumption, formation of by-products and fluctuation of the effluent water quality (Asraf-Snir et al., 2018, Dzyazko et al., 2014, Porada et al., 2013c, Remillard et al., 2018). On the other hand, the *in-situ* generated reactive species such as H<sub>2</sub>O<sub>2</sub> and HOCl, if managed properly, can enable CDI to fulfil its promise of multifunctionality such as micropollutant degradation and/or water disinfection (He et al., 2016b).

Comprehensive understanding of the Faradaic reactions occurring in CDI systems is vital if CDI is to be operated in a stable manner for long periods and with optimal energy consumption. In our previous work, we have investigated the Faradaic reactions in flow-by CDI (He et al., 2016b), membrane CDI (Tang et al., 2017a) and flow electrode CDI (He et al., 2018a, Ma et al., 2016a, Zhang et al., 2017, Zhang et al., 2018d) and, recently, published a review paper on Faradaic reactions in CDI (Zhang et al., 2018a). However, there has been limited investigation of Faradaic processes in CDI systems based on flow-through architecture. As the feedwater is forced to flow directly from one electrode to the other, ion transfer may be expected to differ from that in conventional flow-by CDI, potentially enhancing the rate and extent of Faradaic reactions that occur. As such, the desalination performance and Faradaic reactions in flow-through CDI systems operating under different water flow modes (*i.e.*, forward

and reverse flow) are investigated in this study with variation of solution pH and dissolved oxygen (DO) and the production of  $H_2O_2$  examined. A comprehensive discussion of the side effects and the potential benefits of the Faradaic reactions occurring in these flow-through systems is provided at the end of this work.

## **3.2 Materials and Methods**

## 3.2.1 Cell design

The CDI cell (**Figure 3-1**) used in this study consisted of two parallel commercial carbon cloth electrodes (Nantong Senyou Carbon Fiber Co., Nantong, China) with a macroscopic dimension of  $4.0 \times 4.0 \times 0.3$  cm<sup>3</sup> (**Figure 3-2**). The surface area of carbon cloth electrode measured by Brunauer-Emmett-Teller (BET) method was  $1101 \text{ m}^2 \text{ g}^{-1}$  as reported in our previous work (Tang et al., 2017a). Graphite sheets were attached to the carbon cloth electrodes and served as the current collectors.



Figure 3-1. Photos of the flow-through CDI cell setup.



Figure 3-2. Photo of the carbon cloth electrodes used in the experiment.

For the flow-through CDI cell, laser cut silicone gaskets of dimension  $4.0 \times 4.0 \times 0.2$  cm<sup>3</sup> served as upstream and downstream reservoirs permitting the feedwater to pass evenly through the electrodes and separator. A layer of porous nonconductive nylon sheet (100-mesh, 55 mm × 55 mm× 0.2 mm) was used to electronically isolate the electrodes (**Figure 3-3**). Two operational modes (*i.e.*, forward and reverse flow) were investigated in the flow-through CDI (**Figure 3-3a and b**). In the forward flow-through scenario, the feedwater first passed through the anode, followed by the separator and, finally, the cathode (**Figure 3-3a**). In reverse flow-through scenario, the feedwater flowed in an opposite direction (**Figure 3-3b**). For comparison, a flow-by CDI cell was also fabricated without the use of upstream and downstream reservoirs due the fact that feedwater flows in the separator channel, in parallel with the electrodes (**Figure 3-3c**). In order to prevent the short-circuiting between the two electrodes and provide unobstructed flow pathway for the feed water, two layers of separator is used in flow-by CDI cell. A cross-section view of the flow-through CDI is shown in **Figure 3-3d**.



**Figure 3-3.** Schematic of CDI cell configuration, (a) forward flow-through CDI, (b) reverse flow-through CDI, (c) flow-by CDI, (d) the cross-section of the flow-through CDI cell.

#### **3.2.2 Experimental setup**

In all desalination experiments, a feed solution containing 5 mM sodium chloride with an initial DO concentration of 6.5 mg L<sup>-1</sup> was pumped from the recycling container, passed through the CDI cell, and then returned to the recycling container (**Figure 3-4**). The solution flow rate was controlled by a peristaltic pump (Masterflex, Cole-Parmer, USA) to be 0.78 mL s<sup>-1</sup>. The solution conductivity, pH, and DO were monitored using an electrical conductivity (EC) meter (F-54, HORIBA, Japan), a pH meter (F-51, HORIBA, Japan), and a DO probe (DO-BTA, Vernier Corp.), respectively (**Figure 3-1**) (Zhang et al., 2018b). The cell potential, measured by a digital multimeter (Jaycar Electronics, Australia), was set to 0 V prior to the desalination test. During each charging stage, a constant potential was applied between the anode and the cathode for 15 min using a DC power supply. During the discharging step, the CDI electrodes were

short-circuited for 15 min. Prior to each test, the CDI cell was fully flushed using Milli-Q water.



**Figure 3-4.** Schematic of the flow-through CDI cell setup. Two pieces of carbon cloth served as anode and cathode and a DC power source used to provide a constant voltage (1.2 V). Conductivity and pH sensors were used to detect the solution conductivity and pH in the recycling container.

#### 3.2.3 Analytical methods

The salt adsorption capacity (SAC) was calculated according to the equation:

$$SAC = \frac{\left(C_0 - C_t\right) \times V_s}{m}$$
(3-1)

where  $C_0$  and  $C_t$  are the salt concentrations (mg L<sup>-1</sup>) at the beginning of the experiment and at time *t*, respectively.  $V_s$  is the volume of feedwater (100 mL) used in this work and *m* is the total mass of the two carbon electrodes (g).

The charge efficiency ( $\eta_{charge}$ ) can be calculated as follows:

$$\eta_{charge} = \frac{n \times (C_0 - C_t) \times V_s \times F}{M \times \int i dt} \times 100\%$$
(3-2)

where *n* represents the number of electrons needed for the removal of one mole of NaCl,  $V_s$  is the volume of feed water (100 mL), *F* represents the Faraday constant (96,485 C mol<sup>-1</sup>), *M* is the molecular weight of sodium chloride (58.5 g mol<sup>-1</sup>) and *i* represents the current at time *t* (A). Note that t = 0 was defined as the time point when the electrical adsorption was initiated.

The concentration of  $H_2O_2$  was determined using the Amplex Red (AR)/ horseradish peroxidase (HRP) method (He et al., 2016a). Specially, samples were diluted with 10 mM MOPs buffer (pH 7.0~7.1) and mixed with AR/HRP stock solution in which AR is oxidized by  $H_2O_2$  in the presence of horseradish peroxidase (HRP), exhibiting a fluorescence emission maxima at 587 nm upon excitation at 563 nm, allowing the quantification of  $H_2O_2$  in the solution.

#### **3.3 Results and Discussion**

#### 3.3.1 CDI performance

**Figure 3-5a-c** shows the temporal variation of conductivity of the desalinated water in flow-through and flow-by CDI systems. Obviously, it can be observed that salt was removed more effectively in flow-through CDI mode compared to flow-by CDI mode in all scenarios. For instance, when a potential difference of 1.2 V was applied, the feedwater conductivity first decreased sharply and then reached a relatively steady concentration within 15 min. Flow-through CDI operated in forward flow mode achieved the highest salt adsorption capacity (11.1 mg g<sup>-1</sup>), which is 36.3% and 24.3% higher than that of flow-by CDI (8.2 mg g<sup>-1</sup>) and flow-through CDI operated in reverse flow mode (10.2 mg g<sup>-1</sup>). In addition to greatest overall salt removal in the forward

flow-through mode, higher current and charge efficiency (53.6%) was also observed in flow-through CDI operated under forward flow mode (**Figure 3-6** and **Figure 3-5d**).

In flow-through CDI setup, the fluid flows directly through the two electrodes with the result that the micropore spaces become more accessible to the ions, likely leading to the full use of the active sites of the carbon electrodes and improved salt removal performance (Suss et al., 2012, Zhou et al., 2018b). In comparison, the relatively poor performance in flow-by mode might be due to the fact that the feedwater only flows between anode and cathode, which restricts the ion transport from the bulk solution into the inner parts of the electrodes, resulting in insufficient utilization of the adsorption capability of the carbon electrodes and associated low charge efficiency (Figure 3-5b). In flow-by CDI, ions that have been initially adsorbed near the surface sites might act as barriers for further ion diffusion into the deeper sites. Meanwhile, thicker separator in the flow-by system also slightly increased cell internal resistance, therefore, lowering the salt adsorption capacity. It should also be noted that forward flow operation of flow-through CDI resulted in better desalting performance and higher charge efficiency than that achieved in reverse flow mode. Consideration was therefore given to characterising the competing Faradaic electron transfer reactions occurring during the deionization process.



**Figure 3-5.** Comparison of the temporal variation of conductivity at a constant potential of (a) 0.9 V, (b) 1.2 V, (c) 1.5 V in different scenarios (*i.e.*, flow-through CDI operated in forward flow mode, flow-through CDI operated in reverse flow mode and flow-by CDI); (d) comparison of the charge efficiency in different scenarios under a constant voltage of 1.2 V. Experimental conditions: 900 s charging at a constant potential followed by 900 s discharging by short-circulating the two electrodes.



**Figure 3-6.** Temporal variation of the current between different scenarios (*i.e.*, flow-through CDI operated in forward flow mode, flow-through CDI operated in reverse flow mode, flow-by CDI). Experimental conditions: 900 s charging under a constant potential of 1.2 V and 900 s discharging by short-circulating the two electrodes. Symbols: experiment data; Lines: modelling results.

#### **3.3.2 Variation of pH**

Variations of pH of the desalted water in flow-through and flow-by CDI systems are shown in **Figure 3-7a-c** with the results revealing that the pH of the desalted water in flow-through CDI cell fluctuated more severely than in the case of flow-by CDI. For example, under a constant voltage of 1.2 V, pH increased to a peak value of 9.3 during the charging step and then decreased back to ~8.0 in the discharging step in a flow-through CDI operated in forward flow mode. When operated in reverse flow mode, the pH of the CDI effluent changed in a totally different manner with the pH decreasing to 3.8 in the charging stage followed by a gradual increase to ~6.0 in the discharging stage. In flow-by CDI mode, pH increased slightly (to about 8.2) and then remained relatively stable (**Figure 3-7b**). **Figure 3-7d** demonstrated that pH fluctuation extend gradually decreased during prolonged operation.

It has been reported that the pH fluctuations in CDI cells can be induced by both Faradaic and non-Faradaic processes (Porada et al., 2013c). Specifically, non-Faradaic processes including the selective electrosorption of  $H^+$  and  $OH^-$  and asymmetric removal of anions and cations into the EDLs likely lead to imbalance of  $H^+/OH^-$  and pH variation. In a flow-through CDI system, as one ion is preferentially captured in the first electrodes (*e.g.*, Cl<sup>-</sup> first being stored by the anode in forward flow mode), water dissociation occurs in the opposite electrode in order to maintain electroneutrality with these processes contributing to pH fluctuation (*i.e.*, pH increase in forward flow mode).

Different ions in solution have different diffusion coefficients (mobilities), leading to a difference in ion movement and adsorption rate with the result that pH fluctuations occur. For instance, the diffusion coefficient of  $H^+$  (9.13×10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup>) is significantly larger than that of OH<sup>-</sup> (5.16×10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup>) suggesting that H<sup>+</sup> will be more mobile and be adsorbed at a faster rate than OH<sup>-</sup> with this effect potentially contributing to the initial pH rise.

Faradic reactions, which consume/generate  $H^+/OH^-$  during the desalination process, have been recognized to be major contributors to effluent pH fluctuation. For example, anodic Faradaic reactions associated with the oxidation of carbon electrodes (and/or chloride and water) will take place during the desalination process resulting in the generation of H<sup>+</sup> (Eqs 3-8). Additionally, cathodic Faradaic reactions, particularly those involving oxygen reductions, tend to consume H<sup>+</sup> and generate peroxide or water (Eqs 3-9 to 3-11). Possible Faradaic reactions are summarized below:

Anodic oxidation reactions

$$\frac{1}{2}C + \frac{1}{2}H_2O \rightarrow \frac{1}{2}C = O_{ad} + H^+ + e^- \qquad E^0 = 0.21 \text{ V/SHE (3-3)}$$

$$\frac{1}{4}C + \frac{1}{2}H_2O \rightarrow \frac{1}{4}CO_2 + H^+ + e^- \qquad E^0 = 0.21 \text{ V/SHE (3-4)}$$

$$\frac{1}{2}H_2O_2 \rightarrow \frac{1}{2}O_2 + H^+ + e^- \qquad E^0 = 0.69 \text{ V/SHE (3-5)}$$

$$Cl^{-} \rightarrow \frac{1}{2}Cl_{2} + e^{-}$$
  $E^{0} = 1.36 \text{ V/SHE} (3-6)$ 

$$7 \operatorname{Cl}_2 + \operatorname{H}_2 \operatorname{O} \to \operatorname{HClO} + \operatorname{H}^+ + \operatorname{Cl}^-$$
(3-7)

Cathodic reduction reactions

$$\frac{1}{2}O_2 + H^+ + e^- \rightarrow \frac{1}{2}H_2O_2$$
  $E^0 = 0.69 \text{ V/SHE} (3-8)$ 

$$\frac{1}{2}H_{2}O_{2} + H^{+} + e^{-} \rightarrow H_{2}O \qquad E^{0} = 1.78 \text{ V/SHE (3-9)}$$

$$2H_{2}O + 2e^{-} \rightarrow H_{2} + 2OH^{-} \qquad E^{0} = 0 \text{ V/SHE (3-10)}$$

$$C + H_{2}O + e^{-} \rightarrow C - H + OH^{-} \qquad (3-11)$$

The more extreme pH fluctuations observed in flow-through CDI mode compared to flow-by CDI mode are expected as a result of the more abundant reaction sites and faster mass transfer rate (especially of oxygen) to the electrode surface in the flow-through case. Note that when flow-through CDI is operated in forward-flow mode, feedwater first passes through the anode and then the cathode with the result that the anodic Faradaic reactions (Eqs 3-7) will occur first and generate extra H<sup>+</sup> which, subsequently, will be involved in the oxygen reactions (Eqs 3-8 to 3-10) and consumed rapidly at the cathode. Therefore, after the feedwater flows out of the cell (post-cathode), the solution become alkaline reaching a pH value (9.3) higher than that observed in the flow-by system (8.0). In the reverse-flow case, feedwater first enters the cathode, where there are less  $H^+$  to support the oxygen reduction reactions. Subsequently, the feed stream enters the anode, where carbon oxidation occurs with concomitant H<sup>+</sup> production and associated pH decrease (to 3.8). Meanwhile, the decomposition of  $H_2O_2$ (transported from the cathode) at the anode (the reverse of the reaction shown in Eq 3-8) could also contribute to  $H^+$  formation and pH decrease. In the flow-by system, oxygen reduction reactions would be expected to be dominant compared to carbon oxidation reactions under an applied voltage of 1.2 V, which means that more  $H^+$  will be consumed than generated, leading to an increase in effluent pH. However, since the Faradaic reactions are kinetically limited in flow-by mode, the extent of pH fluctuation is less significant than is the case in flow-through mode.



**Figure 3-7.** Comparison of the temporal variation of pH at a constant potential of (a) 0.9 V, (b) 1.2 V, (c) 1.5 V in different scenarios (*i.e.*, flow-through CDI operated in forward flow mode, flow-through CDI operated in reverse flow mode and flow-by CDI); (d) pH variation when operating the system for 5 cycles under a constant voltage of 1.2 V. Experimental conditions: 900 s charging at a constant potential followed by 900 s discharging by short-circulating the two electrodes.

#### 3.3.3 H<sub>2</sub>O<sub>2</sub> Production and DO Decay

The oxygen reduction activity of carbon cloth was examined by CV in N<sub>2</sub> and O<sub>2</sub> saturated NaCl solution. As shown in **Figure 3-8**, a reduction peak appeared when using O<sub>2</sub>-saturated electrolyte, whereas a featureless curve was observed within the same voltage window in the N<sub>2</sub>-saturated electrolyte, indicating the electrocatalytic activity of carbon electrode for oxygen reduction. The profiles of H<sub>2</sub>O<sub>2</sub> concentration versus time during charging and discharging in the three scenarios are presented in **Figure 3-9a**. It can be observed that H<sub>2</sub>O<sub>2</sub> concentration increased rapidly at the start of

the charging step but then gradually decreased in both flow-through CDI operated in forward flow mode and flow-by CDI, with the maximum  $H_2O_2$  concentration reaching 45 and 37.5  $\mu$ M, respectively. In reverse flow-through mode,  $H_2O_2$  concentration exhibited a relatively slower increase and achieved a peak value of 17.6  $\mu$ M at the end of the charging step. The charge consumed for  $H_2O_2$  production accounted for 4.7%, 1.8% and 4.2% of the total charge applied for forward flow, reverse flow and flow-by system, respectively.



**Figure 3-8.** Cyclic voltammetry (CV) curves of carbon electrodes in  $N_2$  (dash line) and  $O_2$  (solid line) saturated solution with a scan rate of (100 mV s<sup>-1</sup>).

The production of  $H_2O_2$  is expected to be accompanied by a decrease in DO concentration. **Figure 3-9b** presents the temporal variation of DO concentration during charging and discharging cycles in the three scenarios. As expected, DO decreases rapidly in all cases during the charging period. The forward flow-through CDI system showed the largest rate of DO decay, with the DO concentration declining from ~6.5 to ~3.1 mg L<sup>-1</sup>, while the least DO consumption (~6.5 to ~4.2 mg L<sup>-1</sup>) was observed in reverse flow mode. In contrast, the DO decrease rate in the flow-by CDI system was between the flow-through cases.



**Figure 3-9.** Comparison of the temporal variations of (a)  $H_2O_2$  and (b) DO in different scenarios (*i.e.*, flow-through CDI operated in forward flow mode, flow-through CDI operated in reverse flow mode, and flow-by CDI). Experimental conditions: 900 s charging at a constant potential of 1.2 V and 900 s discharging by short-circulating the two electrodes.

In flow-through CDI operated in forward flow mode,  $H^+$  generated from anodic Faradaic reactions will pass directly into the cathode, altering the local feedwater composition and contributing to sequential cathodic Faradaic reactions (**Figure 3-10**). In accord with this, relatively rapid H<sub>2</sub>O<sub>2</sub> production and DO consumption are observed in forward flow mode. However, in reverse flow mode, the solution first enters the cathode, where oxygen reduction and H<sub>2</sub>O<sub>2</sub> formation reactions are expected to occur first (**Figure 3-10**). With this flow pattern, the local H<sup>+</sup> concentration in the cathode will be much lower than is the case in forward flow mode and, as such, the oxygen reduction reaction will, therefore, be somewhat supressed. In addition, once the feedwater passes into the anode, the H<sub>2</sub>O<sub>2</sub> formed at cathode will be further decomposed into water. All these factors presumably contribute to the lower H<sub>2</sub>O<sub>2</sub> generation rate and DO decay rate observed in the reverse flow scenario than in the forward flow case. In the flow-by CDI case, the Faradaic reactions are less significant than in the forward flow configuration as they are constrained by the mass diffusion rate and limited reaction sites.



**Reverse flow mode** 

**Figure 3-10.** Schematic diagram about the capacitive ion storage process and Faradaic reaction processes in flow-through system which operated in (a) forward flow mode, (b) reverse flow mode. Ions are preferentially electroadsorbed and Faradaic reactions are sequentially occurred depending on the flow direction resulting in the pH variation in the system. The black arrows indicate the electrode repulsion of ions with the same charge.

#### **3.3.4 Electrode potentials**

To further investigate the occurrence of these Faradaic reactions, the variations of both anode and cathode potentials were measured using an in situ inserted Ag/AgCl reference electrode. As presented in **Figure 3-11**, asymmetric distributions of applied potential were observed in the CDI system. Both the anode and cathode potentials were

around 0.3 V/SHE prior to the operation, however, on commencement of charging, the anode potentials immediately increased to about 0.8 V while the cathode potentials dropped to -0.4~-0.3 V in all scenarios. Interestingly, the potentials (both anode and cathode) of the forward flow mode were slightly lower than other operational modes, favouring the occurrence of cathodic Faradaic reactions (*i.e.*, oxygen reduction) and supressing the anodic Faradaic reactions (*i.e.*, carbon oxidation). The lower cathode potential would also enhance cation adsorption onto the lower-efficiency cathode, therefore, leading to better salt removal performance. As for the reverse flow mode, higher potentials (anode: ~1.0 V/SHE, cathode: -0.2 V/SHE) were observed during the charging periods, which could result in more severe anodic carbon oxidation and lower effluent pH.



**Figure 3-11.** Variation of the measured anode and cathode potential versus standard hydrogen electrode (SHE) between different scenarios (*i.e.*, flow-through CDI operated in forward flow mode, flow-through CDI operated in reverse flow mode, flow-by CDI). Experimental conditions: 900 s charging at a constant potential of 1.2 V and 900 s discharging by short-circulating the two electrodes.

#### **3.3.5** Environmental implications

Flow-through configurations have been widely applied in a number of fields including microbial fuel cells (Katuri et al., 2011, Zhang et al., 2015a), electrochemical advanced oxidation processes (Gao et al., 2015a, Zaky and Chaplin 2013), electrochemical disinfection (Rahaman et al., 2012, Vecitis et al., 2011) and capacitive desalination (Andelman 2011, Suss et al., 2012). It has been reported that the fluid flow through the carbon electrode enhanced the mass transfer and promoted direct electron transfer, resulting in an increase of electrochemical kinetics and efficiencies by up to 10-fold (Ji et al., 2015, Liu et al., 2013). Additionally, flow-through architecture provides the possibility of full utilization of the active sites of the carbon electrodes.

With regard to desalination, our results demonstrate that using a flow-through design could improve the desalination performance, a finding in line with previous work (Suss et al., 2012). Scope exists for enhancement of the desalination performance using this promising configuration and further work should be undertaken in terms of novel electrode design, operational parameter optimization and fluid modelling.

It should be noted however that the flow-through CDI configuration promotes redox reactions to a greater extent compared to flow-by. This can be a double-edged sword. On one hand, more severe Faradaic reactions can exacerbate the oxidation of the carbon electrodes leading to desalination performance decline and energy loss. In line with more facile redox reactions, larger pH fluctuations were observed in flow-through configuration, potentially leading to more severe precipitation and scaling of the carbon electrodes with these processes reducing the long-term stability of membrane and electrode materials (Cohen et al., 2015, Nir et al., 2015) In addition, these pH variations can also result in a deterioration in water quality as a result of pH values outside the accepted range. Fortunately, a number of strategies including optimization of the voltage window, constant current operation, periodic electrode polarity reversal, and use of a deoxygenation cell can be applied to effectively reduce (or even eliminate) these Faradaic side effects (Zhang et al., 2018a).

On the other hand, if managed properly, some of the Faradaic reactions can be beneficially utilized. For example, the H<sub>2</sub>O<sub>2</sub> produced via cathodic oxygen reduction, when combined with O<sub>3</sub> or UV irradiation, could be potentially applied for water disinfection or contaminant degradation. In forward flow mode, the oxygen reduction reactions were enhanced with a maximum 45  $\mu$ M H<sub>2</sub>O<sub>2</sub> produced. As previous works have shown, this H<sub>2</sub>O<sub>2</sub> concentration, if incorporated with O<sub>3</sub> or UV, is sufficient to promote bacterial inactivation by 0.5-2.0 log units (Cho et al., 2011, Cho and Yoon 2006, Lanao et al., 2008, Rubio et al., 2013). In addition, if the cathode contains elemental iron or an iron oxide, the presence of electrochemically generated H<sub>2</sub>O<sub>2</sub> may initiate a Fenton process with associated *in situ* generation in the CDI cell of powerful oxidants such as the hydroxyl radical which may contribute to both the degradation of any micro-pollutants present and prevention of biofilm growth on the cathode.

## **3.4 Conclusions**

In this study, we have investigated both the desalination and Faradaic processes occurring in a flow-through CDI system operated in different flow modes. A flow-through CDI operated in forward flow mode exhibited the best salt removal performance compared to flow-through CDI operated in reverse flow mode and flow-by CDI. Another outcome is the recognition that pH fluctuations become more severe when adopting the flow-through configuration with the pH of the treated stream increasing to about 9.3 under forward flow mode and decreasing to 4.0 under reverse flow mode. Additionally, the quantities of H<sub>2</sub>O<sub>2</sub> generated exhibited significant differences when applying different configurations and flow modes. Specifically, the

 $H_2O_2$  produced in the CDI was 45, 37.5, and 17.6  $\mu$ M, corresponding to flow-through CDI operated in forward flow mode, flow-by CDI and flow-through CDI operated in reverse flow mode, respectively, with these differences most likely a consequence of the difference in rate and extent of the occurrence of Faradaic reactions in different flow modes. Since much higher  $H_2O_2$  concentrations are generated in forward flow mode compared to the other operational modes, this operational mode combined with  $O_3$  or UV irradiation could potentially contribute to water disinfection or contaminant degradation during desalination.

# Chapter 4. Active chlorine mediated ammonia oxidation revisited: reaction mechanism, kinetic modelling and implications

## 4.1 Introduction

Ammonia removal from wastewaters has attracted much attention in recent decades given the concerns associated with discharge of this critical nutrient with particular problems including eutrophication of receiving waters, the generation of offensive odours and complications associated with the disinfection of water supplies (Buffle et al., 2004, Huang et al., 2008). A variety of ammonia removal technologies including air stripping (Bonmati and Flotats 2003), ion exchange (Jorgensen and Weatherley 2003), adsorption (Wang et al., 2006), chemical precipitation (Li et al., 1999), electrochemical stripping (Tarpeh et al., 2018a, Zhang et al., 2017), biological nitrification/denitrification (Kalyuzhnyi et al., 2006) and break-point chlorination (Pressley et al., 1972) have been applied extensively in the treatment of municipal and industrial wastewaters with each of these technologies exhibiting particular limitations. For example, air stripping consumes large amounts of energy and may result in air pollution problems when ammonia is transformed from aqueous to gas phase. Additionally, this technology exhibits poor removal efficiency at low ammonia concentrations (Obaid-ur-Rehman and Beg 1990). Biological methods require a series of reactors to achieve the range of functions required (i.e., nitrification, denitrification and solid-liquid separation) with the denitrification efficiency largely constrained by the biodegradable organic content in the wastewater (Ruiz et al., 2003). Breakpoint chlorination possesses risks related to the transport, storage and the handling of active chlorine with challenges also associated with the optimization of the dosing of active chlorine.

In recent years, an electrochemical advanced oxidation process (EAOP) has emerged as a promising approach to ammonia removal with advantages including minimal production of secondary waste, amenability to automation, versatility, and safety (Li and Liu 2009, Pérez et al., 2012). It has been reported that EAOPs are effective for the treatment of ammonia-containing wastewaters from tanneries (Vlyssides and Israilides 1997), power plants (Vanlangendonck et al., 2005), municipal sources (Li and Liu 2009) and landfills (Ye et al., 2016).

Ammonia (in either ammonium ion  $(NH_4^+)$  or deprotonated  $NH_{3(aq)}$  forms) can be removed by (i) direct anodic oxidation and/or (ii) indirect oxidation mediated by the electro-generated active chlorine. In the direct oxidation pathway,  $NH_3$  is firstly adsorbed to the anode surface and subsequently decomposed, principally to harmless nitrogen gas, as a result of anodic electron transfer as shown in Eq. 4-1 (Kapałka et al., 2010, Kim et al., 2006, Zöllig et al., 2015b):

$$2NH_3 + 6OH^- \rightarrow N_2 + 6H_2O + 6e^-$$
 (4-1)

However, direct ammonia oxidation requires the adjustment of wastewater pH to values greater than the  $pK_a$  of the NH<sub>4</sub><sup>+</sup>/NH<sub>3</sub> acid-base pair (i.e., pH > 9.25) because NH<sub>4</sub><sup>+</sup> cannot be oxidized directly at the anode (Zöllig et al., 2015a). Furthermore, the low reaction rate and high cost of the electrodes (usually platinum) restricts the practical application of this technology (Zöllig et al., 2015b).

Indirect oxidation, which takes advantage of *in situ* generation of active chlorine at the anode to oxidize ammonia to nitrogen gas, is more commonly used

(Ding et al., 2015, Xiao et al., 2009, Ye et al., 2016). This approach is much faster, more efficient and cost effective than direct oxidation provided sufficient chloride ion (>300 mg  $L^{-1}$ ) is present in the wastewater stream (Kim et al., 2006). The overall reactions resulting in N<sub>2</sub> production are as follows:

$$2\mathrm{Cl}^{-} \to \mathrm{Cl}_{2} + 2\mathrm{e}^{-} \tag{4-2}$$

$$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$$
(4-3)

$$2NH_{4}^{+} + 3HOCl \rightarrow N_{2} + 3H_{2}O + 5H^{+} + 3Cl^{-}$$
(4-4)

Limited insight regarding the precise mechanism and reaction kinetics of the active chlorine-mediated ammonia oxidation process is currently available. Traditionally, it has been considered that the indirect electrochemical ammonia oxidation process (EAOP) occurs via a mechanism similar to that of the intensively studied breakpoint chlorination. That is, ammonia first reacts with the active chlorine species (HOCl or OCl<sup>-</sup>) and, stepwise, generates chloramine species, i.e., monochloramine, dichloramine and trichloramine, and finally nitrogen gas when the active chlorine/ammonia mole ratio gradually reaches 1.5 (Mergerum et al., 1978, Qiang and Adams 2004). However, results of a number of electrochemical indirect ammonia oxidation studies indicate that the transformation of ammonia into nitrogen gas takes place at the very beginning of the electrolysis process and long before an active chlorine/ammonia mole ratio of 1.5 is attained (Kim et al., 2006, Li and Liu 2009, Vanlangendonck et al., 2005). These findings suggest that the mechanism of EAOP differs from that of the conventional breakpoint chlorination process and, as such, requires clarification. Not surprisingly, given the variety of Faradaic reactions that may occur at both anode and cathode as well as the various solution phase reactions that may influence the rate and extent of ammonia oxidation, there has been limited attempt to develop mechanistically-based models of the overall process. As such, the objectives of

this work are to (i) determine the effects of operating parameters such as initial chloride concentration and current density on the rate and extent of ammonia removal, and (ii) development of a detailed mechanistically-based kinetic model providing insight into the complex interactions that occur during electrochemically-mediated ammonia oxidation processes that will assist in optimising implementation of the technology.

## 4.2 Materials and Methods

#### 4.2.1 Chemical reagents

All solutions were prepared using ultrapure 18 M $\Omega$  cm Milli-Q water (MQ, Millipore). Analytical grade chemicals, *i.e.*, ammonium sulfate, sodium sulfate, sodium chlorate, sodium perchlorate, sodium hypochlorite, etc., were purchased from Sigma-Aldrich (or as otherwise stated) and used without further refinement.

#### 4.2.2 Experimental setup

The batch mode experiments were conducted in an open Plexiglass cubic cell at room temperature (25 °C). The commercial RuO<sub>2</sub>/TiO<sub>2</sub>/Ti electrode purchased from BaoJi Changli Special Metal Co., Ltd served as the anode with a size of  $10 \times 10$  cm<sup>2</sup> and a thickness of 0.1 cm. A piece of titanium plate was used as the cathode (BaoJi Changli Special Metal Co., Ltd) with the same dimensions as the anode. Both the anode and cathode were placed vertically and parallel to each other with the gap between the two electrodes maintained at 8 cm (**Figure 4-1**).



**Figure 4-1.** Schematic showing key processes involved in ammonia removal in an undivided electrochemical cell.

#### **4.2.3 Experimental methods and calculations**

A range of factors influencing ammonia removal in the electrochemical advanced oxidation process was investigated including applied current density, initial  $Cl^-$  concentration, initial pH (pH<sub>0</sub>) and initial ammonia concentration. During our experiments, a DC power source was used to provide constant current densities (ranged from  $1 \sim 5 \text{ mA cm}^{-2}$ ) for the electrochemical cell. Initial  $Cl^-$  concentrations varied from 5 mM to 50 mM. Wastewater pH<sub>0</sub> values were adjusted using either 1 M NaOH or 1 M H<sub>2</sub>SO<sub>4</sub>. Each experiment was operated in batch mode and lasted for 90 min. Samples were taken from the electrochemical cell every 5 minutes for analysis of ammonium, nitrite, nitrate, chloride, chlorate and perchlorate concentrations using an ICS-3000 ion chromatograph (Dionex, U.S.). The DPD (N,N-diethyl-p-phenylenediamine) method

was used to determine the concentrations of active chlorine and chloramine that were generated during electrolysis (APHA 2012).

Current efficiency and energy consumption are two key parameters that may be used to evaluate the performance of an electrochemical technology. Current efficiency can be expressed as:

$$CE = \frac{n_i \times F \times (C_0 - C_t) \times V}{M \times \int_0^t IA dt} \times 100$$
(4-5)

where  $C_0$  is the initial concentration (mg L<sup>-1</sup>) of NH<sub>4</sub><sup>+</sup>-N,  $C_t$  is the concentration (mg L<sup>-1</sup>) of NH<sub>4</sub><sup>+</sup>-N at electrolysis time *t* (s), *V* represents the volume of the electrolyte (0.09 L), *M* is the molar mass of NH<sub>4</sub><sup>+</sup>-N (14 g mol<sup>-1</sup>), *I* is the current density (A m<sup>-2</sup>), *A* is the effective surface area of the electrodes (0.01 m<sup>2</sup>), *F* represents the Faraday constant (96485.3 C mol<sup>-1</sup>) and *n* represents the number of electrons needed for the oxidation of one mole of NH<sub>4</sub><sup>+</sup>-N (3 for oxidation of NH<sub>4</sub><sup>+</sup>-N to N<sub>2</sub>). The prediction of required ammonia degradation time was obtained based on kinetic modelling data of time when NH<sub>4</sub><sup>+</sup>-N concentration decreased below 1 mg L<sup>-1</sup>.

Specific energy consumption (kWh kg<sup>-1</sup> N) can be calculated as shown in Eq. 4-6:

$$EC = \frac{\int_0^t UIA dt}{3.6 \times (C_0 - C_t) \times V}$$
(4-6)

where U is the voltage of the electrochemical cell (V).

#### 4.2.4 Kinetics modelling

According to a hypothesized reaction set describing all key chemical reactions occurring in the system, the concentrations of reactants and products (given specific initial conditions and rate constants) predicted to be present at any given time during the electrochemically-mediated active chlorine production and ammonia oxidation processes were determined by numerically solving the differential equations corresponding to the rate expressions for the hypothesized reactions using the kinetic modelling software Kintek Explorer (Qiu et al., 2015).

## 4.3 Results

#### 4.3.1 Chlorine evolution

The electrochemical system was first employed for examination of the evolution of chlorine species in the absence of ammonia at initial Cl<sup>-</sup> concentrations of 10 mM and 20 mM under three different current densities (*i.e.*, 1, 3 and 5 mA cm<sup>-1</sup>). As illustrated in **Figure 4-2**, the gradual loss of Cl<sup>-</sup> with a concomitant increase in active chlorine concentration indicated that Cl<sup>-</sup> was converted into active chlorine at the anode surface (Reactions 1-6 in Table 1). Higher current density and initial Cl<sup>-</sup> concentration resulted in faster active chlorine formation and higher steady state concentrations of active chlorine. For example, when an initial Cl<sup>-</sup> concentration of 20 mM was applied during the electrolysis, steady-state active chlorine concentrations of  $1.4 \sim 1.5$ ,  $2.7 \sim 2.9$  and  $3.3 \sim 3.5$  mM were obtained at current densities of 1, 3 and 5 mA cm<sup>-1</sup> respectively. A similar dependence was observed for the 10 mM Cl<sup>-</sup> case with active chlorine concentrations reaching  $0.8 \sim 0.9$ ,  $1.3 \sim 1.5$  and  $1.5 \sim 1.8$  mM at current densities of 1, 3 and 5 mA cm<sup>-1</sup> respectively.

#### 4.3.2 Active chlorine-mediated ammonia oxidation

**Figure 4-3** demonstrates the effects of current density and Cl<sup>-</sup> concentration on the removal of ammonia during 90-min reaction. It can be seen from these results that a higher current density leads to more rapid ammonia oxidation. When a current density of 1 mA cm<sup>-2</sup> was applied, only 9.0% of NH<sub>4</sub><sup>+</sup>-N could be degraded in 40 min at an initial Cl<sup>-</sup> concentration of 10 mM. The removal rates increased dramatically to 43.2% and 88.0% on increasing the current density to 3 and 5 mA cm<sup>-2</sup> respectively. A similar trend was observed for the 20 mM Cl<sup>-</sup> case while enhanced ammonia removal rates (*i.e.*, 17.8%, 87.5%, and 97.7%) were observed following 90-min operation at current densities of  $1 \sim 5 \text{ mA cm}^{-2}$ .



**Figure 4-2.** Variation of Cl<sup>-</sup> and active chlorine concentrations during the electrolysis of solutions containing different initial concentrations of Cl<sup>-</sup> at current densities of  $1 \sim 5$  mA cm<sup>-1</sup> and initial pH of 6. (a) I = 1 mA cm<sup>-1</sup> and [Cl<sup>-</sup>]<sub>0</sub> =10 mM, (b) I = 3 mA cm<sup>-1</sup> and [Cl<sup>-</sup>]<sub>0</sub> =10 mM, (c) I = 5 mA cm<sup>-1</sup> and [Cl<sup>-</sup>]<sub>0</sub> =10 mM, (d) I = 1 mA cm<sup>-1</sup> and [Cl<sup>-</sup>]<sub>0</sub> =20 mM, (e) I = 3 mA cm<sup>-1</sup> and [Cl<sup>-</sup>]<sub>0</sub> =20 mM and (f) I = 5 mA cm<sup>-1</sup> and [Cl<sup>-</sup>]<sub>0</sub> =10 mM. Solid lines represent the results of kinetic modelling.

The variation of  $NH_4^+$ -N concentrations for different initial Cl<sup>-</sup> concentrations is presented in **Figure 4-4**. An initial Cl<sup>-</sup> concentration of 5 mM was too low to achieve an effective result. When the Cl<sup>-</sup> concentration was higher than 10 mM, the treatment was satisfactory, with the near-complete ammonia removal in 10, 40 and 80 min in the solutions containing 50, 20 and 10 mM Cl<sup>-</sup>, respectively.



**Figure 4-3.**  $NH_4^+$ -N removal at different current densities with initial Cl<sup>-</sup> concentrations of (a) 10 mM and (b) 20 mM. Initial pH 6.0. Solid lines represent the results of kinetic modelling.



Figure 4-4. Variation of  $NH_4^+$ -N using different initial Cl<sup>-</sup> concentrations under constant current density and initial pH of 6.0 in all cases. Solid lines represent the results of kinetic modelling.

Initial pH was observed to exert much less significant influence on ammonia removal than either current density or Cl<sup>-</sup> concentration in our electrochemical system. As can be seen from **Figure 4-5**, the degradation of ammonia exhibited little difference for various initial pH conditions (pH<sub>0</sub> = 3, 6 and 9). Bulk solution pH decreased during the electrolysis process to similar values whatever the initial pH (**Figure 4-6**) with this decrease a result of the abundant generation of H<sup>+</sup> through both hypochlorite generation and indirect ammonia oxidation reactions (reactions 3 and 4) and as a result of other side-reactions such as water splitting (**Figure 4-6**). In addition, the insignificant effect of initial pH on ammonia removal could be attributed to the fact that ammonia degradation mainly takes place close to the anode surface where the local pH is likely to be minimally affected by initial pH. Other investigators have also found that initial pH exerts little impact on ammonia degradation while current density and Cl<sup>-</sup> concentration appear to be the rate-determining parameters (Li and Liu 2009, Xiao et al., 2009). Results showing the effects of initial ammonium concentrations and current density are provided in the supplementary information (**Figure 4-7** and **Figure 4-8**).



Figure 4-5. Effect of initial pH on  $NH_4^+$ -N removal performance. Electrolysis conditions: current density 3 mA cm<sup>-2</sup>, initial Cl<sup>-</sup> concentration 10 mM.



**Figure 4-6.** Variation of the bulk solution pH during the electrolysis process for different initial pH with current density of 3 mA cm<sup>-2</sup> and initial Cl<sup>-</sup> concentration of 10 mM.



**Figure 4-7.**  $NH_4^+$ -N removal at different initial ammonia conditions. Electrolysis conditions: constant current density of 3 mA cm<sup>-2</sup>, initial Cl<sup>-</sup> concentration of 10 mM and initial pH of 6.0. Solid lines represent the results of kinetic modelling.



**Figure 4-8.**  $NH_4^+$ -N concentration variation using different current densities at a constant initial Cl<sup>-</sup> concentration of 10 mM and initial pH of 6.0.

**Figure 4-9** shows the temporal variation in  $Cl^-$  and active chlorine concentrations during ammonia oxidation. In all cases, the concentration of  $Cl^-$  was relatively stable until NH<sub>4</sub><sup>+</sup>-N was completely removed. Specifically, obvious decrease in the Cl<sup>-</sup> concentration occurred following 70 and 40 min reaction at 3 and 5 mA cm<sup>-2</sup> at an initial Cl<sup>-</sup> of 10 mM (**Figure 4-9a**) while increase in the initial Cl<sup>-</sup> concentration to 20 mM resulted in a similar but earlier decrease in Cl<sup>-</sup> concentrations (**Figure 4-9b**). In comparison, when the current density was fixed at 1 mA cm<sup>-2</sup>, no significant change in chloride concentrations was observed with this result likely associated with the residual of ammonia in the solutions over the course of the experiments (**Figure 4-3**).

Active chlorine was also monitored as it plays a crucial role in ammonia removal through the aforementioned reactions (Eqs 4-2 to 4-4). Initially, a low concentration of active chlorine was detected due to its rapid consumption in the indirect ammonia oxidation process while it increased to a relatively high value following the complete degradation of ammonia (**Figure 4-9c** and **d**). With the use of 10 mM Cl<sup>-</sup>, active chlorine began to accumulate from 40 min and 70 min at current densities of 5 and 3 mA cm<sup>-2</sup>, respectively. For a higher initial Cl<sup>-</sup> concentration of 20

mM, the concentration of active chlorine increased earlier (**Figure 4-9d**). It should be noted that the steady-state concentrations of resultant active chlorine were quite comparable to the control experiments (**Figure 4-2**). In contrast, the active chlorine concentrations were low throughout the whole electrolysis process at 1 mA cm<sup>-2</sup>.

It is expected that the electrochemical ammonia oxidation process commences with the anodic oxidation of Cl<sup>-</sup> to active chlorine which subsequently reacts with ammonia resulting in the production of nitrogen gas (Eqs 4-2 to 4-4). Meanwhile, active chlorine is reduced to Cl<sup>-</sup>. The dashed lines in **Figure 4-9** represent the time up until which the Cl<sup>-</sup> concentration does not change significantly and active chlorine does not accumulate as (prior to these critical times) it is reacting with ammonia that is still present As such, Cl<sup>-</sup> can be regarded as a "catalyst" for electrochemical ammonia degradation up to these times. However, once the concentration of ammonia has decreased to zero, the Cl<sup>-</sup> concentration begins to decrease with active chlorine thereafter accumulating in a manner similar to that shown in **Figure 4-2**.

## **4.3.3 By-products generation**

The generation of hazardous by-products such as chlorate and perchlorate is one main drawback of EAOPs applied to water/wastewater containing chloride. In our system, chlorate was the only chloro-species detected in all conditions with the concentrations of perchlorate well below the detection limit.


**Figure 4-9.** Temporal variation of chlorine species in the electrochemical system treating wastewater containing 50 mg  $L^{-1}$  NH<sub>4</sub><sup>+</sup>-N. Chloride with an initial concentration of (a) 10 mM and (b) 20 mM, and active chlorine with an initial Cl<sup>-</sup> concentration of (a) 10 mM and (b) 20 mM. Initial pH 6.0. Solid lines represent the results of kinetic modelling. The dotted lines represent the turning point where the Cl<sup>-</sup> start to decrease and active chlorine concentration begin to accumulate.

The formation of chlorate during the electrolysis of the solution without ammonia is shown in **Figure 4-10a** and **b**. Relatively low concentrations of chlorate were generated at the lowest current density applied (1 mA cm<sup>-2</sup>). Not surprisingly, chlorate concentration increased on increasing the applied current density to 5 mA cm<sup>-2</sup> with 112 and 193  $\mu$ M chlorate produced after 90 min electrolysis of solutions containing 10 mM and 20 mM Cl<sup>-</sup>. Nevertheless, the final chlorate concentrations in this electrochemical cell were less than 1% of the initial Cl<sup>-</sup> concentration, which is one order of magnitude lower than those observed in other similar electrochemical ammonia

removal systems (Jung et al., 2010b, Lin et al., 2016), suggesting that by-products generation was suppressed in our cell.

When ammonia was present in the electrolyte, as shown in **Figure 4-10c** and **d**, the formation of chlorate was initially inhibited but increased rapidly once ammonia had been completely removed (as a result of oxidation by electro-generated chlorine). With an initial Cl<sup>-</sup> concentration of 10 mM, the chlorate concentration reached 0.5, 1.2 and 1.9  $\mu$ M at the time point when most ammonia was removed at current densities of 1, 3 and 5 mA cm<sup>-2</sup>, respectively. For a higher initial Cl<sup>-</sup> concentration (**Figure 4-10d**), the chlorate generation was relatively faster, with 1.2, 2.0 and 2.4  $\mu$ M formed at the end of the ammonia removal period for current densities, respectively, of 1, 3 and 5 mA cm<sup>-2</sup>. These values are lower than the guideline (8.4  $\mu$ M) suggested by WHO (WHO 2011) though once ammonia was exhausted, the chlorate production exhibited a similar trend to the ammonia-free cases (**Figure 4-10a** and **b**) with the chlorate concentrations increasing to more than 100  $\mu$ M following 90 min of reaction.

During the sequential oxidation of ammonia with *in situ* generated free chlorine, most of the ammonia would be expected to convert to  $N_2$  (Reactions 7-10 in Table 1) though a portion could transform into other nitrogenous by-products such as nitrite and nitrate via reactions such as that shown in Eq 4-7:

$$NH_4^+ + 4HOCl \rightarrow NO_3^- + H_2O + 6H^+ + 4Cl^-$$
 (4-7)



**Figure 4-10.** Formation of chlorate at different current densities in solutions containing no ammonia and (a) 10 mM and (b) 20 mM initial chloride, and solutions containing 50 mg  $L^{-1}$  ammonia and (c) 10 mM and (d) 20 mM initial chloride. Initial pH 6.0. Solid lines represent the results of kinetic modelling.

In all experiments described here, the concentration of nitrite was below the detection limit while a small quantity of nitrate was observed. Typical profiles of nitrate formation are shown in **Figure 4-11** with the production of nitrate commencing at the beginning of each experiment and the concentration increasing continuously until a plateau was reached at approximately the time at which ammonia was totally removed. The generation rate of nitrate increased with increase in current density and initial Cl<sup>-</sup> concentration with the nitrate concentration reaching more than 100  $\mu$ M when 5 mA cm<sup>-2</sup> current density and 20 mM Cl<sup>-</sup> were used. Nevertheless, this value is far below drinking water guideline values (806  $\mu$ M) (WHO 2011). Due to very limited

information on steady-state concentration of nitrite, only an overall reaction (Reaction 12 in Table 1) has been introduced to the kinetic model with an excellent description of formation of nitrate achieved from the kinetic modelling of our experimental data (**Figure 4-11**). Chloramine is, potentially, another nitrogen by-product that could be formed during the active chlorine mediated ammonia oxidation process. In our experiments, however, minimal concentrations of chloramine (< 10  $\mu$ M) were detected after 90 min electrolysis with this accounting for less than 0.5% of the initial NH<sub>4</sub><sup>+</sup>-N concentration (data not shown).



**Figure 4-11.** Formation of nitrate at different current densities with initial Cl<sup>-</sup> concentration of (a) 10 mM, and (b) 20 mM. Initial pH 6.0. Solid lines represent the results of kinetic modelling.

#### 4.3.4 Current efficiency and energy consumption

As mentioned earlier, current efficiency and energy consumption are two key parameters used to evaluate the performance of electrochemical processes. As illustrated in **Figure 4-12a**, at a current density of 3 mA cm<sup>-2</sup>, the current efficiency (*CE*) was 2.9% for a 5 mM Cl<sup>-</sup> solution but increased sharply to 6.7%, 14.6%, and 46.1% if higher Cl<sup>-</sup>concentrations of 10, 20 and 50 mM were employed. Results presented in **Figure 4-12b** indicate that the current efficiency first increased with increase in current density and then decreased, with the maximum value achieved at 3 mA cm<sup>-2</sup>. In contrast,

energy consumption exhibits a negative relationship with  $Cl^-$  concentration. The electrochemical cell operated with initial  $Cl^-$  concentration of 50 mM and current density of 3 mA cm<sup>-2</sup> consumed the lowest energy (39.9 kWh kg N<sup>-1</sup>) of the various operating conditions examined with this value one order of magnitude lower than that reported in previous work (Yang et al., 2016b) (**Figure 4-12c** and **d**).



**Figure 4-12.** Current efficiency (a) as a function of  $Cl^-$  concentration at a constant current density of 3 mA cm<sup>-2</sup> and (b) as a function of current density for solutions containing 10 mM and 20 mM Cl<sup>-</sup>. Energy consumption (c) as a function of Cl<sup>-</sup> concentration at a constant current density of 3 mA cm<sup>-2</sup> and (d) as a function of current density. Initial pH 6.0 in all scenarios.

# 4.4 Discussion

Although the electrochemical ammonia oxidation process has now been described by a number of investigators, understanding of the detailed mechanism of

chlorine evolution and ammonia removal remains relatively preliminary. To assist our understanding, we here-in develop a mechanistically-based kinetic model to describe the anodic chlorine evolution and the resultant indirect ammonia oxidation processes. The core components of the model include (i) active chlorine evolution during the electrolysis of NaCl solution (in the absence of ammonia) and (ii) indirect ammonia oxidation by *in situ* generated active chlorine (**Table 4-1**).

#### 4.4.1 Active chlorine evolution

The *in situ* electro-generated free chlorine is recognized to be the principal agent responsible for the oxidation of ammonia. **Figure 4-3** shows the electrolytic generation of chlorine in the absence of ammonia with the observed behaviour following the classical Volmer-Heyrovsky (V-H) mechanism (Hansen et al., 2010, Trasatti 1987). According to this mechanism, chloride ion is first adsorbed on the metal-oxide electrode and is transformed into the chloride radical and, in the process, releases an electron (Reaction 1 in **Table 4-1**):

$$MO_{x} + Cl^{-} \xrightarrow{k_{1}} MO_{x}(Cl^{\bullet}) + e^{-}$$
(4-8)

In the following Heyrovsky step, the generated Cl<sup>•</sup> combines with the Cl<sup>-</sup> near the electrodes to produce chlorine (Reaction 2 in **Table 4-1**):

$$MO_{v}(Cl^{\bullet}) + Cl^{-} \xrightarrow{k_{2}} MO_{v} + Cl_{2} + e^{-}$$
 (4-9)

Alternatively, two Cl<sup>•</sup> radicals can combine and generate chlorine through the Volmer-Tafel reaction (Reaction 3 in **Table 4-1**):

$$MO_x(Cl^{\bullet}) + MO_x(Cl^{\bullet}) \xrightarrow{k_3} 2MO_x + Cl_2$$
 (4-10)

Subsequently, the hydrolysis of Cl<sub>2</sub> occurs (Reaction 4 in **Table 4-1**):

$$Cl_2 + H_2O \xrightarrow{k_4} HOCl + H^+ + Cl^-$$
(4-11)

The hypochlorous acid generated at the anode can then be reduced to chloride ion at the cathode surface (Reaction 5 in **Table 4-1**):

$$HOC1 + 2e^{-} \xrightarrow{k_{5}} C1^{-} + OH^{-}$$

$$(4-12)$$

The main side reactions involve the further anodic oxidation of HOCl/OCl<sup>-</sup> to chlorate (Reaction 6 in **Table 4-1**) (Yang et al., 2016b):

$$MO_{x}(2H_{2}O) + HOC1 \xrightarrow{k_{6}} MO_{x} + CIO_{3}^{-} + 5H^{+} + 4e^{-}$$

$$(4-13)$$

Here, reaction 1 and reaction 5 in Table 1 are the two key reactions that determine formation and decay of active chlorine while reaction 6 has an insignificant effect as the transformation of active chlorine to chlorate is negligible. Indeed, the active chlorine concentration was controlled by the ratio of reactions 1 and 5. By maintaining the ratio of the rate constants for reactions 1 and 5 constant at each current density, we can obtain the values of these rate constants on the basis of best fit to the experimental data for formation of active chlorine and decay of  $Cl^-$  (**Figure 4-3**).

As illustrated in **Table 4-1**, the rate constants of reactions 1 and 5 ( $k_1$  and  $k_5$ ) showed a strong dependency on current density. For instance, the rate constant of Cl<sup>•</sup> formation ( $k_1$ ) increased from 0.2 × 10<sup>-4</sup> s<sup>-1</sup> to 2.3 × 10<sup>-4</sup> s<sup>-1</sup> as the applied current density increased from 1 mA cm<sup>-2</sup> to 5 mA cm<sup>-2</sup>, which was about one order larger than that in previous similar work using a multilayer heterojunction anode (Yang et al., 2016b). Meanwhile, the cathodic chlorine reduction reaction exhibited a rate constant ranging from 1.8 × 10<sup>-4</sup> s<sup>-1</sup> to 11 × 10<sup>-4</sup> s<sup>-1</sup> with its occurrence leading to the achievement of steady-state concentrations of active chlorine (**Figure 4-2**). **Figure 4-13** shows that the values of these rate constants correlate linearly with the current densities ( $R^2$ >0.98).



**Figure 4-13.** Correlation between rate constants  $(k_1, k_5)$  and the current density.

The rate constant for reaction 6 was obtained by fitting the experimental data for chlorate generation (**Figure 4-10a** and **b**). It can be seen from **Table 4-1** that the chlorate formation rate constant ( $k_6$ ) is two orders of magnitude lower than  $k_1$ , which is in line with previous findings that the RuO<sub>2</sub>/IrO<sub>2</sub> anode is conducive to catalysing the generation of active chlorine but, satisfyingly, does little to facilitate the conversion of chlorine to by-products such as chlorate and perchlorate (Bagastyo et al., 2011, Zöllig et al., 2015c).

#### 4.4.2 Chlorine-mediated Ammonia Oxidation

As the identity and rate constants for the key reactions of the traditional breakpoint chlorination process have been reasonably well established, we combined the established ammonia reaction set (reaction 7-12 in Table 1) with the reactions describing the electrochemical active chlorine evolution (reaction 1-6 in Table 1) in order to fully elucidate the mechanism and kinetics of the electrochemically assisted ammonia oxidation processes. It should be noted that reaction 5 in Table 1 actually plays a minor role in the kinetic model of ammonia oxidation since the *in-situ* generated active chlorine will be immediately consumed near the anode surface when ammonia is

present in solution thereby rendering the cathodic chlorine reduction reaction (reaction 5 in **Table 4-1**) unlikely to occur.

As can be seen from **Figure 4-3**, the reaction set we present in **Table 4-1** is able to satisfactorily describe the ammonia degradation data over a range of conditions including different current densities and initial Cl<sup>-</sup> concentrations. The model also provides an excellent description of the time varying concentrations of Cl<sup>-</sup> (Figure 4-9a and b) and active chlorine (Figure 4-9c and d) as well as by-products chlorate (Figure 4-10c and d) and nitrate (Figure 4-11a and b). As illustrated Table 4-1, the in situ generated active chlorine could react with ammonia and form monochloramine and then dichloramine with rate constants for these reactions of  $3.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  and  $1.5 \times 10^2 \text{ M}^{-1}$ s<sup>-1</sup> respectively. Dichloramine, on the one hand, could decompose into NOH, which could combine with monochloramine and dichloramine resulting in formation of harmless nitrogen gas with rate constants of  $8.3 \times 10^3$  M<sup>-1</sup> s<sup>-1</sup> and  $2.8 \times 10^4$  M<sup>-1</sup> s<sup>-1</sup>, respectively. The oxidation of ammonium ions via reaction with Cl<sup>•</sup> is unimportant in our system because of (i) the much higher concentration of Cl<sup>-</sup> than NH<sub>4</sub><sup>+</sup> and (ii) Cl<sup>•</sup> is generated at the anode to which positively charged NH4<sup>+</sup> ions cannot approach. For these reasons, the transformations of Cl<sup>•</sup> into active chlorine (reaction 2 and 3 in Table 1) are the dominant reactions while the reactions between  $Cl^{\bullet}$  and  $NH_4^+$  are of minor importance.

No.	Reaction	Rate constant	References
Active chlorine evolution			
1	$\mathrm{MO}_{\mathrm{x}} + \mathrm{Cl}^{-} \rightarrow \mathrm{MO}_{\mathrm{x}}(\mathrm{Cl}^{\bullet}) + \mathrm{e}^{-}$	1 mA cm <sup>-2</sup> : 0.2×10 <sup>-4</sup> s <sup>-1</sup> 3 mA cm <sup>-2</sup> : 1.3×10 <sup>-4</sup> s <sup>-1</sup> 5 mA cm <sup>-2</sup> : 2.3×10 <sup>-4</sup> s <sup>-1</sup>	This study
	$MO_x(Cl^{\bullet}) + Cl^{-} \rightarrow MO_x + Cl_2 + e^{-}$	$> 1.0 \times 10^5 \ M^{-1} \ s^{-1}$	This study
3	$MO_x(Cl^{\bullet}) + MO_x(Cl^{\bullet}) \rightarrow 2MO_x + Cl_2$	$1.0 \times 10^8 \ M^{-1} \ s^{-1}$	(Wu et al., 1980)
4	$Cl_2 + H_2O \rightarrow HOCl + H^+ + Cl^-$	$0.52 \ M^{-1} \ s^{-1}$	(Wang and Margerum 1994)
5	$HOC1 + 2e^- \rightarrow C1^- + OH^-$	1 mA cm <sup>-2</sup> : 1.8×10 <sup>-4</sup> s <sup>-1</sup> 3 mA cm <sup>-2</sup> : 7.5×10 <sup>-4</sup> s <sup>-1</sup> 5 mA cm <sup>-2</sup> : 11×10 <sup>-4</sup> s <sup>-1</sup>	This study
6	$MO_x(2H_2O) + HOCl \rightarrow MO_x + ClO_3^-$ +5H <sup>+</sup> + 4e <sup>-</sup>	1 mA cm <sup>-2</sup> : 2.4×10 <sup>-6</sup> s <sup>-1</sup> 3 mA cm <sup>-2</sup> : 6.7×10 <sup>-6</sup> s <sup>-1</sup> 5 mA cm <sup>-2</sup> : 12×10 <sup>-6</sup> s <sup>-1</sup>	This study
Activ	e chlorine-mediated ammonia oxidation		
7	$\mathrm{NH}_4^+ + \mathrm{HOCl} \rightarrow \mathrm{NH}_2\mathrm{Cl} + \mathrm{H}^+ + \mathrm{H}_2\mathrm{O}$	$3.1 \times 10^{6} \text{ M}^{-1} \text{ s}^{-1}$	(Qiang and Adams 2004)
8	$\rm NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	$1.5 \times 10^2 \ M^{-1} \ s^{-1}$	(Mergerum et al., 1978)
9	$\text{NHCl}_2 + \text{H}_2\text{O} \rightarrow \text{NOH} + 2\text{H}^+ + 2\text{Cl}^\bullet$	$1.7 \times 10^2 \ M^{-1} \ s^{-1}$	(Zhang et al., 2015b)
10	$\rm NH_2Cl + \rm NOH \rightarrow \rm N_2 + \rm H^+ + \rm Cl^- + \rm H_2O$	$8.3 \times 10^3 \ M^{-1} \ s^{-1}$	(Zhang et al., 2015b)
11	$\mathrm{NHCl}_2 + \mathrm{NOH} \rightarrow \mathrm{N}_2 + 2\mathrm{H}^+ + 2\mathrm{Cl}^- + \mathrm{H}_2\mathrm{C}$	$2.8 \times 10^4 \ M^{-1} \ s^{-1}$	(Zhang et al., 2015b)
12	$\mathrm{NH}_4^+ + 4\mathrm{HOCl} \rightarrow \mathrm{NO}_3^- + 3\mathrm{H}_2\mathrm{O} + 6\mathrm{H}^+ + 4\mathrm{C}_3$	$0.1-0.7 \ M^{-1} \ s^{-1}$	This study

 Table 4-1. Proposed model and rate constants for the electrochemical ammonia

 oxidation process.

#### 4.4.3 Implications of the Model

The mechanistically-based kinetic model developed here provides an effective method to both interpret the experimental data and determine optimal conditions for ammonia oxidation with minimal generation of undesirable by-products. The ammonia degradation times predicted to be required using the kinetic model for complete ammonia removal for a range of initial Cl<sup>-</sup> and ammonia concentrations are shown in **Figure 4-14** for current densities of 3 mA cm<sup>-2</sup> (**Figure 4-14a**) and 5 mA cm<sup>-2</sup> (**Figure 4-14b**). Utilizing **Figure 4-14**, we can readily determine the appropriate operating time for ammonia removal for particular influent water compositions. If the operating time is shorter than that deduced using the model, ammonia is unlikely to be completely oxidized. However, if an operating time longer than that predicated is used, all of the incoming ammonia will be degraded with residual active chlorine transferred to and consumed at the cathode (Eq 4-5 in **Table 4-1**). This not only results in a sharp decrease in current efficiency and increase in energy consumption, but also results in the formation of excessive by-products (**Figure 4-10c** and **d**).



Figure 4-14. Prediction (deduced by use of the kinetic model developed in this work) of the electrolysis time required for complete ammonia oxidation (ammonia concentration < 1 mg/L) as a function of source water chloride and ammonia concentrations at

constant current densities of (a) 3 mA cm<sup>-2</sup> and (b) 5 mA cm<sup>-2</sup>. An initial pH of 6.0 was assumed in all scenarios.

Based on the experimental and modelling results, a reaction mechanism for the electrochemical active chlorine-mediated ammonia oxidation process is proposed and shown in **Figure 4-15**. The initial activation of Cl<sup>-</sup> to Cl<sup>•</sup> results in the formation of active chlorine. The mono/dichloramine generated from the reaction between active chlorine and ammonia undergoes rapid cleavage with the aid of a local excess of active chlorine with eventual transformation to nitrogen gas. Cl<sup>-</sup> can be regenerated during the oxidation of ammonia with the reformation of Cl<sup>-</sup> facilitating the anodic production of active chlorine thereby extending the lifetime of Cl<sup>-</sup> and allowing Cl<sup>-</sup> to be employed in catalytic quantities. Only trace amounts of chlorine and nitrogen by-products are produced.



Figure 4-15. Proposed reaction pathways and reaction rate constants for ammonia degradation by electrochemically generated active chlorine. The schematic shows both

(a) active chlorine evolution at the anode, and (b) active chlorine mediated ammonia oxidation. Final products are indicated in bold characters.

In break-point oxidation of ammonia, when the active chlorine dose to ammonia-nitrogen molar ratio (Cl/N) is lower than 1, active chlorine reacts with ammonia and converts it into chloramine with the concentration of total nitrogen remaining constant while in the transition region (1<Cl/N<1.6), decay of ammonia and chloramine starts to occur. At Cl/N >1.6, complete removal of ammonia nitrogen to nitrogen gas is achieved. In contrast, during the electrochemical ammonia oxidation in the presence of Cl<sup>-</sup>, removal of ammonia nitrogen is initiated at the very beginning of the electrolysis process. This is attributed to the high localized concentration of *in situ* electro-generated active chlorine, with the molar ratio between ammonia nitrogen likely to be higher than 1.6 in the reaction zone close to the anode surface, resulting in the rapid transformation of ammonia to chloramine followed by complete decomposition into nitrogen gas prior to diffusion into bulk solution. It is therefore apparent that the electrochemical oxidation method has advantages over classical break-point chlorination treatment in view of the more efficient use of in situ generated active chlorine, the suppression of generation/accumulation of nitrogen by-products and the ease of operation.

## 4.5 Conclusion

We have demonstrated in this study that the active chlorine-mediated electrochemical oxidation of ammonia can be an effective technology for ammonia removal. The *in situ* generated active chlorine can be used to efficiently convert ammonia into harmless nitrogen gas with concentrations of by-products (i.e., chlorate, nitrate and chloramine) well below WHO guidelines. A mechanistically-based kinetic model has been developed that successfully describes the key underlying reactions occurring in the electrochemical ammonia oxidation system, including active chlorine evolution, ammonia decomposition, and by-product formation. This model can be used to determine operating conditions (current densities, electrolysis times) appropriate to particular feed water compositions (of chloride and ammonia content) that enable complete ammonia removal at optimal current efficiency and minimal by-product formation. These findings contribute to our fundamental understanding of the electrochemical oxidation of ammonia and provide guidance with regard to effective implementation and optimization of this process.

# Chapter 5. Implication of Non-electrostatic Contribution to Deionization in Flow-electrode CDI: Case Study of Nitrate Removal from Contaminated Source Waters

# **5.1 Introduction**

In recent decades, nitrate has become one of the most serious problems affecting water quality globally as a result of the intensification of agricultural activities, particularly with regard to the use of fertilizers (Lado et al., 2017, Oyarzun et al., 2018). While nitrate itself is not particularly toxic, critical concerns exist in the reduction of nitrate in the human digestive system to toxic nitrite (Ward 2005). Several studies have indicated that the occurrence of methaemoglobinaemia to which infants are especially susceptible has a direct relationship with elevated levels of nitrate in drinking water (Sadler et al., 2016). As a result, the maximum contaminant level (MCL) for NO<sub>3</sub>-N in drinking water has been set at 10 mg L<sup>-1</sup> by the U.S. Environmental Protection Agency and 50 mg L<sup>-1</sup> as nitrate (equivalent to 11 mg L<sup>-1</sup> as NO<sub>3</sub>-N) by the World Health Organization (Wang and Chu 2016, Ward 2005). In addition, the presence of nitrate in water bodies can stimulate the excessive growth of algae and other aquatic plants resulting in harm to river and lake ecosystems. In New Zealand, an updated freshwater guideline suggests that 1.0 mg NO<sub>3</sub>-N L<sup>-1</sup> is the limiting chronic nitrate exposure value for pristine environments with high biodiversity (Hickey 2013).

Of the nitrate removal technologies available, biological denitrification is an environmentally friendly and cost-effective method and has been widely applied in biofilters to polish source waters but its efficiency can be significantly affected by a variety of parameters including water temperature, alkalinity and pH. In most cases, the effluent quality from such a process, particularly when operated at high denitrification rates, does not meet the stricter standards (*e.g.*, 1.0 mg NO<sub>3</sub>-N L<sup>-1</sup>) now being either imposed or suggested (Ghafari et al., 2008, Karanasios et al., 2010). Alternatively, physico-chemical technologies such as reverse osmosis (RO) (Schoeman and Steyn 2003), electrodialysis (ED) (Kikhavani et al., 2014) and ion exchange (Ma et al., 2012) can be employed for physico-chemical removal of nitrate from source waters. While high removal rates have been achieved by these methods, the requirement for relatively extreme conditions (*e.g.*, high pressure for RO and high voltage for ED) increases the operating cost. Moreover, the ion exchange method may generate secondary pollution during the regeneration of used sorbents (Kim and Choi 2012).

In recent years, there has been considerable progress in the electrical extraction of ions from brackish waters at low voltages (<1.2~1.6 V) followed by ion immobilization in electrical double layers (EDLs) on carbon electrodes, with one of the recent innovations, flow electrode capacitive deionization (FCDI), gaining in popularity (Hatzell et al., 2015a, Jeon et al., 2013b, Ma et al., 2016b, Rommerskirchen et al., 2015, Yang et al., 2016a). Compared to capacitive deionization (CDI) using a solid electrode, continuous desalting can be achieved in FCDI, largely because of the infinite ionadsorption capacity that can be achieved by pumping uncharged carbon materials into the system (Doornbusch et al., 2016a, Suss et al., 2015a, Yang et al., 2017). In practical applications, a short-circuited method can be implemented to regenerate the flow electrode in a closed cycle with this process resulting in minimization of the amount of carbon materials used (Yang et al., 2017). Another advantage of the electrosorption process relates to the negligible chemical consumption required to maintain the adsorption capacity for charged species in long-term operation (Seo et al., 2010, Zhang et al., 2018c). Recent studies have shown the applicability of CDI for selective nitrate removal from dilute streams with the efficiency further improved with the use of composite electrode materials (Kim and Choi 2012, Oyarzun et al., 2018, Tang et al., 2015a). In contrast, there has been, surprisingly, no investigation of the removal of nitrate using FCDI despite the fact that, given the continuous migration of nitrate and other ions into the flow electrode, high nitrate removal efficiency and water recovery could well be achieved.

In a typical (F)CDI system, electrosorption of ions into EDLs is considered the primary means of salt removal from the brackish stream with the continuous operation of FCDI in short-circuited closed cycle (SCC) mode relying on the full discharge of the flow electrode in the shared recirculation reservoir (Yang et al., 2017). However, carbon is a well-known sorbent, with adsorption occurring non-electrostatically by physico-chemical mechanisms. A number of studies have shown that the physico-chemical removal of nitrate can be induced by the addition of activated carbon into aqueous solutions (Demiral and Gündüzoğlu 2010, Öztürk and Bektaş 2004). As such, it is possible that, following migration across the membrane, nitrate is preferentially adsorbed to the carbon particles, resulting in difficulty in short-circuited operation in fully recovering the adsorption capacity of the flow electrode. Of particular concern is the possibility that deterioration in efficiency of removal of nitrate in FCDI is of considerable importance for better implementation of this technology in potable water production.

In this study, different concentrations of NO<sub>3</sub>-N (50, 20 and 10 mg  $L^{-1}$ ) were used to simulate source waters that have been contaminated to different levels (Lasagna

et al., 2016). An FCDI system was operated in single-pass mode with the flow electrodes recirculated in short-circuited closed cycle. The impacts of current density and hydraulic retention time (HRT) on the process performance were investigated with consideration given to the mechanisms of nitrate removal. Based on the resulting conclusions, viable strategies have been proposed for the continuous operation of FCDI.

# 5.2 Materials and Methods

#### **5.2.1 Materials and Reagents**

All chemicals were purchased from Sigma-Aldrich unless otherwise mentioned. Activated charcoal (Darco, 100 mesh, with an average pore size and BET surface area of 1.44 nm and 917.5 m<sup>2</sup> g<sup>-1</sup> respectively) blended with carbon black at a ratio of 9:1 was used as the carbon material. Each flow electrode contained 8 g of carbon particles in a 1000 mg L<sup>-1</sup> NaCl solution (80 g in total) with this carbon load representing 10 *wt*%. Simulated source water was prepared by mixing an appropriate amount of NaNO<sub>3</sub> and NaCl in Milli-Q water to achieve an initial NO<sub>3</sub>-N concentration of 50, 20 or 10 mg L<sup>-1</sup> with a fixed NaCl concentration of 1000 mg L<sup>-1</sup>.

#### **5.2.2 Experimental setup**

**Figure 5-1** shows the structure of the FCDI cell used in all experiments. The composite flow chambers for the slurry electrode consisted of graphite current collectors and carved serpentine acrylic flow channels (3 mm wide and 3 mm deep resulting in an effective contact area  $A_{eff} = 34.9 \text{ cm}^2$  between the flow electrode and ion exchange membrane from the inlet to the outlet). Ion exchange membranes (CEM-Type I/AEM-Type I, FUJIFILM Europe) were placed respectively against the channels to separate the flow chambers and the spacer (**Figure 5-1**). Simulated water passed through a 0.5 mm thick spacer (100 mesh) made of nylon sheet located between the ion exchange membranes, with silicone gaskets encircling the spacer channel in order to

avoid the leakage of the solution. All parts of the FCDI cell were held together using acrylic end plates (Figure 5-1).





#### 5.2.3 FCDI operation and sample measurement

In all FCDI experiments, the flow electrode was recirculated in SCC mode using a peristaltic pump (Longer pump, Baoding, China) with the flow rate fixed at 80 mL min<sup>-1</sup> (*i.e.*, 40 mL min<sup>-1</sup> each) (**Figure 5-1**). Constant current/voltage was provided by a DC power supply (MP3840, Powertech). The current density was calculated from  $i = I/A_{eff}$  where I is the current (A) and  $A_{eff}$  is the effective area between the flow electrode and ion exchange membrane (34.9 cm<sup>2</sup>). The electrical conductivity of the effluent was measured using a conductivity meter (CON-BTA, Vernier) connected to a data acquisition system (SensorDAQ, Vernier). The concentrations of nitrate-N (NO<sub>3</sub>-N) in aqueous solutions were determined using a UV screening method published by the American Public Health Association (Rice et al., 2012). Prior to measurement of aqueous nitrate concentrations in the flow electrode samples, 0.22  $\mu$ m syringe filters were used to separate the solution and activated carbon particles.

Ion removal in different scenarios. The FCDI performance with regard to nitrate and salt removal from solutions containing 50, 20 and 10 mg NO<sub>3</sub>-N  $L^{-1}$  (and 1000 mg NaCl L<sup>-1</sup>) were initially evaluated at various constant current densities (i = 1.4 $\sim 30.1$  A m<sup>-2</sup>). Because the positively (termed anode) and negatively (termed cathode) charged flow electrodes were recirculated to the shared reservoir (Figure 5-1) for charge neutralization and electrode re-generation after passing through the flow chambers, no extra discharging step was used in this work. Due to the short operation time (20~30 min) of FCDI, the effect of ion accumulation in flow electrodes on desalting performance was not considered. The brackish water was fed into the spacer chamber in single pass mode with the flow rate  $(q_0)$  changing from 0.85 to 3.40 mL  $min^{-1}$ , corresponding to a hydraulic retention time (HRT) from 2.94 to 0.73 min. When the conductivity of the effluent became stable (typically,  $10 \sim 20$  min after setup), 5 mL samples were withdrawn from the effluent and analyzed to quantify the concentrations of NO<sub>3</sub>-N. The energy consumption as a function of productivity (kWh m<sup>-3</sup>) was obtained by integrating the cell voltage and current over the flow rate, as described by Eq. (5-1):

$$E = \frac{IU_{cell}}{q_0} \tag{5-1}$$

Non-electrostatic adsorption of nitrate onto the membrane and carbon. The impact of non-electrostatic adsorption of nitrate in FCDI was investigated by changing the solution in the electrode channels (and the recirculation reservoir). In these 106

experiments, the flow rate of the brackish stream containing 10 mg NO<sub>3</sub>-N L<sup>-1</sup> and 1000 mg NaCl L<sup>-1</sup> was set as 2.55 mL min<sup>-1</sup> (*i.e.* HRT = 0.98 min). The FCDI system firstly ran for 3600 s without use of the flow electrodes to characterize the adsorption of nitrate onto the ion-exchange membrane. Subsequently, a 72 mL "control" flow electrode containing 1000 mg NaCl L<sup>-1</sup> was fed into the system in order to evaluate the diffusion of nitrate into the liquid phase in the absence of an electrical field. Assuming that the physico-chemical adsorption capacity of the membrane for NO<sub>3</sub>-N is fixed (*Q<sub>e,mem</sub>*, mg NO<sub>3</sub>-N m<sup>-2</sup>), the adsorption process may be considered to be pseudo-first order (Ho and McKay 1998) as described in Eqs. 5-2 and 5-3:

$$\frac{\mathrm{d}Q_{t,mem}}{\mathrm{d}t} = k_1 \left( Q_{e,mem} - Q_{t,mem} \right)$$
(5-2)

$$Q_{i,mem} = \frac{\int q_0 \left( C_0 - C_i \right) dt}{A_{mem}} \approx \frac{\sum_{j=1}^{l} \left( C_0 - \frac{C_j + C_{j-1}}{2} \right) q_0 t_j}{A_{mem}}$$
(5-3)

where  $Q_{t, mem}$  (mg NO<sub>3</sub>-N m<sup>-2</sup>) is the dynamic adsorption capacity at time  $t, k_1$  is the pseudo-first-order rate constant (s<sup>-1</sup>),  $q_0 = 2.55$  mL min<sup>-1</sup>,  $C_0$  and  $C_t$  (mg L<sup>-1</sup>) indicate the initial NO<sub>3</sub>-N concentration (10 mg L<sup>-1</sup>) and concentration at time t, j presents the sampling point over the experiment and  $A_{mem}$  is the total surface area of the ion exchange membrane (112 cm<sup>2</sup>). Integrating Eq.5-2 for the boundary conditions (t = 0 to t = t and  $Q_{t,mem} = 0$  to  $Q_{t,mem} = Q_{e,mem}$ ) yields (Eq. 5-4):

$$Q_{t,mem} = Q_{e,mem} \left( 1 - e^{-k_1 t} \right) \tag{4}$$

With regard to the non-electrostatic uptake of NO<sub>3</sub>-N by the carbon particles in the flow electrode, the theoretical increase in the nitrate-N concentration in the flow electrode over time t ( $X_{tot}$ , mg L<sup>-1</sup>) was calculated according to the mass balance (Eq. 5-5). As such, the contribution of membrane adsorption to NO<sub>3</sub>-N removal at time t ( $X_{IEM}$ , mg L<sup>-1</sup>) was normalized by the liquid volume ( $V_{flow} = 72$  mL) of the flow electrode as follows (Eq. 5-6):

$$X_{tot} = \frac{\int q_0 (C_0 - C_t) dt}{V_{flow}}$$
(5-5)

$$X_{\text{IEM}} = \frac{Q_{e,mem} \left(1 - e^{-k_1 t}\right) A_{mem}}{V_{flow}}$$
(5-6)

The physico-chemical adsorption of nitrate in the flow electrode was *ex-situ* evaluated at room temperature. Certain amounts of carbon electrodes were dispersed into 10 mL solutions containing 1000 mg NaCl L<sup>-1</sup> and various concentrations of NO<sub>3</sub>-N. Non-electrostatic adsorption ( $Q_{e,carbon}$ , mg NO<sub>3</sub>-N g<sup>-1</sup>) of nitrate onto the carbon electrode particles was analyzed by fitting the results to a Langmuir isotherm model as follows (Demiral and Gündüzoğlu 2010) (Eq. 5-7):

$$Q_{e,carbon} = \frac{Q_{\infty}bC_e}{1+bC_e}$$
(5-7)

where  $Q_{\infty}$  is the maximum adsorption capacity estimated by the Langmuir model (mg NO<sub>3</sub>-N g<sup>-1</sup>),  $C_e$  is the equilibrium concentration of NO<sub>3</sub>-N (mg L<sup>-1</sup>) and *b* is the Langmuir adsorption equilibrium constant (L mg<sup>-1</sup>). The non-electrostatic contribution of the flow electrode to nitrate removal ( $X_{carbon}$ ) can be determined with the incorporation of Eq. 5-8:

$$X_{carbon} = \frac{Q_{e,carbon}m}{V_{flow}} = \frac{\frac{Q_{\infty}bX_{free}}{1+bX_{free}}m}{V_{flow}}$$
(5-8)

where *m* is the mass of the active materials (*i.e.*, 7.2 g) in the flow electrode and  $X_{free}$  is the free nitrate-N concentration in the recirculation reservoir following electrode discharging. Since  $X_{free}$  relates to the nitrate removed due to the capacitive (and electrodialytic) mechanism, the synthesis of  $X_{\text{IEM}}$ ,  $X_{carbon}$  and  $X_{free}$  should account for  $X_{tot}$ .

Critical parameters influencing continuous performance of the FCDI system. Comparison of the SCC FCDI performance in constant current (CC) mode and constant voltage (CV) mode was conducted, particularly with regard to the fate of nitrate (and other ions) after migration across the membrane. A constant current i = 18.6A m<sup>-2</sup> (or voltage  $U_{cell} = 1.0$  V) was applied during electrosorption with the nitrate concentrations in the effluent and flow electrode measured at predetermined intervals. To avoid accumulation of ions in the liquid phase of the flow electrode leading to ion back diffusion and leakage, aliquots of the electrolyte in the flow electrode ( $\Delta V_{ele}$ ) were replaced by 1000 mg L<sup>-1</sup> NaCl solutions after every 5-h of electrosorption. The water recovery rate ( $\gamma$ ) for FCDI is defined as follows (Eqs. 5-9 and 5-10):

$$\gamma = \frac{\int qdt}{\int qdt + \Delta V_{ele}}$$
(5-9)

$$\int qdt \approx q_0 \int dt - \left( V_{ele,t} - V_{ele,0} \right)$$
(5-10)

where q is the flow rate of the desalted water at time t. Because of the constant water transfer from the spacer into the flow chambers in SCC operation of FCDI (Yang et al., 2017), q should be slightly lower than the influent flow rate  $q_0$ . Therefore, the desalted water yield was estimated according to Eq. 5-10 where  $V_{ele, 0}$  and  $V_{ele, t}$  are the volumes of the electrolyte in the flow electrode (72 mL in this study) initially and at time trespectively.

## 5.3 Results and discussion

# 5.3.1 Salt and nitrate removal for different scenarios

The desalting performance of the FCDI system fed with source waters of different composition is shown in Figure 5-2. For a certain type of water treated at a

fixed HRT, the "steady-state" effluent conductivity decreases with increase in the current density. It can be seen from **Figure 5-2** that the influent nitrate concentration does not affect the desalination rate significantly. While higher ion removal rates can be obtained at longer HRTs, the water productivity is compromised. According to World Health Organization guidelines, water containing TDS concentrations below 1000 mg  $L^{-1}$  (~2000  $\mu$ S cm<sup>-1</sup>) is usually acceptable to consumers, although the palatability of water has been rated by panels of tasters as excellent if the TDS is less than 300 mg/L and good if the TDS is between 300 and 600 mg/L (WHO 1996). Results in **Figure 5-2** show that the FCDI system is capable of reducing the TDS concentration to a very low level, though very low concentrations in the spacer (*i.e.*, conductivity < 100  $\mu$ S cm<sup>-1</sup>) should be avoided as this would lead to a dramatic increase in operating voltage and energy consumption (**Figure 5-3**). For example, when an influent NO<sub>3</sub>-N concentration of 10 mg L<sup>-1</sup> and HRT of 0.98 min were used, the effluent conductivity of the system decreased from 125.1 to 50.3  $\mu$ S cm<sup>-1</sup> with the current density increasing from 20.1 to 21.5 A m<sup>-2</sup> (**Figure 5-2**).

However, the cell voltage increased sharply from 1.00 to 1.88 V (**Figure 5-3**). The relationship between the energy consumption and "steady-state" effluent conductivity is shown in **Figure 5-4**. Overall, it can be concluded that an increase in either the treatment efficiency (*i.e.*, lower effluent conductivity) or the productivity (*i.e.*, shorter HRT) would lead to an increase in energy consumption.



Figure 5-2. Change of the effluent conductivity by using FCDI when the feed water contains (a) 50, (b) 20 or (c) 10 mg NO<sub>3</sub>-N L<sup>-1</sup>. All experiments were conducted in a single-pass, constant-current mode. Flow electrode = 10 *wt*% carbon in 1000 mg NaCl L<sup>-1</sup> electrolyte. The legends in the figures indicate different HRTs. The operating time for electrosorption is 1200 ~ 1800 s. Lines serve to guide the eye.



**Figure 5-3.** Change of the average cell voltage as a function of the current density. Initial influent NO<sub>3</sub>-N concentration: (a) 50, (b) 20 and (c) 10 mg L<sup>-1</sup>. The legends in figures indicate different HRTs. Experimental conditions: single-pass, constant-current mode and operating time =  $1200 \sim 1800$  s. Lines serve to guide the eye.



**Figure 5-4.** Energy consumption to achieve different effluent conductivity at an influent NO<sub>3</sub>-N concentration of (a) 50, (b) 20 and (c) 10 mg L<sup>-1</sup>. The legends in figures indicate different HRTs. Experimental conditions: single-pass, constant-current mode and operating time = 1200 ~ 1800 s. Lines serve to guide the eye.

The "steady-state" nitrate-N concentrations in the FCDI system with feed water of different NO<sub>3</sub>-N concentrations are shown in **Figure 5-5**. It can be seen that NO<sub>3</sub>-N concentrations in the effluent all decreased with an increase in current density and/or HRT, which is similar to the change of the effluent conductivity (**Figure 5-2**). The energy consumption values required to meet different NO<sub>3</sub>-N standards in the three scenarios are provided in **Figure 5-6**. For example, at an HRT of 0.98 min, a current input of 20.2 A m<sup>-2</sup> (*i.e.*, energy consumption = 0.49 kWh m<sup>-3</sup>) is required to reduce the NO<sub>3</sub>-N concentration from 50 to <10 mg L<sup>-1</sup> that complies with most guideline MCLs (Ward 2005). However, further decreasing the effluent NO<sub>3</sub>-N concentration to meet higher standards such as 1.0 mg NO<sub>3</sub>-N L<sup>-1</sup> considered necessary to protect pristine environments with high biodiversity and conservation value (Hickey 2013) is not without challenges because this would lead to very low effluent conductivity and unnecessary water splitting. In contrast, NO<sub>3</sub>-N concentrations can be reduced to a very low level (< 0.1 mg L<sup>-1</sup>) provided that the source water is less contaminated. Specifically, the energy consumptions are 0.90 and 0.46 kWh m<sup>-3</sup> respectively for feed waters containing 20 and 10 mg NO<sub>3</sub>-N L<sup>-1</sup> respectively at an HRT of 0.98 min (**Figure 5-6**). As shown in **Figure 5-5**, the "steady-state" effluent concentrations of NO<sub>3</sub>-N all exhibit a current-independent drop, especially evident at low current densities (where electrosorption is less effective) and at longer HRT. A plausible explanation for this effect could relate to the physico-chemical removal of nitrate by the membrane and/or carbon in the system with longer HRT facilitating the mass transfer from feed water to the flow electrode through the anion exchange membrane. As such, consideration was given to the non-electrostatic adsorption of nitrate in FCDI and its impacts on system performance. Unless otherwise stated, the following studies were carried out to treat feed waters initially containing 10 mg NO<sub>3</sub>-N L<sup>-1</sup> (and 1000 mg NaCl L<sup>-1</sup>).



Figure 5-5. Change of the effluent NO<sub>3</sub>-N concentration at an influent NO<sub>3</sub>-N concentration of (a) 50, (b) 20 and (c) 10 mg NO<sub>3</sub>-N  $L^{-1}$ . All experiments were conducted in single-pass, constant-current mode. The legends in figures indicate different HRTs. The operating time for electrosorption is 1200 ~ 1800 s.



**Figure 5-6.** Energy consumption to obtain different "steady-state" NO<sub>3</sub>-N concentrations when the feed water contains (a) 50, (b) 20 or (c) 10 mg NO<sub>3</sub>-N L<sup>-1</sup>. The legends in the figures indicate different HRTs. Experimental conditions: single-pass, constant-current mode, flow electrode = 10 *wt*% carbon in 1000 mg NaCl L<sup>-1</sup> electrolyte and operating time = 1200 ~ 1800 s. The standards and low-impact guidelines refer to the MCLs in Ward (2005) and Hickey (2013).

#### **5.3.2** Non-electrostatic adsorption of nitrate

In an FCDI system, ions in the feed water are expected to migrate through the ion-exchange membranes and end up in the liquid phase of the flow electrode (Ma et al., 2018) or associate with the electrical double layer (EDL) of the carbon electrode particles (Jeon et al., 2013b) during electrosorption. While FCDI SCC operation can regenerate the electrode capacitance with most of the EDL-associated ions eventually released into the electrolyte (He et al., 2018c, Yang et al., 2017), electrode regeneration might be expected to be compromised under conditions where non-electrostatic adsorption plays a vital role in ion removal. **Figure 5-7a** shows the change of the effluent NO<sub>3</sub>-N concentration in the FCDI system in the absence of flow electrode solution and particles and with no applied external electrical field. While rapid decrease in the nitrate concentration was initially observed (as a result, presumably, of nitrate adsorption to the anion exchange membrane), the adsorption sites on the membrane

gradually became saturated with the effluent nitrate-N concentration increasing to 8.5 mg L<sup>-1</sup> after 3600 s. The physico-chemical adsorption of nitrate onto the membrane can be well described by the pseudo-first-order kinetics model (Eq.5-4 and Figure 5-7b). O<sub>e</sub>, mem and  $k_1$  were determined to be 65.4 mg NO<sub>3</sub>-N m<sup>-2</sup> and 0.0012 s<sup>-1</sup> respectively. The contribution of membrane adsorption to NO<sub>3</sub>-N removal at time t ( $X_{\text{IEM}}$ , mg L<sup>-1</sup>) was then estimated (see below) using Eq. 5-6. Subsequently, a 72 mL saline solution containing 1000 mg NaCl  $L^{-1}$  (*i.e.*, essentially the solution phase of the flow electrode) was added into the electrode chambers. Because of the concentration gradient across the membrane, nitrate in the spacer chamber gradually diffused into the electrolyte circulating in the electrode chambers. As shown in Figure 5-8a, the effluent NO<sub>3</sub>-N concentration reached the lowest value at 1200 s (7.0 mg  $L^{-1}$ ) and then went up to 8.8 mg L<sup>-1</sup>. There was a good relationship between the total amount of NO<sub>3</sub>-N (*i.e.*,  $X_{tot}$ calculated from (Eq. 5-5) removed from the brackish stream and that transferred into the electrolyte (Figure 5-8b), indicating that (i) the anion exchange membrane was sufficiently saturated following 3600-s operation (Figure 5-7a) and (ii) the passive nitrate transfer is negligible when the concentration gradient across the membrane becomes insignificant.

The non-electrostatic contribution of the flow electrode to nitrate removal  $(X_{carbon})$  was evaluated in the FCDI unit by undertaking studies in the absence of an electrical field ( $i = 0 \text{ A m}^{-2}$ ). It can be seen from **Figure 5-9a** that the presence of carbon in the flow electrode significantly improves the removal of nitrate, despite the absence of removal via electrosorption. Even though the membrane adsorption capacity was exhausted following 3600-s operation (**Figure 5-9b**), the effluent NO<sub>3</sub>-N concentration was still substantially lower compared to the influent. The theoretical NO<sub>3</sub>-N concentration in the flow electrode ( $X_{tot}$ ) and the concentration of nitrate on the

membrane ( $X_{IEM}$ ) were respectively calculated according to Eqs. 5-5 and 5-6 with  $X_{free}$  determined based on the aqueous NO<sub>3</sub>-N concentration in the flow electrode at time *t*. Results in **Figure 5-9b** suggest that a large fraction of NO<sub>3</sub>-N removed in FCDI should not be ascribed to  $X_{IEM}$  and  $X_{free}$ , with this result highlighting the importance of non-electrostatic adsorption of nitrate to the carbon particles present in the flow electrode chamber.

As such, the adsorption isotherm of nitrate from aqueous solutions by activated carbon was measured at room temperature (**Figure 5-10**), with the experimental data fitting well with the Langmuir model (Eq.5-7). Parameters  $Q_{\infty}$  (1.10 mg g<sup>-1</sup>) and b (0.073 L mg<sup>-1</sup>) were then used to characterize the nitrate removal by carbon adsorption  $(X_{carbon})$  in FCDI (Eq. 5-8). Mechanisms that may contribute to the non-electrostatic adsorption process include exchange between nitrate and (i) ions associated with polar functional groups on the carbon surface and/or (ii) ions in the EDLs of the carbon in the flow electrode (Gierak and Lazarska 2017). Both mechanisms could negatively influence the effectiveness of FCDI for nitrate removal; for example, the exhaustion of active sites on the carbon particle surface may result in deterioration of process performance, and the pre-accumulation of nitrate in the EDLs would be expected to affect the capacitive kinetics of nitrate removal when an electrical field is applied.



**Figure 5-7.** Evaluation of the contribution of membrane adsorption to NO<sub>3</sub>-N removal in FCDI: (a) Change of the effluent NO<sub>3</sub>-N concentration and (b) mass balance of NO<sub>3</sub>-N removal. The red lines indicate the results of pseudo-first-order kinetic modeling. The system was operated in single-pass mode at i = 0 A m<sup>-2</sup>. Experimental conditions: influent NO<sub>3</sub>-N concentration = 10 mg L<sup>-1</sup> and HRT = 0.98 min.



**Figure 5-8.** Diffusion of nitrate into the solution phase of the flow electrode as a result of the concentration gradient. (a) The time-course results of the effluent NO<sub>3</sub>-N concentration and (b) mass balance of NO<sub>3</sub>-N removal in the flow electrode initially containing 1000 mg NaCl L<sup>-1</sup>. The experiment was carried out following the membrane reaching the adsorption capacity (as shown in Fig. 4). The red line in SI Fig. S4b stands

for the results according to the mass balance calculation (Eq. 5-5). Experimental conditions: influent NO<sub>3</sub>-N concentration = 10 mg L<sup>-1</sup>, i = 0 A m<sup>-2</sup>, single-pass and HRT = 0.98 min.



**Figure 5-9.** Nitrate removal in FCDI at i = 0 A m<sup>-2</sup>. (a) Effluent NO<sub>3</sub>-N concentration and (b) mass balance of nitrate in the flow electrode. For comparison, the effluent NO<sub>3</sub>-N concentration at 18.6 A m<sup>-2</sup> is also provided in **Figure 5-9a** (blue inverted blue triangles).  $X_{tot}$ ,  $X_{IEM}$ ,  $X_{free}$  and  $X_{carbon}$  were determined according to Eqs. 5-5, 5-6 and 5-8. Experimental conditions: influent NO<sub>3</sub>-N concentration = 10 mg L<sup>-1</sup>, single-pass, flow electrode = 10 *wt*% carbon in 1000 mg NaCl L<sup>-1</sup> electrolyte and HRT = 0.98 min.



**Figure 5-10.** Langmuir modeling of nitrate adsorption by the active carbon materials in the flow electrode at room temperature.

# 5.3.3 Comparison of XIEM, Xfree and Xcarbon during nitrate removal

Figure 5-11a depicts the time-course results of salt and nitrate removal in the FCDI system under constant current mode. The effluent conductivity and NO<sub>3</sub>-N concentration initially decreased to very low levels. Subsequently, slight deterioration in ion removal efficiency was observed with the effluent NO<sub>3</sub>-N concentration gradually exceeding the MCL (1 mg  $L^{-1}$ ) for environments with high biodiversity and conservation value (Hickey 2013). An overview of the fate of nitrate within the FCDI system is presented in **Figure 5-11b**. The theoretical NO<sub>3</sub>-N removal amount ( $X_{\text{IEM}}$  +  $X_{free} + X_{carbon}$ ) is estimated to be a little higher than the experimentally determined value  $(X_{tot})$  with this discrepancy likely ascribed to the fact that  $X_{carbon}$  was estimated under assumed equilibrium conditions (Eq. 5-8). In SCC FCDI, the flow electrodes are continuously charged in the cell and re-generated in the shared reservoir (Figure 5-1) with ions in the electrical double layers (EDLs) released into the electrolyte when discharging occurs in the shared reservoir (He et al., 2018c, Yang et al., 2017). The ions released during this discharging process may be re-immobilized on the carbon particles once they re-enter to charged environment of the electrode flow channels. As such, aqueous NO<sub>3</sub>-N concentration in the flow electrode is constantly changing with the short contact time between carbon and electrolyte in the shared reservoir likely insufficient for the physico-chemical adsorption process to achieve equilibrium with the result that the calculated  $X_{carbon}$  was, in all likelihood, somewhat higher than the actual amount of nitrate adsorbed on the carbon. Overall, X<sub>IEM</sub> became insignificant at extended times (Figure 5-11b) although it is expected that the membrane's affinity for nitrate will continue to facilitate the selective transfer of nitrate across the membrane.  $X_{carbon}$  accounted for a major part of the nitrate removed with results in Figure 5-12 indicating that nitrate on the carbon is difficult to be electrostatically desorbed, even

when the current is reversed. Therefore, consideration was given to the question of how the FCDI performance changes once the capacity of the carbon electrode particles to non-electrostatically adsorb nitrate has been exhausted.



**Figure 5-11.** Comparison of  $X_{\text{IEM}}$ ,  $X_{free}$  and  $X_{carbon}$  in nitrate removal in FCDI. (a) Change of voltage and treatment efficiency and (b) mass balance of nitrate removed with the electrolyte in flow electrode consisting of 1000 mg NaCl L<sup>-1</sup>. (c) Change of voltage and treatment efficiency and (d) mass balance of nitrate removed with the electrolyte in flow electrode consisting of 100 mg NO<sub>3</sub>-N L<sup>-1</sup> and 1000 mg NaCl L<sup>-1</sup>. Experimental conditions: influent NO<sub>3</sub>-N concentration = 10 mg L<sup>-1</sup>, single-pass, HRT = 0.98 min and i = 18.6 A m<sup>-2</sup>.



**Figure 5-12.** Electro-desorption of NO<sub>3</sub>-N in the carbon by reversing the current. (a) Change of cell voltage and effluent conductivity and (b) change of the concentrations of effluent nitrate and nitrate in the liquid phase of flow electrode. The effluent NO<sub>3</sub>-N concentration was only slightly higher than the influent, indicating that nitrate on the carbon was difficult to be electrostatically desorbed. Experimental conditions: initial NO<sub>3</sub>-N concentration = 10 mg L<sup>-1</sup>, single-pass, HRT = 0.98 min, *i* = 18.6 A m<sup>-2</sup> from 0 to 7200 s and -18.6 A m<sup>-2</sup> from 7200 to 14400 s.

A flow electrode suspension consisting of 10 *wt*% carbon materials, 100 mg NO<sub>3</sub>-N L<sup>-1</sup> and 1000 mg NaCl L<sup>-1</sup> was continually mixed on a magnetic stirrer for at least 12 h prior to use in order to achieve adsorption equilibrium. **Figure 5-11c** and **d** summarize the temporal change of the treatment efficiency and mass balance of nitrate on using this "nitrate-equilibrated" suspension in the flow electrode. Compared to the results in **Figure 5-11a**, while a similar trend in the variations of effluent conductivity and NO<sub>3</sub>-N concentration was observed, the FCDI efficiency decreased due to the presence of nitrate in the flow electrode. For example, the lowest effluent NO<sub>3</sub>-N concentration in **Figure 5-11c** was 1.22 mg L<sup>-1</sup> at 1200 s, consistently higher than that in **Figure 5-11a**. In this latter case, the sum of  $X_{\text{IEM}} + X_{free}$  provide a reasonable explanation for  $X_{tot}$ , indicating that the formation of EDLs in SCC FCDI was less

affected due to the exhaustion of the physico-chemical adsorption capacity of the carbon particles in the flow electrode chamber. While one might speculate that nitrate migration under this condition is essentially an electrodialysis process, previous studies have confirmed that the capacitive mechanism dominates in SCC FCDI (i.e., Xfree) in view of the much lower efficiency observed when only electrodialysis occurs (He et al., 2018c). Nevertheless, the effluent NO<sub>3</sub>-N concentration exceeded 1 mg  $L^{-1}$  over the whole experiment (Figure 5-11c) and, even when X<sub>carbon</sub> contributed to nitrate removal, deterioration in the process performance still occurred (Figure 5-11a). It should be noted that as a result of nitrate (and salt) transfer into the electrolyte, the ionic resistance in the flow electrode constantly decreased during the desalting process. The cell voltage in Figure 5-11c (0.75~0.50 V) is much lower than that in Figure 5-11a (1.5~0.79 V). In classical CDI (and MCDI), a constant effluent salt concentration could be achieved under constant current mode, largely due to the buildup of electrical potential at the Stern plane  $(\Delta \varphi_d)$  (Tang et al., 2016b, Tsouris et al., 2011, Zhao et al., 2012a). According to the modified Donnan model (Porada et al., 2013b, Wang et al., 2018), there is a positive correlation between the excess salt adsorption ( $\Gamma$ ) and both the effective micropore volume (relative to total electrode volume)  $(p_{mi})$  and the nondimensional Donnan potential within the micropores ( $\Delta \varphi_D$  that relates to  $\Delta \varphi_d$ ). With regard to charge neutralization and electrode re-generation in SCC FCDI, constant  $p_{mi}$ would be expected to be maintained during the desalting process. However, the decrease in cell voltage when the FCDI system is operated in constant current mode would lead to the re-distribution of electrical potential with subsequent shrinkage in  $\varphi_d$ . Therefore, stable effluent quality cannot be guaranteed for SCC FCDI when operated in constant current mode.
# 5.3.4 Critical parameters influencing FCDI performance under continuous operation

To obtain a stable desalting performance, the FCDI system was operated in constant voltage mode with the charging voltage (1.0 V) comparable to the initial cell voltage under the constant current mode at i = 18.6 A m<sup>-2</sup> (Figure 5-11a). It can be seen from Figure 5-13 that, with the migration of ions into the flow electrode, the current in the circuit gradually increased due to the decrease in the internal ionic resistance (Dykstra et al., 2016a). A fairly stable effluent quality (NO<sub>3</sub>-N < 1 mg L<sup>-1</sup>) was obtained when operated in constant voltage mode, with the results in reasonable agreement with those in the initial stage of operation under constant current mode (Figure 5-5). As such, operation in constant voltage mode is recommended for SCC FCDI in water purification.



Figure 5-13. Operation of FCDI in constant voltage mode. Experimental conditions: influent NO<sub>3</sub>-N concentration = 10 mg L<sup>-1</sup>, single-pass, HRT = 0.98 min and cell voltage = 1.0 V.

Specific energy consumption and water recovery are two key indicators that may be used to evaluate the performance of (M)CDI with regard to removal of ions from contaminated water sources (Suss et al., 2015a). While one advantage of FCDI is the continuous desalting operation, the generation of a waste stream in SCC FCDI relates to the accumulation of ions in the liquid phase of the flow electrode (Doornbusch et al., 2016a) that likely results in (i) water transfer and dilution of the carbon content in the flow electrode (Yang et al., 2017) and (ii) back-diffusion and leakage of ions that deteriorate the coulombic efficiency (Tedesco et al., 2016). Using the definition of SCC FCDI water recovery rate ( $\gamma$ ) provided in Eqs. 5-9 and 5-10, we compare the performance (with regard to both effluent nitrate concentration and energy consumption) for water recovery rates of 97.7% and 91.4% (see Figure 5-14 and Figure 5-15). At an extremely high water recovery rate (97.7%), the current density initially increases with ion migration into the solution phase of the flow electrode (Figure 5-15). However, the over accumulation of ions in the flow electrode likely results in an increase in the internal (polarization) resistance with the subsequent current density and nitrate removal efficiency decreasing over time. It is also possible that there is an excess number of ions in the electrolyte compared to the available sites on the carbon  $(p_{mi})$  at extremely high water recovery rates with this leading to the lesseffective electrodialysis process playing a more important role in ongoing ion removal. In comparison, SCC FCDI works well at a "relatively lower" water recovery rate of 91.4% (still significantly higher than (M)CDI) (Porada et al., 2013b, Suss et al., 2015a). The effluent NO<sub>3</sub>-N concentration was constantly lower than 1 mg  $L^{-1}$  at reasonable energy consumption (~ 0.5 kWh m<sup>-3</sup>) and productivity (HRT < 1 min) (Figure 5-14).



**Figure 5-14.** Energy consumption and nitrate removal efficiency of SCC FCDI at different water recovery rates. Experiments were conducted following that in SI Fig. S7 to reduce  $X_{carbon}$ . The electrolyte was partially replaced with 1000 mg NaCl L<sup>-1</sup> solution every 5 hours. Experimental conditions: initial NO<sub>3</sub>-N concentration = 10 mg L<sup>-1</sup>, single-pass, cell voltage = 1.0 V and HRT = 0.98 min. Lines serve to guide the eye.



**Figure 5-15.** Current density and effluent conductivity of SCC FCDI at different water recovery rates. Experiments were conducted following that in SI Fig. S7 to reduce  $X_{carbon}$ . The electrolyte was partially replaced with 1000 mg NaCl L<sup>-1</sup> solution every 5

hours. Experimental conditions: initial NO<sub>3</sub>-N concentration = 10 mg L<sup>-1</sup>, single-pass, cell voltage = 1.0 V and HRT = 0.98 min. Lines serve to guide the eye.

# 5.4 Conclusions

In this study, SCC FCDI was used to remove nitrate from source waters containing different nitrate concentrations. Results indicate that FCDI is well suited to removing nitrate to levels consistent with extremely stringent standards (< 1 mg NO<sub>3</sub>-N L<sup>-1</sup>) though a less onerous target of, say, 10 mg L<sup>-1</sup> would be more cost-effective under conditions where the influent nitrate concentration is high (50 mg NO<sub>3</sub>-N L<sup>-1</sup>). Investigation of the fate of nitrate indicated that non-electrostatic adsorption of nitrate to the carbon particles initially plays a vital role in nitrate removal in FCDI. Nevertheless, the exhaustion of non-electrostatic adsorption capacity with ongoing operation did not lead to significant deterioration in performance with this result likely ascribed to the continued retention of nitrate in the EDLs of the carbon particles in the flow anode. In continuous operation of SCC FCDI, constant voltage mode is better suited to maintaining stable effluent quality. Through periodic replacement of the electrolyte at a water recovery of 91.4%, the FCDI system can achieve a continuous desalting performance with the effluent NO<sub>3</sub>-N concentration below typical target MCLs at low energy consumption (~0.5 kWh m<sup>-3</sup>) but high productivity (HRT < 1 min).

# Chapter 6. Capacitive membrane stripping for ammonia recovery (CapAmm) from dilute

wastewaters

# 6.1 Introduction

A rapidly increasing world population and improvement in living standards have resulted in the demand for greater food production with this production strongly dependent on the utilization of fertilizers rich in nitrogen (N) and phosphorus (P) to maintain soil fertility and increase crop yields (Jin et al., 2014, Tilman et al., 2002). However, the traditional Haber-Bosch process for the production of ammonia, the key component in the synthesis of most popular N fertilizers (including urea, ammonium nitrate and ammonium sulfate), is responsible for 1.5-2.5% of the annual global energy consumption and more than 1.6% of global CO<sub>2</sub> emissions (Agency 2007, Luther et al., 2015, Zhou et al., 2017a). Considering that the demand for nitrogen fertilizer is expected to increase at an average annual growth rate of 1.5% over the next decade (Garcia-Gonzalez and Vanotti 2015, Heffer and Prud'homme 2016), the issue of how to produce ammonia in a sustainable manner represents a global challenge.

While expenditure on ammonia production for fertilizer use is increasing, water contamination has become increasingly severe, especially in recently industrialized countries such as China and India, with ammonia nitrogen recognized to be one of the principal contaminants. It has been reported that 2.5 million tonnes of ammonia nitrogen is discharged annually to waterbodies in China (Jin et al., 2014), with the injection of this major nutrient resulting in severe eutrophication, acute and chronic toxicity to aquatic organisms and production of toxic byproducts during drinking water disinfection (Ji et al., 2017, Kim et al., 2006). Though a great number of robust technologies such as nitrification/denitrification, electrochemical oxidation and breakpoint chlorination have been developed to remove ammonia from wastewaters (Gao et al., 2010, Kapałka et al., 2010, Pressley et al., 1972, Zhang et al., 2012, Zhu et al., 2008), this practice would seem unsustainable in view of the lifecycle of ammonia mentioned above. In light of both the problems associated with removal of ammonia from waters and the increasing demand for ammonia-based fertilizers, there is increased interest in ammonia recovery (and production) from dilute wastewaters in view of the economic and environmental benefits (Ledezma et al., 2015, Wang et al., 2017, Zhang and Angelidaki 2015a).

The first step in the recovery of ammonia from low-strength wastewaters involves pre-concentration of the ammonia. While ion exchange adsorption by zeolites and membrane separation (e.g., reverse osmosis and nanofiltration) may be used to generate ammonia-rich solutions (Booker et al., 1996, Häyrynen et al., 2009), these technologies either suffer from high energy cost and/or require large quantities of chemicals for regeneration purposes and, as a result, are less feasible for ammonia recovery from dilute waste streams. Recently, flow-electrode capacitive deionization (FCDI) has attracted interest given its potential applications in seawater desalination and energy storage (Hatzell et al., 2015b, Häyrynen et al., 2009, Jeon et al., 2013a, Ma et al., 2016a). FCDI is particularly effective in accumulating ions in the flow electrodes with cations such as Na<sup>+</sup> and NH4<sup>+</sup> concentrated in the cathode chamber and anions such as Cl<sup>-</sup> concentrated in the anode chamber. In addition to this capacitive mechanism, electron exchange at the surface of the flow electrodes may well result in the consumption and/or production of protons.(Zhang et al., 2018a) An increase in pH in the cathode chamber (as is typical as a result, in part, of the reduction of oxygen) (He et

al., 2016b, Zhang et al., 2018a) would result in change in speciation from  $NH_4^+$ dominance at pH < pK<sub>a</sub> (of 9.3) for the  $NH_4^+$ - $NH_3$  acid-base pair to  $NH_3(aq)$  dominance at pH > pK<sub>a</sub>. Equilibrium will rapidly be established between dissolved and gaseous ammonia in the cathode chamber with the possibility of subsequent removal of  $NH_3(g)$ by interfacing the solution with a gas permeable membrane.

In this study, we develop a process for capacitive membrane stripping for ammonia recovery (CapAmm) from dilute wastewaters (**Figure 6-1**) in which ammonia undergoes migration across a cation exchange membrane and selective accumulation in the cathode chamber of a flow electrode followed by transformation to dissolved NH<sub>3</sub> with subsequent stripping via membrane contactor and recovery in acid solution (for example, as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>). A number of operational parameters associated with the performance of CapAmm are investigated with specific consideration given to the mass flow of ammonia from the influent wastewater to the acidic receiving solution. An overall evaluation of the operating cost and economic benefit of the ammonia produced highlights the opportunities and challenges of CapAmm in sustainable water, resource and energy management.



(1) Composite current collector (graphite paper)
(2) Composite current collector (acrylic plate flow channel)
(3) Cation exchange membrane (CEM)
(4) Desalination chamber
(5) Anion exchange membrane (AEM)
(6) End plate

**Figure 6-1.** Schematic representations of (a) our flow-electrode capacitive deionization (FCDI) cell, (b) the composite current collector made of graphite paper and acrylic sheet with serpentine flow channels carved by a laser cutter and (c) the FCDI system and (d) cross-section schematic of the FCDI cell.

# 6.2 Materials and methods

#### **6.2.1 Experiment Setup**

The structure of the CapAmm apparatus is shown in **Figure 6-1** and **Figure 6-2**. A silicone gasket and a nylon sheet (100-mesh) were bounded by two ion-exchange membranes (CEM-Type I/AEM-Type I, FUJIFILM Europe) with the gap between the ion exchange membranes acting as a spacer chamber (thickness of ~500  $\mu$ m) through which the wastewater flowed (**Figure 6-1b**). Acrylic sheets with carved serpentine channels for flow electrodes were placed against the graphite current collectors (**Figure 6-1a**). The cross-section of each channel was 3 mm × 3 mm with an effective contact area between the ion-exchange membrane and the flow electrodes of 34.9 cm<sup>2</sup>. These parts were held together with the use of acrylic end plates (**Figure 6-1a**). The flow electrodes were continuously cycled between the flow channels and the circulation tanks, with the polypropylene (PP) hollow-fiber membrane contactor (**Figure 6-1c**) placed in the negatively charged flow electrode circulation tank. The total length of the membranes used in this work was 30 cm, with outer diameter of 2 mm, wall thickness of 0.1 mm, pore size of 0.45  $\mu$ M and total effective surface area of 18.8 cm<sup>2</sup>.

#### **6.2.2 Operating Conditions**

Synthetic wastewater containing 1000 mg NaCl  $L^{-1}$  and 40 mg NH<sub>4</sub><sup>+</sup>-N  $L^{-1}$  was fed into the spacer chamber in single-pass mode. The effect of different wastewater flow rates (of 0.85 to 2.55 mL min<sup>-1</sup> with corresponding hydraulic retention time (HRT) of 2.94 to 0.98 min) was evaluated in this study. The electrical conductivity of this stream was continuously measured at the outlet with the use of a conductivity meter (CON-BTA, Vernier) connected to a data acquisition system (SensorDAQ, Vernier). The flow electrodes were composed of 10 wt% 100-mesh DARCO activated carbon (average particle diameter of 18.5 µm) and 90 wt% Milli-Q water and were prepared according to our preliminary studies (Ma et al., 2016a). In all experiments, the flow electrodes (65 mL) were recirculated respectively using a dual-head peristaltic pump (Longer pump, Baoding, China) at a constant flow rate of 50 mL min<sup>-1</sup>. In one operating cycle, electrosorption was carried out at a constant current density (3.0-17.2 A m<sup>-2</sup>) using a DC power supply (MP3840, Powertech). For ammonia recovery, the membrane module was immersed in the cathode flow-electrode slurry while 65 mL of receiving solution (0.5 M sulfuric acid) was continuously circulated (at 50 mL min<sup>-1</sup>) inside the hollow fibre membranes (Darestani et al., 2017, Rezakazemi et al., 2012).



Figure 6-2. Cross-section schematic of the FCDI cell used in the CapAmm system.

The gas permeable membrane separates two circulating solutions, with the cathode flow-electrode suspension passing over the exterior of the membrane and the receiving solution (sulfuric acid) flowing inside the membrane. The pores of the gas permeable membrane are filled with air and cannot be wetted by the aqueous solution. During operation,  $NH_4^+$  in the wastewater is first removed and accumulates in the cathode flow-electrode, where the pH is high and enhances the transformation  $NH_4^+$  to  $NH_3$ .  $NH_3$  evaporates near the aqueous-membrane interface, diffuses through the

membrane pores and reacts with the sulfuric acid thereby generating ammonium sulfate. At the low pH of the acidic receiving stream, the concentration of NH<sub>3</sub> is very low with the difference in NH<sub>3</sub> partial pressure between the flow-electrode and acid receiving solution representing the driving force for ammonia transport across the membrane (**Figure 6-3**).



Figure 6-3. Mechanism of ammonia recovery by the gas permeable.

#### 6.2.3 Analytical Methods and Calculations

The voltage (*U*) across the electrical circuit was recorded every five seconds using a Vernier voltage probe connected to the SensorDAQ. The variation of pH in the flow electrode was monitored by an F-51 pH meter (Horiba, Japan). Samples from the influent, effluent, cathodic flow electrode, and acidic receiving solution were collected every 30 min. All samples were filtered through 0.45  $\mu$ m filters (Millipore) prior to further analysis. Ammonium ion concentrations were determined by ion chromatography (ICS-3000, Dionex, U.S.) with the instrument used equipped with guard column CG16 (5 × 50 mm) and separation column CS16 (5 × 250 mm). Sodium concentration was measured by ICP-OES (Agilent Varian vista pro 710). Current efficiency and energy consumption are two key parameters used to evaluate the performance of the CapAmm system. Current efficiency (%) can be expressed as:

$$\eta = \frac{\sum n_i \times F \times v \times \int_0^t (C_{i,inf} - C_{i,eff}) dt}{M \times \int_0^t IA dt} \times 100$$
(6-1)

where  $C_{i,inf}$  is the initial influent concentration (mg L<sup>-1</sup>) of ion species *i*,  $C_{i,eff}$  the effluent concentration (mg L<sup>-1</sup>) of ion species *i*, *v* the flow rate (m<sup>3</sup> s<sup>-1</sup>) of the wastewater stream, *I* the applied current density (A m<sup>-2</sup>),  $M_i$  is the molar mass of ion species *i* (g mol<sup>-1</sup>), *A* is the effective current area between the ion-exchange membrane and the flow electrodes (0.0035 m<sup>2</sup>), *F* the Faraday constant (96485.3 C mol<sup>-1</sup>) and  $n_i$  the charge of certain ion species (*i.e.*, 1 for NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup>). The electrical energy consumption for wastewater treatment (and deionization) (kWh m<sup>-3</sup>) was calculated according to:

$$EC = \frac{\int_{0}^{t} U_{t} \times IA dt}{3600000 \times \int_{0}^{t} v dt}$$
(6-2)

where  $U_t$  is the voltage (V) across the circuit of the CapAmm system, *I* the applied current density (A m<sup>-2</sup>), *A* is the effective current area between the ion-exchange membrane and the flow electrodes (0.0035 m<sup>2</sup>), *v* is the flow rate (m<sup>3</sup> s<sup>-1</sup>) of the wastewater.

The specific energy consumption for  $NH_4^+$ -N recovery (kWh kg<sup>-1</sup> N) can be calculated as:

$$EC_{\mathrm{NH_4^+-N, recovery}} = \frac{\int_0^t U_t \times IAdt}{3.6 \times C_{\mathrm{NH_4^+-N, acid}} \times V_{acid}}$$
(6-3)

where  $U_t$  is the voltage across circuit of the CapAmm system, I is the current density,  $C_{\text{NH4+-N,acid}}$  is the ammonia concentration (mg L<sup>-1</sup>) in the acidic receiving solution at time *t*,  $V_{\text{acid}}$  is the volume of the receiving solution (0.065 L). The removal efficiency of certain ion (%) was determined according to:

$$RE_{i} = (1 - \frac{C_{i,eff}}{C_{i,inf}}) \times 100$$
(6-4)

The ion selectivity can be expressed by the ratio of the ion removal efficiency, *i.e.*, the  $NH_4^+$ -N selectivity towards  $Na^+$  was calculated as  $RE(NH_4^+-N)/RE(Na^+)$ .

The ammonia recovery efficiency ( $\rho$ , %) can be calculated according to:

$$\rho_{\mathrm{NH}_{4}^{+}-\mathrm{N}} = \left(\frac{C_{\mathrm{NH}_{4}^{+}-\mathrm{N},acid} \times V_{acid}}{v \times t \times C_{\mathrm{NH}_{4}^{+}-\mathrm{N},\mathrm{inf}}}\right) \times 100$$
(6-5)

The average ammonia removal rate  $(g N m^{-2} d^{-1})$  can be calculated according to:

$$R_{\rm NH_4^+-N, removal} = \frac{86400 \times (C_{\rm NH_4^+-N, inf} - C_{\rm NH_4^+-N, eff}) \times v}{A}$$
(6-6)

Where  $C_{\text{NH4+-N,inf}}$  is the initial influent  $\text{NH}_4^+$ -N concentration (mg L<sup>-1</sup>),  $C_{\text{NH4+-N,eff}}$  the effluent  $\text{NH}_4^+$ -N concentration (mg L<sup>-1</sup>) of ion species *i*, *v* the flow rate (m<sup>3</sup> s<sup>-1</sup>) of the wastewater stream, *A* is the effective area of the ion exchange membrane membrane (0.00349 m<sup>2</sup>).

The average ammonia recovery rate  $(g N m^{-2} d^{-1})$  can be calculated according to:

$$R_{\mathrm{NH_4^+}-\mathrm{N},\mathrm{recovery}} = \frac{86.4 \times C_{\mathrm{NH_4^+}-\mathrm{N},acid} \times V_{acid}}{A \times t}$$
(6-7)

 $C_{\text{NH4+-N,acid}}$  is the ammonia concentration (mg L<sup>-1</sup>) in the acidic receiving solution at time *t*,  $V_{\text{acid}}$  is the volume of the receiving solution (0.065 L), *A* is the effective area of the ion exchange membrane membrane (0.00349 m<sup>2</sup>).

Finally, the distribution of the ions (ammonia and sodium) in the effluent, acid solution, cathode electrolyte was obtained by dividing the total amount of a particular ion contained in the effluent, acid solution, cathode electrolyte with the total amount of that ion in the influent. Through the mass balance principle, the remaining ions were considered to be the amount of ions absorbed on the carbon particles or stripped into the air (these parameters cannot be measured directly).

## 6.3 Results and discussion

#### 6.3.1 Ammonia Removal from the Dilute Wastewater

Results for salt removal performance in the CapAmm system at different charging current densities and HRTs are summarized in **Figure 6-4 and Figure 6-5**. Relatively stable effluent conductivity was observed under all experimental conditions, with higher current densities and longer HRTs resulting in greater reduction in feed water conductivity (**Figure 6-4**). Meanwhile, increases in both applied current densities and HRTs also exert positive effects on NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> removal. It is also revealed that CapAmm has a higher selectivity for NH<sub>4</sub><sup>+</sup>-N compared to Na<sup>+</sup> removal, particularly at lower current density and/or HRT (**Figure 6-5a and b**). For instance, the ratio of removal efficiency between NH<sub>4</sub><sup>+</sup>-N and Na<sup>+</sup> (*i.e.*, *RE*(NH<sub>4</sub><sup>+</sup>-N)/*RE*(Na<sup>+</sup>)) was 2.5 at a current densities of 5.8, 11.5 and 17.2 A m<sup>-2</sup>. A similar trend was observed for the effect of change in HRT with *RE*(NH<sub>4</sub><sup>+</sup>-N)/*RE*(Na<sup>+</sup>) declining from 1.6 to 1.0 on increase in HRT from 0.98 to 2.94 min.

It has previously been reported that ions with a smaller hydrated radius are transported more rapidly from the feed water into the cathodic flow electrode under a fixed electrical field, provided that they have the same valence charge (Tran et al., 2015). Additionally, smaller ions are more readily electrosorbed by activated carbon particles than larger ions because of their easier access to the micro-pores of these particle electrodes (Hou and Huang 2013, Zhou et al., 2018a). The fact that  $NH_4^+$  has a slightly smaller hydrated radius (3.31 Å) than  $Na^+$  (3.58 Å) may account for the observation that the electrosorption

process in our CapAmm system exhibits a higher selectivity towards  $NH_4^+$  compared to  $Na^+$  at lower current densities/shorter HRTs (Nightingale Jr 1959).



**Figure 6-4.** Effluent conductivity variation of CapAmm system in single-pass mode (a) at different charging current densities (*i.e.*, 3.0, 5.8, 11.5 and 17.2 A m<sup>-2</sup>) with the HRT of the feed wastewater fixed at 1.48 min, and (b) at a constant current density of 11.5 A m<sup>-2</sup> with different HRTs (*i.e.*, 0.98, 1.48, 1.96, and 2.94 min).

#### 6.3.2 Ammonia Transformation in the Flow Electrode

**Figure 6-5c and d** indicate that the pH of the cathode gradually changed from neutral to alkaline during operation. The shaded areas represent the region where the pH was higher than the  $pK_a$  of NH<sub>4</sub><sup>+</sup> (9.3). In this region, almost all of the NH<sub>4</sub><sup>+</sup> will be deprotonated and transformed into dissolved NH<sub>3</sub>, thereby providing ideal prerequisites for ammonia separation and recovery from the bulk solution via membrane stripping.

According to recent studies, Faradaic reactions such as oxygen reduction take place at the cathode even when the cell voltage is relatively low (e.g. < 1.0 V), consuming H<sup>+</sup> and resulting in pH increase (Dykstra et al., 2017, Holubowitch et al., 2017, Nativ et al., 2017, Zhang et al., 2018a). It is to be expected that higher current densities (and higher charging voltages) facilitate oxygen reduction leading to a more rapid rise in pH in the cathode. In contrast, changing HRTs does not influence the duration for which the flow electrode is exposed to a particular applied potential (as the flow electrode is recirculated at a constant rate) and, as such, would not be expected to significantly influence the pH.



**Figure 6-5.** Average removal efficiencies for ammonium and sodium ions in the CapAmm system (a) under different current densities (*i.e.*, 3.0, 5.8, 11.5 and 17.2 A m<sup>-2</sup>) with a constant HRT of 1.48 min, and (b) at a constant current of 11.5 A m<sup>-2</sup> with HRTs of 0.98, 1.48, 1.96 and 2.94 min. The blue symbols are the ratio of removal efficiency of *RE* (NH<sub>4</sub><sup>+</sup>-N)/*RE* (Na<sup>+</sup>) with this ratio representing the selectivity of NH<sub>4</sub><sup>+</sup> compared to Na<sup>+</sup>. Temporal change of pH in the cathode chamber of the CapAmm system operated (c) under different current densities (*i.e.*, 3.0, 5.8, 11.5 and 17.2 A m<sup>-2</sup>) with a constant HRT of 1.48 min, and (d) under a constant current of 11.5 A m<sup>-2</sup> with different HRTs (*i.e.*, 0.98, 1.48, 1.96, and 2.94 min). The shade area represents the pH range >9.3, indicating the deprotonation of NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub>.

#### 6.3.3 Ammonia Recovery and Energy Consumption

As shown in **Figure 6-6**, it can be concluded that ammonium ions removed from the feed stream were effectively transferred to the acidic receiving solution, with the recovered NH<sub>4</sub><sup>+</sup>-N concentrations finally reaching  $51.1 \pm 1.2$ ,  $100.1 \pm 9.6$ ,  $147.2 \pm 0.6$  and  $174.9 \pm 11.4$  mg L<sup>-1</sup> at 3.0, 5.8, 11.5 and 17.2 A m<sup>-2</sup> respectively (**Figure 6-6a** and **b**). The average ammonia recovery rate increased from 5.7 to 19.5 g N m<sup>-2</sup> d<sup>-1</sup> when the current density increased from 3.0 to 17.2 A m<sup>-2</sup>. In the first hour, the NH<sub>4</sub><sup>+</sup>-N concentration in the acid solution increased relatively slowly, presumably because the initial low pH in the cathode chamber (**Figure 6-6a** and **d**) hindered the transformation of NH<sub>4</sub><sup>+</sup> into NH<sub>3</sub> and the subsequent diffusion of ammonia across the gas membrane. On analysing the NH<sub>4</sub><sup>+</sup>-N concentration in the cathode solution, a sharp increase was observed in the first hour and then reached a relatively stable concentration of 35-40 mg L<sup>-1</sup> in the following three hours (**Figure 6-6a**). Similar trends were observed when operated under different HRTs (**Figure 6-6c** and **d**).

From **Figure 6-7a**, we can clearly see that the applied current density plays an important role in ammonia recovery. At current density higher than 11.5 A m<sup>-2</sup>, 55-65% ammonia can be recovered by the membrane contactor as ammonium fertilizer, while about 15% of the ammonia is still present in the cathode and 20% was not detected (presumably either because it is electro-absorbed on the carbon particles or because it has been air-stripped). It is therefore of great significance to recover the ammonia that remains in the cathode chamber (~35% of the total) in our future studies. As is clear from **Figure 6-7b**, HRTs have a minor influence on the ammonia recovery efficiency, especially when the HRT is longer than 1.48 min, with a similar recovery rate at these long HRTs of 50~60%.

An overview of the effluent water quality, NH4<sup>+</sup>-N recovery efficiency, energy consumption and average ammonia removal/recovery rate over a range of operating



conditions is provided in **Table 6-1**. Overall, the energy required for water desalination ranged from 0.05-1.95 kWh m<sup>-3</sup>, depending on the applied current densities and HRTs.

**Figure 6-6.** Temporal variation of ammonia concentrations in (a) the cathode chamber and (b) acidic receiving solution of the CapAmm system operated under different current densities (*i.e.*, 3.0, 5.8, 11.5 and 17.2 A m<sup>-2</sup>) with a constant HRT of 1.96 min, and ammonia concentrations in (c) the cathode chamber and (d) acidic receiving solution of the system charged at a constant current density of 11.5 A m<sup>-2</sup> with different HRTs (*i.e.*, 0.98, 1.48, 1.96 and 2.94 min).



**Figure 6-7.** Fate and distribution of ammonia in the CapAmm system (a) at different current densities (*i.e.*, 3.0, 5.8, 11.5, and 17.2 A m<sup>-2</sup>) with a constant HRT of 1.96 min, and (b) at a constant current of 11.5 A m<sup>-2</sup> with different HRTs (*i.e.*, 0.98, 1.48, 1.96, and 2.94 min).

At applied current densities of 3.0, 5.8, and 11.5 A m<sup>-2</sup> (for HRT fixed at 1.48 min), the energies consumed for ammonia recovery were 6.1, 9.9 and 21.7 kWh Kg<sup>-1</sup> N with the recovery efficiencies reaching 18.7%, 38.1% and 55.1% respectively, and the average recovery rates attained calculated (respectively) to be 5.7, 11.3 and 16.5 g N m<sup>-2</sup> d<sup>-1</sup>. The energy consumption of the CapAmm system is comparable with the energy required for N fixing by Haber-Bosch processes (10.3-12.5 kWh kg<sup>-1</sup> N) (Mulder et al., 2003) as well as other ammonia removal/recovery systems. For instance, conventional WWTPs, which typically rely on two-stage nitrification/denitrification processes to covert ammonia (and other reactive nitrogen species) back to N<sub>2</sub> gas, generally require an energy input of ~12.5 kWh kg<sup>-1</sup> N (including the cost of electricity, internal water recycling, etc) while the use of external carbon sources (*e.g.*, methanol) would result in a much higher energy consumption of 30.3 kWh kg<sup>-1</sup> N (Maurer et al., 2003). Air-stripping requires the addition of extra base (to raise the pH to 9.5-12) and/or heating to

25-85 °C to covert ammonium (NH<sub>4</sub><sup>+</sup>) to its volatile form (NH<sub>3</sub>), resulting in high energy consumption (3.9-28.2 kWh kg<sup>-1</sup> N) (Antonini et al., 2011, Başakçilardan-Kabakci et al., 2007).

Meanwhile, the energy consumption of the CapAmm system is comparable with other electrochemical ammonia recovery systems. An integrated system composed of a hydrogen gas  $(H_2)$  recycling electrochemical cell (recycling of the  $H_2$  generated at the cathode to the anode) and a gas permeable membrane contactor was found to achieve an ammonia recovery efficiency of 60-73% and an average ammonia recovery rate 110.2 g N  $m^{-2} d^{-1}$  at an energy requirement of 10.0 kWh kg<sup>-1</sup> N (Kuntke et al., 2017). However, this system required the injection of additional H<sub>2</sub> and the application of a noble catalyst to enable stable operation with these components representing an additional energy cost (Kuntke et al., 2017). Another ammonia recovery system that combined an electrochemical cell (EC) and air-stripping was able to recover 96% ammonia at a recovery rate of 120 g N  $m^{-2} d^{-1}$  and exhibited an energy consumption of 20 kWh kg<sup>-1</sup> N (with 13 kWh kg<sup>-1</sup> N for EC and 9 kWh kg<sup>-1</sup> N for air-stripping) (Desloover et al., 2012). More importantly, it should be noted that most of these ammonia recovery systems were focussed on harvesting ammonia from high ammonia concentration (~3400 mg L<sup>-1</sup> N) streams (such as urine) with relatively low concentrations of competing ions (~1400 mg  $L^{-1}$  K<sup>+</sup> and ~1600 mg  $L^{-1}$  Na<sup>+</sup>) with the competitive cations and  $NH_4^+$ -N mole ratio as low as 0.43. However, the influent of our CapAmm system contains 40-50 mg L<sup>-1</sup> NH<sub>4</sub><sup>+</sup>-N (~80 times lower than that in urine) and  $\sim$ 390 mg L<sup>-1</sup> Na<sup>+</sup> ( $\sim$ 1000 mg L<sup>-1</sup> NaCl) resulting in a high Na<sup>+</sup>/NH<sub>4</sub><sup>+</sup>-N mole ratio of 5.7. This means that a larger part of the energy will be consumed for water desalination (salt removal) thereby resulting in relatively lower ammonia recovery rate. In our future studies, we will examine the applicability (and energy usage) of the

CapAmm process to recovery of ammonia from medium/high ammonia concentration waste streams.

In contrast, bioelectrochemical systems (BES), which take advantage of electrochemically active bacteria to degrade organic matter and generate electricity, can recover ammonia at much lower energy demand compared to traditional EC systems and the CapAmm system introduced here (Kuntke et al., 2014, Kuntke et al., 2012, Ledezma et al., 2017, Zamora et al., 2017). In BES systems however, the ammonia recovery rate is relatively slow (3-5 g N m<sup>-2</sup> d<sup>-1</sup>) due to the limited current density produced by the anaerobic bacteria at the anode (Kuntke et al., 2012, Zhang and Angelidaki 2015a). Additionally, the biological process is very sensitive to a range of environmental factors including, pH, carbon loading, chemical toxicity (e.g., ammonia present in the influent) and temperature, restricting the practical application of these technologies. Indeed, the CapAmm process may have an advantage over bioelectrochemical systems in view of its greater stability, predictability and flexibility and the opportunity for automatic control of the reactor.

 Table 6-1. Comparison of effluent water quality, ammonia recovery efficiency, energy

 consumption and ammonia removal/recovery rate over a range of operating conditions

Operation parameter	$\begin{array}{c} Effluent \\ NH_4^+-N \\ (mg \ L^{-1} \ ) \end{array}$	Effluent NaCl (mg L <sup>-1</sup> )	NH4 <sup>+</sup> -N recovery efficiency (%)	Energy demand for water desalination (kWh m <sup>-3</sup> )	Energy demand for NH4 <sup>+</sup> -N recovery (kWh Kg <sup>-1</sup> N)	Ammonia removal rate (g N m <sup>-2</sup> d <sup>-1</sup> )	Ammonia recovery rate (g N m <sup>-2</sup> d <sup>-1</sup> )
HRT: 1.48 min <i>I</i> : 3.0 A m <sup>-2</sup>	18.7	719.4	18.7	0.05	6.1	17.1	5.7
HRT: 1.48 min <i>I</i> : 5.8 A m <sup>-2</sup>	12.9	561.7	38.1	0.16	9.9	21.1	11.3
HRT: 1.48 min <i>I</i> : 11.5 A m <sup>-2</sup>	4.0	281.8	55.1	0.51	21.7	27.3	16.5
HRT: 1.48 min <i>I</i> : 17.2 A m <sup>-2</sup>	1.9	34.3	64.5	1.35	48.4	28.8	19.5
HRT: 0.98 min <i>I</i> : 11.5 A m <sup>-2</sup>	8.6	476.9	34.6	0.31	13.6	36.2	16.0
HRT: 1.96 min <i>I</i> : 11.5 A m <sup>-2</sup>	1.6	75.8	52.4	0.78	46.8	21.8	11.7
HRT: 2.98 min <i>I</i> : 11.5 A m <sup>-2</sup>	1.4	51.3	46	1.95	206.8	14.6	6.62

In contrast, bioelectrochemical systems (BES), which take advantage of electrochemically active bacteria to degrade organic matter and generate electricity, can recover ammonia at much lower energy demand compared to traditional EC systems and the CapAmm system introduced here (Kuntke et al., 2014, Kuntke et al., 2012, Ledezma et al., 2017, Zamora et al., 2017). In BES systems however, the ammonia recovery rate is relatively slow (3-5 g N m<sup>-2</sup> d<sup>-1</sup>) due to the limited current density produced by the anaerobic bacteria at the anode (Kuntke et al., 2012, Zhang and Angelidaki 2015a). Additionally, the biological process is very sensitive to a range of environmental factors including, pH, carbon loading, chemical toxicity (e.g., ammonia present in the influent) and temperature, restricting the practical application of these technologies. Indeed, the CapAmm process may have an advantage over bioelectrochemical systems in view of its greater stability, predictability and flexibility and the opportunity for automatic control of the reactor.

#### **6.4 Environmental Implications**

Our study demonstrates that the CapAmm process can be a very effective alternative for ammonia removal and recovery from dilute wastewaters. Compared with other ammonia recovery systems that require additional chemical dosing to adjust the pH and which use energy-intensive air stripping to extract ammonia, CapAmm allows for the selective ammonia removal and preconcentration in the cathode chamber, with the elevation in pH that occurs as a result of intrinsic Faradaic processes favouring the conversion of NH<sub>4</sub><sup>+</sup> in to dissolved NH<sub>3</sub>. Given the rapidity with which solution phase ammonia equilibrates with gaseous ammonia, NH<sub>3</sub>(g) will readily diffuse through a gas-permeable membrane into an acid solution and may be recovered as an ammonium salt which can be readily marketed as a fertilizer. In addition, our experimental setup is less complex than other experimental setups which utilize energy intensive air-stripping processes or require the use of multiple absorption vessels. While sulphuric acid was used in this study as an example for ammonia recovery, alternatives (such as phosphoric acid or nitric acid) could be considered in order to produce higher-value fertilizers.

# Chapter 7. Continuous Ammonia Recovery from Wastewaters Using an Integrated Capacitive Flow Electrode Membrane Stripping System

# 7.1 Introduction

While nitrogen gas constitutes about 78% of the terrestrial atmosphere, the availability of its active forms (*i.e.*, ammonium, nitrite and nitrate) as essential nutrients for agricultural plant growth and other anthropogenic uses is limited (Gruber and Galloway 2008). The invention of the Haber-Bosch process in the early twentieth century enabled the manufacture of ammonia (an important raw material for N-based fertilizers) on an industrial scale with the ready availability of this essential nutrient dramatically enhancing global agricultural productivity and consequently economic growth (Erisman et al., 2008, Galloway et al., 2008, Gruber and Galloway 2008). However, the Haber-Bosch process involves the chemical combination of nitrogen and hydrogen gas under high temperature (~500 °C) and high pressure (200-300 atm) conditions, accounting for about 2% of the world energy consumption and 1.6% of global greenhouse gases emissions (Luther et al., 2015, Zhou et al., 2017b). With the continuous increase in world population and improvement in living standards, the demand for nitrogen fertilizer is projected to increase by 50% by 2050 (Sutton and Bleeker 2013). Therefore, the development of more sustainable, efficient, and economic routes for the production of ammonium-based fertlizers is of great significance (Guo et al., 2018, Luo et al., 2018, Sengupta et al., 2015).

From a lifecycle perspective, most food proteins are degraded to ammonium ions and/or urea in metabolic processes and end up in sewage. It is reported that the waste stream accounts for 18-21% of the N-fertilizers that are produced by industrial nitrogen fixation (Mulder 2003) with the discharge of sewage containing even dilute concentrations of nitrogen into waterbodies created various environmental issues on a global scale, including the deterioration of water quality and loss of biodiversity (Duce et al., 2008, Erisman et al., 2008, Larsen et al., 2013, Zhao et al., 2015). While conventional wastewater treatment plants might take advantage of nitrification/denitrification processes to convert reactive nitrogen back to N2, this practice essentially attempts to reverse the ammonia production process from which most of the sewage nitrogen is derived (Galloway et al., 2004). Therefore, processes that enable the direct recovery of ammonia from sewage/urine and effectively close the loop between fertilizer production and wastewater treatment rather than using N2 as an intermediate have attracted increasing attention in view of the potential enormous economic and environmental benefits.

Of the technologies available, air-stripping followed by acid adsorption is a well-established process that has been intensively studied in last decade. However, airstripping requires the addition of extra base (to raise the pH to 9.5-12) and/or heating to 25-85 °C to covert ammonium (NH<sub>4</sub><sup>+</sup>) to its volatile form (NH<sub>3</sub>), resulting in high energy consumption (3.9-28.2 kWh kg<sup>-1</sup> N) (Antonini et al., 2011, Başakçilardan-Kabakci et al., 2007). Ion exchange is another recovery method with ammonium ions first being selectively adsorbed (by materials such as zeolites, resins and biochar) followed by chemical desorption to generate a concentrated ammonium stream (Tarpeh et al., 2017, Wang and Peng 2010). The drawbacks of this technology relate to the need for a large amount of chemicals (such as NaCl and NaOH) to regenerate the adsorbents. Recently, electrochemical ammonia removal (and recovery) technologies have gained in popularity as a result of advantages such as efficient ammonium enrichment driven by the electrical field and concomitant pH increase that enables ammonia recovery (*e.g.*, by methods such as membrane stripping). In a dual-chamber electrochemical system,  $NH_4^+$  migrates to the negatively charged chamber where it is then transformed to  $NH_3$  and recovered as value added products, with an average energy consumption ranging from 10 to 30 kWh kg<sup>-1</sup> N (Desloover et al., 2015, Desloover et al., 2012, Kuntke et al., 2017, Luther et al., 2015, Matassa et al., 2015, Rodriguez Arredondo et al., 2017). Bio-electrochemical systems (BES), which use bacteria at the anode to oxidize organic matter and produce electricity, can recover ammonia at an lower energy demand (< 5 kWh kg<sup>-1</sup> N) (Kuntke et al., 2014, Kuntke et al., 2012, Ledezma et al., 2017, Ma et al., 2017, Zamora et al., 2017) though the recovery rate still need to be further improvement.

Capacitive membrane stripping for ammonia recovery (CapAmm), first proposed by Waite's group (Zhang et al., 2017), is composed of a flow-electrode capacitive deionization unit and a gas-permeable membrane contactor. This technology allows simultaneous salt removal and ammonia recovery from dilute wastewaters. While the mechanism involving NH4<sup>+</sup> migration and transformation are similar to those reported in conventional electrochemical systems (Luther et al., 2015), the capacitive ion immobilisation and extraction from wastewaters as a result of the formation of electrical double layers on the charged flow-electrode sustains a high coulombic efficiency in the CapAmm system (Zhang et al., 2018a, Zhang et al., 2017). Results of our previous study showed that with the use of a hollow-fibre membrane contactor, the CapAmm process could achieve an ammonium recovery rate of ~60% with a relatively low energy requirement (Zhang et al., 2017). Although the CapAmm process is highly competitive with regard to ammonia recovery from dilute wastewaters in view of its moderate operating conditions (*e.g.*, low voltage and temperature independence) and high energy efficiency, consideration should be given to (i) simplification of the CapAmm configuration, (ii) optimisation of operating conditions, particularly in relation to minimization of energy consumption, (iii) potential application of the CapAmm for ammonia recovery from high-strength wastewaters (*i.e.*, urine, digestate and landfill leachate) and (iv) the possibility of continuous (long-term) operation before this method could be recommended as a viable choice for large-scale ammonia recovery from wastewaters.

As a result, an integrated CapAmm system was developed in this study (**Figure 7-1**). Compared to the previous configuration that requires *ex-situ* ammonia stripping (Zhang et al., 2017), a flat-sheet gas-permeable membrane was simply inserted into an electrochemical unit in the new design, thus providing a more compact and cost-effective means of ammonia recovery. Impacts of different operating conditions on the performance of this modified CapAmm process were evaluated in order to ascertain the effect of particular parameters on ammonia recovery and energy demand. Finally, continuous ammonia recovery (and/or water desalination) was then carried out using the optimal operating conditions with detailed analysis of the opportunities and challenges likely to be encountered in use of a scaled-up CapAmm process. The overarching goal of this study was to ascertain how to best implement the CapAmm process such that ammonia and water recovery were maximized and energy usage minimized.

# 7.2 Materials and methods

#### 7.2.1 Experiment Setup

The structure of the CapAmm apparatus is shown in **Figure 7-1**. It is a fourchambered parallel plate reactor in which four square silicon gasket frames and three membranes (*i.e.*, anion exchange membrane (AEM), cation exchange membrane (CEM) and flat-sheet gas membrane (FGM)) were bolted together between two acrylic end plates to create the anode, desalination, cathode and acid chambers respectively (**Figure 7-1a** and **b**). AEM-Type I and CEM-Type I were provided by FUJIFILM Europe and the FGM was obtained from Ningbo Changqi Porous Membrane Technology Co., Ltd (Ningbo, China). The effective contact area ( $A_{eff}$ ) between flow electrode and the membrane was 58.0 cm<sup>2</sup>. The desalination chamber (~2.5 mL) consisted of a nylon spacer sheet (100-mesh, 160 mm × 70 mm) residing within the silicone gasket (500 µm thickness) sandwiched between the AEM and CEM (Ma et al., 2016a, Tang et al., 2015b). The flow electrodes were continuously cycled between the graphitic flow channels and the circulation reservoirs (**Figure 7-1a** and **c**). Similar to the desalination chamber, the acid chamber also consisted of a nylon spacer sheet (100-mesh, 160 mm × 70 mm) placed within a silicone gasket (500 µm thickness) between the FGM and the acrylic end plate (**Figure 7-1a**).

#### 7.2.2 Operating Conditions

In this study, aqueous solutions for the saline wastewater and flow-electrode electrolyte were prepared using 18.2 M $\Omega$  cm Milli-Q water (Millipore) and NaCl and NH<sub>4</sub>Cl solutes (>99.0%, ACS grade) from Sigma Aldrich. The effects of operation parameters (carbon contents, current densities, HRTs and operational modes) were first investigated with the CapAmm operated in single-pass mode with synthetic dilute wastewater containing ~1000 mg L<sup>-1</sup> NaCl and ~43 mg L<sup>-1</sup> NH<sub>4</sub><sup>+</sup>-N (similar to that of real AnMBR effluent) running through the desalination chamber at different flow rates with corresponding hydraulic retention times (HRT) of 0.98, 1.48, 1.96, and 2.94 min. The electrical conductivity of the treated wastewater was continuously monitored with the use of a conductivity meter (CON-BTA, Vernier) connected to a data acquisition system (SensorDAQ, Vernier). To evaluate the effect of carbon content on CapAmm

performance, three carbon mass loadings (of 2, 5, and 10 wt%) were chosen and tested. Before all experiments, the flowable electrodes were continually mixed using a magnetic stirrer to achieve homogeneous carbon suspensions (Ma et al., 2016a). A 40 mL receiving solution (0.5 M sulfuric acid) was continuously recirculated at 50 mL min<sup>-1</sup> between the acid chamber and a stirred acid reservoir (**Figure 7-1a**).

In this study, ammonia removal and recovery in CapAmm were carried out at a constant current density (1.8-10.4 A m<sup>-2</sup>) using a DC power supply. The performance in two operational modes, *i.e.*, isolated closed-cycle (ICC) and short-circuited closed-cycle (SCC) modes (Figure 7-1c) were compared as reported in previous works (Doornbusch et al., 2016b, He et al., 2018b, Jeon et al., 2014). In ICC mode, 40 mL positively and negatively charged flow electrodes were individually recirculated between the CapAmm Cell and two stirred reservoirs. A 2-hour charging stage was followed by reversecurrent discharging ( $\sim 0.3$  h) to regenerate the electrodes and recover part of the energy. In SCC mode, 80 mL carbon suspension was pumped in parallel through the anodic and cathodic flow channels and then returned and mixed in the reservoir with this approach resulting in charge neutralization and regeneration of the electrodes (Figure 7-1c). However, the acid and base produced by Faradaic reactions in the flow-electrode chamber will also be neutralized, resulting in a stable solution pH of around 7. Therefore, when operated in SCC mode, 0.5 mL 2 M NaOH solution was periodically added into the flow electrodes to maintain an average pH value around 11 that is similar to that in ICC mode. Control experiments were conducted under similar conditions but without addition of NaOH solutions.

Real wastewater collected from a local AnMBR wastewater treatment plant was then treated by CapAmm under the optimal conditions obtained from the studies on synthetic wastewater. The water quality of the real wastewater used is provided in Table S1. Meanwhile, the possibility of ammonia recovery from high-strength wastewaters (in this case synthetic urine) using CapAmm was also tested. In order to achieve better removal/recovery performance, lower current density (27.2 A  $m^{-2}$ ) and longer HRT (5.88 min) were applied.

Finally, continuous operation of the CapAmm was conducted in ICC mode over 50 hours (25 cycles) of operation. Each cycle involved the sequence of (i) 2-h charging for electrosorption at a constant current density, (ii) regeneration of the electrodes by mixing the charged slurry and replacement part of the electrolyte after sedimentation, and (iii) equal division of the mixed electrodes into the reservoirs. The analytical methods and calculations are presented in Supporting Information.

#### 7.2.3 Analytical Methods and Calculations

The voltage (*U*) across and current (*i*) through the electrical circuit was recorded using a Vernier voltage probe connected to the SensorDAQ. The pH in the flow electrodes was monitored using an F-51 pH meter (Horiba, Japan). Samples from the effluent, cathodic flow electrode and acidic receiving solution were collected every 20 min. All samples were filtered through 0.45  $\mu$ m filters (Millipore) prior to further analysis. Cation concentrations were measured by ion chromatography (ICS-3000, Dionex) with the instrument equipped with a guard column CG16 (5 × 50 mm) and a separation column CS16 (5 × 250 mm).

The removal efficiency (in %) of a particular ion was determined according to:

$$RE_{i} = (1 - \frac{C_{i,eff}}{C_{i,inf}}) \times 100$$
(7-1)

where  $C_{i,inf}$  is the influent concentration (mg L<sup>-1</sup>) of ion species *i* and  $C_{i,eff}$  the effluent concentration (mg L<sup>-1</sup>) of ion species *i*.

Current efficiency and energy consumption are two key parameters used to evaluate the performance of the CapAmm system. Current efficiency (%) can be expressed as:

$$A = \frac{\sum \frac{n_i \times F \times v \times \int_0^t (C_{i,inf} - C_{i,eff}) dt}{M_i}}{\int_0^t IA dt} \times 100$$
(7-2)

where  $n_i$  is the charge of certain ion species (*i.e.*, 1 for NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup>), *F* the Faraday constant (96485.3 C mol<sup>-1</sup>), *v* the flow rate (m<sup>3</sup> s<sup>-1</sup>) of the wastewater stream,  $M_i$  the molar mass of ion species *i* (g mol<sup>-1</sup>), *A* the effective area between the ion-exchange membrane and the flow electrode (0.0058 m<sup>2</sup>) and *I* the applied current density (I = i/A, A m<sup>-2</sup>). The electrical energy consumption for ammonia removal (and deionization) (kWh m<sup>-3</sup>) and NH<sub>4</sub><sup>+</sup>-N recovery (kWh kg<sup>-1</sup> N) can be calculated according to:

$$EC_{removal} = \frac{\int_0^t U_t \times IA dt}{3600000 \times \int_0^t v dt}$$
(7-3)

$$EC_{recovery} = \frac{\int_{0}^{t} U_{t} \times IA dt}{3.6 \times C_{\text{NH}_{4}^{+}-\text{N}, acid} \times V_{acid}}$$
(7-4)

where  $U_t$  is the voltage (V) across the circuit of the CapAmm system at time t,  $C_{\text{NH4+-}}_{\text{N,acid}}$  the NH4<sup>+</sup>-N concentration (mg L<sup>-1</sup>) in the acidic receiving solution at time t and  $V_{\text{acid}}$  the volume of the receiving solution (0.04 L). The energy recovery during a discharging step in ICC mode was determined by integrating the reversed current and potential difference over time. Note that SCC does not require a nominal discharging step as charge neutralization (*i.e.*, short-circuited contact) of the flow electrodes acts to regenerate the carbon particles. The ammonia recovery efficiency (R, %) can be calculated according to:

$$R_{\mathrm{NH}_{4}^{+}-\mathrm{N}} = \left(\frac{C_{\mathrm{NH}_{4}^{+}-\mathrm{N},\,acid} \times V_{acid}}{v \times t \times C_{\mathrm{NH}_{4}^{+}-\mathrm{N},\,inf}}\right) \times 100$$
(7-5)

The average ammonia removal rate (g N m<sup>-2</sup> d<sup>-1</sup>) and recovery rate (g N m<sup>-2</sup> d<sup>-1</sup>) were determined according to:

$$r_{\rm NH_4^+-N, removal} = \frac{86400 \times (C_{\rm NH_4^+-N, inf} - C_{\rm NH_4^+-N, eff}) \times v}{A}$$
(7-6)

$$r_{\mathrm{NH}_{4}^{+}-\mathrm{N},\ recovery} = \frac{86.4 \times C_{\mathrm{NH}_{4}^{+}-\mathrm{N},acid} \times V_{acid}}{A \times t}$$
(7-7)

# 7.3 Results and Discussion

### 7.3.1 Integrated Design of CapAmm.

In this study, we developed an innovative and compact electrochemical system for ammonia recovery (and N-based fertilizer production) from wastewaters. Graphite plates carved with cut-through serpentine flow path channels (3 mm wide and 3 mm deep) (**Figure 7-1d**) were used as current collectors. This design allows efficient electron transfer between the flow electrodes and current collectors on the side walls of the flow channels. Meanwhile, in the cathode chamber, the flow electrode can readily contact with both a CEM and flat-sheet gas membrane (FGM) in the flow channels with the arrangement providing an effective pathway for ammonium migration from the desalination chamber to the cathode chamber followed by transport into the acid chamber during *in-situ* membrane stripping (**Figure 7-1b**). The FGM used in this study was comprised of a thin expanded polytetrafluoroethylene (ePTFE) active layer and a nonwoven fabric support layer with a total membrane thickness of 80 µm. The average pore size and porosity of the ePTFE active layer were 0.45 µM and 90% (**Figure 7-1e**), respectively. The FGM was highly hydrophobic with a contact angle of approximate 127.8 degrees (**Figure 7-1f** and **g**), indicating the ability of allowing the migration of ammonia across the membrane whilst preventing the permeation of water, dissolved ions and carbon particles, thus guaranteeing the production of high purity ammonia in the receiving solution.

With regard to the essential transformation of ammonium to volatile ammonia (NH<sub>3</sub>) in the cathode chamber prior to the recovery process (**Figure 7-1b**), at room temperature (*i.e.*, 293 K), pH is the key factor determining the fraction of NH<sub>3</sub> in the total ammonia nitrogen (TAN) present ([NH<sub>3</sub>]/[TAN] =  $10^{\text{pH}}/(e^{21.3}+10^{\text{pH}})$ ) (Ahn et al., 2011). While elevated pHs (pH >11) have been reported in the recirculation tank of the cathode in CapAmm as a result of concomitant Faradaic reactions (Nativ et al., 2017), it should be noted that the local pH near the current collector (and flow channels) can be much higher than that of the bulk carbon suspension in the recirculation tank. Therefore, it is expected that the integrated design will favour the transformation and subsequent recovery of ammonia *in-situ*.



**Figure 7-1.** Schematic representations of (a) the integrated capacitive membrane stripping process for ammonia recovery (CapAmm), (b) ammonia migration, transformation and recovery in the CapAmm system, and (c) isolated closed-cycle (ICC) and short-circuited closed-cycle (SCC) operation of the flow-electrode. (d) A photograph of the graphite current collector carved with cut-through serpentine flow channels. (e) SEM image of the active layer surface of the FGM. (f) A photograph of small water droplets on the surface of the FGM with the contact angle shown in (g). AEM, CEM and FGM represent anion exchange membrane, cation exchange membrane and flat-sheet gas membrane respectively.

#### 7.3.2 Optimisation of CapAmm System

**The Effects of Carbon Content in Flow Electrode. Figure 7-2** and **Figure 7-3**-7 summarise the ion removal and ammonia recovery performance using flow

electrodes of different carbon contents. Under a constant charging current density of 6.8 A m<sup>-2</sup> and HRT of 1.48 min, an increase in the carbon content has positive effects on ion removal, with much lower steady-state effluent conductivity (<1000  $\mu$ s cm<sup>-1</sup>) and higher NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup> removal efficiencies observed at higher carbon mass loadings of 5 *wt*% and 10 *wt*% (**Figure 7-3** and **Figure 7-2a**). The current efficiencies of the CapAmm system were relatively low (63.7% and 71.9%) at carbon contents of 0 *wt*% and 2 *wt*% but rose to higher values (~90%) at 5 *wt*% and 10 *wt*% (**Figure 7-2b**).



**Figure 7-2.** The variations of (a) average removal efficiencies of  $NH_4^+$  and  $Na^+$  and (b) dynamic current efficiency ( $\Lambda$ ) and electric energy consumption for ammonia recovery as a function of carbon content in the flow electrode (*i.e.*, 0 *wt%*, 2 *wt%*, 5 *wt%* and 10 *wt%*). All experiments were performed in ICC mode at a constant current density of 6.8 A m<sup>-2</sup> and HRT of 1.48 min.

Meanwhile, cathode pH can increase to higher than the  $pK_a$  of NH<sub>4</sub><sup>+</sup> (9.3) in all cases (**Figure 7-4**), leading to the successful recovery of ammonia in the acid chamber (**Figure 7-5** and **Figure 7-6**). Although our investigation into the fate of ammonia revealed that the majority was recovered as ammonium sulfate in the acid chamber in all cases, the use of higher carbon contents led to a slightly decrease in recovery efficiency due to the adsorption/trapping of ammonia on the carbon particles (**Figure 7-6**). In

addition, an increase in the carbon content significantly reduced the cell voltage and electric energy consumption (**Figure 7-7**). Specifically, the control experiment at 0 *wt*% carbon (similar to the electrodialysis process) required a high electric energy consumption of 45.2 kWh kg<sup>-1</sup> N but decreased to 35.8, 24.8 and 21.2 kWh kg<sup>-1</sup> N at carbon contents of 2 *wt*%, 5 *wt*% and 10 *wt*%, respectively (**Figure 7-2**b).



**Figure 7-3.** Temporal variation of effluent conductivity during the operation of CapAmm cell using flow electrodes with different carbon contents (*i.e.*, 0 wt%, 2 wt%, 5 wt% and 10 wt%). The experiments were performed in ICC mode at a constant current density of 6.8 A m<sup>-2</sup> and HRT of 1.48 min.

Overall, it can be concluded that increasing the carbon content enhances the ion removal and ammonia recovery efficiency in the integrated CapAmm system with this effect largely attributed to the increased extent of direct contact between carbon particles that is achieved at the higher carbon loadings. Indeed, it has been reported that the formation of a conductive 3D interconnected particle network at high carbon densities in flow electrodes can facilitate electron transfer and decrease the internal resistance of the whole cell (Hatzell et al., 2017, Presser et al., 2012). Note that using 5 wt% carbon loading achieved very similar performance to that of 10 wt% carbon (Figure 7-2). Therefore, in view of the low residual NH4<sup>+</sup>-N retained on the carbon
particles, superior current efficiency and lower risk of pipe and flow channel blocking, a flow-electrode with a 5 *wt*% carbon content was used in following experiments unless otherwise stated.



**Figure 7-4.** Temporal variation of cathode pH during the operation of CapAmm cell using flow electrodes with different carbon contents (*i.e.*, 0 wt%, 2 wt%, 5 wt% and 10 wt%). The experiments were performed in ICC mode at a constant current density of 6.8 A m<sup>-2</sup> and HRT of 1.48 min.



**Figure 7-5.** The variation of NH<sub>3</sub>-N (and NH<sub>4</sub><sup>+</sup>) concentration in (a) cathode chamber and (b) acid chamber as a function of time during the operation of CapAmm cell using flow electrodes with different carbon contents (*i.e.*, 0 wt%, 2 wt%, 5 wt% and 10 wt%).

The experiments were performed in ICC mode at a constant current density of 6.8 A  $m^{-2}$  and HRT of 1.48 min.



**Figure 7-6.** Fate and distribution of ammonia in the CapAmm system using flow electrodes with different carbon contents (*i.e.*, 0 wt%, 2 wt%, 5 wt% and 10 wt%). The experiments were performed in ICC mode at a constant current density of 6.8 A m<sup>-2</sup> and HRT of 1.48 min.



**Figure 7-7.** Temporal variation of voltage during the operation of CapAmm cell using flow electrodes with different carbon contents (*i.e.*, 0 wt%, 2 wt%, 5 wt% and 10 wt%). The experiments were performed in ICC mode at a constant current density of 6.8 A m<sup>-2</sup> and HRT of 1.48 min.

The Effects of Current Density and HRT. Figure 7-8a and b clearly show that both current density and HRT have a positive effect on ion removal, with higher NH<sub>4</sub><sup>+</sup> removal efficiency achieved than Na<sup>+</sup> due to the fact that NH<sub>4</sub><sup>+</sup> has a slightly smaller hydrated radius (3.31 Å) than Na<sup>+</sup> (3.58 Å) (Tran et al., 2015, Zhou et al., 2018a). More importantly, Faradaic reactions such as O<sub>2</sub> reduction occurring in cathode flow electrode resulted in the cathodic pH increasing to values higher than the p $K_a$  of NH<sub>4</sub><sup>+</sup> thus providing ideal conditions for ammonia transformation and extraction via membrane stripping (**Figure 7-8c** and **d**).



**Figure 7-8.** Average removal efficiencies for ammonium and sodium ions in the CapAmm system (a) under different current densities (*i.e.*, 1.8, 3.4, 6.8 and 10.4 A m<sup>-2</sup>) with a constant HRT of 1.48 min, and (b) at a constant current of 6.8 A m<sup>-2</sup> with HRTs of 0.98, 1.48, 1.96 and 2.94 min. Temporal change of pH in the cathode chamber of the

CapAmm system operated (c) under different current densities (*i.e.*, 1.8, 3.4, 6.8 and 10.4 A m<sup>-2</sup>) with a constant HRT of 1.48 min, and (d) under a constant current of 6.8 A m<sup>-2</sup> with different HRTs (*i.e.*, 0.98, 1.48, 1.96, and 2.94 min). The shade area represents the pH range >9.3, indicating the deprotonation of NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub>.

It can be seen from Figure 7-9 that negligible accumulation of ammonia (~20 mg  $L^{-1}$ ) in cathode was observed in all experiments. In contrast, continuous increase in ammonia concentrations was found in the acid chamber. At a current density of 6.8 A m<sup>-2</sup> and HRT of 1.48 min, nearly 150 mg L<sup>-1</sup> ammonia nitrogen was recovered in the acid chamber, which represents a 3.5 fold increase in concentration to that of the feed wastewater. A summary of the ammonia distribution in the CapAmm system is provided in Figure 7-10a and b, which clearly shows that the majority of ammonium ions removed from the feed wastewater were finally transferred to the acid chamber. For example, 65.8% of the influent ammonia was transferred and fixed as ammonium sulfate in the acid chamber at an applied current density of 6.8 A  $m^{-2}$  and HRT of 1.48 min, while 6.2% remained in the liquid phase of the cathode with the missing portion (16.8%) electrosorbed on the carbon particles and/or escaped into the air. Meanwhile, higher current density and/or longer HRT relates to more efficient desalination that lowers the conductivity of the solution in the desalination chamber (*i.e.*,  $< 200 \ \mu S \ cm^{-1}$ at a current density of 10.4 A m<sup>-2</sup> and HRT of 2.94 min) which, in turn, increases the cell internal resistance and voltage across the cell (Figure 7-11) (Galama et al., 2013). Electric energy consumption for ammonia recovery can be calculated was 9.6, 13.3, 24.8 and 48.9 kWh kg<sup>-1</sup> N corresponding to 1.8, 3.4, 6.8 and 10.4 A m<sup>-2</sup> respectively (Figure 7-10c). On extending the HRT from 0.98 to 2.94 min, the energy consumption increased by 3.2 times (from 18.7 to 79.1 kWh kg<sup>-1</sup> N) (Figure 7-10d). In summary, taking the ion removal efficiency, ammonia recovery performance and energy consumption into

consideration, a current density of 6.8 A  $m^{-2}$  and HRT of 1.48 min was chosen as the optimal operating conditions for the CapAmm system.



**Figure 7-9.** Temporal variation of ammonia concentrations in (a) the cathode chamber and (b) acidic receiving solution of the CapAmm system operated under different current densities (*i.e.*, 1.8, 3.4, 6.8 and 10.4 A m<sup>-2</sup>) with a constant HRT of 1.48 min, and ammonia concentrations in (c) the cathode chamber and (d) acidic receiving solution of the system charged at a constant current density of 6.8 A m<sup>-2</sup> with different HRTs (*i.e.*, 0.98, 1.48, 1.96 and 2.94 min).



**Figure 7-10.** Fate and distribution of ammonia in the CapAmm system at different (a) current densities with a constant HRT of 1.48 min and (b) HRTs with a constant current of 6.8 A m<sup>-2</sup>. Variations of electric energy consumption as a function of (c) current densities at constant HRT of 1.48 min and (d) HRTs at a constant current density of 6.8 A m<sup>-2</sup>.

Significance of ICC Operation of the Flow Electrode. While it is reported that SCC operation of the flow electrode is conducive to maintaining the "infinite" capacitance of the flow electrode in the charging step as a result of the continuous charge neutralization and electrode regeneration in the *ex-situ* apparatus (Jeon et al., 2014), there is a critical concern that the circumneutral pH value of the SCC flow electrode is unfavourable for the ammonia

transformation and recovery in CapAmm. Therefore, comparison of the ICC and SCC operation of the flow electrode was conducted under the optimal conditions determined above (*i.e.*, a charging current density of 6.8 A m<sup>-2</sup> and HRT of 1.48) (**Figure 7-1c**). A control experiment involving adjustment of the pH of SCC flow electrode to ~11(similar to the average cathode pH of ICC mode) was carried out in parallel. **Figure 7-12** depicts the results of a 2-h charging stage followed by a 20-min reverse-current discharging step to recover energy. In ICC mode, 87.4% of the influent ammonia was removed while 77.8% could be effectively recovered in the acid chamber due to the higher cathode pH. However, the recovery ratio in SCC mode dropped to 12.6% without pH adjustment though the use of pH adjustment led to 68.9% recovery of ammonia (**Figure 7-12a** and **b**).



**Figure 7-11.** Temporal variation of cell voltage (a) under different current densities (*i.e.*, 1.8, 3.4, 6.8 and 10.4 A m<sup>-2</sup>) with a constant HRT of 1.96 min and (b) a constant current density of 6.8 A m<sup>-2</sup> with different HRTs (*i.e.*, 0.98, 1.48, 1.96 and 2.94 min).

The application of a short-term discharging step process (20 min) resulted in further improvement in ammonia recovery efficiency to ~80% in ICC mode (**Figure 7-12b**). This finding can be largely ascribed to the desorption and migration of the trapped ammonia on the carbon surface on increasing the cathode potential to zero or even positive values. The change in cell voltage in ICC mode from the charging stage to discharging stage indicated that only a small amount of energy could be recovered (2.1%, as shown in **Figure 7-12c**) with this low percentage possibly a result of (i) the self-discharging of the flow electrode during recirculation and (ii) loss of charge at the electrode/electrolyte interface as a result of the occurrence of Faradaic reactions (Jeon et al., 2014, Ma et al., 2018). Overall, the net electric energy consumption was 20.4, 11.0 and 70.4 kWh kg<sup>-1</sup> N respectively for ICC mode and SCC operation with and without pH adjustment of the flow electrode (**Figure 7-12d**). Although the SCC mode with pH adjustment consumed the lowest electrical energy, it should be noted that extra chemicals (~5 kg NaOH kg<sup>-1</sup> N, equivalent to ~60 kWh kg<sup>-1</sup> N) were required to drive the ammonia recovery process. It can be therefore concluded that the ICC mode is more favourable for recirculation of the flow electrode in the CapAmm system.



**Figure 7-12.** The variations of (a) pH in the cathode (or pH in the combined flow electrode in SCC mode), (b) ammonia distribution, (c) cell voltage and (d) electrical energy consumption in three different operation modse (*i.e.*, ICC mode and SCC operation with/without pH adjustment of the flow electrode). Experimental conditions: Carbon content = 5 *wt*%, Current density = 6.8 A m<sup>-2</sup> at the charging stage (Current density = -6.8 A m<sup>-2</sup> at the discharging stage, if applicable) and HRT = 1.48 min.

**Ammonia Recovery from Real Domestic Wastewater.** The performance of CapAmm was tested in terms of its potential for low-strength domestic wastewater (real AnMBR effluent) treatment. As shown in **Table 7-1** and **Figure 7-13**, stable effluent was achieved during the electrolysis process with 80% of the ions (*i.e.*, NH<sub>4</sub><sup>+</sup>-N, Na<sup>+</sup>,

 $K^+$  and  $Ca^{2+}$ ) and 43% of the TOC being removed. Meanwhile, 62.5% of the ammonia was harvested as ammonium sulfate in the acid chamber with the final concentration reaching more than 120 mg L<sup>-1</sup>, whereas other competing cations (*i.e.*, Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>) present in the real wastewater accumulated in the cathode chamber but not detected in the acid chamber. The average energy consumption for ammonia recovery and water treatment (water desalination) were 25.1 kWh kg<sup>-1</sup> N and 0.67 kWh m<sup>-3</sup> of water.

**Table 7-1.** The concentration of different ions ( $NH_4^+$ -N,  $Na^+$ ,  $K^+$ ,  $Ca^{2+}$ ), TOC concentrations, conductivity in the CapAmm influent (real AnMBR permeate) and effluent (after treatment).

	NH4 <sup>+</sup> -N (mg L <sup>-1</sup> )	Na <sup>+</sup> (mg L <sup>-1</sup> )	K <sup>+</sup> (mg L <sup>-1</sup> )	Ca <sup>2+</sup> (mg L <sup>-1</sup> )	TOC (mg L <sup>-1</sup> )	Conductivity (µs cm <sup>-1</sup> )
Influent	42.5	325	110	16	8.1	2198
Effluent	10.5	83	17	2.9	4.6	405



**Figure 7-13.** Temporal variation of (a)  $NH_4^+$ -N, (b)  $Na^+$ , (c)  $K^+$ , (d)  $Ca^{2+}$  concentration in effluent, cathode electrolyte and acid chamber when using CapAmm to treat real domestic wastewater (AnMBR effluent). Experimental conditions: Carbon content = 5 *wt*%, Current density = 6.8 A m<sup>-2</sup> and HRT = 1.48 min.

Ammonia Recovery from High-strength Wastewater. The possibility of using CapAmm to harvest ammonia from higher-strength wastewaters (in these studies, synthetic urine) was also investigated. Single-pass experiments with synthetic urine demonstrated that ammonia nitrogen can be efficiently and selectively removed and recovered via capacitive desalination and the electrochemical stripping processes (**Figure 7-14**). 58.3% of the total ammonia in the influent was recovered in the acid chamber after 2 h treatment at a low ammonia recovery energy consumption of 7.8 kWh  $kg^{-1}$  N.



**Figure 7-14.** Temporal variation of ammonia concentrations in effluent, cathode chamber and acidic receiving solution of the CapAmm system for treatment of synthetic urine. Experimental conditions: Carbon content = 5 *wt*%, Current density = 27.2 A m<sup>-2</sup> and HRT = 2.88 min.

The proportion of major cation species transported across the CEM is shown in **Figure 7-15a**. For dilute wastewaters (synthetic domestic wastewater and real domestic wastewater), the majority of charge (~70%) was consumed by the transportation of Na<sup>+</sup>, while less than 20% of the charge is available for NH<sub>4</sub><sup>+</sup>-N extraction. This is due to the fact that the Na<sup>+</sup>/NH<sub>4</sub><sup>+</sup>-N mole ratio in these dilute wastewaters is higher than 5, which indicates that Na<sup>+</sup> will become a strong competitor compared to NH<sub>4</sub><sup>+</sup>-N in the electrical field, resulting in a higher charge/energy cost for Na<sup>+</sup> removal. However, when treating medium/high-strength wastewater such as urine, the transport of NH<sub>4</sub><sup>+</sup>-N accounts for the majority (~75%) of charge consumption as ammonium is the dominant species present (Na<sup>+</sup>/NH<sub>4</sub><sup>+</sup>-N mole ratio <0.3). Ammonia nitrogen flux across the membranes is

an important parameter to describe the electrochemical ammonia removal and recovery performance. As shown in **Figure 7-15b**, nitrogen fluxes across the CEM were 15.8, 13.3 and 264.7 g N m<sup>-2</sup> d<sup>-1</sup> for the treatment of synthetic domestic wastewater, real domestic wastewater and synthetic urine, respectively. In contrast, nitrogen fluxes across the FGM were slightly lower than that across the CEM. As for energy consumption, extracting ammonia from high-strength wastewaters (*i.e.*, urine) required 61.8% less energy (compared to that for dilute wastewater (*i.e.*, domestic wastewater), mainly because of the lower competition from other cation ions such as Na<sup>+</sup>. Current efficiencies were similar (75%-90%) in each of the three scenarios, indicating the effectiveness of the CapAmm system described here.



**Figure 7-15.** A comparison of (a) proportion of major cation ions transported across the CEM and (b) CEM nitrogen flux, FGM nitrogen flux, energy consumption and current efficiency when treating three different wastewaters (*i.e.*, synthetic domestic wastewater, real domestic wastewater and synthetic urine) using CapAmm system.

# 7.3.3 Continuous Operation of the CapAmm System with Synthetic Dilute Wastewater

Results of continuous operation for 25-cycles (using ICC mode and the optimal parameters obtained above) provide some insight into the likely long-term performance of the CapAmm system. Stable effluent conductivity, Na<sup>+</sup> concentration and NH<sub>4</sub><sup>+</sup>-N concentration were achieved over 50 h operation (**Figure 7-16**). Cathode pH exhibited a

similar repeating pattern with the value increasing from near neutral to around 12 during each cycle, providing the conditions required for continuous recovery of ammonia (Figure 7-17a). As shown in Figure 7-17b, ammonia concentration kept increasing (almost linearly) over the 25-cycles of operation with the final concentration reaching 3386 mg  $L^{-1}$ , a concentration 78 times of that in the dilute wastewater. The average electricity consumed was 20.6 kWh kg<sup>-1</sup> N with a high water recovery of ~87%. In our future work, long-term operation will be conducted to achieve an ammonia concentration of > 50 g/L (close to the saturated solutions) and continuously separate ammonium sulfate crystals from the systems. The steady cell voltage that was attained after a few minutes of charging decreased slightly over ensuing cycles with the decrease mainly attributed to the increasing ion concentration in the flow-electrodes, which reduced the overall resistance of the CapAmm cell (Figure 7-14). Noting that the separation of ammonia from the system is an alkalinity consuming process, which might cause an imbalance between the protons produced at anode and the hydroxide ions left in cathode. Therefore, a slight pH decreasing after electrode regeneration (via anode/cathode flow-electrode mixing) will be observed at the end of each operation cycle.



Figure 7-16. The variation of (a) conductivity, (b) sodium concentration and (c) ammonium concentration in the effluent as a function of operation time under a constant current density of 6.8 A  $m^{-2}$  and HRT of 1.48 min during a 25 cycle (50 h in total) operation.



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**Figure 7-17.** The variation of (a) cell voltage, (b) cathode pH and (c) ammonia concentration in the acid chamber during the 25 cycles (50 hours in total) operation. The shade area represents the pH range >9.3, indicating the deprotonation of  $NH_4^+$  to  $NH_3$ . Experimental conditions: Carbon content = 5 *wt*%, Current density = 6.8 A m<sup>-2</sup> at the charging stage and HRT = 1.48 min.

#### 7.3.4 Comparison with Alternative Methods

In this section, a detailed and comprehensive comparison of the CapAmm process with other alternative methods of ammonia removal/recovery is provided (Table 7-2 and Figure 7-18). Electrochemical methods have previously been used for ammonia removal and, in some cases, recovery from dilute wastewaters. Electrochemical advanced oxidation, which takes advantage of *in situ* generated active chlorine to preferentially degrade ammonia, requires an extremely high energy input of 383 kWh kg<sup>-1</sup> N due to the occurrence of unwanted Faradaic reactions (such as water electrolysis) (Yang et al., 2016b). Ren et al. developed an innovative electrochemical reactor with the electrolyte cyclically flowing in the electrode compartment (packed with activated carbon) to continuously concentrate ammonium and phosphate ions and generate struvite from domestic wastewater. During this process, the system required a high electricity input of 220.2 kWh kg<sup>-1</sup> N. Meanwhile, the ammonium recovery efficiency was below 20% due to the large ammonium to phosphate ion ratio (>>1) in the influent stream (Ren et al., 2017). In contrast, our CapAmm cell only required 20.6 kWh kg<sup>-1</sup> N for electricity under optimal operating conditions. The average electricity energy consumption for the wastewater treatment (desalination) was 0.54 kWh m<sup>-3</sup>, much lower than other similar technologies in treating dilute streams.



**Figure 7-18.** Correlation of current density and nitrogen flux across the CEM. Data collected from current work (blue symbols) and previous studies (grey symbols). The inserted figure enlarged from the red area represents the relation between current density and nitrogen flux of CapAmm treating low-strength wastewaters.

When it comes to handling high-strength wastewaters such as urine, digestate, landfill leachate and animal waste, there are a number of competitive approaches. These methods generally include an electrochemical unit (*i.e.*, bioelectrochemical systems (BESs), electrodialysis and capacitive deionization) to transport ammonium ions towards the cathode (where pH automatically increase without base addition) and an ammonia separation unit (*i.e.*, air stripping system, gas membrane contactor and air cathode) to selectively recover ammonia. BES-based processes (*i.e.*, MFC, MEC and MDC), which produce electricity from the microbial oxidation of organic matter, concentrate ammonia in the cathode enabling ammonia recovery at extremely low energy consumption (< 5 kWh kg<sup>-1</sup> N). (Kuntke et al., 2012, Sotres et al., 2015, Zhang and Angelidaki 2015a,b) These technologies have emerged as a promising pathway for simultaneously treating wastewater (COD removal), harvesting electricity and recovering resources. The low ammonia nitrogen flux obtained in MFCs can be increased

by converting the system to a MEC as a result of the higher bio-current generated (Kuntke et al., 2014). Other non-biological electrochemical systems (ESs) are capable of providing higher current densities (10-100 A m<sup>-2</sup>) and enabling larger nitrogen fluxes (>100 g N m<sup>-2</sup> d<sup>-1</sup>) (Kuntke et al., 2018, Tarpeh et al., 2018b). Electricity energy demand and nitrogen flux for these ESs can range from 6 to 25 kWh kg<sup>-1</sup> N, depending on the applied current densities (**Figure 7-18**) and wastewater type. It should be noted that the ammonia separation unit will also require either extra chemicals (such as sulfuric acid) or additional electricity consumption. Ammonia separation via a gas membrane contactor is expected to be a better option due to the fact that only a small amount of additional chemicals is requires extra electricity energy for aeration. Our CapAmm system, which combines FCDI with a gas membrane, exhibited a competitive performance with other similar alternatives; at a current density of 27.2 A m<sup>-2</sup>, an electricity energy demand of 7.8 kWh kg<sup>-1</sup> N was required with an ammonia flux of 264 g N m<sup>-2</sup> d<sup>-1</sup> and recovery efficiency of 58%.

#### 7.4 Environmental Implications

Domestic wastewater is increasingly being considered as a potential resource (i.e., a source of energy, fertilizing nutrients and reclaimed water) rather than as a waste. One approach that appears feasible involves the use of AnMBR for COD removal and biogas production (energy recovery) followed by the use of CapAmm for nitrogen and phosphate capture (fertilizing nutrients recovery) and salt removal (water recovery). While this approach is relatively complex and the electric energy input high, it does enable maximum resource recovery from wastewaters.

Methods	Wastewater type	Current density (A m <sup>-2</sup> )	Nitrogen flux across CEM (g N $m^{-2} d^{-1}$ )	NH4 <sup>+</sup> -N removal/recovery efficiency (%)	Electricity consumption for ammonia recovery (kWh kg <sup>-1</sup> N)	Electricity consumption for water treatment $(kWh m^{-3})^{a}$	Reference
Electrochemical oxidation Electrochemical oxidation CDI-like electrochemical reactor	Synthetic domestic Synthetic domestic	250 30	n.a. n.a.	~100 95	383.0 39.9	64.3 1.9	(Yang et al., 2016b) (Zhang et al., 2018b)
	Synthetic domestic	2.1	7.8	<10	220.2	n.r.	(Ren et al., 2017)
CapAmm	Synthetic domestic	3.4	11.7	38	13.3	0.35	This study
CapAmm CapAmm CapAmm (with energy recovery)	Synthetic domestic	6.8	15.8	66	24.8	0.71	This study
	Synthetic domestic	10.4	16.9	79	48.8	1.83	This study
	Synthetic domestic	6.8	15.8	78	20.6	0.69	This study
CapAmm	Real domestic (AnMBR eflluent)	6.8	13.2	62	25.1	0.67	This study
MFC + air stripping	Real pig slurry	0.07	3.7	n.r.	n.r.	n.r.	(Sotres et al., 2015)
MFC + air stripping	Synthetic urine	0.5	3.3	<i>n.r</i> .	-1.0 <sup>b</sup>	n.r.	(Kuntke et al., 2012)
MEC + air stripping	Synthetic wastewater	2.7	5.1	n.r.	2.9	n.r.	(Zhang and Angelidaki 2015a)
MDC + air stripping	Synthetic urine	7.6	80	88	-0.10	-0.7	(Zhang and Angelidaki 2015b)
MEC + membrane stripping	Real urine	1.6	27	26	1.1	n.r.	(Zamora et al., 2017)
MEC + Nickel-based membrane electrodes	Synthetic side stream centrate	2.4	36.2	n.r.	1.6	n.r.	(Hou et al., 2018)
MEC + NH4HCO3 crystals	Synthetic urine	29	n.r.	14	9.51	n.r.	(Ledezma et al., 2017)
ES + air stripping	Synthetic urine	30	142	41	16.8	34.4	(Desloover et al., 2012)
ES + air stripping	Digestate	30	94	63	25.0	80.6	(Desloover et al., 2012)
ES + air stripping	Synthetic urine	30	253	53	9.5	31.0	(Luther et al., 2015)
ES + air stripping	Real urine	40	235	75	14.7	52.9	(Luther et al., 2015)
ES+ membrane stripping	Real urine	50	335	63	13.6	34.3	(Rodriguez Arredondo et al., 2017)
ES + membrane stripping	Real urine	100	937°	30°	8.5	20.4	(Tarpeh et al., 2018b)
HRES + membrane stripping	Real urine	20	151	73	7.3	18.1	(Kuntke et al., 2017)
HRES + membrane stripping	Real urine	50	342	60	15.6	31.8	(Kuntke et al., 2017)
HRES + membrane stripping	Synthetic urine	100	598	58	6.5	12.9	(Kuntke et al., 2018)
CapAmm	Synthetic urine	27.2	264	58	7.8	16.7	This study

**Table 7-2.** Comparison of energy consumption and ammonia removal/recovery performance using different methods aimed at ammonia removal/recovery from wastewaters.

n.a. not applicable, n.r. not reported and too little information provided to calculate. MFC: microbial fuel cell, MDC: microbial desalination cell, MEC: microbial electrolysis cell, ES: nonbiological electrochemical system, HRES: hydrogen recycling electrochemical system

<sup>a</sup> Electricity energy consumption for wastewater treatment (*i.e.*, water desalination), unit kWh m<sup>-3</sup>.

<sup>b</sup>Minus means energy gain, while positive means energy cost.

<sup>c</sup>Calculated according to the data reported.

An alternative approach we consider worthy of further investigation involves the recovery of nitrogen and phosphate directly from high-strength streams (e.g. source separated urine) using CapAmm followed by biological treatment (e.g. AnMBR, A/A/O) for organic matter degradation. This approach appears more attractive because the high ammonia concentrations and low concentrations of competing ions (Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup>) in urine result in much lower electric energy consumption (Kuntke et al., 2017, Ledezma et al., 2017, Tarpeh et al., 2018a). In this scenario, as most of the nutrients from urine (accounting for ~80% of the nutrient input in municipal WWTP) have been recovered before the waste stream enters the WWTP, it may beneficially impact the cost of domestic wastewater treatment as there will be little need for further N removal.

One major limitation of the FCDI approach is the poor electrical conductivity of the carbon flow electrodes (several orders of magnitude lower than conventional static electrodes) (Porada et al., 2014, Xu et al., 2008), with this restricting the ion removal/recovery efficiency and increasing the internal resistance and, ultimately, resulting in higher energy consumption. In addition, pumping of the flow carbon particles consumes energy, which must be taken into account in the overall energy budget of the technology (Hatzell et al., 2015b). Scale-up from small bench size units to full-sized modules will also obviously be required. It is envisaged that CapAmm cells could be stacked together to provide the required throughput but challenges will need to be overcome, particularly with regard to optimizing flow electrode composition (*i.e.*, electrolyte, carbon loading and active electrode materials), flow cell design (*i.e.*, slurry flow rate, charging/discharging time control). Of particular attraction however is the low voltage, direct current requirements of the technology rendering it suitable for direct use of photovoltaic power supply with associated reduction in energy costs.

# Chapter 8. The role of absorbents on ammonia recovery performance in capacitive membrane stripping system

#### 8.1 Introduction

Global water scarcity and resource shortages caused by population explosion and industrial development have become a great challenge for human society in the 21<sup>st</sup> century. In response to this challenge, research scientists and engineers have focused on exploring multiple sources of freshwater and nutrients in recent decades (Elimelech and Phillip 2011, Shahzad et al., 2017, Vorosmarty et al., 2010). In particular, it is recognised that wastewater contains abundant nutrients (especially of nitrogen and phosphorous) and certainly represents a reusable water resource (Verstraete et al., 2009). Excessive nutrients in wastewater, if discharged to the environment, will result in eutrophication that deteriorates water quality and ecosystem structure and function in natural waterbodies such as lakes, rivers and estuaries (Chen et al., 2017c, Kavvada et al., 2017, Xie et al., 2016). One survey undertaken by the International Lake Environmental committee revealed that 54%, 53%, 48%, 41% and 28% of lakes and reservoirs are eutrophic in Asia and the Pacific, Europe, North America, South America and Africa, respectively (Nikitin et al., 2015). It is reported that the potential economic losses associated with eutrophication in U.S. freshwaters, conservatively, reached \$2.2 billion annually.

Paradoxically, while the presence of excessive nutrients, such as ammonia, in wastewaters and the discharge of these wastewaters to receiving waters constitute a major environmental problem, the production of ammonia for fertilizer use represents 1.5-2.5% of the annual global energy consumption and more than 1.6% of global CO<sub>2</sub> emissions (Galloway et al., 2008, Gruber and Galloway 2008, Guo et al., 2018). Additionally, the ability to recover ammonia from wastewaters represents a means of both remediating damaged aquatic environments and assisting in reduction of greenhouse gas emissions as a result of a reduction in need for ammonia manufacture by traditional means.

As described earlier in this thesis, we have developed an innovative and costeffective system for ammonia recovery (termed CapAmm) utilising a flow-electrode capacitive desalination (FCDI) cell and gas-permeable membrane contactor (Zhang et al., 2017, Zhang et al., 2018e). FCDI, involving the application of flowable carbon electrodes, is a new technology capable of desalinating wastewater via electrosorption of the ionic species (including nutrients such as ammonium ions) in the electric double layers (EDLs) of the charged carbon particles (Hatzell et al., 2015b, Häyrynen et al., 2009, Jeon et al., 2013a, Ma et al., 2016a). Importantly, Faradic reactions occur in the electrochemical cell, causing pH variation in the flow-electrode. For instance, an increase in pH in cathode chamber occurs due to the reduction of oxygen and/or water leads to a change in ammonia speciation from NH<sub>4</sub><sup>+</sup> dominance at pH <  $pK_a$  (of 9.3) to NH<sub>3(aq)</sub> dominance at pH >  $pK_a$  (Sleutels et al., 2016, Vanotti et al., 2017, Zhang et al., 2017). Equilibrium is rapidly established between dissolved and volatile gaseous ammonia, which diffuses through a hydrophobic membrane (incorporated in the cathode chamber) and can be recovered in a receiving solution.

As described in Chapters 6 and 7, two types of CapAmm configuration have been employed in our preliminary studies (Zhang et al., 2017, Zhang et al., 2018e). In our first-generation system, a hollow-fiber gas membrane was immersed in the cathode flow-electrode container. An ammonia recovery efficiency of ~60% can be achieved with a specific energy consumption of 9.9 to 21.1 kWh kg N<sup>-1</sup> (Zhang et al., 2017). In the second-generation system, a flat-sheet gas membrane was employed and inserted into the FCDI cathode chamber, with an integrated CapAmm cell being fabricated. The integrated CapAmm cell exhibits an extraordinary ammonia removal efficiency (~90%) and recovery efficiency (~80%) (Zhang et al., 2018e). Energy consumptions were comparative to other technologies, with 20.4 kWh kg<sup>-1</sup> N for low-strength (*i.e.*, domestic) and high-strength (*i.e.*, synthetic urine) wastewaters, respectively. In both scenarios, sulfuric acid was applied as the receiving solution and continuously circulated on the lumen side of the gas contactors, with ammonium sulfate as the endproduct. However, concern has been expressed regarding the quality and potential market value of the currently recovered products. For example, ammonium sulfate, the most common end-product extracted from ammonia-containing wastewater, is of relatively low value (~0.12 USD kg<sup>-1</sup>).

Higher value products such as compound fertilizer or ammonia solution could potentially be produced if alternative absorbents (acids) such as H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub> and even H<sub>2</sub>O were to be used. For example, the prices for compound fertilizers (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and NH<sub>4</sub>NO<sub>3</sub> are 0.65 USD kg<sup>-1</sup> and 0.2 USD kg<sup>-1</sup>, respectively. Additionally, the application of H<sub>2</sub>CO<sub>3</sub>\* (H<sub>2</sub>CO<sub>3</sub> and CO<sub>2(aq)</sub>) as an ammonia absorbent could be a way to capture CO<sub>2</sub> gas as well as producing NH<sub>4</sub>HCO<sub>3</sub> while ammonia solution, the product of ammonia absorbed by water, is a valuable chemical widely used in textile and plastic manufacturing, agricultural production, food processing and water treatment and has great market demand with an extremely high price of 0.5-0.7 USD kg<sup>-1</sup> (Zhang et al., 2019b). As such, there is a need for a comprehensive comparison and evaluation of the different end-products that could be retrieved through use of various absorbing solutions. In the study described in this chapter, a variety of ammonia receiving solution (*i.e.*, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, HCl, H<sub>2</sub>CO<sub>3</sub>\* and H<sub>2</sub>O) are applied for the recovery of ammonia or ammonium salts using the previously described CapAmm system. Particular attention is given to the effects of absorbents on salt removal performance, fate and distribution of ammonia and mass fluxes across the gas membranes. An overall evaluation of the operating costs including chemical expenses and potential revenues from the end-products highlights the opportunities and challenges of CapAmm in sustainable water, resource and energy management.

#### 8.2 Materials and methods

### 8.2.1 Reagents

Artificial ammonia-containing wastewater (containing ammonia) and flowelectrodes electrolyte were prepared using 18.2 M $\Omega$  cm Milli-Q water (Millipore). Analytical reagent grade chemicals (*i.e.*, NaCl, NH<sub>4</sub>Cl, H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl) used in current all experiments were purchased from Sigma Aldrich and directly used without any further purification. The flow-electrodes were prepared by adding 5 g solid carbon materials (100 mesh DARCO® activated carbon charcoal blended with carbon black powder with a mass ratio of 9:1) into Milli-Q water (95 g) with this carbon load representing 5 *wt*%. To completely wet the carbon particles surface, the flow-electrodes were continually mixed on a magnetic stirrer for more than 1 day prior to experimentation. The artificial wastewater was prepared by dissolving an appropriate amount of NH<sub>4</sub>Cl and NaCl in Milli-Q water to achieve an initial NH<sub>4</sub><sup>+</sup>-N concentration of ~43 mg L<sup>-1</sup> and NaCl concentration of ~1000 mg L<sup>-1</sup> (similar to dilute wastewater such as anaerobic membrane bioreactor (AnMBR) effluent).

#### 8.2.2 Experiment setup

The structure of an FCDI system, which is composed of two graphite current collectors (160 mm  $\times$  70 mm, thickness: 5 mm), two ion exchange membranes (AEM-Type II /CEM-Type II, FUJIFILM Europe) and one hydrophobic gas membrane (150 mm  $\times$  70 mm  $\times$  0.08 mm), is shown in Figure 8-1. Two acrylic endplates were applied to hold all these components together in a manner similar to that reported in our previous work with four chambers (anode chamber, desalination chamber, cathode chamber and acid chamber) formed between the three membranes and two endplates (He et al., 2018a, Song et al., 2019). Serpentine flow channels (3 mm width, 3 mm depth, with 570 mm in total length) were carved on the graphite current collectors using a CNC machine. Flowable carbon suspensions in the anode and cathode chambers respectively formed between the flow-channels and AEM and CEM constitute the flow electrodes. The contact area between the current collector and each IEM (A) is 66.3  $\text{cm}^2$  while the effective contact area between the flow channel and IEM  $(A_{eff})$  is 34.9 cm<sup>2</sup>. The artificial wastewater passed through the nylon spacer (100mesh, 160 mm  $\times$  70 mm  $\times$  0.5 mm) located between the CEM and AME with a silicone gasket (0.5 mm thickness) encircling the spacer in order to prevent water leakage. Similarly, to provide a flow path for the acid solution, a similar nylon spacer sheet is placed between the gas membrane and endplate (Figure 8-1). All experiments were undertaken in single-pass mode unless specifically mentioned. The flow rate was controlled at 0.8 mL min<sup>-1</sup> using a dual-head peristaltic pump (Longer pump, Baoding, China) resulting in a constant hydraulic retention time (HRT) of 1.48 min. During operation, 40 mL 5 wt% flow-electrodes were respectively recirculated between the FCDI electrode chambers and the stirred reservoir. Constant current density (I = i/A, 6.8 A cm $^{-2}$ ) was applied to the circuit by a DC power supply (MP3840, Powertech).



**Figure 8-1.** Schematic representation of the CapAmm system for salt removal and ammonia recovery. AEM and CEM stand for the anion and cation exchange membrane, respectively.

#### 8.2.3 Ammonia recovery in different scenarios

Different receiving solutions (ammonia absorbents) including volatile acids [HNO<sub>3</sub> (1 M) and HCl (1 M)], nonvolatile acids [H<sub>3</sub>PO<sub>4</sub> (0.33 M) and H<sub>2</sub>SO<sub>4</sub> (0.5 M)], dissolved CO<sub>2</sub> solution (H<sub>2</sub>CO<sub>3</sub>\*), and Milli-Q water (degassing by using nitrogen gas before use) were tested in this study. The receiving solution (40 mL) was continuously recirculated between the acid chamber and a stirred acid reservoir at a constant flow rate of 50 mL min<sup>-1</sup>. The CapAmm performance with regard to conductivity and voltage variation, ion removal performance and ammonia separation efficiency were initially evaluated under different absorbent conditions. The fate and distribution of ammonia in the CapAmm system were then investigated.

#### 8.2.4. Analytical Methods and Calculations

The voltage (*U*) across the electrical circuit was recorded every five seconds using a Vernier voltage probe connected to the SensorDAQ. The variation of pH in the flow electrode was monitored by an F-51 pH meter (Horiba, Japan) (He et al., 2018a, Song et al., 2019). Samples from the influent, effluent, cathodic flow electrode and acidic receiving solution were collected every 30 min. All samples were filtered through 0.45 µm filters (Millipore) prior to further analysis. The effluent conductivity was determined using a conductivity meter (CON-BTA, Vernier) connected to a data acquisition system (SensorDAQ, Vernier). The concentrations of ions (i.e., NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup>) were measured by ion chromatography (ICS-3000, Dionex) with the instrument equipped with a guard column CG16 (5 × 50 mm) and a separation column CS16 (5 × 250 mm).

The removal efficiency (in %) of a particular ion was determined according to:

$$RE_{i} = (1 - \frac{C_{i,eff}}{C_{i,inf}}) \times 100$$
(8-1)

where  $C_{i,inf}$  is the influent concentration (mg L<sup>-1</sup>) of ion species *i* and  $C_{i,eff}$  the effluent concentration (mg L<sup>-1</sup>) of ion species *i*.

The ammonia separation factor (selectivity) can be determined by:

$$\rho = \frac{RE_{\mathrm{NH}_{4}^{+}-\mathrm{N}}}{RE_{\mathrm{Na}^{+}}}$$
(8-2)

Current efficiency and energy consumption are two key parameters used to evaluate the performance of the CapAmm system. Current efficiency (%) can be calculated as follows:

$$\Lambda = \frac{\sum \frac{n_i \times F \times v \times \int_0^t (C_{i,inf} - C_{i,eff}) dt}{M_i}}{\int_0^t IA dt} \times 100$$
(8-3)

where  $n_i$  is the charge of certain ion species (*i.e.*, 1 for NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup>), *F* the Faraday constant (96485.3 C mol<sup>-1</sup>), *v* the flow rate (m<sup>3</sup> s<sup>-1</sup>) of the wastewater stream,  $M_i$  the molar mass of ion species *i* (g mol<sup>-1</sup>), *A* the effective area between the ion-exchange membrane and the flow electrode (0.0058 m<sup>2</sup>) and *I* the applied current density (I = i/A, A m<sup>-2</sup>).

The electrical energy consumption for ammonia removal (and deionization) (kWh  $m^{-3}$ ) and NH<sub>4</sub><sup>+</sup>-N recovery (kWh kg<sup>-1</sup> N) can be calculated according to:

$$\eta_{removal} = \frac{\int_0^t U_t \times IA dt}{3600000 \times \int_0^t v dt}$$
(8-4)

$$\eta_{recovery} = \frac{\int_0^t U_t \times IA dt}{3.6 \times C_{\text{NH}_4^+ - \text{N, acid}} \times V_{acid}}$$
(8-5)

where  $U_t$  is the voltage (V) across the circuit of the CapAmm system at time *t*,  $C_{\text{NH4+-}}_{\text{N,acid}}$  the NH4<sup>+</sup>-N concentration (mg L<sup>-1</sup>) in the acidic receiving solution at time *t* and  $V_{\text{acid}}$  the volume of the receiving solution (0.04 L). The energy recovery during a discharging step in ICC mode was determined by integrating the reversed current and potential difference over time. Note that SCC mode does not require a nominal discharging step as charge neutralization (*i.e.*, short-circuited contact) of the flow electrodes acts to regenerate the carbon particles. The ammonia recovery efficiency (*R*, %) can be calculated according to:

$$R_{\mathrm{NH}_{4}^{+}-\mathrm{N}} = \left(\frac{C_{\mathrm{NH}_{4}^{+}-\mathrm{N},\,acid} \times V_{acid}}{v \times t \times C_{\mathrm{NH}_{4}^{+}-\mathrm{N},\,inf}}\right) \times 100$$
(8-6)

The average ammonia recovery flux (g N  $m^{-2} d^{-1}$ ) was determined according to:

$$F_{\mathrm{NH}_{4}^{+}-\mathrm{N},flux} = \frac{86400 \times (C_{\mathrm{NH}_{4}^{+}-\mathrm{N},acid,initial} - C_{\mathrm{NH}_{4}^{+}-\mathrm{N},acid,final}) \times \nu}{A}$$
(8-7)

# 8.3 Results and discussion

#### **8.3.1 Salt removal performance**

The desalting performance of the CapAmm system current density =  $6.8 \text{ A m}^{-2}$ and HRT = 1.48 min using different acidic receiving solutions are presented in **Figure** 8-2 and Figure 8-3. It is noted that the effluent conductivity rapidly decreased from ~2400 to a steady value of ~600  $\mu$ S cm<sup>-1</sup> in all scenarios (Figure 8-2a). Meanwhile, all cell voltages were stabilized at  $\sim 1.2$  V (Figure 8-2b). Similarly, it can be observed from Figure 8-2c and Figure 8-3 that the application of various acids had no obvious effects on ion removal efficiencies (~60% for Na<sup>+</sup> and ~90% for NH<sub>4</sub><sup>+</sup>) with a stable Na<sup>+</sup> concentration of  $<150 \text{ mg } \text{L}^{-1}$  and  $\text{NH}_4^+$  concentration of  $<5 \text{ mg } \text{L}^{-1}$  in the effluent stream. The ammonia removal selectivity factors ranged from 1.4 to 1.6 in all cases. These results are not surprising as the CapAmm desalination performance is mainly determined by operating parameters (e.g., current density and HRT), flow-electrode properties (e.g., carbon content, conductive additive and electrolyte), ion exchange membrane properties (membrane thickness, resistance, and selectivity) and operational modes (e.g., short-circuited closed-cycle and isolated closed-cycle) (Zhang et al., 2018e). In a CapAmm cell, the acid receiving solutions were completely separated from the cathode flow-electrodes by placing a hydrophobic gas membrane between, and therefore, it is expected that acid absorbent used should play a negligible role in salt removal processes.



**Figure 8-2.** Temporal variation of the (a) FCDI voltage and (b) effluent conductivity when using different acids as ammonia adsorbents. Experiment conditions: Carbon content = 5 *wt*%; Current density = 6.8 A m<sup>-2</sup>; HRT = 1.48 min. (c) Average removal efficiencies for ammonium and sodium ions in the CapAmm system when using different ammonia acid absorbents. The grey symbols are the ratios of removal efficiency [ $RE(NH_4^+-N)/RE(Na^+)$ ] with this ratio representing the selectivity of NH<sub>4</sub><sup>+</sup> compared to Na<sup>+</sup>. Experiment conditions: Carbon content = 5 *wt*%; Current density = 6.8 A m<sup>-2</sup>; HRT = 1.48 min.



**Figure 8-3.** Temporal variation of (a) the effluent Na<sup>+</sup> concentration and (b) the effluent NH4<sup>+</sup>-N concentration when using different acids as ammonia adsorbents. Experiment conditions: Carbon content = 5 *wt*%; Current density =  $6.8 \text{ A m}^{-2}$ ; HRT = 1.48 min.

# 8.3.2 Fate and distribution of ammonia in the CapAmm system

The effects of different acid types on the fate and distribution of ammonia and its recovery performance were comprehensively investigated in this section. At a constant room temperature (*i.e.*, 25 °C), the ammonia species in the wastewater is mainly determined by solution pH (**Figure 8-4**) with the fraction of NH<sub>3</sub> to total ammonia nitrogen (TAN = NH<sub>3</sub> +NH<sub>4</sub><sup>+</sup>) expressed as: [NH<sub>3</sub>]/[TAN] =  $10^{\text{pH}}/(e^{21.3}+10^{\text{pH}})$ . To achieve the efficient recovery of ammonia via use of a gas membrane, a prerequisite is the conversion of ammonia into its deprotonated form (NH<sub>3</sub>) at pH higher than 9.3 (*pK*<sub>a</sub> of the NH<sub>4</sub><sup>+</sup>-NH<sub>3</sub> acid-base pair) (Garcia-Gonzalez and Vanotti 2015).

The variations of the pH in cathode flow-electrodes are presented in **Figure 8-5**. It is has been widely reported that the concomitant Faradaic reactions in the desalination system will result in pH fluctuations in the flow-electrodes. For instance, pH increase cathodic flow-electrode can be mainly attributed to the reduction of oxygen with values reaching higher than 9.3 (shaded parts in **Figure 8-5**) attained in less than 20 min. Similar pH variations (from ~7 to ~12) were observed in all scenarios except the  $H_2CO_3^*$  case. The sluggish pH rise when using  $H_2CO_3^*$  as extractant, however, is not

surprising as  $H_2CO_3^*$  could easily evaporate and diffuse back through the gas membrane, dissolve into the cathode electrolyte (a OH<sup>-</sup>/NH<sub>3</sub> consuming processes) resulting in a slight decrease in pH (to ~10). While elevated base production was observed in the recirculation reservoir, the local pH in the flow-channels (close to the gas membrane) is expected to be much higher than that in the bulk flowable-electrode in the recirculation reservoir, facilitating the recovery of ammonia.



**Figure 8-4.** Distribution of nonvolatile  $(NH_4^+)$  and volatile ammonia  $(NH_3)$  with the variation of pH under a constant temperature of 25 °C.



**Figure 8-5.** Temporal variation of the cathode pH in the CapAmm system when using different acids for ammonia recovery. The shaded area represents the pH range of >9.3,

indicating the deprotonation of  $NH_4^+$  to  $NH_3$ . Experiment conditions: carbon content = 5 *wt*%; current density = 6.8 A m<sup>-2</sup>; HRT = 1.48 min.

In the CapAmm system, ammonia in influent wastewater is expected to migrate through the ion-exchange membranes and end up in the cathode chamber (either dissolved in the liquid phase of the flow-electrode and/or partially stored in the electrical double layer (EDL) of the suspended carbon particles), followed by membrane stripping and extraction by different absorbents. Temporal variations of ammonia concentrations in the cathode and acid chambers are illustrated in Figure 8-6. For ammonia absorption using nonvolatile absorbents ( $H_2SO_4$  and  $H_3PO_4$ ), the ammonia concentrations in the cathode chamber first demonstrated a gradual increase in the first 40 min and then were stabilized at a relatively low concentrations of ~20 mg L<sup>-1</sup>. In contrast, the application of volatile absorbents such as  $HNO_3$ , HCl,  $H_2CO_3^*$  and  $H_2O$ resulted in a continuous increase in the cathode ammonia concentration, with final values reaching 40-60 mg  $L^{-1}$  (Figure 8-6a). As for the ammonia concentrations in the acid chamber, unexceptionally, use of nonvolatile absorbents (H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) led to the best ammonia capture performances, with the ammonia concentrations continually increasing to  $\sim 160 \text{ mg L}^{-1}$ . However, relatively sluggish ammonia accumulation was observed in other scenarios when using volatile absorbents (HNO<sub>3</sub>, HCl), H<sub>2</sub>CO<sub>3</sub>\* and H<sub>2</sub>O as the absorbent. Specifically, in the initial phase (0-40 min), limited ammonia was transferred into the acid chamber (Figure 8-6b).

To further evaluate the influence of different absorbents on the performance of the CapAmm module, ammonia distributions were calculated based on mass balance equations described in Section 2. As depicted in **Figure 8-7**, nearly 10% of the ammonia in the wastewater still remained in the effluent in all scenarios. The majority of ammonia flowed into acid chamber in form of ammonium salts or ammonia solution (the green bar). The best recovery performance was achieved when using nonvolatile absorbents with recovery efficiencies of 74.7% for  $H_3PO_4$  and 72.9% for  $H_2SO_4$ , respectively. Volatile absorbents such as HNO<sub>3</sub> and HCl resulted in quite similar recovery efficiencies (~58.0%) while slightly lower recovery efficiency (48.3%) was observed in the  $H_2CO_3^*$  case. Using water as the absorbent, however, had the least recovery efficiency (35.0%). Moreover, it should not be noted that there is a considerable amount of ammonia left in the cathode chamber (either being dissolved in the catholyte (blue bar) or adsorbed by the flowable carbon particles (grey bar)) which can be further harvested if properly managed.



Figure 8-6. Temporal variation of the ammonia concentration in (a) the cathode chamber and (b) the acidic receiving solution of the CapAmm system when using different ammonia absorbents. Experiment conditions: carbon content = 5 wt%; current density = 6.8 A m<sup>-2</sup>; HRT = 1.48 min.



Figure 8-7. Fate and distribution of ammonia in the CapAmm system when using different ammonia absorbents. Experiment conditions: carbon content = 5 wt%; current density = 6.8 A m<sup>-2</sup>; HRT = 1.48 min.

#### 8.3.3 Mass fluxes across the gas membrane

The fluxes of different substances (i.e., water, sodium, absorbents and ammonia) across the gas membrane were further investigated with result shown in **Figure 8-8**. Based on the volume variations of the cathode flow-electrodes and acid absorbents before and after the operation, the transport of water across the gas membrane can be determined. As expected, no obvious water transfer was observed when using nonvolatile acids (H<sub>3</sub>PO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub>), carbonic acid (H<sub>2</sub>CO<sub>3</sub>\*) and water as ammonia absorbents due to the low water permeability of the extremely hydrophobic gas membrane under similar water vapor partial pressures across the membrane. Surprisingly, for the volatile acids, obvious water transfer from the cathode chamber to the acid chamber was observed with a significant increase in acid absorbent volumes from ~40 to ~58 mL. The average water flux across the membrane was calculated in these cases to be  $1.3 \text{ Lm}^{-2} \text{ h}^{-1}$ . Acids such as HNO<sub>3</sub> and HCl could easily volatilise into the membrane pores and be condense in the pores, leading to a higher local acid

concentration. As a result, a higher water vapor partial pressure difference would form between the cathode electrolyte and the acid solution, with this pressure difference providing a driving force to transport water across the hydrophobic membrane. Based on calculations according to Eq. 8-6 and 8-7, ammonia fluxes across the gas membrane were 11.2, 12.1, 9.1, 9.3, 7.6, and 5.6 g m<sup>-2</sup> d<sup>-1</sup>, when using H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>, HCl, H<sub>2</sub>CO<sub>3</sub>\* and H<sub>2</sub>O respectively. Volatile acids showed lower ammonia fluxes (23.4%) compared to nonvolatile acids (H<sub>3</sub>PO<sub>4</sub>) with this difference mainly attributed to the strong competition of water migration. In the H<sub>2</sub>CO<sub>3</sub>\* case, the competition of CO<sub>2</sub> back-diffusion as well as the sluggish cathode pH increase (Section 3.2) led to the observed inferior ammonia flux and recovery efficiency.

In actuality, ammonia extraction by absorbents is always accompanied by a series of complex physicochemical processes. For instance, ammonia capture by  $H_2CO_3^*$  is likely to involve a sequence of chemical reactions (Han et al., 2013a) with possible formation of ammonium salts such as ammonium carbamate (NH<sub>4</sub>COONH<sub>2</sub>), ammonium carbonate ((NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>) and ammonium bicarbonate (NH<sub>4</sub>HCO<sub>3</sub>) with the proportion of these species present dependent upon the particular ionic composition and temperature and pressure. In our experiments, the final products we recovered contained a total carbonate concentration of 9.17 mM and total ammonia nitrogen concentration of 7.49 mM with the final pH reached 8.5. Based on MINITEQ calculation, the distribution of carbonate and ammonia species can be easily obtained. As shown in Table S1, 97.5% of carbonate was in HCO<sub>3</sub><sup>-</sup> form and 85.9% of ammonia nitrogen was present as ionic NH<sub>4</sub><sup>+</sup>, indicating that the predominate endproduct should be NH<sub>4</sub>HCO<sub>3</sub>. Solid forms of the ammonium salts may precipitate after prolonged operation or, more likely, in a recovery process in which excess water is removed (**Figure 8-9**).



**Figure 8-8.** Schematic representation of mass transfer fluxes across the hydrophobic gas membranes when using (a) non-volatile acid (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>), (b) volatile acid (HNO<sub>3</sub>, HCl), (c) dissolved greenhouse gas (H<sub>2</sub>CO<sub>3</sub>\*) and (d) Milli-Q water (H<sub>2</sub>O).



**Figure 8-9.** Schematic illustration associated with the NH<sub>3</sub>–CO<sub>2</sub>–H<sub>2</sub>O equilibrium in cathode and acid chamber.
#### 8.3.4 Economic analysis of the CapAmm process using different acids

On the basis of the results obtained, we can make a comprehensive economic analysis (with regard to operating cost, chemical cost, products offset) thereby providing an effective approach to interpret our observations, compare systems and further identify the drawbacks and merits of different scenarios. As shown in Figure 8-10, lower operational costs (with respect mainly to electricity consumption) were observed (\$1.1~1.4 kg<sup>-1</sup> N) when using strong acid absorbents (H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub> and HCl) compared to those of weak absorbents ( $H_2CO_3^*$  and  $H_2O$ ) within this difference in costs mainly due to higher ammonia adsorption/capture efficiency. However, the specific acid consumptions required for ammonia capture were 3.5, 7.0, 4.5 and 2.6 kg of acid kg<sup>-1</sup> N, corresponding to application of H<sub>2</sub>SO<sub>4</sub> (98 wt%), H<sub>3</sub>PO<sub>4</sub> (85 wt%), HNO<sub>3</sub> (68 wt%) and HCl (36 wt%) with the dosage of these strong absorbents costing  $0.8 \sim 2.3 \text{ kg}^{-1}$  N, respectively. In contrast, because ammonia extraction using  $H_2CO_3$  contributed to the fixation of  $CO_2$  (greenhouse gases reduction), the chemical expense can be regarded as negative (earning  $0.37 \text{ kg}^{-1} \text{ N}$ ). When considering the products offsets, use of  $H_3PO_4$  and  $H_2O$  for adsorption generates high value end products such as (NH<sub>3</sub>)<sub>2</sub>HPO<sub>4</sub> and NH<sub>3</sub>.H<sub>2</sub>O, with high specific profits of \$5.3 and \$5.0 kg<sup>-1</sup> N, respectively, whereas other products such as (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, NH<sub>4</sub>NO<sub>3</sub> and NH<sub>4</sub>HCO<sub>3</sub> were actually of low-value. Therefore, the overall net revenues calculated were \$1.4, \$2.4, \$2.5, \$1.6, \$0.3, and  $-2.5 \text{ kg}^{-1} \text{ N}$  when using H<sub>2</sub>SO<sub>4</sub>, H<sub>3</sub>PO<sub>4</sub>, HNO<sub>3</sub>, HCl,  $H_2CO_3^*$  and  $H_2O$  as ammonia extractants. Interestingly, although the ammonia capture efficiencies for the H<sub>2</sub>CO<sub>3</sub>\* and H<sub>2</sub>O scenarios were relatively unsatisfying (<60%), the net profits obtained were greater than those obtained when using strong acid absorbents with this result a function of negligible chemical expenses and high end-products returns.

It is worth mentioning that the market prices of fertilizer are highly variable with the fluctuations a result of the global supply and demand for fertilizer. Considering that the demand for fertilizers are expected to increase at an annual growth rate of 1.5% over coming decades, the price of industrial products such as ammonia solution, ammonium salts and phosphate salts will continue to increase. From this respect, the harvesting of ammonia from wastewaters by our CapAmm system will be of increasing attractiveness in light of the growing economic and environmental benefits.



Figure 8-10. Economic analysis of the CapAmm process using different acids as ammonia absorbents. Data collected from Alibaba.com.

#### 8.3.5. Continuous operation using Milli-Q water as absorbents

Based on the previous results, ammonia capture via water adsorption should be the most economically effective option. As such, a trial of continuous operation of the CapAmm cell with Milli-Q water as the ammonia absorbents was then conducted. Cell discharging was completed by mixing the anode flow-electrode and cathode flowelectrode every two hours (one cycle) resulting in release of the absorbed ions and regeneration of exhausted carbon particles. As presented in **Figure 8-11**, the steadystate ammonia concentration was below 2 mg L<sup>-1</sup> in the effluent stream while continuous increase in ammonia concentrations were observed in both the cathode and acid chambers with the final concentrations reaching 99.6 mg  $L^{-1}$  and 136.2 mg  $L^{-1}$ , respectively. It should be noted that the cathode pH will decrease after discharge (pH neutralization), resulting in a slight back-diffusion of ammonia into the cathode chamber at the beginning of each cycle. As the adsorption capacity of water is limited, further concentration (possibly by a method such as forward osmosis) is required to produce more concentrated ammonia-solution products.



**Figure 8-11.** Variations of the ammonia concentration in the effluent stream, cathode chamber and acid chamber when operating the FCDI at a carbon content of 5 *wt%*. Experimental conditions: current density =  $11.5 \text{ A m}^{-2}$  at the charging stage,  $-17.2 \text{ A m}^{-2}$  at the discharging stage; HRT = 1.48 min; charging time = 120 min. The discharging of the FCDI cell was achieved by mixing the anode and cathode flow electrodes.

#### 8.4 Conclusions

In this study, a CapAmm system process was developed to remove salts and recover ammonia from wastewaters using different ammonia absorbents. Results indicate that absorbents have negligible influence on salt removal performances and cell voltages with a steady effluent  $NH_4^+$  concentration of <5 mg L<sup>-1</sup> and sodium concentration of <150 mg L<sup>-1</sup> achievable at constant current density = 6.8 A m<sup>-2</sup> (and

HRT = 1.48 min). Further investigation of the fate of ammonia indicated that the majority of ammonia flowed into the acid chamber and was fixed as ammonium salts or ammonia solution. Volatile absorbents (HNO<sub>3</sub> and HCl) showed lower recovery efficiencies compared to nonvolatile absorbents, due to the significant water migration across the gas membrane when volatile absorbents are used. Back-diffusion of CO<sub>2</sub> and  $NH_3$  in the  $H_2CO_3^*$  and  $H_2O$  scenarios also led to a deterioration in ammonia recovery performance with this finding likely ascribed to competitive occupation of the gas membrane pores and a decrease in catholyte pH. Economic analysis further confirmed that use of strong acid adsorbents was less economically attractive compared to use of H<sub>2</sub>CO<sub>3</sub>\* and H<sub>2</sub>O as ammonia absorbents in regards to the high chemical costs and low products revenues in the case of the strong acids. In continuous operation of CapAmm using H<sub>2</sub>O absorbents, the system can achieve a continuous ammonia removal and recovery performance, with the effluent  $NH_3^+$ -N concentration below 2 mg  $L^{-1}$  and a linear increase in ammonia concentration in the recovery chamber.

# Chapter 9. Ammonia-rich Solution Production from Wastewaters Using Chemical-free Flowelectrode Capacitive Deionization (FCDI)

#### 9.1 Introduction

Ammonia, one of the most important industrial chemicals and carbon-free energy carriers, has a worldwide annual production of about 150 million tons, with the demand projected to continue increasing due to the booming world population and improvement in living standards (Erisman et al., 2008, Galloway et al., 2008, Gruber and Galloway 2008). Ammonia synthesis is traditionally based on the Haber-Bosch process, which combines high purity N<sub>2</sub> and H<sub>2</sub> under harsh conditions (*i.e.* high pressure, high temperature and metal-based catalysts), with this process accounting for  $\sim$ 1% of the global energy consumption and 1.6% of the world's CO<sub>2</sub> emissions (Agency 2007, Luther et al., 2015, Zhou et al., 2017a). Of this ammonia production,  $\sim$ 20% ends up in sewage with the large-scale influx of this reactive nitrogen species into the aquatic environment resulting in serious deterioration of water quality. In view of the value of ammonioa as a resource and its deleterious impact when discharged to the environment, there is renewed interest in recovering ammonia from wastewaters.

In recent decades, a variety of approaches have been developed for ammonia removal/recovery from wastewaters including crystallization, air-stripping, ionexchange, membrane separation and/or (bio)electrochemical methods with these technologies typically aimed at producing products of value (such as ammonium sulfate and struvite) (Kelly and He 2014, Ward et al., 2018, Zhang et al., 2018b).

Crystallization via the formation of, for example, struvite relies on the use of an appropriate precipitator (*i.e.* MgCl<sub>2</sub>) to react with solubilized ammonia and phosphate species at a stoichiometric ratio of Mg:N:P of 1:1:1 under optimum pH conditions (8.5-10.5) (Mehta and Batstone 2013, Romero-Guiza et al., 2015). However, this method requires expensive chemicals (i.e. Mg and an alkali) and is likely to be uneconomic unless the influent phosphate concentration is over 100 mg  $L^{-1}$  (Pastor et al., 2010, Ronteltap et al., 2010). The effectiveness of air stripping, which involves the physical transfer of  $NH_{3(aq)}$  from wastewaters to gas phase followed by acid adsorption, is strongly dependent on operating factors such as feed pH (>10.5), feed temperature (~45 °C), ratio of air to feed (600-700:1) and feed characteristics (Zarebska et al., 2014, Zhang et al., 2012). There are also major technical challenges in ammonia-stripping relating to the scaling and fouling of the stripping towers (Bonmati and Flotats 2003, Vaneeckhaute et al., 2017). (Bio)electrochemical systems take advantage of an electrical field to transfer and concentrate ammonium ions in the cathode chamber where NH4<sup>+</sup> is transformed to NH3 under the concomitant alkaline environment and then may be recovered via coupled processes such as gas stripping(Hou et al., 2018, Kuntke et al., 2017, Ledezma et al., 2017, Ledezma et al., 2015, Zhang and Angelidaki 2015a). Although the use of alkali chemicals can be largely avoided, the effectiveness of these (bio)systems is constrained by the relatively low ammonia flux and the requirement for acidic receiving solutions (e.g. sulfuric acid), thus increasing the operating cost and complexity, especially in decentralized scenarios(Hou et al., 2018, Ledezma et al., 2015, Tarpeh et al., 2018b). In addition, there has been continued argument with regard to the quality and market value of the end-products. For example, ammonium sulfate, a common product recovered from wastewaters that is widely used as an agricultural fertilizer, is of low value ( $\sim 0.13$  USD kg<sup>-1</sup>).

Ammonia solution, also known as aqueous ammonia  $(NH_{3(aq)})$ , is a valuable chemical that is widely used in plastics and textile manufacturing, food production and water treatment. Given these various applications, recovery of ammonia from wastewaters as ammonia solution would seem far preferable compared to recovering as an ammonium salt. Conventional ammonia solution production systems typically consist of two compartments; that is, an air stripper for ammonia separation from wastewaters and an absorber to trap gaseous ammonia and accumulate to generate a concentrated ammonia solution. To increase the recovery efficiency, the stripper should be operated under low pressure and high temperature conditions and the absorber operated at high pressure and low temperature with this arrangement of conditions exceptionally complex and energy-intensive.

An alternative to the traditional approaches of ammonia removal and recovery involves the use of a flow-electrode capacitive deionization (FCDI) system. This approach has gained increasing popularity as a means of concentrating (and, in some instances, recovering) selected ions. Indeed, in our previous FCDI studies, we have shown, at bench scale at least, that this approach is effective for the removal of ammonium ions from wastewaters with subsequent recovery through use of gaspermeable membranes as an ammonium salt solution (Wang et al., 2017, Zhang et al., 2017, Zhang et al., 2018d). As mentioned above however, ammonium salts are of limited value. As such, we focus in this work on the recovery of solutions with high concentration ratios of ammonia to other ions from dilute wastewater using FCDI with specific consideration given to the effects of different operating conditions on the process performance and energy efficiency. Evaluation of the performance of a continuously operated bench-scale unit was then undertaken over nine successive charging/discharging cycles. The overarching goal of the present work is to present a proof of concept of this proposed approach that enables production of high-value ammonia-rich products stream from wastewaters by a chemical-free method.

#### 9.2 Materials and methods

#### 9.2.1 Experiment Setup

The structure of the FCDI cell is shown in **Figure 9-1a**. Basically, it is a threechambered unit in which three silicon gasket frames and two ion exchange membranes (AEM-Type II/CEM-Type II, FUJIFILM Europe) were incorporated together between two acrylic end plates creating the anode, desalination and cathode chambers respectively. The current collectors were made of graphite plates which were carved with serpentine channels (3 mm wide and 3 mm deep) through which suspensions of carbon particles were circulated and constituted the flowable electrodes. The contact area between the current collectors and each membrane (*A*) was 66.3 cm<sup>2</sup> while the effective contact area ( $A_{eff}$ ) between the flow channels and each membrane was equal to 34.9 cm<sup>2</sup>. Wastewaters passed through a 0.5 mm thick spacer (100 mesh) made of a nylon sheet located between the two membranes.

#### 9.2.2 Operating Conditions

Synthetic wastewater containing ~1000 mg L<sup>-1</sup> NaCl and ~43 mg L<sup>-1</sup> NH<sub>4</sub><sup>+</sup>-N was fed into the desalination chamber in a single-pass mode. The hydraulic retention time (HRT) of the wastewater was controlled at 1.48 min. The carbon materials in the flow electrodes were composed of 100-mesh DARCO® activated carbon, Norit® chemically activated charcoal and carbon black powders with a mass ratio of 8:1:1. During the experiment, 40 mL positively and negatively charged flow-electrodes (with the current collectors connected to the anode and cathode of a DC power supply during the charging period as shown in **Figure 9-1**, were individually recirculated between the FCDI cell and two stirred reservoirs. Four carbon content levels (0, 2, 5 and 10 *wt*%)

with the bulk solution prepared using 18.2 M $\Omega$  cm Milli-Q water) were tested to examine their influence on the ammonia recovery performance in one operating cycle comprising 120-min charging (electrosorption) and 60-min discharging (desorption and electrode regeneration by reversal of the polarity). The charging and discharging current densities were respectively fixed at *i* = 6.0 and -9.0 A m<sup>-2</sup>. Subsequently, continuous operation was undertaken using 5 *wt*% carbon content with consideration given to two charging/discharging alternatives (*i.e.* 120min/60min and 120min/40min). Production of ammonia-rich solution via FCDI was further examined using real domestic wastewater (with effluent collected from a local anaerobic membrane bioreactor). On the basis of the results obtained, a continuous experiment over nine successive cycles (~25 h) was carried out. The analytical methods and calculations are provided in Section S1 in Supporting Information.



**Figure 9-1.** Schematic representations of (a) the structure of the FCDI cell and (b) cross-section schematic of the cell and (c) charging and (d) discharging alternation for selective ammonia recovery.

#### 9.2.3 Analytical Methods and Calculations

The effluent conductivity was measured by a conductivity meter (CON-BTA, Vernier) and the cell voltage (U) was monitored by a voltage probe (CON-BTA, Vernier). Both of them were connected to a data acquisition system (SensorDAQ, Vernier). pH variation in the flow-electrode was measured using an F-51 pH meter (Horiba, Japan). Samples from the influent, effluent and cathodic flow electrode were

collected every 30 min. All samples were filtered through 0.45  $\mu$ m filters (Millipore) prior to further analysis. Both ammonium and sodium ion concentrations were determined by ion chromatography (ICS-3000, Dionex, U.S.) with the instrument used equipped with guard column CG16 (5 × 50 mm) and separation column CS16 (5 × 250 mm).

The specific energy consumption for ammonia recovery (kWh  $kg^{-1}$  N) can be calculated as:

$$E = \frac{\int_{0}^{t_{c}} U_{c} i_{c} A dt + \int_{0}^{t_{d}} U_{d} i_{d} A dt}{3.6 \times C_{N,cat} \times V_{cat}}$$
(9-1)

where  $U_c$  and  $U_d$  represent the cell voltage (V) during charging and discharging stage,  $i_c$ and  $i_d$  are the applied current density (A m<sup>-2</sup>) during charging and discharging stage,  $t_c$ and  $t_d$  represent the operation time (s) of the charging and discharging stage, A is the contact area between the current collectors and each membrane (0.00663 m<sup>2</sup>),  $C_{N,cat}$  is the final ammonia concentration (mg L<sup>-1</sup>) in the cathode after discharging,  $V_{cat}$ represents the volume (0.04 L) of cathodic flow-electrode. The selectivity of ammonia towards other ions can be expressed as:

$$\eta = \frac{C_{\text{N,cat}} / C_{\text{N,inf}}}{C_{\text{i,cat}} / C_{\text{i,inf}}}$$
(9-2)

where  $C_{N,cat}$  and  $C_{N,inf}$  represent the NH<sub>4</sub><sup>+</sup>-N (and NH<sub>3</sub>-N) concentrations (mg L<sup>-1</sup>) in the cathode chamber (after completion of discharging) and the influent stream respectively, and  $C_{i,cat}$  and  $C_{i,inf}$  the ions (such as Na<sup>+</sup>, K<sup>+</sup> or Ca<sup>2+</sup>) concentrations (mg L<sup>-1</sup>) in the cathode chamber (after completion of discharging) and the influent stream respectively. The distributions of the ions in the effluent (during charging), those back diffused into the desalination chamber (during discharging), and those trapped in the cathode chamber were obtained by dividing the total amount of a particular ion contained in the effluent (during charging), the waste stream (during discharing), the cathode electrolyte with the total amount of ions in the influent. According to the mass balance principle, the remaining, unknown portions may relate to the adsorption of ions on the carbon particles and/or escape (of  $NH_{3(g)}$ ) into the air.

Charge efficiency (%) during the charing process can be expressed as:

$$\Lambda = \frac{\sum \frac{n_i \times F \times v \times \int_0^{t_c} (C_{i,inf} - C_{i,eff}) dt}{M_i}}{\int_0^{t_c} i_c A dt} \times 100$$
(9-3)

where  $n_i$  is the charge of certain ion species (*i.e.*, 1 for NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup>), *F* the Faraday constant (96485.3 C mol<sup>-1</sup>), *v* the flow rate (m<sup>3</sup> s<sup>-1</sup>) of the wastewater stream,  $M_i$  the molar mass of ion species *i* (g mol<sup>-1</sup>), *A* the effective area between the ion-exchange membrane and the flow electrode (0.00663 m<sup>2</sup>) and *I* the applied current density (I = i/A, A m<sup>-2</sup>).

#### 9.3 Results and discussion

#### 9.3.1 Selective Ammonia Recovery in FCDI

In this study, we used a flow-electrode system for selective ammonia recovery and ammonia-rich solution production (**Figure 9-1a** and **b**). As proposed in Figure 1c, during the charging step, when a positive current density is applied, cations (Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup>) migrate through the cation exchange membrane (CEM) and are accumulated in the cathode chamber. Due to unavoidable Faradaic reactions (particularly oxygen reduction), the cathode pH increases to values >  $pK_a$  of ammonium (9.25) with this high pH facilitating the transformation of NH<sub>4</sub><sup>+</sup> to uncharged NH<sub>3</sub> (Zhang et al., 2019a, Zhang et al., 2017). During the discharging step, a reversed current density is applied. Most of Na<sup>+</sup> in the cathode will be released back to the desalination chamber with the uncharged ammonia, however, rejected by the CEM and thereby selectively concentrated in the cathode chamber.

Figure 9-2 and Figure 9-3 show the temporal variations of  $NH_4^+$  and  $Na^+$ concentrations in the effluent stream and cathode electrolyte when the FCDI was operated using different carbon contents. In the charging stage,  $NH_4^+$  and  $Na^+$ concentrations exhibited similar trends with the ions being continuously removed from the desalination chamber and their concentrations increasing linearly in the cathode chamber (Figure 9-2). In contrast, during discharging, the variation of NH4<sup>+</sup> concentration was dependent on the carbon content; that is, at low carbon contents (e.g. 0 wt% in Figure 9-2a), trapping of  $NH_4^+$  (or  $NH_3$ ) in the cathode did not occur with the nitrogen concentration in the effluent increasing along with a continuous concentration decrease in the cathode. For higher carbon contents (e.g. 5 wt%), insignificant ammonia loss from the cathode was noted within the initial 40-min of discharging (Figure 9-2b). Carbon contents, however, have limited influence on Na<sup>+</sup> migration during charging/discharging. Overall, NH4<sup>+</sup> demonstrated a slightly higher removal rate compared to  $Na^+$  in the charging stage with a much slower release rate during discharging at higher carbon contents. By decanting the ammonia-rich electrolyte from the flow cathode (following the removal of the carbon particles by sedimentation or membrane filtration), selective ammonia recovery can be achieved in the chemical-free FCDI system.



**Figure 9-2**. Variations of the ammonia concentrations in the effluent and cathode at carbon contents of (a) 0 *wt*% and (b) 5 *wt*% and sodium ion concentrations at carbon contents of (c) 0 *wt*% and (d) 5 *wt*%. Variations of ion concentrations at 2 and 10 *wt*% are shown in **Figure 9-3**. (e) Time-course results of voltages and (f) energy consumption (whole period) and charge efficiency (charging period) for ammonia-rich solution production as a function of carbon contents in the flow electrodes. Experimental conditions: HRT = 1.48 min; charging time = 120 min and discharging time = 60 min. The shaded sections of the plots represent the behavior during the discharging process.



**Figure 9-3.** Variations of the ammonia and sodium ion concentrations in the effluent stream and the cathode electrolyte at carbon contents of (a) 2 *wt*% and (b) 10 *wt*%. Experimental conditions: HRT = 1.48 min; charging time = 120 min and discharging time = 60 min. The shaded parts represent the discharging process.

#### 9.3.2 Significance of High Carbon Contents in Flow-electrode

As indicated in **Figure 9-2e**, an increase in the carbon content from 0 to 10 *wt*% significantly reduced the charging cell voltage from 3.4 to 2.0 V as well as the discharging cell voltage (at 180 min) from -3.3 to -1.3 V. This can be ascribed to the fact that higher carbon contents result in a conductive 3D interconnected particle network in the flow electrodes thus facilitating the electron/ion transfer and decreasing the cell internal resistance (Hatzell et al., 2017, Ma et al., 2018). In a capacitive system, the coupling of charge ( $e^-$ ) and counter ions (NH<sub>4</sub><sup>+</sup> and Na<sup>+</sup>) in the electrical double layers (EDLs) may compete with the Faradaic reactions (such as the reduction of O<sub>2</sub>) that generate OH<sup>-</sup>. The use of higher carbon contents enhanced the capacitive effects and suppressed the Faradaic process with much smaller pH fluctuations being observed (**Figure 9-4**), which is of great significance during the discharging step. For example, at

carbon content of 5 *wt*%, the cathode pH increased from 7.0 to 11.9 at the charging stage but slowly decreased to 9.2 during discharging as a result of the retarded production of protons. However, for 0 *wt*% carbon content, pH first increased to 12.6 during charging but quickly dropped to 4.2 following the polarity reversal. As such, the protonated ammonium migrated back to the desalination chamber (**Figure 9-2a**).

Results of this study indicated that most of the NH<sub>4</sub><sup>+</sup> present in the influent stream from wastewaters could be transformed to and sustained in the uncharged form during the charging/discharging operation of FCDI thus enabling the production of ammonia-rich solution by selectively releasing the charged ions back into the desalination chamber while retaining the uncharged NH<sub>3</sub> in the flow electrode. According to our calculations (**Figure 9-3**), the energy consumptions were 94.4, 79.5, 38.5 and 35.4 kWh kg<sup>-1</sup> N respectively at carbon contents of 0, 2, 5 and 10 *wt*% (**Figure 9-2f**). Meanwhile, charge efficiency during the charging period improved from 63.8% to 78.5% when the carbon loading increased from 0 to 10 *wt*% (**Figure 9-2f**). Note that the use of flow electrodes containing 5 *wt*% carbon led to a similar performance to 10 *wt*% carbon. As a result, 5 *wt*% carbon content was used in the following experiments unless otherwise stated.



Figure 9-4. Temporal variations of the cathode pH during the charging/discharging operation of the FCDI cell at different carbon contents (*i.e*, 0, 2, 5 and 10 *wt%*).

Experimental conditions: HRT = 1.48 min; charging time = 120 min and discharging time = 60 min. The shaded parts represent the discharging process.

#### 9.3.3 Influence of Charge/Discharge Time Ratio

In regard to the potential transformation of NH<sub>3</sub> and leakage at prolonged discharging times (Figure 9-2b), two charging/discharging options (120min/40min and 120min/60min) were evaluated. It can be seen from Figure 9-5 and Figure 9-6 that repeating changes of cell voltages and cathode pH were achieved during operation of the FCDI system. For the 120min/40min scenario, the final voltage and pH at the end of each cycle (following discharging) were ~0.8 V and 11.8, which provide the ideal prerequisites for the enrichment of ammonia in the catholyte (Figure 9-5a and b). An approximately linear increase in the aqueous ammonia concentration (with a final value of 263 mg  $L^{-1}$ ) is observed in the cathode due to the retardation in NH<sub>3</sub> back diffusion across the membrane (Figure 9-5c and d). In contrast, when extending the discharging time to 60 min, the cathode pH cannot be sustained at a high value due to the concomitant Faradaic reactions that generate protons, resulting in the protonation of ammonia followed by back diffusion into the desalination chamber (Figure 9-6c and d). Mass balance calculations showed that ammonia was mainly present in the catholyte, especially at the optimized discharging time (45.3% at 40 min), with insignificant accumulation of Na<sup>+</sup> observed (Figure 9-7).



**Figure 9-5.** Temporal variations of (a) the cell voltage, (b) cathode pH, (c) ammonia concentrations in the effluent and the catholyte and (d) sodium ion concentrations in the effluent and the catholyte during 3-cycles operation with a charging time of 120 min and discharging time of 40 min. Experimental conditions: HRT = 1.48 min; carbon content = 5 wt%; The shaded parts represent the discharging process.



**Figure 9-6.** Temporal variations of (a) the cell voltage, (b) cathode pH, (c) ammonia concentrations in the effluent and the catholyte and (d) sodium ion concentrations in the

effluent and the catholyte during 3-cycles operation with a charging time of 120 min and discharging time of 40 min. Experimental conditions: HRT = 1.48 min; carbon content = 5 wt%; The shaded parts represent the discharging process.



Figure 9-7. Distribution of the ammonia and sodium after 3-cycles operation at different charging/discharging alternations. Experimental conditions: carbon content = 5 wt%; HRT = 1.48 min.

#### 9.3.4 Ammonia-rich Solution Production from Domestic Wastewater

The production of an ammonia-rich solution via FCDI was further examined using real domestic wastewater (effluent collected from a local anaerobic membrane bioreactor wastewater treatment plant). After FCDI treatment, stable effluent was obtained with a low concentration of residual  $NH_4^+$ . As shown in **Figure 9-8**, all ions accumulate in the cathode during the charging process, while only the uncharged ammonia trapped during the discharging stage. After three-cycles of operation, the selectivity of ammonia to  $Na^+$ ,  $K^+$  and  $Ca^{2+}$  achieved was 3.7, 2.0 and 11.4, respectively. The superior selectivity of ammonia to  $Ca^{2+}$  could be partly attributed to the precipitation of  $CaCO_3(s)$  on the flow electrodes, thus reducing the dissolved  $Ca^{2+}$ concentrations in the cathode as described elsewhere (He et al., 2018a).



**Figure 9-8.** Variations of (a) Na<sup>+</sup>, (b) NH<sub>3</sub>-N (NH<sub>4</sub><sup>+</sup>-N), (c) K<sup>+</sup> and (d) Ca<sup>2+</sup> concentrations in the effluent and the catholyte when using FCDI to treat the real wastewater (AnMBR effluent) at carbon content of 5 *wt*%. Experimental conditions: HRT = 1.48 min; Carbon content = 5 *wt*%; charging time = 120 min and discharging time = 40 min. The shaded parts represent the discharging process.

#### 9.3.5 Continuous operation

On the basis of the results obtained, the FCDI system was operated for nine successive cycles (~25 h) to further evaluate ammonia recovery performance. It can be seen from **Figure 9-9** that cathode pH showed excellent repeatability during the operation. Ammonia was successfully accumulated in the cathode with the final concentration reaching 927 mg  $L^{-1}$ , while most of the Na<sup>+</sup> was released into the desalination chamber with this process resulting in a high N/Na<sup>+</sup> selectivity of 5.1 (**Figure 9-10**).



**Figure 9-9.** Time-course results of the cathode pH during nine-successive-cycles continuous operation of FCDI. Experimental conditions: HRT = 1.48 min; Carbon content = 5 *wt*%; charging time = 120 min and discharging time = 40 min.



**Figure 9-10.** Variations of (a) NH<sub>3</sub>-N (NH<sub>4</sub><sup>+</sup>-N) and (b) Na<sup>+</sup> concentrations in the effluent and the flow cathode during continuous operation of FCDI. Experimental conditions: HRT = 1.48 min; Carbon content = 5 wt%; charging time = 120 min and discharging time = 40 min. The shaded parts represent the behavior during the discharging process.

#### 9.4 Implications and Outlook

This study provides a chemical-free alternative to the production of ammoniarich solutions from wastewaters by taking advantage of the differential rates of migration of ammonium ions and other cations during the FCDI charging and discharging Operating conditions carbon processes. (e.g. content and charging/discharging time ratio) have significant impacts on process performance. Although a small portion of the ammonia transported to the cathode chamber may be physically adsorbed by the carbon particles, the use of higher carbon contents results in much smaller pH excursions, especially during discharging, resulting in the successful entrapment and concentration of ammonia in the cathode chamber.

While the results presented here provide proof-of-concept of the suitability of FCDI for recovery of ammonia-rich solution, more effort is required to improve the recovery efficiency and to optimize the selectivity of the FCDI process with respect to competing ions. Further long-term tests using real high-strength substrates (*i.e.*, urine, manure, leachate) need to be undertaken and scale-up to a practical size is vital. Other challenges lie in reducing the energy associated with pumping the suspended carbon particles and with rapidly separating the concentrated ammonia solution form the carbon slurry. Development of mathematic models of the process would also be of use in optimizing pH variation and energy consumption, both of which are key factors in developing a sustainable ammonia recovery technology.

## **Chapter 10. Conclusions**

This thesis collectively presents all the work completed during my PhD with the studies described herein focused on fundamental electrochemical mechanisms, performance investigation, process optimization, economic evaluation and exploration of application niches when using electrochemically-based technologies (CDI and EAOPs) for nutrient abatement and/or recovery. The results demonstrate that these approaches hold great promise for energy efficient and economically efficient water treatment and resource recovery in the future.

Chapters 2-3 describe the electrochemical processes (Faradaic and non-Faradaic reactions) occurring in typical electrochemical systems and, in particular, in the CDI cell. In Chapter 2, we provide detailed insight into both the positive and negative effects of these reactions. Guidelines and strategies that could be used to reduce or eliminate the negative side effects of Faradaic reactions are presented and approaches to best utilizing Faradaic reactions in a positive manner (e.g., nutrients removal/recovery, disinfection and contaminants degradation) are described.

In Chapter 3, we have investigated both the desalination and Faradaic processes occurring in an innovative flow-through CDI system operated in different flow modes. A flow-through CDI operated in forward flow mode exhibited the best salt removal performance compared to flow-through CDI operated in reverse flow mode and flow-by CDI. Another outcome is the recognition that pH fluctuations become more severe when adopting the flow-through configuration with the pH of the treated stream increasing to about 9.3 under forward flow mode and decreasing to 4.0 under reverse flow mode. Additionally, the quantities of  $H_2O_2$  generated exhibited significant differences when applying different configurations and flow modes with these differences most likely a consequence of the difference in rate and extent of the

occurrence of Faradaic reactions in different flow modes. Since much higher  $H_2O_2$  concentrations are generated in forward flow mode compared to the other operational modes, this operational mode combined with  $O_3$  or UV irradiation could potentially contribute to water disinfection or contaminant degradation during desalination.

Chapters 4-5 focus on the application of electrochemical methods to selectively sequester nutrients ions such as ammonium and nitrate. In Chapter 4, we have demonstrated an effective ammonia removal approach using an active chlorine-mediated electrochemical oxidation process. With the *in situ* generated active chlorine near the anode, ammonia can be efficiently converted into harmless nitrogen gas with concentrations of by-products (i.e., chlorate, nitrate and chloramine) well below WHO guidelines. A mechanistically-based kinetic model has been developed that successfully describes the key underlying reactions occurring in the electrochemical ammonia oxidation system including active chlorine evolution, ammonia decomposition, and by-product formation. This model can be used to determine operating conditions (current densities, electrolysis times) appropriate to particular feed water compositions (of chloride and ammonia content) that enable complete ammonia removal at optimal current efficiency and minimal by-product formation.

In Chapter 5, SCC FCDI was used to remove nitrate from source waters containing different nitrate concentrations. Results indicate that FCDI is well suited to removing nitrate to levels consistent with extremely stringent standards (< 1 mg NO<sub>3</sub>-N  $L^{-1}$ ). Investigation of the fate of nitrate indicated that non-electrostatic adsorption of nitrate to the carbon particles initially plays a vital role in nitrate removal in FCDI. Nevertheless, the exhaustion of non-electrostatic adsorption capacity with ongoing operation did not lead to significant deterioration in performance with this result likely ascribed to the continued retention of nitrate in the EDLs of the carbon particles in the

flow anode. In continuous operation of SCC FCDI, constant voltage mode is better suited to maintaining stable effluent quality. Through periodic replacement of the electrolyte at a water recovery of 91.4%, the FCDI system can achieve continuous desalting with the effluent NO<sub>3</sub>-N concentration below typical target MCLs at low energy consumption (~0.5 kWh m<sup>-3</sup>) but high productivity (HRT < 1 min).

New approaches for ammonia recovery, either as ammonium salts or ammonia solution, are described in Chapter 6-9. In Chapter 6, a capacitive membrane ammonia stripping (CapAmm) system, which is composed of a FCDI cell and a hollow-fiber membrane contactor, was found to be a very effective alternative for ammonia removal and recovery from dilute wastewaters. Compared with other ammonia recovery systems that require additional chemical dosing to adjust the pH and which use energy-intensive air stripping to extract ammonia, CapAmm allows for the selective ammonia removal and preconcentration in the cathode chamber, with the elevation in pH that occurs as a result of intrinsic Faradaic processes favouring the conversion of NH<sub>4</sub><sup>+</sup> to dissolved NH<sub>3</sub>. Given the rapidity with which solution phase ammonia equilibrates with gaseous ammonia, NH<sub>3</sub>(g) will readily diffuse through a gas-permeable membrane into an acid solution and may be recovered as an ammonium salt which can be readily marketed as a fertilizer. In addition, this experimental setup is less complex than other experimental setups which utilize energy intensive air-stripping processes or require the use of multiple absorption vessels.

In Chapter 7, we extend this earlier study (Chapter 6) with description of an FCDI system with integrated flat sheet gas permeable membrane with comprehensive assessment of ammonia recovery performance from both dilute and concentrated wastewaters. The integrated CapAmm cell exhibited excellent ammonia removal and recovery efficiencies (up to ~90% and ~80% respectively). The energy consumptions for ammonia recovery from low-strength (*i.e.*, domestic) and high-strength (*i.e.*,

synthetic urine) wastewaters were 20.4 kWh kg<sup>-1</sup> N and 7.8 kWh kg<sup>-1</sup> N, respectively, with these values comparable to those of more conventional alternatives. Stable ammonia recovery and salt removal performance was achieved over more than two days of continuous operation with ammonia concentrated by ~80 times that of the feed stream. These results demonstrate that the integrated CapAmm system described here could be a cost-effective technology capable of treating wastewaters and realizing both nutrient recovery and water reclamation in a sustainable manner.

In Chapter 8, a CapAmm process was used to remove salts and recover ammonia from wastewater using different ammonia absorbents. Results indicated that absorbents have negligible influence on salt removal performances and cell voltages. Further investigation of the fate of ammonia indicated that the majority of ammonia flowed into the acid chamber and was fixed as ammonium salts or ammonia solution. Volatile absorbents (HNO<sub>3</sub> and HCl) showed lower recovery compared to nonvolatile absorbents due to the significant water migration across the gas membrane. Meanwhile, obvious back-diffusion of CO<sub>2</sub> and NH<sub>3</sub> in the H<sub>2</sub>CO<sub>3</sub>\* and H<sub>2</sub>O scenarios led to a deterioration in ammonia recovery performance with this result likely ascribed to competitive occupation of the gas membrane pores and the decrease of cathode flow-electrode pH. Economic analysis further revealed that using strong acid adsorbents was less economically attractive compared to using H<sub>2</sub>CO<sub>3</sub>\* and H<sub>2</sub>O as ammonia absorbents in view of the high chemical costs of these acids and the low value of the products.

In Chapter 9, a chemical-free alternative to the production of ammonia-rich solutions from wastewaters was developed by taking advantage of the differential rates of migration of ammonium ions and other cations during the FCDI charging and discharging processes is described. Operating conditions (e.g. carbon content and charging/discharging time ratio) have significant impacts on process performance. Although a small portion of the ammonia transported to the cathode chamber may be physically adsorbed by the carbon particles, the use of higher carbon contents results in much smaller pH excursions, especially during discharging, resulting in the successful entrapment and concentration of ammonia in the cathode chamber.

Despite the great advances achieved in this study, it should be noted that these electrochemical nutrients removal/recovery technologies, especially FCDI, are still in their infancy. A number of obstacles prevent them from practical application. First, one major limitation of FCDI systems relates to the discontinuous electrical network of the flow-electrodes, particularly the commonly utilized activated carbons particles, resulting in the conductivity of the flow-electrodes being a few orders of magnitude lower than that of conventional static carbon electrodes. Although a higher loading of active materials in the flow electrode slurry might improve the flow electrode conductivity resulting in enhanced salt removal performance, it also significantly increases the viscosity of the flow-electrode with the risk for flow-electrode blocking increased. Increased efforts will be required to solve this critical issue in our future work with possible approaches including utilizing a fluidized bed, performing surface modification of the carbon particles and introducing additives such as redox shuttles, carbon black or carbon nanotubes (CNTs).

Secondly, there is still no effective solution to efficiently and rapidly separate the flowing carbon particles from the brine stream and achieve real continuous operation of the FCDI cell. Future work will investigate effective carbon separation methods which will allow for the continuous and stable operation of FCDI. Possible approaches include use of microfiltration membrane separation, magnetic separation and gravity separation.

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Thirdly, optimal design of the FCDI unit will be required with coupled modelling of the hydraulic conditions in the cell together with the transport of ions through the ion exchange membranes and subsequently toward the surface of the mobile electrode particles likely gaining increasing interest. The hydraulic condition of the carbon particles in the CDI cells will also be modelled and used to assist in identifying the optimum geometry of the electrodes as well as the optimal loading of particles in the FCDI unit. Computational fluid dynamics (CFD) will be an effective tool to assist these modelling and design tasks.

Last but not least, pumping of the flow carbon particles consumes energy, which must be taken into account in the overall energy budget of the technology scaling up from small bench size units to full-sized modules. It is envisaged that CapAmm cells could be stacked together to provide the required throughput but significant challenges remain. Of particular attraction however is the low voltage and, direct current requirements of the technology rendering it suitable for direct use of photovoltaic power supply with associated reduction in energy costs.

# **Publications and patents during PhD study**

#### **Publications**

1. **Zhang, C.**, He, D., Ma, J.; Tang, W., Waite, T.D\*., Faradaic reactions in capacitive deionization (CDI) - problems and possibilities: A review. Water Res. 2018, 128, 314-330. **[Nature Index Journal**; IF **7.015**; Citation **79**; Hot Paper]

2. Zhang, C., Ma, J., He, D., Waite, T.D\*., Capacitive membrane stripping for ammonia recovery (CapAmm) from dilute wastewaters. Environ. Sci. Technol. Lett. 2017, 5(1), 43-49. [IF 5.869; Citation 17; Highly cited paper]

3. Zhang, C., He, D., Ma, J., Waite, T.D\*., Active chlorine mediated ammonia oxidation revisited: Reaction mechanism, kinetic modelling and implications. Water Res. 2018, 145, 220-230. [Nature Index Journal; IF 7.015; Citation 8]

4. **Zhang, C.**, Ma, J., Song, J., He, C., Waite, T.D\*., Continuous ammonia recovery from wastewaters using an integrated capacitive flow electrode membrane stripping System. Environ. Sci. Technol. 2018, 52(24), 14275-14285. [Nature Index Journal; IF 6.653; Citation 4]

5. **Zhang, C.**, He, D., Ma, J., Tang, W., Waite, T.D\*., Comparison of faradaic reactions in flow-through and flow-by capacitive deionization (CDI) systems. Electrochim. Acta 2019, 299, 727-735. [IF **5.116**; Citation **4**]

6. **Zhang**, C., Ma, J., Waite, T.D\*., Ammonia-Rich solution production from wastewaters using chemical-free flow-electrode capacitive deionization. ACS Sustain. Chem. Eng. 2019. DOI: 10.1021/acssuschemeng.9b00314. [IF **6.140**; Citation **0**]

8. Tang, W., He, D., **Zhang, C.**, Kovalsky, P., Waite, T.D\*., Comparison of Faradaic reactions in capacitive deionization (CDI) and membrane capacitive deionization (MCDI) water treatment processes. Water Res. 2017, 120, 229-237. [Nature Index Journal; IF 7.015; Citation 63; Hot paper]

9. Tang, W., He, D., **Zhang, C.**, Waite, T.D\*., Optimization of sulfate removal from brackish water by membrane capacitive deionization (MCDI). Water Res. 2017, 121, 302-310. [Nature Index Journal; IF 7.015; Citation 28]

10. He, C<sup> $\dagger$ </sup>., Ma, J<sup> $\dagger$ </sup>., **Zhang, C**., Song, J., Waite, T.D<sup>\*</sup>., Short-circuited closed-cycle operation of flow-electrode CDI for brackish water softening. Environ. Sci. Technol. 2018, 16, 9350-9360. [Nature Index Journal; IF 6.653; Citation 11]

11. Ma, J., He, C., He, D., **Zhang, C.**, Waite, T.D\*., Analysis of capacitive and electrodialytic contributions to water desalination by flow-electrode CDI. Water Res. 2018, 144, 296-303. [Nature Index Journal; IF 7.015; Citation 12]

12. Ma, J., He, D., Tang, W., Kovalsky, P., He, **Zhang, C**., Waite, T.D\*., Development of redox-Active flow electrodes for high-performance capacitive deionization. Environ. Sci. Technol. 2016, 24, 13495-13501. [Nature Index Journal; IF 6.653; Citation 28]

13. Song, J., Ma, J., **Zhang, C.**, He, C.; Waite, T.D\*., Implication of non-electrostatic contribution to deionization in flow-electrode CDI: Case Study of Nitrate Removal from Contaminated Source Waters. Front. Chem. 2019, 7, 146. [IF **3.994**; Citation **0**]

14. **Zhang,** C., Ma, J., Waite, T.D\*., The roles of acid types on ammonia recovery performance of the capacitive membrane stripping system. (Under review)

15. **Zhang, C.**, Wu L., Ma, J., Pham, N., Wang, M., Waite, T.D\*., An integrated flowelectrode capacitive deionisation-microfiltration module for continuous salt removal: system performance and limitations. (**In preparation**)

16. **Zhang, C.**, Ma, J., Waite, T.D\*., Flow electrode capacitive deionization (FCDI) for energy-efficient salt removal and resource recovery: is it viable? (**In preparation**)

17. **Zhang, C.**, Cheng, X., Ma, J., Waite, T.D\*., Phosphate recovery from wastewater using flow electrode capacitive deionization (FCDI). (**In preparation**)

#### Patents

1. Waite, T.D\*., Zhang, C., Ma, J., He, D., Ammonia recovery apparatus and method . AUS patent, The University of New South Wales. (**Under review**)

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