

**Nutrients Recovery from Municipal Wastewater Effluent using
Electrochemical and Freeze Concentration Approaches**

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ABSTRACT

Municipal wastewater (MWW) is now being re-evaluated as a potential multi-resource for water, energy and nutrients. Anaerobic membrane bioreactors (AnMBRs) are increasingly being investigated as a cost-effective biological option with strong potential for the recovery of energy and removal of pathogens and contaminants from MWW. However, the recovery of nutrients by AnMBRs is typically negligible. This thesis focused on the simultaneous removal of nutrients from the effluent of AnMBRs for MWW treatment. Three approaches were proposed, namely, electrodeionization (EDI), freeze concentration (FC), as well as using FC as a preconcentration step for electrodialysis(ED). Synthetic effluents from AnMBR for MWW treatment were used as feed in the EDI, FC, and integrated FC/ED studies in this thesis.

In the investigation of EDI approach, the effect of the scan rates on limiting current (I_{lim}) determination and effects of 110% of I_{lim} , I_{lim} and 90% of I_{lim} were studied. At the recommended I_{lim} over 3 h, the removal efficiency of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, Ca^{2+} and Mg^{2+} , was 74.4%, 100%, 92.3%, and 58.8%, respectively, with a specific energy consumption of 0.74 kWh/m³ of feed wastewater. The results demonstrated that the EDI process is very promising for the removal of ionic nutrients and hardness ions from wastewater similar to municipal wastewater.

For FC approach, synthetic feed water containing the single impurities ($\text{H}_x\text{PO}_4^{y-}\text{-P}$, $\text{NH}_4^+\text{-N}$ and COD causing glucose) and the multiple impurities with different concentrations were tested at various mixing

conditions. The average achieved removal efficiencies of $H_xPO_4^{y-}$ -P, NH_4^+ -N and COD in single impurity tests were 99.9%, 96.5% and 100%, respectively. In multiple impurities tests, the average removal efficiencies of $H_xPO_4^{y-}$ -P, NH_4^+ -N and COD ranged 99.9% - 90.6%, 96.2% - 90.2%, and 100% - 88.2%, respectively. The experimental results indicated a potential that FC was efficient to remove nutrients from municipal wastewater effluent.

An approach of using freeze concentration as a preconcentration step for electrodialysis (ED) was also investigated. The removal efficiencies of NH_4^+ -N, $H_xPO_4^{y-}$ -P, and Ca^{2+} at a current from 90% to 110% of limiting current over 3 h, ranged from 93.9% - 97.1%, 56.4% - 62.3%, and 88.6% - 94.5%, respectively. The results of experiments with synthetic MWW without freeze concentration revealed that preconcentration was prerequisite for improving the performance of ED for dilute solutions, particularly for the removal of $H_xPO_4^{y-}$ -P. Freeze concentration as a preconcentration step for ED offers a promising approach for the treatment of MWW via ED.

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LIST OF ABBREVIATIONS AND SYMBOLS

AEM	Anion Exchange Membranes
AnMBRs	Anaerobic Membrane Bioreactors
BOD	Biochemical Oxygen Demand
C_0	Initial Concentration
CAS	Conventional Activated Sludge
CEDI	Continuous Electrodeionization
CEM	Cation Exchange Membranes
C_f	Final Concentration
C_i	Impurity Concentration in the Ice Phase
C_L	Impurity Concentration in the Unfrozen Liquid
COD	Chemical Oxygen Demand
CSTR	Completely Stirred Tank Reactor
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
EBPR	Enhanced Biological Phosphorus Removal
EC	Electrocoagulation
ED	Electrodialysis
EDI	Electrodeionization
EDR	Electrodialysis Reversal

EGSB	Expanded Granular Sludge Bed
EO	Electrochemical Oxidation
ER	Electrochemical Reduction
HRT	Hydraulic Retention Time
I_{lim}	Limiting Current
MBR	Membrane Bioreactors
MF	Microfiltration Membranes
MWW	Municipal Wastewater
NF	Nanofiltration
OLR	Organic Loading Rate
PAOs	Polyphosphate Accumulating Organisms
PFC	Progressive Freeze Concentration
PLE	Polymeric Ligand Exchanger
Re	Removal Efficiency
RO	Reverse Osmosis
SEC	Specific Energy Consumption
SFC	Suspension Freeze Concentration
SRT	Sludge Retention Times
TDS	Total Dissolved Solids
TMP	Transmembrane Pressure

TOC	Total Organic Carbon
TS	Total Solids
TSS	Total Suspended Solids
UASB	Up-Flow Anaerobic Sludge Blanket Reactor
UF	Ultrafiltration Membranes
V_0	Volume of Feed Water
V_i	Volume of Melted Ice
V_L	Volume of Unfrozen Liquid

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Chapter 1. Introduction

1.1 Current problems associated with municipal wastewater treated by conventional anaerobic processes

Rather than being treated as a form of waste, municipal wastewater (MWW) is now being re-evaluated as a potential multi-resource for water, energy (e.g., methane or biogas), and nutrients (primarily nitrogen and phosphorus) [1-3]. MWW is principally characterized as having: (1) a higher fraction of particulate chemical oxygen demand (COD); (2) moderate biodegradability of the contained organic compounds; (3) relatively low strength organic and nutrients loads with varying concentrations; and (4) relatively low temperatures [4].

Conventional aerobic treatment systems are commonly implemented for the low organic strength MWW to meet stringent effluent standards.

Theoretically, MWW with typical COD values (400-500 mg/L) possesses a potential chemical energy of 1.5-1.9 kWh/m³ of wastewater [5]. In practice, for conventional activated sludge (CAS) systems with anaerobic sludge digestion, the typical energy demand is 0.6 kWh/m³, of which 0.3 kWh/m³ is consumed by aeration [2]. In a case study of Oslo, Norway [6], the energy demand ranged from 0.67-0.87 kWh/m³ of wastewater, which was utilized for pumping, mixing, aeration, anaerobic digestion, sludge handling, space heating, lighting and general maintenance. Thus the potential chemical energy of MWW is almost twice of the energy demand.

Another form of potential energy contained in MWW is thermal energy. The potential thermal energy for heat-pump extraction is 7.0 kWh/m^3 of wastewater [2]. Typically, energy recovered by heat pumps in the form of heat is 3-4 times the electrical energy consumed [2,3]. Hence, the net energy that might be achieved by heat pumps is about $5.25\text{-}5.6 \text{ kWh/m}^3$, which exceeds the potential chemical energy of MWW. However, thermal energy must be reused within a short distance between the heat source and heat sink [3,7]. Moreover, if electricity production is highly dependent on alternative heating fuels, such as natural gas or fuel oil, and the fuels are much less expensive than electricity, it becomes uneconomical to recover energy from MWW via heat pumps [2,3]. Hence, much less attention will be paid to the thermal energy of MWW in this review.

Due to the drawbacks of high energy consumption, large volumes of sludge yield, and failure to recover nutrients, it was concluded from the screening of MWW treatment plants that spanned nine European countries along the River Danube, that CAS systems were uneconomical and unsustainable [1].

In contrast, anaerobic treatment has the advantages of low energy demand and less sludge yield. This may be illustrated through a quantitative comparison from the study conducted by McCarty *et al.* [2]. The results revealed that the biogas energy generated from full anaerobic treatment (1 kWh/m^3) was approximately twice the energy that was required for plant operations (0.4 kWh/m^3), on the basis of a summary of typical domestic wastewater energy characteristics. For CAS with sludge digestion, however, the energy produced (0.5 kWh/m^3) was less than the energy consumed (0.6 kWh/m^3). Hence, the conclusion was that anaerobic treatment had the capacity for achieving a net energy production for the removal of organic matters, in which case reuse for irrigation was suggested [2]. Additional energy

consumption or cost (e.g. chemical dosage for phosphate precipitation), which are higher than that of organic matters, are needed to recover nutrients in wastewater plants where direct irrigation is not always available or economic due to the long transportation distance. Although more energy or cost are needed for nutrients recovery, from the viewpoint of life cycle assessment, nutrients recovery relieves the depletion of natural resources for the production of traditional fertilizers, such as phosphate ores, energy and water. Consequently, energy and water are actually saved.

Among anaerobic treatment processes, the high-rate up-flow anaerobic sludge blanket reactor (UASB) and expanded granular sludge bed (EGSB) have been applied to directly treat full-scale MWW, particularly UASB in countries with constant and relatively warm temperatures [8,9,20]. Although these processes offer great promise, a number of barriers restrain their wide application to direct MWW treatment, including: (1) the attainment of sustained low temperatures in temperate and cold regions; (2) longer sludge retention times (SRT) are required to maintain microbial populations for the rate-limiting hydrolysis of the retained particulates; (3) the high fraction of suspended solids in MWW decreases sludge activity within the reactor, thus additional pre-treatment is suggested; (4) effluent has high nutrients content, pathogens and relatively high COD as well as biochemical oxygen demand (BOD), which cannot achieve the discharge standards [10-12].

The effects of low temperature, primarily ambient or psychrophilic (<20°C), have been investigated since 1976 [4]. One review paper concluded that satisfactory performance was achievable without additional heating in low temperature, however, removal efficiencies, effluent quality and methane-rich biogas generation were decreased [10]. This was further confirmed in the studies of Takahashi *et al.*,

who conducted a pilot experiment with municipal sewage at ambient temperatures (10.6°C -27.7°C) for more than 1100 days [13,14]. A stable COD removal efficiency of 63±13% was achieved, and longer SRT was regarded as favorable for the degradation of refractory substances, such as cellulose [13]. The COD removal efficiency of another bench-scale experiment conducted by Bandara *et al.*, at temperatures of 6°C to 31°C over 18 months was lower at ~ 40%-60% [14].

During anaerobic processes, organic nitrogen and phosphorous are mineralized to ammonia and orthophosphate, which are not removed from the system. This is the main reason for the low removal efficiency of nutrients by anaerobic treatment. However, these effluent resident mineralized nutrients are beneficial when reused in the form of fertilizers for agricultural irrigation [8,9,15].

1.2 An alternative for enhancing the quality of effluent subsequent to anaerobic treatment

Various post treatment methods have been considered for enhancing the quality of effluent subsequent to anaerobic treatment [9,16-18]. Membrane technologies, an alternative for polishing the effluent of anaerobic reactors, have also received considerable attention. Anaerobic membrane bioreactors (AnMBRs), integrating different types of anaerobic reactors, particularly UASB, are increasingly being investigated as a cost-effective option with the potential to recover energy and remove pathogens and contaminants for MWW [15,19].

No aeration is required for AnMBRs, and further, due to the coupling of anaerobic bioreactors with microfiltration membranes (MF) or ultrafiltration membranes (UF), pathogens are completely removed from the effluent. Biomass may be effectively retained within the reactor for additional biodegradation

to produce biogas, and an almost infinite SRT becomes possible. All of these factors enable AnMBRs to maximize energy recovery from wastewater and to achieve higher effluent quality to meet stringent standards, save for the nutrients. AnMBRs provide an alternative solution for the major problems that are encountered by anaerobic processes at low temperatures, fed with low strength MWW and a high proportion of particulate substances.

1.3 Objectives

To date, various novel wastewater treatment processes and nutrients recovery methods are proposed and studied. However, research specifically on how to integrate both maximized energy production, water and nutrients recovery from MWW are very limited. Therefore, from the viewpoint of sustainable development, developing new methods or integrating the existing methods for resources recovery from large amount of low strength MWW in a more efficient way is of great importance. The main research objectives of this study are as follows:

- (1) Explore an expanded electrodeionization (EDI) cell for the efficiently simultaneous removal of nutrients and other ionized species (such as hardness ions) from a synthetic effluent of AnMBR for MWW treatment.
- (2) Investigate the effectiveness of freeze concentration (FC) in the removal of nutrients from MWW-like wastewater and study the possible effects affecting the performance of FC, primarily including mixing conditions and initial concentrations of impurities in the synthetic feed water.

(3) Propose FC as a preconcentration step for electrodialysis (ED) for the removal of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$ and Ca^{2+} from synthetic effluent of AnMBR for MWW treatment.

1.4 Scope of this thesis

This thesis is composed of six chapters. The research background and study objectives are presented in this chapter. In the following Chapter 2, a comprehensive literature review will be provided. Information on AnMBRs for energy recovery, pathogens and organic contaminants removal will be covered, followed by the analysis of presently available nutrients recovery technologies, of which EDI, ED and FC are recommended. Chapter 3 to 5 will present the experimental studies of nutrients removal utilizing EDI, FC, as well as using FC as a preconcentration step for ED, respectively. Finally, Chapter 6 will summarize the results and provide recommendations for future research on the basis of the experimental studies.

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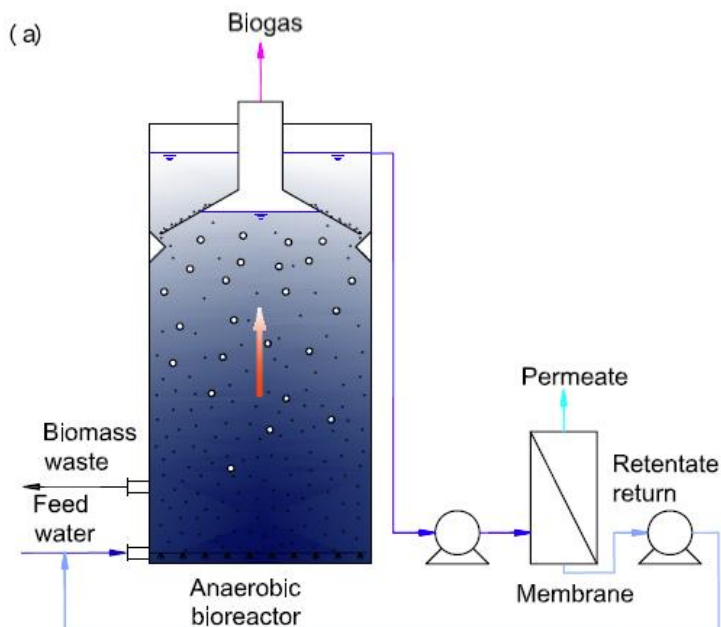
Chapter 2. Literature review

2.1 Utilizing AnMBRs for energy recovery, pathogens and organic contaminants removal

The first pilot scale AnMBR was developed by Dorr-Oliver in the early 1980's for the treatment of high-strength whey processing wastewater. It consisted of a completely mixed suspended growth anaerobic bioreactor, which was combined with external cross-flow membrane filtration [1]. Subsequently, research on AnMBRs has been conducted with different wastewaters, including MWW.

2.1.1 AnMBRs configurations and membrane selection

AnMBRs are categorized as three configurations: (1) pressure-driven external cross-flow (Fig. 2.1a); (2) vacuum-driven internal submerged (Fig. 2.1b); (3) vacuum-driven external submerged (Fig. 2.1c) [1].



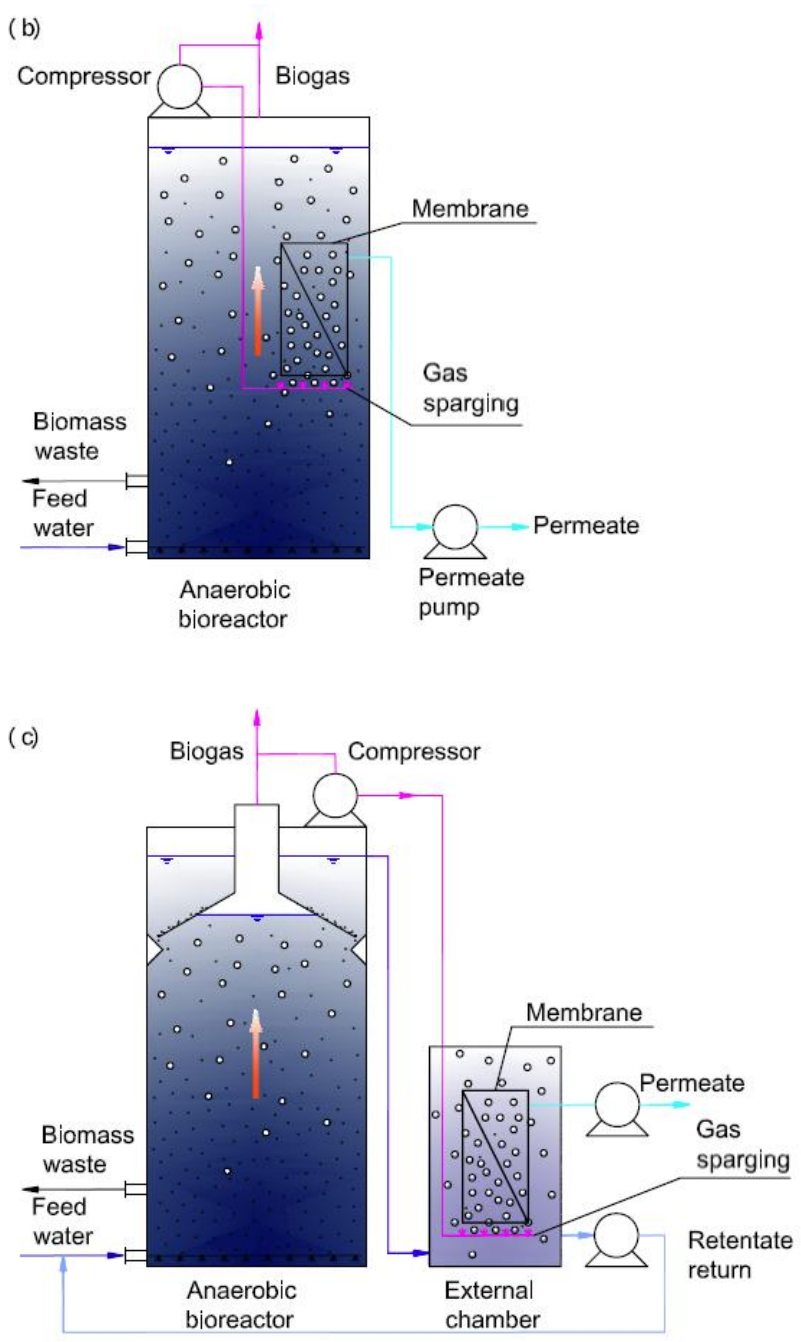


Fig. 2.1 AnMBRs configurations

Regardless of the configurations, AnMBRs may integrate with different types of anaerobic reactors. For MWW treatment, Ozgun *et al.* comprehensively evaluated integration strategies from the literature in

terms of biological performance and membrane aspects. A completely stirred tank reactor (CSTR) with equal hydraulic retention time (HRT) and SRT is most commonly studied in AnMBR system. It has the advantages of higher permeate rates and potential of substrate conversion to biogas. However, it causes heavy membrane fouling and low flux due to the direct exposure of the membrane to the bulk sludge. On the other hand, UASB provides for biomass retention in the sludge bed. Since the suspended solids loads on membranes may be decreased, membrane fouling might be alleviated. This makes UASB a promising option for AnMBRs systems [2].

The two most common types of membranes used in AnMBRs are MF and UF, which have been widely installed or employed in aerobic membrane bioreactors (MBR) for MWW treatment on a global scale [3-7]. Despite the abundant practical experience that has been accumulated for MBR processes, very limited full-scale AnMBRs applications have been reported. Among the full-scale AnMBRs systems reported, a treatment capacity of 378 m³/d for food industry wastewater (as the largest installation) was completed by ADI [8].

The membranes commonly used in AnMBRs are flat-sheet, hollow fiber, and tubular. Regarding the materials, polymeric membranes have garnered more attention over much more expensive ceramic or metallic membranes. The preferred polymeric materials are polyvinylidene difluoride (PVDF) and polyethersulfone (PES) (~75% of total products). Other polymeric materials, such as polyethylene (PE), polypropylene (PP) and polysulfone (PSF) have also been studied [8]. Various investigations have indicated that membrane materials may impact the degree of membrane fouling [2,9].

In bench-scale AnMBRs systems challenged with different types of wastewater, the membrane pore sizes ranged from 20,000 Dalton to 10 μ m, with 0.4 μ m as the median [2,8,10]. The filtration area of the membranes varied in the reactors with different working volumes, from 0.013 m² to 100 m² [2,10]. The reported membrane permeate flux in the experiments had a rather wide range, from the low 1.3 L/m²·h (LMH), to extremely high 450 LMH [10]. The range of transmembrane pressure (TMP) was less than 200 kPa and typically less than 70 kPa [2,10]. Specifically, the sustainable permeate flux for MWW treatment was suggested to be ~5-15 LMH [8,9,11] with a recommendation not exceeding 7 LMH for a long stable operation with a gas sparging velocity of 62 m/h for a 14.8 gTSS/L biomass concentration [2]. These figures are equivalent to ~50% of the overall permeate flux that was used in an aerobic membrane bioreactor system (10-25 LMH) [6]. Hence, a larger membrane filtration area is required for AnMBRs systems, which in turn significantly increases the cost of the overall system. This is because membrane costs account for the greatest fraction of the capital cost (~72.3%) with a designed flux of 10 LMH [11].

2.1.2 Energy recovery

In anaerobic systems, energy is recovered through the continuous generation of methane or biogas. In contrast to conventional anaerobic reactors (e.g., UASB), AnMBRs exhibit excellent sludge-liquid separation via MF or UF membranes. Thus the high concentrations of suspended biomass in MWW are retained in the anaerobic reactor, for the sake of anaerobic microorganisms that have slow growth rates, to further convert the substrate into methane. This also enables the complete separation control of SRT and HRT, thereby facilitating achievement of infinite SRT within the reactor. The hydrolysis of the

retained particulates principally at low temperature, is considered to be the rate-limiting step, thus longer SRT is required [2,9]. Therefore, methane production in AnMBRs is generally higher than in conventional anaerobic processes. This was evidenced by a comparison of methane yields at low temperatures for sewage treatment. The range was 0.16-0.27 LCH₄/gCOD_{removal} in UASB [12,13], and 0.23-0.33 LCH₄/gCOD_{removal} in AnMBRs [8].

In order to achieve a net energy production for low strength MWW, it is necessary to operate AnMBRs at low temperatures without additional heating [9,10,14]. This, on the other hand, reduces methane yields due to the lower growth rate of anaerobic microorganisms and higher methane solubility in low strength MWW. For a typical biogas methane content of 70%, methane is ~1.5 times more soluble at 15 °C than at 35 °C [8].

Membrane fouling comprises an additional obstacle for AnMBRs in decreasing energy demand. It also limits the full-scale application of AnMBRs in wastewater treatment. Biofouling (organic and inorganic fouling), which typically forms simultaneously, are proposed as the main fouling mechanisms in AnMBRs [1,8], where membrane fouling increases the TMP. Prevention measures, such as membrane relaxation and membrane backflushing and/or biogas sparging, require energy input. All of these factors make membrane fouling control the most energy intensive demand in AnMBRs systems [9]. In order to achieve higher net energy yield, the obstacle of membrane fouling needs to be addressed.

2.1.3 Pathogens and contaminants removal

Pathogens and bacteria are totally free within the effluent following the filtration by MF and UF

membranes [2].

For the removal of contaminants, the effluent quality in AnMBRs is much higher than in conventional anaerobic reactors. For municipal wastewater, the concentration ranges of COD, total suspended solids (TSS), NH₄-N, and P in anaerobic treatment effluents were reported to be 100-200 mg/L, 50-100 mg/L, 30-50 mg/L, 10-17 mg/L, respectively [15]. In AnMBRs, the concentration ranges of COD, TSS, NH₄-N and P in the effluent may be 20-150 mg/L, 0-15 mg/L, 10-70 mg/L, 1-15 mg/L, respectively [8]. Generally COD in AnMBRs sewage treatment effluent is less than 100 mg/L [1]. It is obvious that AnMBRs may remove both COD and TSS to a significant degree. In AnMBRs systems, the removal of COD and TSS might exceed 85% and 99%, respectively; however, the removal of TN or TP is typically negligible [8,16], which is also evidenced from Table 2.1.

Table 2.1 Performance of AnMBRs at low temperature for MWW-like treatment with nutrients information

Type of wastewater	Contaminants/ Concentrations	Treatment processes	Operation conditions	Performance	Ref.
Municipal wastewater with glucose addition	pH: 6.8±0.1 COD: 630±82 mg/L NH ₄ -N: 61.5±10 mg/L TP: 8.2±0.9 mg/L	Submersible Mesophilic and psychrophilic flat sheet, UF	Mesophilic: T: 35°C 0.6-1.1 g COD/L.d Psychrophilic: T: 20°C OLR: 0.5-0.9 g COD/L.d Flux: 7 LMH	Permeate: COD: <80 mg/L NH ₄ -N: 67.4±8.2 mg/L TP: 7.1±0.7 mg/L Under both temperatures, the COD removal was close to 90%.	[17]
Simulated and actual domestic wastewater (DWW)	pH: 7±0.2 simulated DWW COD: 440±68mg/L actual DWW COD: 259±82 mg/L NH ₄ -N: 27±7 mg/L TP: 21±2 mg/L	Submersible Psychrophilic Flat sheet, MF	T: 15.0±0.1°C OLR: 660 mg COD/(L.d) HRT: 16 h Flux: 7 LMH	Simulated DWW: COD removal: 92±5% permeate COD: 36±21 mg/L Actual DWW: COD removal: 69±10% Nutrients were not removed.	[16]
Synthetic municipal wastewater	pH: 6.8-7.1 COD:500mg/L TN: 40 mg/L TP: 10 mg/L	External Ambient Tubular, MF	T: 25±1°C OLR: 1-2kg COD/(m ³ .d) HRT: 12-6 h Flux: 5, 8 LMH	Permeate COD: <40 mg/L Longer HRT and SRT may be favorable for methane recovery and sludge reduction.	[18]
Municipal secondary wastewater	pH: 7.0±0.2 COD:342-527 mg/L NH ₄ -N: 32.4±11.6 mg/L TP: 4.3±0.5 mg/L	Submersible Mesophilic Flat sheet membrane	T: 30±3°C OLR: ~1 kg COD/(m ³ .d) HRT: 10 h Flux: 12 LMH	Effluent COD: ~60 mg/L NH ₄ -N: 31.1±12.3 mg/L TP: 3.8±0.7 mg/L	[11]
Synthetic municipal wastewater	pH: 6.8-7.1 COD:500mg/L TN: 40 mg/L TP: 10 mg/L	External Ambient Tubular, MF	T: 25±1°C T: 15±1°C OLR: 1 kg COD/(m ³ .d) HRT: 12 h	Total COD removal: >95% (25°C), >85% (15°C) Methanogenic activity: lower at 15°C compared to 25°C.	[19]

Municipal wastewater with glucose addition	pH: 6.6 ± 0.1 COD: 612 ± 97 mg/L NH ₄ -N: 42.3 ± 8.0 mg/L TP: 5.7 ± 1.3 mg/L	Submersible Psychrophilic flat sheet, UF	Flux: 5 LMH Psychrophilic: T: 20°C OLR: 0.5-0.9 g COD/L.d Flux: 7 LMH	Permeate: COD: <80 mg/L NH ₄ -N: 44.9 ± 12.1 mg/L TP: 5.0 ± 1.4 mg/L	[20]
Municipal wastewater	pH: 6.4 ± 0.2 Soluble COD: 39-120 mg/L NH ₄ -N: 10-55 mg/L NO ₃ ⁻ -N: 15-35 mg/L PO ₄ ³⁻ -P: 2-8 mg/L	External Ambient Tubular	T: 25°C OLR: 0.03-1.64kg COD/(m ³ .d) HRT: 12-24 h	Permeate: NH ₄ -N: 8.9-51.8 mg/L NO ₃ ⁻ -N: <0.4 mg/L after 131 days PO ₄ ³⁻ -P: similar to influent AnMBR had similar removal rate of soluble COD with MBR at same HRT.	[21]
Municipal wastewater	pH: 6.9-7.3 COD: 350-500 mg/L TN: 10.6-11.8 mg/L PO ₄ ³⁻ -P: 3-4.5 mg/L T: 5-14°C	External Mesophilic flat sheet, MF	T: 35 ± 2 °C Flux: 80-450 LMH HRT: 16.67 h	Permeate: COD: ~30 mg/L TN: 9-9.85 mg/L PO ₄ ³⁻ -P: ~0.8 mg/L AnMBR was concluded to be more useful than conventional activated sludge process in Erzurum city at cold temperature.	[22]
Municipal wastewater	pH: 6.9-7.3 COD: 162.3-603.2 mg/L NH ₄ -N: 27.5 ± 13.6 mg/L TP: 4.2 ± 1.4 mg/L	Submersible Psychrophilic tubular non-woven fabric membrane	T: 15-20°C Flux: 5 LMH OLR: 2.36 kg COD/(m ³ .d) HRT: 2.6 h	Permeate: COD: 77.5 ± 29.5 mg/L NH ₄ -N: 27.6 ± 12.5 mg/L TP: 3.2 ± 1.3 mg/L	[23]
Dilute municipal wastewater	pH: 7.5 Soluble COD: 38-131 mg/L NH ₄ -N: - PO ₄ ³⁻ -P: 2-9 mg/L	External Membrane pore size: 0.1 μm	T: - OLR: 0.03-0.16kg COD/(m ³ .d) HRT: 0.5-2 days	Neither temperature nor heating was mentioned. Permeate: Average soluble COD removal rate: 64% NH ₄ -N: 8.9-51.8 mg/L PO ₄ ³⁻ -P: 2-9 mg/L	[147]

Municipal wastewater	Soluble COD: 501 ± 165 mg/L NH ₄ -N: 71 ± 14 mg/L PO ₄ ³⁻ -P: 10 ± 2 mg/L	Submersible, external Psychrophilic Tubular UF	T: $18 \pm 2^\circ\text{C}$ Flux: 10-14 LMH OLR: 2-2.5kg COD/(m ³ .d) HRT: 7 h	Permeate: COD: 122 ± 36 mg/L NH ₄ -N: 104.02 mg/L PO ₄ ³⁻ -P: 23.8 ± 14.6 mg/L	[24]
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T: Temperature

OLR: Organic loading rate

The research on AnMBRs has concentrated primarily on treatment performance, membrane fouling, and biogas production affected by various COD and TSS concentrations in the influent. Nutrients (TN and TP) is set at a fixed proportion with COD for synthetic wastewater, or kept at relatively constant concentrations for actual wastewater. Under mesophilic and thermophilic operation conditions, the ratio of COD: N: P = 100:2.6:0.4 is often maintained to sustain the nutrients concentrations required for anaerobic microorganisms growth [25]. This is difficult for real MWW as the nutrients concentrations in MWW always fluctuate. However, the effects of various nutrients concentrations on normal operation of AnMBRs are still not clear, only a qualitative statement in regard to AnMBRs having low nutrients requirement is available [8]. Furthermore, the effect of low temperature to the nutrients requirement for AnMBRs is not clear too. The proportion of ammonium in AnMBRs substrate increases with decreased temperature while the activity of microorganisms decreases when the temperature decreases. As nutrients concentrations are essential to maintain the normal activity of microorganisms, it is of great interest to investigate the suitable nutrients concentration range for the normal operation of AnMBRs at low temperature.

Additionally, low temperatures act to lower the removal efficiencies and effluent quality (Table 2.1).

2.2 Nutrients recovery from MWW effluent

2.2.1 Analysis of presently available nutrients recovery technologies

A number of review papers [26-28] broadly assessed the available nutrients recovery technologies for waste streams, and described commonly used technologies such as chemical precipitation, enhanced

biological phosphorus removal (EBPR), struvite crystallization, adsorption and ion-exchange, membrane filtration, and electro dialysis.

2.2.1.1 Chemical precipitation

Chemical precipitation [29] is typically employed for the removal of phosphorus only. The metal ions most commonly used are aluminum, iron and calcium, which may be dosed into wastewater to precipitate with soluble phosphate. The major disadvantages associated with this process include the high operational cost of chemical dosage, increased salinity in the effluent, and increased sludge production (up to 35 vol%). Due to the strong bonding between P and aluminum- based or iron-based coagulants that are currently used in MWW, the generated sludge is difficult to utilize. Hence, in order to improve its bioavailability, an additional release step is required [26]; otherwise sludge disposal is needed, with both options incurring additional costs.

Chemical precipitation is more efficient in the treatment of wastewater with higher phosphorus concentrations. Therefore, conventional biological treatment processes might be upgraded to the EBPR process so as to enhance phosphorus concentrations in waste streams [29].

Metal ions may also be introduced into wastewater through the use of sacrificial electrodes (e.g., Al and Fe) in the electrocoagulation process, which is discussed in section 2.2.2.1. Since no chemicals are required in electrocoagulation, the disadvantages of chemical precipitation mentioned above are effectively eliminated. Compared to the high operational cost caused by chemical dosage in chemical precipitation process, the operational cost caused by electricity and metal electrodes in

electrocoagulation process is much lower.

2.2.1.2 EBPR process

EBPR is widely used in MWW to remove up to 80-90% of soluble P through assimilation and accumulation, primarily via polyphosphate accumulating organisms (PAOs) [26], which are relatively inexpensive and environmentally sustainable. However, when the simultaneous biological removal of nitrogen is required, it is difficult for EBPR to resolve the conflicts between the removal of N and P in terms of SRT demand, nitrate inhibition of phosphate release, and competition for carbon sources [30]. Additionally, EBPR requires alternating anaerobic conditions for the PAOs to release P, and subsequently aerobic/anoxic conditions for the PAOs to uptake excess P and adequate amounts of organic carbon [31]. However, in AnMBRs, no aerobic condition exists with only anaerobic condition being available. This makes EBPR an unfeasible option for the removal of phosphorus from AnMBRs effluent.

2.2.1.3 Struvite crystallization

Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) crystallization is one of the most widely recommended technologies for the recovery of phosphorus from sludge digester supernatants particularly in wastewater treatment plants with EBPR [32]. The products obtained by struvite crystallization may either be used as an effective slow release fertilizer, or be accepted readily by the phosphorus industry [28,30]. According to the equimolar stoichiometry of struvite formation [33], the magnesium concentrations in MWW are usually deficient, hence an additional supplement of magnesium is required. Nevertheless, in most

cases, $\text{NH}_4\text{-N}$ would be excessive for the reaction. Therefore, water resident N and P may not be effectively simultaneously recovered. The recovery of P is high (e.g., 60-90% [32,34,35]) while the recovery of N is relatively low (20-30% removal of soluble ammonium [26]).

Struvite precipitation is cost-effective for sludge digestion supernatants with high concentrations of N and P ($(\text{P-PO}_4 > 50 \text{ mg/L})$ [26,35], but is not suitable for the removal of low concentrations of P in AnMBRs effluents, which are generally less than 17 mg/L for MWW. Additional P concentration process is required to achieve a reasonable recovery efficiency of struvite precipitation, such as adsorption, which may complicate the whole treatment process greatly and lead to much high capital investment and operational cost. Therefore, struvite precipitation is not recommended to recover nutrients from AnMBRs effluent for MWW.

2.2.1.4 Adsorption and ion-exchange

During adsorption and ion-exchange, ions are transferred from the solvent to insoluble adsorbents in a fixed bed [26]. Although various adsorbents such as inorganic ion exchangers, activated alumina, surfactant-modified zeolites, industrial and agricultural wastes have been extensively investigated for wastewater nutrients removal, polymeric resins are more feasible for practical wastewater treatment, as they have higher adsorption and regeneration capacities, mechanical strength and selectivity [36-38].

In Comparison with chemical or biological methods, adsorption and ion-exchange are more effective for the removal of both soluble N and P at much lower concentrations [36,38], particularly for phosphate which is required to be less than 0.1 mg/L prior to discharge in many countries [38]. In

addition to the high quality of effluent that may be discharged directly, especially for the low strength AnMBRs effluent with little TSS, adsorption produces no additional sludge and has adaptability to the shocks of flow rate, nutrients loading, and temperature [37,38].

The drawbacks of ion-exchange are associated with additional chemical regeneration during operation, such as high operational cost associated with chemical consumption, several hours of system shut down, a large footprint for chemicals storage, pumping facilities, and waste streams that contain high concentrations of regenerant chemicals [39]. Generally, regenerant chemicals (acids, bases or salts) with concentrations of 2 - 8% by weight are used [40], which are over 200 times that of the nutrients concentrations in MWW (less than 100 mg/L). An acidic or basic waste streams have the requirement to be neutralized prior to discharge and salty waste streams increase undesired salinity in the effluent. These drawbacks associated with chemical regeneration may be overcome in electrodeionization process. Continuous electro-regeneration in situ can replace chemical regeneration, such that no chemicals are required. Further details are discussed in section 2.2.2.4.

Experiments on the recovery of nutrients using ion exchange resins are summarized in Table 2.4.

2.2.1.5 Membrane filtration

Membrane filtration, primarily nanofiltration (NF) and reverse osmosis (RO) membranes, for soluble N and P recovery [26,41], have also been researched. The removal of ammonium and nitrates by NF and RO membranes is higher than 80% [26]. This pressure-driven process has the advantage of obtaining superior effluents. Its disadvantages, however, are intensive energy demands and the high cost of

membrane replacement. According to a survey of existing membrane installations based on integrated membrane systems for MWW reuse, the specific energy demands for a RO filtration unit ranges 0.29-1.2 kWh/m³ of permeate [3]. Additionally, undesired contaminants and salts are also accumulated in the concentrate, which is unsuitable for direct reuse; thus requiring additional treatment [26].

2.2.1.6 Electrodialysis

In contrast to non-selective RO or NF separation, electrodialysis may be operated as a selective desalination process which possesses a low chemical demand for membrane regeneration and higher water recovery than RO [42]. This indicates a much less concentrate volume which would facilitate the transportation dramatically. Furthermore, the simultaneously but separately collected concentrate (ammonium in one concentrate compartment, phosphate and nitrate in another concentrate compartment) leads to easier use as fertilizers, without the need of additional operations to make the concentrate suitable for specific soil conditions. As a result, the whole treatment process can be significantly shortened and simplified. This provides a great potential to reduce the overall cost and energy demand.

Electrodialysis (ED) is applicable for the selective recovery of all nutrients at low concentration. Segregated cation and anion concentrate species may be used as fertilizers [26]. However, due to the inherent concentration polarization phenomenon, the energy demands are relatively high. Although the demand for the chemical regeneration of the membranes is lower than RO, it is still required. To overcome this, electrodialysis-based electrodeionization (EDI) is developed. Further details are discussed in section 2.2.2.4.

2.2.1.7 Freeze concentration

It has long been known that freezing can purify and concentrate aqueous solution. A simple natural example is that sea-ice has a much lower salt content than sea-water. The separation of pure water and impurities is achieved by the crystallization of ice from water. Most of the solutes and suspended solids are rejected from the small dimensions of the ice crystal lattice and concentrated in the unfrozen liquid [43].

Freeze concentration has been widely used in food processing industry for years [44-46]. It is also recognized as a potential option for water/wastewater treatment. Freezing is featured with the following advantages: (a) high separation factor; (b) high energy efficiency due to the low latent heat of freezing (333.5 kJ/kg) compared to evaporation (2256.7 kJ/kg); (c) no chemical addition and little maintenance for corrosive resistance system which lead to low operation cost; (d) low capital investment attributed to the absence of chemical pre-treatment and inexpensive materials for the system at low temperature [47,48]. However, industrial application of freeze concentration in water/wastewater treatment is very limited. Development in pilot-scale research of freezing has been reported [48-54]. The major possible reasons are conservative approach to the adoption of new technology and the perception of a mechanically complex process which in practice has been greatly improved with recent development [47,48].

2.2.1.8 Other nutrients recovery technologies

The use of plants for nutrients accumulation is greatly dependent on temperature, oxygen, and type of

wetland; hence it is difficult to develop stable and versatile mass extraction systems. Liquid-liquid extraction, gas-permeable membranes, and liquid-gas stripping are only suitable for high nutrients concentrations in water [26].

Each of the technologies described above has its own set of advantages and disadvantages. A great amount of research has been conducted toward the development of new processes or combinations thereof to overcome the disadvantages. For examples, an innovate fluidized bed reactor was developed for struvite crystallization [55], biological nutrients removal was combined with induced crystallization [56], phosphorus was recovered from membrane concentrates via struvite crystallization [34], nanofiltration was combined with low pressure wet oxidation [57], nutrients were recovered with bioelectrochemical systems [58], an osmotic membrane bioreactor was studied for the direct recovery of phosphorus from MWW [30], etc. Electrochemical methods have also been integrated to improve nutrients recovery technologies, such as electrocoagulation for phosphorus recovery [59], ammonia nitrogen and phosphorus removal from MWW using electrochemical oxidation [60], and nitrate removal through electrochemical reduction [61]. Special attention has been paid to electrochemical methods as they are suitable for the extraction of low concentration of nutrients in MWW, and are more efficient and cost-effective than the commonly used processes such as chemical precipitation, ion-exchange and membrane filtration.

2.2.2 Electrochemical methods for nutrients recovery

Emerging electrochemical methods are considered as promising alternatives for the removal of nutrients in water and wastewater due to their advantages such as environmental compatibility, high

efficiency, ambient operation conditions, amenability with automatic control, and quick start-up [62].

Generally, there are four fundamental electrochemical methods employed in water/wastewater treatment: electrocoagulation (sometimes coupled with electroflotation), electrochemical oxidation, electrochemical reduction, electrodialysis, and electrodialysis-based technologies.

2.2.2.1 Electrocoagulation

In the electrocoagulation (EC) process, an electric current is introduced to sacrificial electrodes (such as Al and Fe) to generate metal ions, which act as coagulants [63]. The released metal ions react immediately with hydroxide ions in solution to produce metallic hydroxides (e.g. $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$). The accumulated metallic hydroxides then polymerize and coagulate with water contaminants primarily through adsorption, surface complexation or co-precipitation; similar to chemical coagulants such as alum and ferric chloride [62,64]. Hence no chemical dosage is required and sludge production may be reduced. EC has been used in MWW water for the removal of COD, SS, and ionic phosphorus [65]. The recommended current density is 20-25 A/m^2 in order to sustain the operation of EC for extended periods without maintenance [65,66].

Nitrate may not be removed by conventional chemical coagulation; however, it can be removed by EC. Lacasa *et al.* [67] concluded that the chief reasons included: (1) The more than three folds higher increase in conductivity by chemical coagulation, than EC, decreased the widths of double layers around the precipitate particles; (2) The dosed anions during coagulation competed with nitrates for adsorption onto the growing metal hydroxide precipitates [64]. This adsorption was regarded as the

primary mechanism for relatively high nitrate removal efficiency [67]. However, the cost of nitrate removal by EC was much higher due to the low efficiency of utilizing the electrochemically induced reagents, hence nitrate removal by EC was not suggested [64].

Aluminum electrodes possessed higher phosphate removal rates and removal efficiencies than iron electrodes [62], but iron electrodes were more economical than aluminum electrodes for the removal of phosphate at low current density [64].

Due to large capital investments and high energy demands, the application of EC was hampered worldwide prior to the 1950s. Currently, emergent EC processes have drawn attention for their high treatment capacities with relatively low cost [65]. According to research conducted by Koparal and Ogutveren [148], EC was more cost efficient than electroreduction for the removal of nitrate.

Combined biological-electrochemical treatment:

The removal of total phosphorus at the pilot laboratory scale was demonstrated by Tran *et al.*, who used EC from spiked MWW effluent following a biofiltration process [68]. Investigation into EC toward improvements in the quality of secondary clarifier municipal wastewater influent was conducted by Al-Shannag *et al.* [69].

2.2.2.2 Electrochemical oxidation

The electrochemical oxidation (or electrooxidation) (EO) of pollutants involves direct oxidation and/or indirect oxidation. It is often used to eliminate biorefractory organic compounds and ammonia nitrogen.

Electrochemical advanced oxidation processes (EAOPs), based on EO, have been developed to treat recalcitrant organic contaminants; however, the removal of nitrogen species has not been discussed in EAOPs [63,70,71]. Therefore, EAOPs are not considered a suitable choice for the simultaneous recovery of nutrients.

The direct oxidation of organic compounds may occur directly at anodes either through electron transfers from the electrode to the compound molecules, or through the generation of physically adsorbed hydroxyl radicals ($\cdot\text{OH}$) or chemisorbed MO_{x+1} in the electrode oxide lattice [72]. During indirect oxidation (or mediated oxidation), strong oxidizing species are generated at the anode surface that subsequently degrade organics in the bulk solution where two reaction mechanisms may coexist [73]. Generally, indirect EO has been shown to be more effective than direct EO [72]. The applied current density in the literature varies significantly (typically from 5 to more than 1000 A/m^2), and has been subject to specific experiment conditions, such as different contaminant concentrations, chloride concentration and target removal levels [66]. Relatively high energy consumption is the central drawback of the EO process [73].

The molecular chlorine that is formed by chloride ions at the anode is a common active oxidant. The removal of ammonia by EO takes place primarily due to the indirect EO mechanism [73-75]. During the EO process, in the normal pH range of MWW (6-7.5), chloride is transformed into chlorine, which immediately reacts with water to form hypochlorite. The overall reaction occurring between hypochlorite and ammonia at the anode may be expressed as equation (2.1) [74]:



The presence of mediators such as chloride makes the selection of electrode material highly important, as they have significant influence on the selectivity and efficiency of EO [72,73]. Titanium and other noble metal-based substrates such as Pt, PbO₂, IrO₂, SnO₂, and boron-doped diamond (BDD) are intensely studied anode materials [66,72]. In terms of electrode material costs, those in EO might be the most expensive among EC, EO, and electrochemical reduction systems [62].

Chloride concentration should be high enough (typically > 3000 mg/L) to ensure efficacious treatment for indirect oxidation [66], where chloride concentrations in low strength MWW fail to attain this level. Therefore, an additional chloride dosage is required to enhance the treatment efficiency [66]. On the other hand, trihalomethane (THM), a carcinogenic by-product of the reaction, has been detected (maximum concentration 1.7 mg/L) at high chloride concentrations [74]. Because of this and the aforementioned reasons, EO has been less applied than EC for water and wastewater treatment, particularly for the removal of nitrites and phosphates [62].

Consequently, EO is not recommended as optimal method for the treatment of nutrients in AnMBRs effluent.

Combined biological-electrochemical treatment:

Ammonia removal by EO has been investigated by Li and Liu, which showed that EO had the capacity to reduce ammonia, from 32 mgN/L, to less than 0.5 mgN/L, after 2 h in the effluent from aerobic or

anaerobic reactors that treated MWW [76].

2.2.2.3 Electrochemical reduction

Electrochemical reduction (or electroreduction) (ER) is typically applied to reduce nitrate to nitrogen gas at the cathode surface [62]. Nitrite, ammonia, and other nitrogen species might also be generated as by-products during the process, which is considered as the major limitation of the application of ER for the removal of nitrate [77,78]. To enhance the selectivity of nitrate to nitrogen gas, NaCl may be added to aid the oxidation of produced ammonia and nitrite by the ER process at the anode [77,78], where the reaction of ammonia oxidation follows the aforementioned equation (2.1). This implies that the high removal efficiency of nitrate is actually achieved through the combination of ER and EO processes. Another alternative might involve the synergistic interactions of key parameters, such as the distance between electrodes, applied voltage, initial pH, and reaction time [79]. The practical application of these two laboratory methods for large scale MWW treatment remains distant as the quality of actual MWW is always variable.

Combined biological-electrochemical treatment:

Distinct from the conventional ER discussed above, autotrophic microorganisms in bio-electrochemical reactors (BERs) utilize hydrogen gas, which is produced at the cathode surface, as an electron donor to reduce nitrate to nitrogen gas. The net reaction of denitrification on the cathode, and the overall reaction in BERs are shown in equations (2.2) and (2.3), respectively [80].





The summaries of detailed cases in BER research have been summarized by Mook *et al.* and Ghafari *et al.* [77,80]. Most of the tested samples were synthetic water.

Various ER methods have been studied, where the great potential for nitrate removal was shown; however, ER has been constrained only to nitrate removal to date. Other nutrients in MWW, such as phosphate, have not been investigated in ER.

Studies on the above mentioned electrochemical methods for the removal of nutrients from wastewater are summarized in Table 2.2.

Table 2.2 Electrocoagulation, electrochemical oxidation and electrochemical reduction for nutrients removal from wastewater

Types of wastewater	Contaminants/Concentration	Electrochemical methods/Electrode	Operation conditions	Findings	Ref.
EC for nitrate or phosphate:					
Synthetic solution containing NaNO ₃	Nitrate: 100-300 mg/L	ER Cathode: carbon cloth cathode Anode: graphite rod	pH: 5-11 Applied potential: 2.9 V Retention time: 0-100 min	Nitrate was mainly converted to N ₂ gas. Higher removal rates were achieved at lower pH with relatively low energy consumption. Energy consumption was higher with lower solution concentrations.	[148]
	Nitrate: 100-300 mg/L	EC Anode: Fe	pH: 5-11 Applied potential: 20-80 V Retention time: 0-100 min	Nitrate was removed with the precipitation of Fe(OH) ₃ produced in water by soluble anode. The optimum pH was between 9 and 11. Although higher potential applied in EC, EC was concluded as more cost efficient with typical energy consumption about 0.5x10 ⁻⁴ kWh/g with less duration time.	
Groundwater	Nitrate: 25 mgN/L (Na ₂ SO ₄ : 3000 mg/L as supporting electrolyte)	EC Electrodes: Fe and Al	Current densities: 0.1-5.0 mA/cm ² Retention time: 0-4000 min	Nitrate removal was mainly due to the adsorption onto growing metal hydroxide precipitates. The adsorption isotherm fitted to the Freundlich Isotherm for iron and aluminum electrodes. Current density did not influence the nitrate removal. pH was not a primary factor.	[67]
Synthetic solution containing KH ₂ PO ₄	PO ₄ -P: 25-150 mg/L	EC Electrodes: Al/ Fe plates	Initial pH: 3 Current densities: 0.25-1.0 mA/cm ² Electrodes gap: 5 mm Retention time: 0-40 min	Aluminum electrode had higher removal rates and efficiencies than iron electrode. Increasing current density could increase removal efficiencies. 100% removal efficiency was obtained by using Al electrodes for all initial phosphate concentrations, but the	[81]

Spiked MWW (with KH ₂ PO ₄)	Soluble COD: 16.3 ± 1.6 mg/L Phosphorus: 2-50 mgP/L	EC flocculation Electrodes: mild steel plates (bipolar configuration)	and pH: 7.0±0.1 Current densities: 12-95 mA/cm ² Retention time: 5-30 min	efficiency was decreased with Fe electrode. Bath operation: more than 96% TP was removed combined with flocculation Optimal operation conditions: current density at 38.2 mA/cm ² for 20 min and 0.01 g/L cationic polymer addition subsequently Continuous operation: more than 98% TP could be removed	[68]
EO: Diluted municipal landfill leachate	COD: 773-3799mg/L NH ₄ ⁺ : 487-2020mg/L Cl ⁻ : 1420-8571mg/L	EO Anode: Boron doped diamond (BDD) Cathode: stainless steel (316L)	pH: 7.51, 8.35 Current densities: 15-90 mA/cm ² Electrodes gap: 5 mm Retention time: 0-480 min	Almost half of the initial ammonia was transformed to nitrate. Additional Cl ⁻ enhanced ammonia removal efficiency and caused less NH ₄ ⁺ oxidized to NO ₃ ⁻ . Ammonia in effluent can be less than 15mg/L.	[82]
Synthetic solution; Effluent from aerobic or anaerobic reactors treating MWW	NH ₄ ⁺ : 32-1053 mgN/L Cl ⁻ : 30-300mg/L	EO Anode: RuO ₂ /Ti Cathode: stainless steel	pH: 3.0-9.3 Current densities: 3.8-15.4 mA/cm ² Electrodes gap: 10 mm Retention time: 0-24 h	Indirect oxidation of HOCl was the primary mechanism for ammonia oxidation. N ₂ gas is the main product. The reaction followed pseudo zero-order kinetics for Cl ⁻ <300mg/L and NH ₄ ⁺ <100mg/L. The ammonia was reduced to less than 0.5 mgN/L after 2 h.	[76]
Synthetic solution	NH ₄ ⁺ : 1 M (Na ₂ SO ₄ : 0.1 M)	EO Anode: RuO ₂ , IrO ₂ and Pt Cathode: Ti (with and without a cation exchange membrane)	pH: 3-12 Current densities: 20-140 mA/cm ² Retention time: 0-90 min	Ammonia was oxidized to N ₂ gas with highest efficiency at a current density of 80 mA/cm ² . Electrode performance order: RuO ₂ ≈IrO ₂ >Pt Better removal efficiencies were achieved in electrolytic cell with a membrane or with higher chloride concentrations which exerted less influence from about 10 g/L.	[83]
Seawater from a	NH ₄ ⁺ : 8 mg/L	EO	pH: 6.9	Trihalomethanes (THM) was detected, with a maximum	[74]

sea hatchery	bream	COD: 54.8 mg/L Cl ⁻ : 26167 mg/L NO ₂ ⁻ : 80 mg/L SO ₄ ²⁻ : 35000 mg/L	Anode: BDD on silicon Cathode: BDD	Current densities: 5-50 A/m ² Retention time: 0-280 min	concentration of 1.7 mg/L. NH ₄ -N followed a second order kinetics while COD and nitrite removal followed zero order kinetics. BDD anode showed considerable improvements on oxidation kinetics and energy saving for ammonia, nitrite and COD removal.
MWW dosed with sodium chloride		NH ₄ ⁺ : 45.84 ± 8.45 mg/L COD: 686 ± 67 mg/L NaCl: 2%	EO Anode: Ti/Pt Cathode: Stainless Steel 304	pH: 6, 7, 8 Retention time: 0-400 min	NH ₄ -N was reduced by almost 100% at pH 6 and 8 in two hours. Although high removal of phosphate removal was observed, the phosphate precipitation was probably due to the pH shift to the alkaline region rather than the EO.
ER for nitrate					
Synthetic solution (NaNO ₃ + NaClO ₄)		Nitrate: 10 ⁻³ to 10 ⁻¹ M NaClO ₄ : 0.5 M	ER Cathode: copper	pH: 7-13 Current densities: 0-70 mA/cm ²	Confident values of the diffusion coefficient of nitrate ions (D) were assessed which can be used to determine the electrons number as 2 for reduction peak at -0.9 V/SCE (reduction to nitrate), 6 for peak at -1.2 V/SCE (reduction to hydroxylamine) and 8 for peak at -1.3 V/SCE (reduction to ammonia).
Synthetic solution (NaNO ₃ + H ₂ SO ₄)		Nitrate: 5 mM H ₂ SO ₄ : 0.5 M	ER Cathode: Pt(1 1 1) and Cu-modified Pt(1 1 1) electrodes		Cyclic voltammetry technique was used to study the kinetics and mechanism of nitrate reduction on Pt based electrodes. In sulphuric and perchloric acids, nitrate was essentially reduced to NO and ammonia. 4 orders of magnitude current occurred on Cu-modified Pt(1 1 1) in perchloric acid solutions than pure Pt at 0.12 V.
Simultaneous removal:					
Synthetic solution		Phosphate: 25 mg/L	EC	Initial pH: 3-9	Higher initial pH and current density increased removal

containing KNO ₃ and KH ₂ PO ₄	Nitrate: 25-100 mg/L NaCl: 3.5%	Electrodes: Al	Current densities: 0.78-2.34 mA/cm ² Retention time: 0-50 min	efficiencies. Higher initial phosphate and/or nitrate concentrations decreased removal efficiencies. Kinetics: first order rate equation
Domestic wastewater (DWW), pond water containing algae (PW)	DWW: COD: 36.5 mg/L NH ₄ ⁺ : 23.09 mg/L PW: COD: 46 mg/L TN: 4.4 mg/L DWW: TP: 4.5 mg/L PW: TP: 0.296 mg/L	EO Anode: Ti coated with Ti/RuO ₂ -TiO ₂ Cathode: stainless steel	Voltage: 500 V, 25 kHz Electrodes gap: 2 cm Retention time: 15 min Current densities: 3 mA/cm ² Electrodes gap: 2 cm Retention time: 15 min	A pilot scale EO treatment system (0.3 m ³ /h) using high voltage pulse power had been developed. The removal of TN, TP, NH ₄ -N and COD from the two types of water was approximately 90%. Phosphate was removed by Fe(OH) ₃ or Fe(OH) ₂ produced by electrocoagulation.

2.2.2.4 Electrodialysis and electrodeionization

(1) Electrodialysis

Electrodialysis (ED) has been utilized as a mature technology for desalination for more than a half century on an industrial scale [87,88]. The treatment capacity of ED and ED-based processes varies from less than 100 m³/d to more than 20,000 m³/d [40,88]. As shown in Fig. 2.2, in ED cell, an electrical field is applied to force anions and cations to transport from a dilute compartment to a concentrate compartment through an anion exchange membrane and cation exchange membrane, respectively [89]. In addition to desalination, ED might also be used to remove nutrients in water.

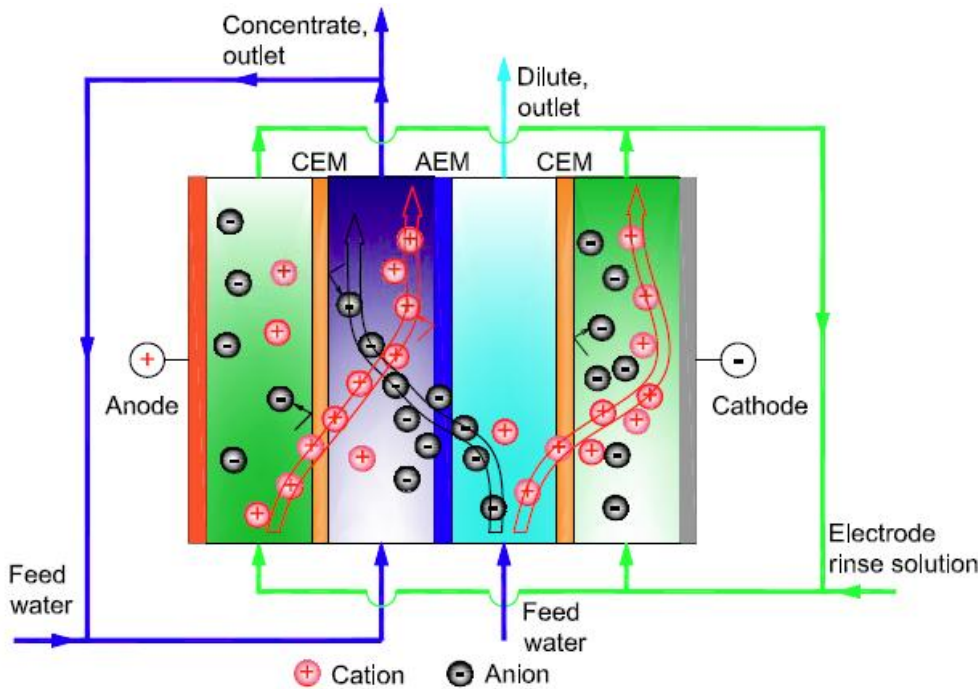


Fig. 2.2 Schematic of ED process

For nitrogen species, examples include the removal of nitrate [89,90], ammonium [91] in drinking

water, ammonium in swine manure effluent [92], nitrate, nitrite, and ammonium together in synthetic solutions [93]. Research indicated that it was challenging to separate NO_3^- from Cl^- and $\text{H}_x\text{PO}_4^{x-}$ from SO_4^{2-} via conventional ED [87]. Competition between NO_3^- and Cl^- in ED process was also encountered by Cheikh *et al.* [90]. Different types of ED membranes were tested by Chon *et al.* who adjusted the pH of solution and the duration of ED to increase the selectivity of dissolved inorganic nitrogen by ED [93]. A novel anion exchange membrane was synthesized by Kikhavani *et al.* who used Amberlite IRA-400 anion exchange resin as functional group agent for the selectivity of NO_3^- to Cl^- at 4.68 in ED [42]. Copolymer solutions consisting of vinyl- benzyl chloride, styrene and hydroxyethyl acrylate to aminate, with four aminating agents was investigated by Park *et al.* [94]. Among the most newly synthesized anion exchange membranes, membranes aminated with tributylamine had the highest permselectivity for nitrate. A method for estimating the monovalent anion selectivity of ED system was proposed by Takagi *et al.* [95].

Conventional electro dialysis was investigated to recover phosphate from excess sludge solutions, which achieved almost complete recovery in batch operations or a 95.8% recovery ratio under a low feed rate of 10 mL/min, in continuous operation [96]. To increase the phosphate recovery ratio in the struvite reactor, selectrodialysis (SED) was used to selectively concentrate phosphate to exceed the required minimum of 40 mg/L from the UASB effluent. The phosphate concentration was reduced from 2.5 mmol/L to 0.5 mmol/L by the combination of SED and struvite reactor, with high recovery efficiency (93%) under a low current density of 31.25 A/m². Monovalent selective anion exchange membranes (MVA) were applied to fractionate phosphate from chloride and bicarbonate [35].

In addition to ionic nutrients ions separation, the segregation of ionic nutrients from organic compounds [87] and organic nitrogen from inorganic nitrogen [93] have also been studied.

Membrane types, sample pH, and the duration of operation were key factors in the performance of ED [93]. The water recovery rate of ED-based system was between 90% and 95% [39,88].

Generally, the useful life of ED-based stacks under operational conditions is normally 5-8 years [39,88], longer than that of RO modules. And the removal efficiency of ED-based technologies is higher than RO. Another advantage of ED-based systems over competing RO technology is that much fewer pretreatments are required due to minimum membrane fouling or scaling, which may be achieved via a reverse polarity operation [88].

In Comparison with other membrane processes for ion separation, such as reverse osmosis (RO) and nanofiltration (NF), the cost-effectiveness of ED in water desalinization is limited to the specific feed water quality and product water requirements, otherwise, energy demands would be quite high [88]. Electrodeionization (EDI) comprises an alternative with the capacity to enhance the competitiveness for the treatment of low strength wastewater.

(2) Electrodeionization

Electrodeionization (EDI) is an electro dialysis-based separation technology that integrates electro dialysis (ED) with ion-exchange to decrease the drawbacks of each technology. A representation of the EDI process is depicted in Fig. 2.3. The introduction of ion exchange resins into the dilute

compartments of EDI increases the conductivity of the compartments by several orders of magnitude higher [97] such that concentration polarization might be prevented for the most part. The energy consumption for EDI is also reduced, which makes it suitable for solutions that possess very low electrolyte concentrations [98].

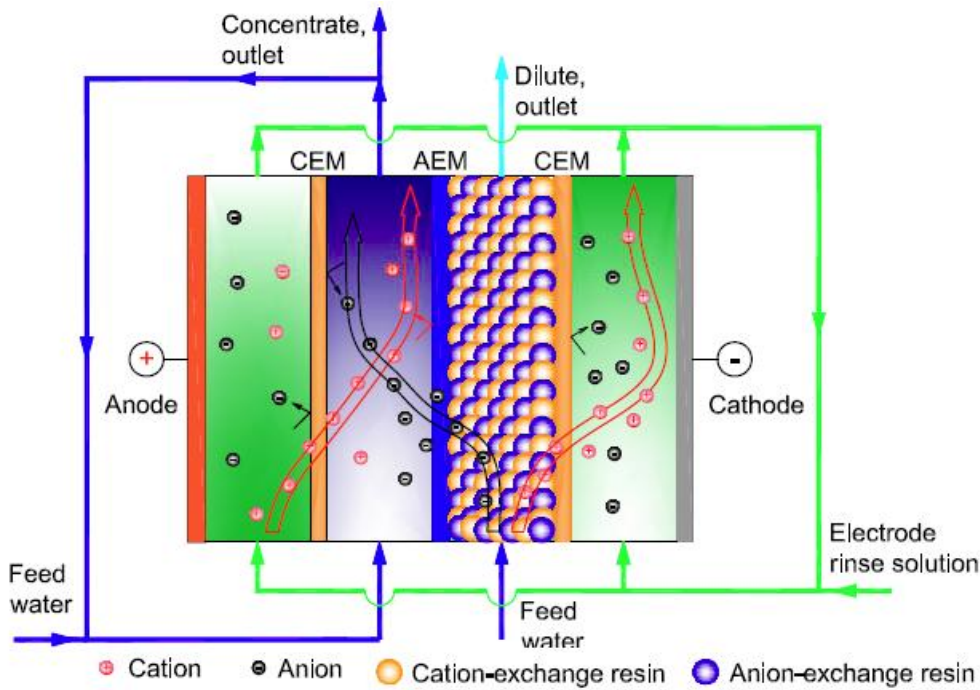


Fig. 2.3 Schematic of EDI process

The protons and hydroxyl ions produced by ED may act to continuously regenerate resins in situ to some extent, so that additional chemical regeneration can be prevented. Hence, EDI is more energy efficient and environmentally compatible. EDI has been widely used to produce ultrapure water [99] and is garnering increased attention for the removal of heavy metal ions from wastewater [100,101]. The typical energy consumption of an EDI system is $\sim 0.25 \text{ kWh/m}^3$ of pure water product [40], and the value varies from $0.05\text{-}0.8 \text{ kWh/m}^3$ of pure water product, which can vary subject to influent quality

and the requirements of the product water [100].

Research into the modeling of the EDI process has drawn considerable attention. The development of EDI and proposed new models were briefly summarized by Lu *et al.* [97,102], which included a simulation of the effects of water dissociation in a single cell with cation exchange resins in a dilute compartment for the separation of cations (such as heavy metals), and mixed cation and anion exchange resins for ultrapure water production. Unlike ED, which is usually operated below the limiting current density due to the concentration polarization effects [88], EDI commonly operates above the limiting current density, and is thus characterized by water dissociation and concentration polarization [97].

Higher removal efficiencies may be achieved with elevated water dissociation [103]. In general, however, the water splitting in EDI is not capable of generating sufficient H^+ and OH^- for resin regeneration. For example, the regeneration rate was only 60% in [104], and a fraction of H^+ and OH^- recombine prior to resin regeneration. The transport number of H^+ , $t_{H^+} = 4 \times 10^{-5}$ -0.11 for cation-exchange membranes, whereas transport number of OH^- , $t_{OH^-} = 0.03$ -0.6 for anion-exchange membranes [99]. According to the calculation model by Lu *et al.*, this leads to a water dissociation rate at the surface of the anion-exchange membranes that is far larger than that at the surface of cation-exchange membranes [97]. Therefore, water dissociation is excessive on anion-exchange membranes while insufficient on cation-exchange membranes for target removal rates [102]. Higher water dissociation may be obtained under a higher current density, which results in a lower current efficiency [103]. To overcome these drawbacks, a bipolar membrane with a much higher water splitting

efficiency (t_{H^+} , t_{OH^-} =0.9-0.96) may be introduced into the EDI system. In a bipolar membrane EDI system configuration, cation and anion exchange resins are placed in separate compartments, thus the opportunities for the recombination of generated H^+ and OH^- are rare [99]. An example of the EDI configuration with bipolar membranes for ultrapure water production is illustrated in Fig. 2.4.

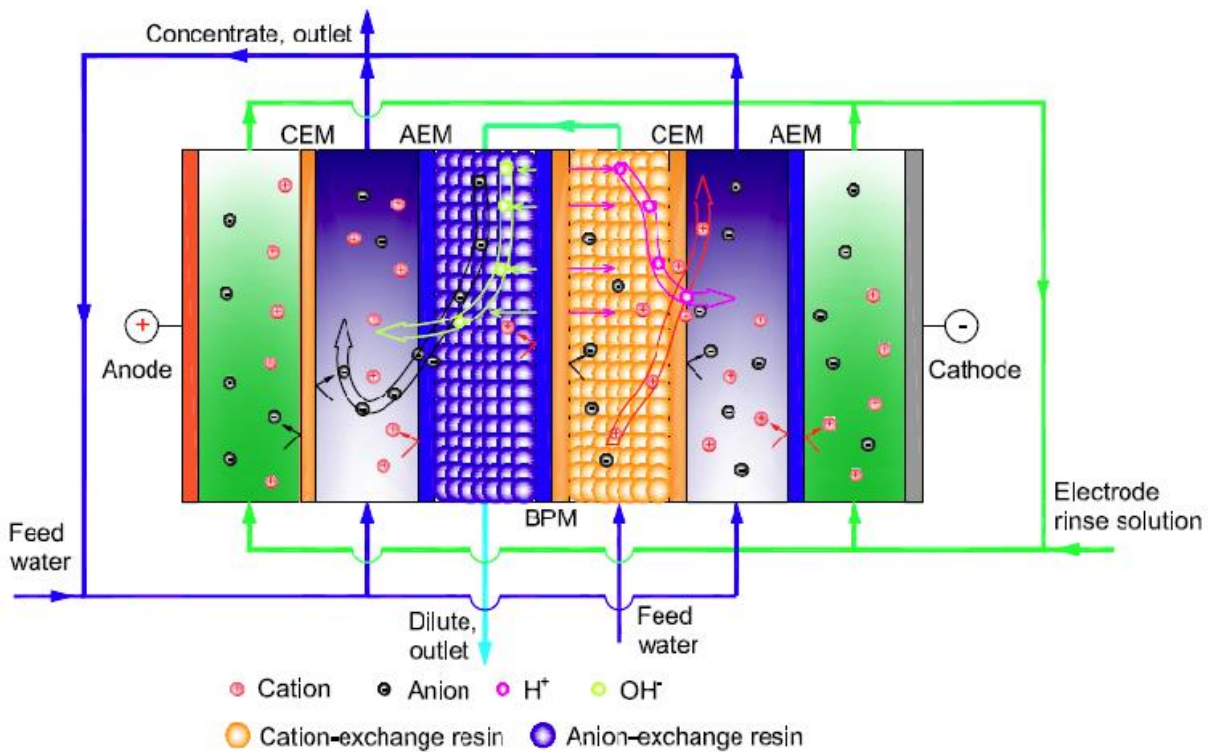


Fig. 2.4 EDI configuration with bipolar membrane (BPM) for desalination

Several studies on nutrients removal via EDI have concentrated on the removal of ammonia [149-151] and nitrate [104-106,151,152]; however, few studies have reported phosphate recovery from low strength water by EDI. One study that described phosphoric acid purification by EDI from phosphoric solutions (54% and 11% P_2O_5) was reported by Elleuch *et al.* [107].

The major parameters affecting EDI performance were summarized as: current strength, flow velocity (in the dilute and concentrate compartments), temperature, and TDS, in the influent and product water [100].

In deionization, EDI footprints are only half the size required by the conventional ion exchange resin (IX) process, and the energy consumption costs for EDI are lower than the cost of regeneration (with associated labor), and chemicals. Therefore, both capital investment and operational cost expenditures related to EDI are lower than that of conventional IX processes. Furthermore, cost of EDI has been recently significantly reduced due to module improvements [40].

Combined biological-electrochemical treatment:

The combination of ED and Column of Immobilized Biomass on Granular Activated Carbon (CIBGAC) bioreactor to remove nitrate continuously was studied by Cheikh *et al.* [90]. A synthetic solution containing nitrate (100 mg/L), chloride (200-400 mg/L), and sulphate (200-400 mg/L) was initially run through ED, subsequently, the concentrate of ED was treated by the CIBGAC process. The competition between nitrate and chloride in ED was observed, which were monovalent ions with closed ionic mobility. In contrast, the influence of sulfate (a divalent ion) was negligible, which was explained in terms of divalent ions having lower capacity for electromigration, in comparison to monovalent ions. The final nitrate concentration was lower than 50 mg/L following treatment.

A study on ammonium removal by ED was undertaken by Khaoua *et al.*, who conducted pilot scale experiments with biological filters using the effluent of a drinking water treatment plant [91]. A novel

ED (SED) was implemented by Zhang *et al.* to selectively concentrate phosphate from UASB effluent [35]. Conventional electro dialysis (CED) was introduced by Wang *et al.* into an enhanced biological phosphorus removal (EBPR) process to concentrate phosphate from a synthetic solution, which was then integrated with electro dialysis, which incorporated bipolar membranes (EDBM) to produce phosphoric acid and an alkali solution for multiple reuses [96].

Research on electro dialysis (ED) and electrodeionization (EDI) for the removal of nutrients from wastewater are summarized in Table 2.3.

Table 2.3 Electrodialysis and electrodeionization for nutrients removal from wastewater

Types of wastewater	Contaminants/ Concentration	Electrochemical methods/Electrode & membrane	Operation conditions	Findings	Ref.
Conventional ED:					
Synthetic solution (Na ₃ PO ₄ ·12H ₂ O, Na ₂ HPO ₄ ·12H ₂ O, NaH ₂ PO ₄ ·2H ₂ O)	PO ₄ ³⁻ : 100 mg of P/L	Electrodes: Ti coated with Ru Conventional ED: CEM: JCM-II-07 AEM: JAM-II-07 ED with bipolar membrane	Current densities: 10-50 mA/cm ² Voltage: 24.5-75.0 V Retention time: 0-300 min	Phosphate was converted into phosphorus acid by ED with bipolar membrane and recovery ratio could reach 95.8% under continuous operation.	[96]
RO concentrate	NaNO ₃ : 0.31 mmol/L Na ₂ HPO ₄ : 0.44 mmol/L TOC: 0 or 120 g/L	AEM: nonselective membrane (SA), membrane selective for monovalent anions (MVA)	Current densities: 46.9-78.1 A/m ² Voltage: 24.5-75.0 V Retention time: 0-300 min	It was difficult to separate NO ₃ ⁻ from Cl ⁻ and H _x PO ₄ ^{y-} from SO ₄ ²⁻ by SA and MVA membrane in ED. 85% of TOC was separated by ED from real RO concentrates.	[87]
Effluent from biological treatment plant	NH ₄ ⁺ : <8.5 mg/L	CEM: CMX AEM: AFN	Initial pH: 8-8.5 Current densities: <45 A/m ² Retention time: 0-25 min	Ammonium in ED effluent can be 0.037 mg/L. And TDS was also significantly reduced.	[91]
Swine manure	NH ₄ ⁺ -N: 3200 mg/L	ED and air stripping CEM: CR67HMR AEM: AR204SZRA	Initial pH: 8.5 Current densities: <40 mA/cm ²	95% of NH ₄ ⁺ -N was removed from the swine manure.	[92]
Synthetic solution	KNO ₃ : 100 mg/L Cl ⁻ : 200-400 mg/L SO ₄ ²⁻ : 200-400 mg/L	ED and CIBGAC CEM: not specified AEM: not specified	Current densities: 2.4-14.5 A/m ² Retention time: 0-40 min	Nitrate concentration was less than 50 mg/L and nitrite concentration was less than 10 µg/L after treated by the hybrid process.	[90]
UASB effluent	Na ₂ HPO ₄ : 2.7	SED-struvite combined	Current density: 31.25	The initial phosphate concentration was	[35]

	mmol/L Cl ⁻ : 70 mmol/L HCO ₃ ⁻ : 21-27 mmol/L	system standard CEM, standard AEM, monovalent selective AEM	A/m ² Retention time: 62 h	reduced to around 0.1 mmol/L in the presence of chloride by the combined system.
Synthetic solution	NaNO ₃ : 0.01M NaCl: 0.01M	Newly synthesized heterogeneous AEM CEM: PC-SK	Membranes gap: 0.5 mm	The newly synthesized anion exchange membrane had a nitrate to chloride selectivity of 4.68 at low voltages. [42]
EDI:				
Synthetic solution containing (NH ₄) ₂ SO ₄	NH ₄ ⁺ : 173-272mg/L	Two-stage EDI Electrodes: platinized Ti CEM: CR 67 AEM: AR 103 Resins: mixed	Current densities: 5-30 mA/cm ² Retention time: 6 h	Ammonium removal could be greater than 96.8% in two stage unit for 6 h run time at current density less than 10 mA/cm ² . [149]
Blow-down of PWR nuclear power plants	Ammonia: about 1000 ppb	Continuous EDI	pH: 4-10	Ammonia could be reduced from 1000 ppb to 3-4 ppb. [150]
Fertilizer plant wastewater	NH ₄ ⁺ : 300 mg/L NO ₃ ⁻ : 1010 mg/L	membrane-less electrostatic shielding ED and then EDI Electrodes: platinized Ti grids	pH: 5 Current densities: 15-30 A/m ² for ED, 50 A/m ² for EDI Retention time: 28 min for ED	During ED process, NH ₄ ⁺ and NO ₃ ⁻ were reduced to 11.6 mg/L and 38.4 mg/L respectively. [151] Then the dilute of ED was further treated by EDI where NH ₄ ⁺ and NO ₃ ⁻ were decreased to less than 1 mg/L respectively.
Synthetic solution containing NaNO ₃	NO ₃ ⁻ : 124 mg/L	Anode: Ti with precious metal oxide Cathode: stainless steel CEM & AEM: IONAC™ Resins: mixed	Current densities: 0.5-0.91 mA/cm ² Membranes gap: 1-2 mm Retention time: 0-400 min	Nitrate could be treated to below the required 45 mg/L. [105] The impact of main parameters was studied. Larger membranes gap resulted in lower flux and higher energy consumption. Lower nitrate concentrations increased the

Two natural water streams dosed with NaNO ₃ , NaCl and CaSO ₄	Each species: 2-6 meq/L	Anode: Ti with precious metal oxide Cathode: stainless steel CEM & AEM: IONAC™ Resins: mixed	Applied voltage: 2-5 V Membranes gap: 1 mm Retention time: 0-50 min for most experiments	energy consumption due to higher water dissociation at lower ionic strength. The applied voltage affected the process selectivity and energy efficiency greatly. Ion-selective resins in EDI made the process more nitrate selective and energy efficient. The composition of natural water affected the nitrate selectivity and energy consumption of EDI. Natural water with less dissolved solids required less energy and was more selective for nitrate removal.	[106]
Drinking water dosed with NaNO ₃	NO ₃ ⁻ : about 80 mg/L Ca ²⁺ : 122.7 mg/L HCO ₃ ⁻ : 366 mg/L Cl ⁻ : 57.7 mg/L	CEM: CDS Morgane AEM: ADS Morgane Resins: mixed	Applied voltage: 9-24.5 V Retention time: 0-150 min	EDI had faster nitrate extraction rate and higher nitrate removal efficiency than ED. Nitrate removal efficiency was about 99% in EDI while 80% in ED.	[152]
Tap water dosed with NaNO ₃	NO ₃ ⁻ : 50 mg/L	Electrodes: Ti/Ru Anion exchange resin: Amberlite IRA-400 Cation exchange resin: Purolite A520E	Applied voltage: 50 V Retention time: 0-90 h	Nitrate concentration was decreased from 50 mg/L to 10 mg/L after 20 h in EDI. The regeneration rate was 60% after 90 h under 50 V in EDI.	[104]

CEM: cation exchange membrane
AEM: anion exchange membrane

For EDI, the key is the use of ion exchange resins in the dilute compartment [100]. Thus the resins used for nutrients removal are provided as follows:

(1) Ammonium

Typically, strong acid cation (SAC) resins are employed for ammonium recovery. In contrast to studies on the selective recovery of nitrates and phosphates with ion exchange resins, reports on the selective concentration of ammonium from aqueous solutions are quite rare. This may be due to the fact that other cations, such as Ca^{2+} and Mg^{2+} , are multivalent, while NH_4^+ is monovalent and SAC resin is more selective for multivalent cations. In spite of this, SAC resins have still been considered a suitable choice for the recovery of ammonium due to their high exchange capacity and rapid regeneration. In terms of selective ammonium removal, natural zeolites have demonstrated improved performance over SAC [108]. Experiments on ammonium recovery with commercial ion exchange resins are summarized in Table 2.4.

(2) Nitrate and phosphate

A newly developed Polymeric Ligand Exchanger (PLE) for the selective removal of both nitrate and phosphate was investigated by Kney *et al.* who explained the selectivity mechanism was due to the Lewis-acid base interaction (through the formation of inner sphere complexes) between the two anions and the copper (II) ions that were introduced in the PLE [109]. However, the high cost of PLE has hindered its extensive use. A later commercialized hybrid anion exchanger (HAIX) gained more attention for the selective recovery of phosphate from various types of wastewater [110-113]. In

addition to HAIX, other ion exchange resins were studied to selectively remove phosphate [36,37,55]. Ion exchange was combined as a polishing method for MBR effluent by Johir *et al.* to recover phosphate and nitrate [114]. Purolite A500P was applied to remove organic matter and recover phosphate, whereas Purolite A-520E was used in the recovery of nitrate. Recovery rates of more than 95-97% phosphate and nitrate were achieved with 20 bed volumes with 1% NaCl or with four bed volumes with 2-3% NaCl. Experiments involving the recovery of nutrients with ion exchange resins are summarized in Table 2.4.

Table 2.4 Recovery of nutrients with conventional ion exchange resin methods

Wastewater	Contaminants/ Concentrations	Resin type	Findings	Ref.
Ammonium recovery:				
Synthetic solution containing NH ₄ Cl	Ammonia: 20 mg/L	SAC resin Na-type Dowex HCR-S (Dow chemical Co.)	Ammonia removal was greatly affected by initial pH and initial ammonia concentration in the solution. The more complex isotherm of the modified Langmuir version and that of Jossens <i>et al.</i> described the data better.	[115]
Synthetic industrial effluent	NH ₄ ⁺ : 40mg/L PO ₄ ³⁻ : 20 mg/L Humic acid: 40 mg/L	strong macroreticular exchange Amberlite IRA910 SAC resin: Amberjet 1200 Na	basic anion resin: Phosphorus removal was reduced by Cl ⁻ , CO ₃ ²⁻ , SO ₄ ²⁻ and humic acid.	[116]
Semi-aerobic landfill leachate	COD: 2380-2850 mg/L BOD: 40-160 mg/L NH ₃ -N: 1820-2200 mg/L	SAC resin: INDION 225 Na (Ion Exchange (INDIA) Ltd.)	The adsorption kinetics followed the pseudo-second-order equation. The adsorption capacity was 12.56 mg/g. NH ₃ -N removal rate was 94.2%.	[117]
Synthetic and real municipal wastewater	For synthetic municipal wastewater:	SAC resin: KU-2-8 (analogue of Amberlite IR-120,	For real municipal wastewater: the removal efficiency could be 95.8%~99.9%.	[108]

	NH ₄ -N: 40 mg/L	Diaion SK-1A, Dowex 50)	
Synthetic solution containing organic compounds and NH ₄ -N	NH ₄ ⁺ : 50mg/L Citric acid: 533 mg/L Whey protein: 20mg/L	Cationic gel resin, Dowex50w-x8 (Dow Chemical) macronet cationic exchanger MN500 (Purolite)	Citric acid reduced about 50% of breakthrough capacity of MN500 but didn't affect Dowex 50w-x8. Whey protein didn't affect the process.
Synthetic solution and Nitrate and phosphate recovery:	NH ₄ ⁺ : 25-150 mg/L	Cation exchange resin C150H (Purolite)	Ammonium removal could be 80-90 %.
Secondary municipal wastewater effluent	PO ₄ ³⁻ : 1.5 ~5.0 mg/L (as P) NO ₃ ⁻ : 2.0~ 5.0 mg/L (as N)	Newly developed Polymeric Ligand Exchanger (PLE)	A highly selective removal of phosphate was achieved by PLE. The affinity sequence for the PLE: HPO ₄ ²⁻ > NO ₃ ⁻ > SO ₄ ²⁻
Synthetic water and domestic wastewater effluent	Synthetic water NO ₃ ⁻ : 50 mg N/L PO ₄ ³⁻ : 15 mg P/L wastewater NO ₃ ⁻ : 12.9 mg N/L PO ₄ ³⁻ : 5.9 mg P/L	Purolite A500P anion exchange resin hydrous ferric oxide (HFO) columns	Purolite A500P selectively recovered nitrate and HFO selectively recovered phosphate. The removal efficiency was close to 100% in spite of the presence of other competing anions (Cl ⁻ and SO ₄ ²⁻).
Synthetic solution	20 mg/L each of KH ₂ PO ₄ , KNO ₃ , NaCl, and NaF	Newly developed polymeric anion-exchange resin based on AMP16-OH (Samyang)	The synthetic resin showed higher exchange capacity and selectivity for phosphate.
Synthetic solution	NO ₃ ⁻ : 20 mgN/L PO ₄ ³⁻ : 10 mgP/L	Purolite A500PS Purolite A520E	Purolite A520E had higher nitrate removal (<85%) and lower phosphate removal (48%), while Purolite A500PS had lower nitrate removal (about 65%) and higher phosphate removal (65%).
Phosphate recovery:			
Diluted secondary wastewater	Phosphorus: 260 µg/L	Hybrid anion exchanger (HAIX)	HAIX had much higher selectivity of phosphate over sulfate. The typical secondary wastewater pH (around 7.5) is the best for HAIX.
Synthetic solution	5.0~75.0 (mg/L as P)	HAIX DOW-HFO	The three resins showed higher selectivity of orthophosphate than

Human urine, diluted urine	Phosphorus: 7.7-668 mg/L	DOW-HFO-Cu SAC resin hybrid anion exchange (HAIX-Fe)	sulfate. More than 90% phosphate was removed by HAIX-Fe resin. More than 92% phosphate desorbed from the resin during regeneration.	[112]
Synthetic human urine	Total PO ₄ ³⁻ : 5-20 mg/L	PhosXnp or LayneRT HAIX resin (SolmeteX)	HAIX rapidly removed phosphate in 5 min with 97% efficiency without being affected by high concentrations of chloride or sulfate.	[113]
Synthetic solution	PO ₄ ³⁻ : 5-30 mg P/L	Purolite FerrIX A33E	External mass transfer was the main control factor of the adsorption of Purolite FerrIX A33E.	[55]

To date, research efforts into nutrients recovery from wastewater have focused on only one or two components. EC may be used to remove organic compounds, phosphorus, and nitrate. EO has the capacity to eliminate biorefractory organic compounds, nitrite, and ammonia nitrogen. ER is primarily applied for the reduction of nitrate to nitrogen gas. ED and ED-based processes are utilized either to recover ammonium, or nitrate and phosphate. No research on the simultaneous recovery of these three nutrients by ED or ED-based processes has yet been reported.

Research efforts on ED and EDI in water and wastewater treatment can be categorized into three areas:

(1) water treatment, such as the production of ultrapure water from tap water or other sources of water containing very low concentrations of impurities or desalination from sea water with high concentrations of salts; (2) removal of multivalent ions from industrial wastewater, such as heavy metal ions; (3) recovery and concentration of some specific matters, such as the concentration of organic acids and nutrients. Generally, ED based technologies are either utilized to recover nutrients from high concentration wastewater such as swine manure or to remove nutrients from low concentration water such as groundwater to meet the standards of ultrapure water or drinking water. Nutrients concentration

in MWW is lower than swine manure but higher than groundwater, research on applying EDI to recover nutrients from feed water with similar concentration range to MWW and meet the standards of wastewater effluent is very limited. Compared to RO, much fewer pretreatment is required as membrane fouling or scaling of EDI is less, thus utilizing EDI for the effluent of AnMBRs treating MWW has the potential to achieve a shortened treatment process as a whole. Moreover, modifying the EDI system from the much stricter standards of drinking water to standards of wastewater effluent indicates a great potential to reduce energy demand. Therefore, EDI is proposed to optimize the overall treatment process and modification of EDI system to meet standards of wastewater effluent is proposed to further reduce energy demand.

Recently, EDI designs have been developed for different treatment purposes [99,100,121]. The recent development of EDI configurations and the development of selective nutrients recovery through the use of novel ion exchange membranes (particularly bipolar membranes and resins) from wastewater, indicate a great potential for EDI to simultaneously recover nutrients from MWW much more efficiency.

2.2.3 Applications of freezing in water/wastewater treatment

2.2.3.1 Desalination

Processes of freeze concentration for desalination were reviewed in [48]. Suspension freeze concentration (SFC) and progressive freeze concentration (PFC) have commercial applications in food processing industry [44] and chemistry industry [48], with 100,000 tons paraffin/year as the largest static melt crystallization plant developed by Sulzer Chemtech [122]. In SFC (Fig. 2.5, a), known as

Niro process in the industry, ice nuclei are formed in the initial phase (nucleation). The small ice nuclei gradually grow to the bigger ice crystals which are then separated from the concentrate in the wash column [44]. Instead of many small ice crystals in SFC, only a large single ice crystal (ice layer) is formed and grown on a cold surface in PFC (Fig. 2.5 b) [44]. The ice layer is controlled by the ice front one dimensionally, which enables an easy operation [123]. The falling-film crystallization, based on progressive freezing principles, can be categorized as PFC method.

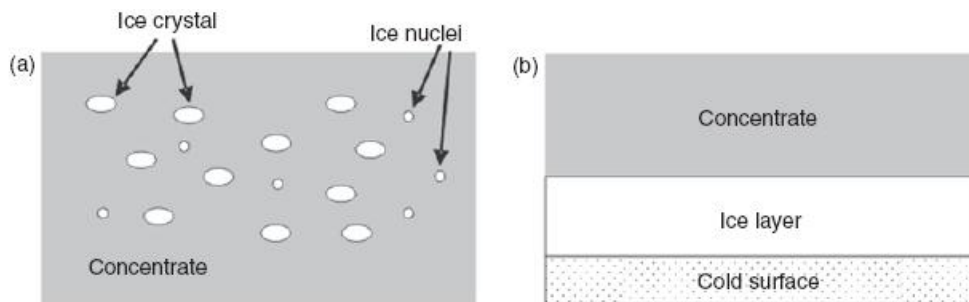


Fig. 2.5 Two methods of freeze concentration [44]

(a) Suspension freeze concentration; (b) Progressive freeze concentration

Although SFC has higher productivity than PFC [46,49], the system is complicated and requires expensive initial capital investment. Thus, its practical application has been limited [46]. By contrast, the easy separation of ice layer from concentrate and simple operation system in PFC could reduce the process cost substantially [46]. Hence, it has drawn more attention in desalination and wastewater treatment research.

A new freeze desalination process, HybridICE™, was developed in 2013 to save a fresh water stream that is usually required to wash the ice crystals in the traditional SFC system [49,124]. The pilot test

results of batch experiment in [49] indicated an average salt removal of 96% for feed water containing sodium chloride in the range of 1-25 g/L. The average salt removal in continuous operation mode with 2.3%-10% sodium chloride solution was 82.8%, a bit lower than that in the batch operation mode [124].

With an attempt to utilize the cold weather during the winter months in Canada, Beier *et al.* designed a trickle freeze separation equipment to remove salts from mine waste water [125]. They found that melting was more effective at removing salts than freezing. At ambient temperature of -15°C , 80% salts could be removed after melting 9% of the produced ice for feed water containing NaCl no higher than 3000 mg/L or after melting 27% of the produced ice for feed water containing 20,000 mg/L NaCl [125].

Rich's group developed a static ice layer crystallizer for the desalination of sea water [54]. Under the initial temperature of -0.5°C and final temperature of -2°C , after crystallization (10 h) and sweating (35 min), the salinity of feed water was decreased from 7.01g/kg to product water that met the European drinking water standards with a good safety margin.

A coupled method, unidirectional-freezing (ice layer grows from top to bottom) was combined with ice crushing and centrifugation (CIAC), was introduced to improve the quality of the produced ice for brackish water. For brackish water (1320 mg/L -8350 mg/L), the freezing removed 48.38% - 57.88% of total dissolved solids (TDS), and CIAC could further remove 30.91% - 47.28% of TDS [126].

Williams *et al.* [47] modified a commercial ice maker K40 to simplify the freezing concentration

system for actual reverse osmosis (RO) brine. An ice layer was formed and grown over the upper surface of the inclined plate, and the feed was concentrated to near brackish water or sea water standards instead of drinking water standards. As a result, the volume of the concentrated brine needed to be disposed of was reduced, and the product water was recycled back to join the main feed stream for the RO plant.

2.2.3.2 Wastewater treatment

It was reported that two commercial plants for petroleum waste stream treatment had been built by Niro (Oxfordshire, UK) with SFC system since 1997 [153]. At present, the Niro process has been widely used in food industry [48].

On the basis of the lab experiment, Wakisaka *et al.* [50] conducted a pilot freezing plant to test the treatment of synthetic wastewater with glucose. Ice layer was produced in each ice making cylinder and then was detached by the gaseous coolant. 1.4 fold concentrated solution was obtained for the feed water with COD in the range of 2600-5800 mg/L. The removal efficiency of glucose varied from ~99% to ~93% for the feed water of 2600 mg/L and 5800 mg/L, respectively.

Lorain *et al.* [127] explored the potential of freezing in the treatment of synthetic wastewater, urban wastewater and cutting oil wastewater. For the urban wastewater after primary settling, the removal efficiency was 88.3%. For the samples after secondary settling, the removal efficiency was higher and reached 93.3%.

Facey and Smith [128] used unidirectional freezing method to simulate the treatment of Kraft pulp mill

effluents by semi-natural freezing. When the feed water was frozen slowly and thawed fast from predominantly the bottom-up, the method could remove 73% of color in the top 70% liquid fraction. Gao [129] also used unidirectional freezing method to study the treatment of membrane concentrate. At -7°C, conductivity, total solids (TS) and total organic carbon (TOC) were removed 70-80% in the ice samples with freezing ratio at 80% and 40-60% were removed with freezing ratio at 90%. Same freezing method was employed by Xue *et al.* [130] to investigate the partition of dissolved organic matter (DOM) in liquid and ice phase. They found that lower freezing temperature and higher dissolved organic carbon (DOC) caused more DOM was captured in the ice phase. In addition, changes of the quantity, optical properties, and chlorine reactivity of DOM by freezing were observed.

Spray freezing method was also evaluated in the industrial wastewater treatment. Gao *et al.* [131] compared the partial and complete spray freezing treatment for the oil sands tailings pond water. They found that the degree of spray freezing was a significant factor that affected the removal efficiencies of COD, TOC, conductivity, Cl⁻ and SO₄²⁻. No removal of impurity content was observed for the complete spray freezing. Further research extended spray freezing to treat pulp mill effluent and oil sands tailings pond water [132]. More than 60% of impurities were removed when 70% of the feed water was frozen. With the same freezing ratio at 70%, Gao *et al.* compared the removal efficiencies of two freezing methods, spray freezing and unidirectional downward freezing (UDF), with the secondary petroleum refinery and pulp mill effluents as feed water [133,134]. Despite the different concentrations of the feed water (about 10 times), the treatment efficiencies were similar. 85%-96% impurities were removed by UDF with mixing and 75%-91% treatment efficiency was achieved in the final 50% of the melt water

after two weeks storage. The freezing temperature (-15°C and -25°C) also showed no significant influence on the treatment efficiencies [133,134]. The *E. coli* inactivation capacity by freezing was also studied [135].

Nutrients removal by freeze concentration

Lind *et al.* [136] used unidirectional downward freezing to concentrate nutrients from human urine and reduce the volume of the urine. At freezing temperature of -14°C, approximately 80% of the nutrients were concentrated in 25% of the initial volume. On the basis of the results from Lind *et al.*, Ganrot *et al.* [137] combined struvite precipitation and nitrogen adsorption by zeolite or active carbon to optimize the nutrients recovery. The operation condition of freezing in the experiment was set at -18°C and 60% of the nutrients were concentrated in 40% of the feed volume.

Gulyas *et al.* [138] investigated the concentration of nutrients in separately collected urine (“yellow water” from no-mix toilets) with falling film concentrator and stirred vessel freeze concentrator. The results showed that the stirred vessel freeze concentrator was more effective to recover nutrients and high salinity in feed urine led to high urine constituents incorporated in the ice phase.

To investigate the distribution of inorganic nutrients and dissolved organic carbon in sea ice, Zhou *et al.* [139] reproduced the formation of natural sea ice in the Hamburg Ship Model Basin, Hamburg (19 days). 21 polyethylene experimental mesocosms with a volume of 1.2 m³ each were used (without mechanical mixing). Under this simulated natural freezing condition, the enrichment factor of dissolved compounds (nitrate, nitrite, ammonium, phosphate, silicate, and DOC) into the sea ice deviated from 1,

which meant that the dissolved compounds hadn't behaved conservatively with respect to salinity when they were incorporated into the sea ice. They concluded that the brine convection and stratification affected the incorporation of the dissolved compounds.

One of the promising advantages of freezing process is that the natural low winter temperatures in cold regions (natural cool energy) can be utilized to greatly reduce the energy demand. Zhang *et al.* [140] conducted the natural frozen sewage treatment experiment in HuLun Lake area of Inner Mongolia, which is in the northeast of China. The designed process removed more than 80% of TN, TP and COD in the first freezing stage, more than 94% of TN, TP and COD after the second stage, more than 97% of TN, TP and COD after the third stage.

2.2.3.3 Factors influencing the performance of progressive freeze concentration

During the process of PFC, impurities are rejected from ice crystals, which results in a concentration differential between that of ice and liquid phases. This phenomenon is known as concentration polarization, which is schematically shown in Fig. 2.6.

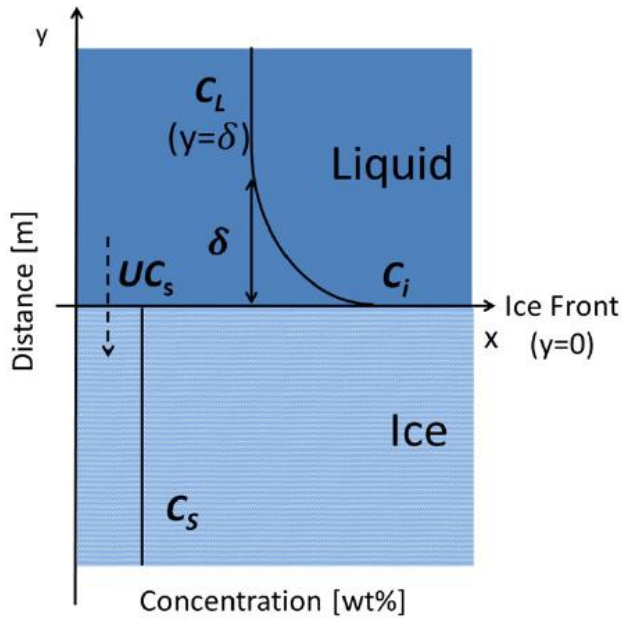


Fig. 2.6 The concentration gradient near the ice front in PFC [123]. C_L : the concentration of liquid; C_i : the concentration of the ice front; C_s : the concentration of the ice; U : the advance speed of the ice front.

The advance speed of the ice front U , the circumferential velocity of the stirrer U_r (or mixing intensity) and initial concentration (C_0) are thus considered as the key parameters of PFC.

(1) The advance speed of the ice front

Theoretically, the advance speed of the ice front should be low enough to ensure that the impurities are rejected by the growing ice crystals at the interface of ice and water. Additionally, the structures of ice crystals are different with different freezing rate. Ice crystals grow in columns with flat ice/water interface at lower advance speed of the ice front. They turn into multi-crystalline array of dendrite structure at higher freezing rate [126]. The work of Bogdan *et al.* achieved the in situ visualization of this dendrite-like structure [141]. The reason may be that dendrite structure could form ice crystals

faster with larger interface between ice crystals and liquid. This leads to the entrapment of solutes and suspended solids in the gap between the growing ice crystals [126,142].

Freezing rate directly depends on freezing temperature. The lower the freezing temperature, the faster the freezing front moves. Experiment results showed that increasing impurities concentration in ice with decreasing temperature [126,128,130].

(2) Initial impurity concentration

The initial concentration of impurities in the feed liquid is important for the performance of PFC. At the same freezing temperature, higher removal efficiency can be obtained when PFC is fed with solution at lower initial concentration [126,130]. This may be attributed to the increases of impurities accumulated at the ice/liquid interface caused by the increases of viscosity of water and quantity of potential crystal nucleus in water with increasing impurity concentration. This leads to lower diffusion of impurities to liquid phase and easier entrapment in the ice phase [130].

(3) Mixing speeds

Mixing reduces the concentration of impurities near the interface of ice/liquid and increases the diffusion from the boundary region through strengthened convective mass transfer. As a result, the effectiveness of PFC could be improved [123,143,144].

Except the mechanical mixing method, ultrasonic mixing method was also studied in PFC. The research of Kawasaki *et al.* [145] showed that PFC performance was improved via the increasing

intensity of ultrasonic irradiation.

(4) Other factors

Super-cooling and ice seeding:

The phenomenon of super-cooling was observed in the initial stage of PFC without ice seeding before the ice crystal formation. The impurities would be trapped in the gap between the dendrites ice crystals that would be suddenly formed under certain circumstances, resulting in the poor quality of ice [126]. Ice seeding is usually conducted to prevent the occurrence of super-cooling [50,126]. Other methods such as using a cooling plate with many small holes was also reported [154].

Sweating or thawing:

Ice sweating (partial melting) or thawing reduces the concentration of impurities in the ice, which was proved by the results of research [54,126,128,146]. The partial melting of ice phase could improve the purity of ice. For example, ~78% of salinity in the ice sample was removed after 2 h of melting at 0 °C in the study of [54].

Multi-stage freezing:

Based on freezing in one stage, multi-stage freezing could enhance the performance of PFC [54] [140]. For the removal of TN, TP and COD in the original water, more than 80% was achieved through single stage, more than 94% was achieved through second stage freezing and more than 97% was achieved through third stage freezing [140].

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Chapter 3. Simultaneous recovery and removal of nutrients and hardness ions from synthetic municipal wastewater using electrodeionization

3.1 Introduction

Municipal wastewater (MWW) is now being re-evaluated as a potential multi-resource for water, energy (e.g., methane or biogas), and nutrients (primarily nitrogen and phosphorus) [1-3]. Anaerobic treatment is increasingly being investigated as a potential technique for MWW. It has the advantages of low energy demand and low sludge yield. Studies by McCarty *et al.* have indicated that net energy generation is achievable for MWW using anaerobic treatment [2]. The primary challenges of anaerobic processes in the treatment of MWW are low temperatures (<20°C), low organic strength, and a high proportion of particulates [4]. An anaerobic membrane bioreactor (AnMBR) provides an alternative solution to address these problems, as it integrates anaerobic reactors with membranes; typically microfiltration membranes (MF) or ultrafiltration membranes (UF). The pore sizes of MF or UF in the reported research ranged from 20,000 Dalton to 10µm, with 0.4µm as the median [5-7], which are smaller than pathogens. Due to the separation of membranes, the pathogens are completely free in the effluent, and suspended solids may be effectively retained within the reactor for further biodegradation to produce biogas, which indicates an almost infinite solids retention time (SRT) in the reactor. As a result, additional energy recovery from MWW and higher effluent quality are achievable in an AnMBR [4].

As with other anaerobic treatment processes, nutrients concentrations in the effluent of AnMBRs for

MWW treatment are typically higher than the discharge standard. The explanation for this is that influent resident organic nitrogen and phosphorous are mineralized to ammonium and orthophosphate during the anaerobic process, which are not removed from the system. These ionized nutrients may pass through the pores of MF or UF and give rise to high N and P concentrations in the effluent [5,8,9]. Therefore, additional measures should be considered to recover the nutrients in the effluent in order to satisfy stringent discharge standards.

Various nutrients recovery technologies from MWW have been proposed and assessed, including chemical precipitation, enhanced biological phosphorus removal (EBPR), struvite crystallization, adsorption and ion-exchange, membrane filtration, and electrodialysis (ED) [10-12]. Each technology has its own set of advantages and disadvantages. One strategy to overcome the disadvantages might be the development of new processes or combinations thereof. For example, ion exchange is a simple and efficient method for the removal of soluble N and P species toward high effluent quality. This is suitable for the low strength effluent of AnMBR in the treatment of MWW contains minimal suspended solids. Moreover, it is resistant to the fluctuations in flow rate, nutrients loading, and temperature, and no additional sludge is produced [13,14]. However, due to the additional chemical regeneration during operation, each ion exchange bed has the requirement of being shut down for several hours. High operational cost is necessary for chemical consumption and the treatment of waste streams that contain high concentrations of regenerant chemicals [15]. In electrodialysis (ED) stacks with ion selective membranes, under the influence of an applied electric potential difference, ions are separated and purified from the feed water with high efficiency. For wastewater containing low concentrations of

ionized species, however, the energy demand might increase significantly [16].

The integration of ED with ion-exchange to decrease the drawbacks of each technology leads to the development of electrodeionization (EDI). Ion exchange resins packed in EDI beds increase the conductivity of the compartments by several orders of magnitude higher, such that more rapid electro-migration of ionized species and higher removal efficiencies than ED are achievable [17]. Energy consumption is also reduced for dilute solutions [18]. Since the resins are continuously electro-regenerated in situ with the generation of H^+ and OH^- ions from water splitting, no additional chemicals are required [17]; hence, EDI is more energy efficient and environmentally compatible. This technology has been widely employed for the production of ultrapure water and is garnering increased attention for the removal of heavy metal ions from wastewater [19-22].

Very few researchers have explored EDI as an approach for the removal of the relatively low concentration of nutrients in the effluent of AnMBR for MWW treatment, in which most of the total nitrogen and phosphorus are mineralized to ionic forms, no pathogens and few suspended solids are contained. The aim of this study was to investigate the continuous removal of ammonium and orthophosphate with an expanded EDI cell [23], which possessed the capacity to simultaneously separate and recover cations and anions in cation and anion concentrate compartments, respectively. The segregation of cations and anions in separate concentrate compartments was critical for this wastewater study, as it may alleviate the possible membrane fouling due to precipitation initiated by hardness ions (e.g. Ca^{2+} and Mg^{2+}) and anions (e.g. orthophosphate). Despite the general requirement of low concentrations of hardness ions in the feed water for the EDI process, the effective removal of

hardness ions has been demonstrated with EDI and with electrodeionization reversal (EDIR) [23-25].

According to the results of one study [26], it is difficult to separate phosphate from SO_4^{2-} under the operation of conventional ED. Moreover, it is challenging to directly apply ED for the removal of low concentrations of phosphate in wastewater (such as MWW), and very few reports of relevance can be found. Similarly, as relates to the removal of phosphate species via EDI, only small number of studies can be found. One pertinent study investigated an EDI configuration that combined ion-exchange membranes and textiles to eliminate metallic impurities from phosphoric acid solutions (54% P_2O_5 and 11% P_2O_5), rather than using EDI to remove phosphate species from an aqueous solution [27]. One explanation for the low number of studies on phosphate removal by EDI may be that, typically, phosphate cannot compete with other anions (e.g., sulphate and chloride) in solution, when using common commercial resins. All of the aforementioned reasons may lead to the relatively low phosphate removal efficiency.

Conversely, developing phosphate selective resins have proved to possess a high affinity for phosphate over competing anions. Therefore, EDI that is packed with the phosphate selective resins might be considered as a possible option for the removal of phosphate from wastewater. To the best of our knowledge, the removal of phosphate in MWW using EDI has not been investigated to date. In this study, we explored the application of a commercially available iron-based oxide phosphate selective ion exchange resin (Purolite FerrIX™ A33E) in the EDI process.

Further, we systematically investigated the effects of applied currents on the removal of nutrients

(ammonium and orthophosphate) and hardness ions (Ca^{2+} and Mg^{2+}) in the EDI system following the determination of the limiting current.

3.2 Experimental Section

3.2.1 Materials and chemicals

The ion selective membranes employed in these experiments were cation exchange membranes (CMI-7000S) and anion exchange membranes (AMI-7001S), both from Membranes International Inc. The CMI-7000S membrane consisted of gel polystyrene that was cross linked with divinylbenzene, with sulphonic acid functional groups, and a total exchange capacity of 1.6 ± 0.1 meq/g. The AMI-7001S membrane possessed the same matrix with divinylbenzene, with quaternary ammonium functional groups, and a total exchange capacity of 1.3 ± 0.1 meq/g, and fibers were used to reinforce both membranes.

Mixed resins were packed within the EDI cell, including a cation exchange resin (Amberlite[®] 200C Na), and a strong acidic macroreticular exchanger with a total exchange capacity of 1.7 meq/mL, which was purchased from Rohm and Haas Company. Purolite FerrIX[™] A33E, a highly porous hybrid anion exchanger infused with iron oxide, was kindly provided by Purolite Corporation, which was initially designed for the selective removal of arsenic. It was found that the resin could also be applied for the selective removal of phosphate [28]. The total exchange capacity of the anion exchanger with the polymer structure of the polystyrene that was cross-linked with divinylbenzene, was 0.5 - 4 g As per liter.

The experiments were conducted with synthetic solution containing NH_4Cl , KH_2PO_4 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, which were used to simulate the effluent of AnMBR for MWW treatment. The NH_4Cl was purchased from ACP, whereas the other chemicals were purchased from Sigma-Aldrich as analytical grade reagents. All other chemicals used in the experiment were of reagent grade and used as supplied. The ultrapure water (18.2 $\text{M}\Omega \text{ cm}$) used in the preparation of all solutions was purified by a Nanopure Diamond[®] water system.

The target ions and their concentrations in the synthetic solution are given in Table 3.1. The pH of the synthetic water was 4.96, which varied according to the exposure time to the ambient air due to the possible dissolution of CO_2 from the air into solution. No additional adjustments to the pH were made. Therefore, $\text{H}_x\text{PO}_4^{y-}\text{-P}$ was employed to express the phosphate ions, as phosphate ions in this pH range have a mixture of H_2PO_4^- (dominant species) and HPO_4^{2-} .

Table 3.1. Target ions and concentrations in synthetic feed water

Target ions	Concentration (mg/L)
$\text{NH}_4^+\text{-N}$	50
$\text{H}_x\text{PO}_4^{y-}\text{-P}$	20
Ca^{2+}	75
Mg^{2+}	25

3.2.2 Analytical methods

The $\text{NH}_4^+\text{-N}$ concentration in the samples was determined by the standard Phenate method (APHA 1999) using a UV-Visible spectrophotometer (Cary 50) with a 4 cm^3 quartz cuvette. The concentrations of Ca^{2+} , Mg^{2+} , and P were analyzed using Inductively Coupled Plasma Atomic Emission Spectroscopy

(ICP-AES) (Varian Vista Pro). The pH in the solutions was measured with a VWR[®] SympHony[™] SB20 pH meter. Both the current-voltage curve and time-voltage curves were recorded using a Voltalab (PGZ 402 Universal Potentiostat).

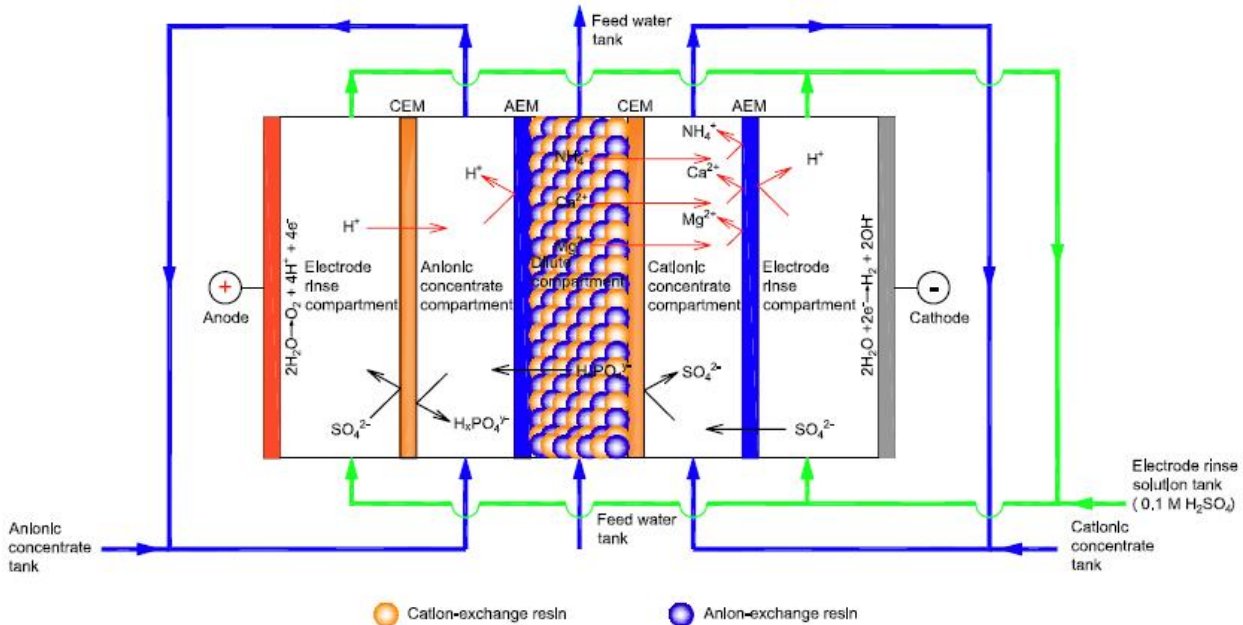
3.2.3 Pretreatment of ion exchange membranes and resins

The cation and anion exchange membranes were immersed in 0.1 M H₂SO₄ and 0.1 M KOH for 24 h, respectively, to allow for membrane hydration and expansion, and then rinsed with deionized water just prior to their installation into the EDI cell to remove any excess reagents. The cationic resin (Amberlite[®] 200C Na) was initially immersed in 0.1 M H₂SO₄ and stirred for 1 h, while the anionic resin (Purolite FerrIX[™] A33E) was immersed in 0.1 M KOH and stirred for 1h. Subsequently, the two resins were separately rinsed twice with stirring using deionized water (1 h for each rinse), separated from the water via filtration, and completely dried at a temperature of 50°C.

3.2.4 EDI cell setup

A lab-scale EDI cell comprised of a plate-and-frame module, described in a previous study [23], was utilized in continuous mode. The continuous electrodeionization (CEDI) system may be seen in Scheme 3.1. Two cation exchange membranes (CEM) and two anion exchange membranes (AEM) were alternately placed between the two electrodes. For each membrane, the active surface area was 60 cm² (6 cm x 10 cm). The compartments between two membranes, from the middle of the cell to the electrodes, were the dilute compartment, concentrate compartments, and electrode rinse compartments, with thicknesses of 10 mm, 10 mm, and 15 mm, respectively. The dilute compartment was packed with 40 g of mixed resins (cationic and anionic) at a ratio of 1:1 by weight. The EDI cell was controlled by a

Voltalab (PGZ 402 Universal Potentiostat) with a constant current through the cathode (stainless steel plate, 6 cm x 10 cm) and the anode (Ti/Ta₂O₅-IrO₂, 6 cm x 10 cm).



Scheme 3.1. EDI system for the removal of nutrients and hardness ions

3.2.5 Operation of CEDI system

A 250 mL volume of synthetic solution was circulated by a peristaltic pump through the dilute compartment, while 100 mL of synthetic solution in each concentrate tank was separately circulated through each concentrate compartment. A 250 mL volume of 0.1 M H₂SO₄ was employed as the electrode rinse solution and circulated through the two electrode rinse compartments for all experiments. The flow rates of the four distinct circuits were maintained at a constant 9 mL/min. Samples were periodically taken from the dilute tank of the recirculation line to monitor the concentrations of NH₄⁺-N, H_xPO₄^{y-}-P, Ca²⁺, and Mg²⁺.

According to previous studies, the removal of specific ions might be also initiated through the absorption by unsaturated resins [22,23]. Therefore, in order to test the efficiency of EDI, the resins were saturated prior to their packing into the dilute compartment of the EDI cell. The cationic and anionic resins were separately saturated in the synthetic feed solution. Once completely saturated and extracted, the resins were fully mixed and packed into the dilute compartment. A constant current was repeatedly applied to the packed EDI cell until no further decrease of the cell voltage was observed, which revealed the ion exchange equilibrium of the resins.

The EDI experiments were operated in batch mode. Following each run, a cleaning solution of 0.1 M HCl was circulated through the concentrate compartments to remove any possible precipitation on the membranes; subsequently ultrapure water was circulated to remove any residues in the compartments.

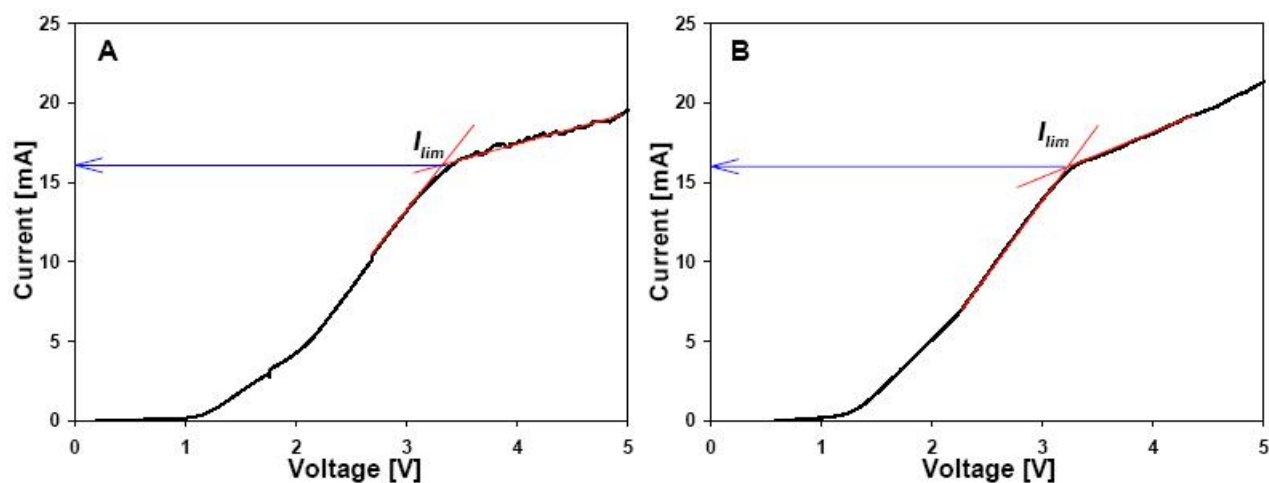
3.3 Results and discussion

3.3.1 Determination of limiting current

Typically, the limiting current (I_{lim}) is experimentally determined, principally because it depends on self-selecting parameters such as membrane and solution properties, EDI configuration, flow rate, and operation temperature [20], which makes theoretical predictions very complicated. In addition to the Cowan-Brown plot method (electrical resistance or pH in dilute compartment vs. reciprocal current), limiting current may also be analyzed from the current-voltage (I-V) curve, which was used in this study. Different scan rates were tested for the determination of the limiting current (e.g. 3.3 mV/s and 1 mV/s) [21,29]. Therefore, prior to the experiments, the effects of different scan rates were investigated,

as the concentration of the feed water in this study was not in the typical range for ED or EDI processes.

A 250 mL volume of feed water was circulated through the dilute compartment, while 250 mL of feed water in each concentrate tank was separately circulated through each concentrate compartment. A 250 mL volume of 0.1 M H₂SO₄ was employed as the electrode rinse solution. The flow rates of the four separate circuits were maintained at a constant 10 mL/min. The volumes of the concentrate solutions and flow rate were different from those described in 3.2.5. The I-V curves at scan rates of from 1 mV/s to 15 mV/s are presented in Fig. 3.1, and the limiting currents of 1 mV/s, 2 mV/s, 5 mV/s, 10 mV/s, and 15 mV/s were determined to be 16.1 mA, 16.1 mA, 18.9 mA, 21.5 mA, and 25.5 mA, respectively. Obviously, the limiting currents were constant at scan rates of 1 mV/s and 2 mV/s. However, when the scan rate was above 2 mV/s, the limiting current was increased as the scan rates were increased. Small peaks were observed in Fig. 3.1D and Fig. 3.1E, which made an accurate determination of the limiting current difficult. Therefore, a low scan rate (1 mV/s) was selected for the following experiments.



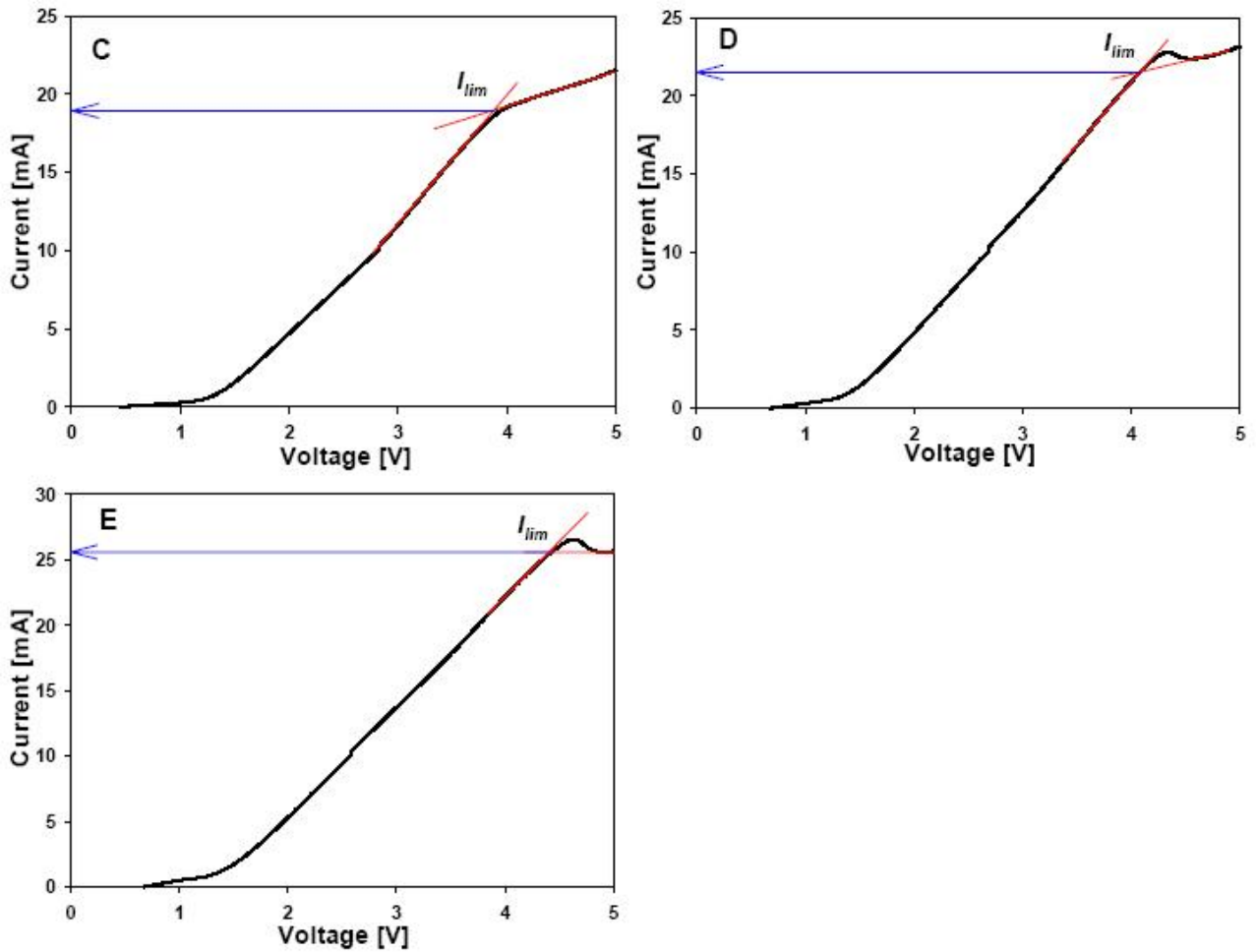


Fig. 3.1. Current vs. voltage curves of the ED experiments at a flow rate of 10 mL/min and the scan rates of (A) 1 mV/s, (B) 2 mV/s, (C) 5 mV/s, (D) 10 mV/s, and (E) 15 mV/s.

For the EDI experiment, the operational conditions were the same as described in section 3.2.5, where the flow rates of all compartments were 9 mL/min. Current was supplied to the electrode plates by DC power, with a stepwise increase of voltage from 0 to 5 V at a rate of 1 mV/s. The limiting current determination is illustrated in Fig. 3.2.

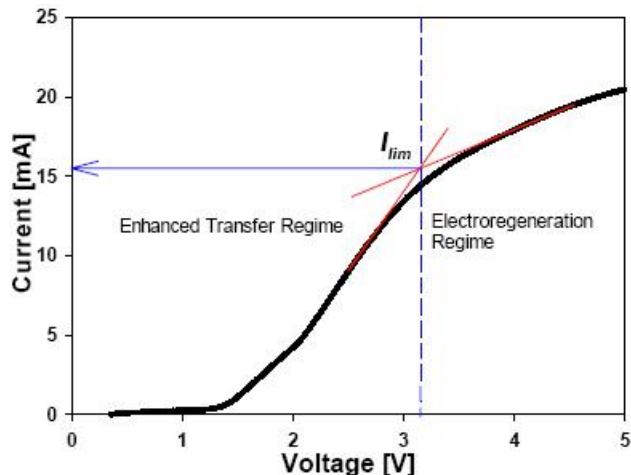


Fig. 3.2. Experimental current vs. voltage curve in the EDI cell illustrating the determination of limiting current at a flow rate of 9 mL/min and a scan rate of 1 mV/s

As can be seen in Fig.3.2, the current was close to zero when the voltage was below 1.3 V. During this period, the applied power primarily contributed to the charging of the ion exchange membranes and electrodes. From 1.3 to 2.1 V, the current increased linearly with the increase of applied voltage according to Ohm's law, and the slope was less than that of the current increase between 2.1 and 2.8 V. In these linear increase regions, the current was not limited and the charged ions were transported from the bulk solution to the resin/solution and membrane/solution interfaces. As the voltage further increased and once the I_{lim} was attained, however, a much smaller increase in current was observed, and the current was limited. This resulted from ions depletion in the layer adjacent to the membrane surface in the dilute compartment due to concentration polarization, as well as the occurrence of water splitting [16]. The I_{lim} could be obtained from the point of intersection of the two tangents crossing in correspondence to the I-V curve, which was determined to be 15.50 mA.

Ion exchange resins are required to be electro-regenerated with the H^+ and OH^- generated by water splitting. Theoretically, higher removal efficiencies are obtained with higher electroregeneration; however, the current efficiency is decreased [30]. Thus, limiting currents of (15.50 mA) and 110% of I_{lim} (17.05 mA) were selected in the following experiments. An experiment with 90% of I_{lim} (13.95 mA) was also conducted to verify whether the decreased electroregeneration caused by current below I_{lim} would reduce the removal efficiencies of the target ions.

3.3.2 Removal efficiencies

The concentrations of NH_4^+-N , $H_xPO_4^{y-}-P$, Ca^{2+} and Mg^{2+} in the dilute compartment of the CEDI cell at different currents over four hours are depicted in Fig. 3.3. The removal efficiencies of the target ions are presented in Fig. 3.4. In general, as anticipated, with higher the applied currents, higher removal efficiencies were achieved, albeit the trends of $H_xPO_4^{y-}-P$ and Ca^{2+} were not as distinct as that of NH_4^+-N and Mg^{2+} . This illustrated that higher removal efficiencies were due to enhanced water splitting when the CEDI cell was charged with a higher current.

Removal efficiency (Re) was used to evaluate the CEDI performance, by using Eq. (3.1).

$$Re (\%) = \frac{C_0 - C_f}{C_0} \times 100 \quad (3.1)$$

Where: C_0 represents the initial concentration and C_f is the final concentration in the dilute compartment.

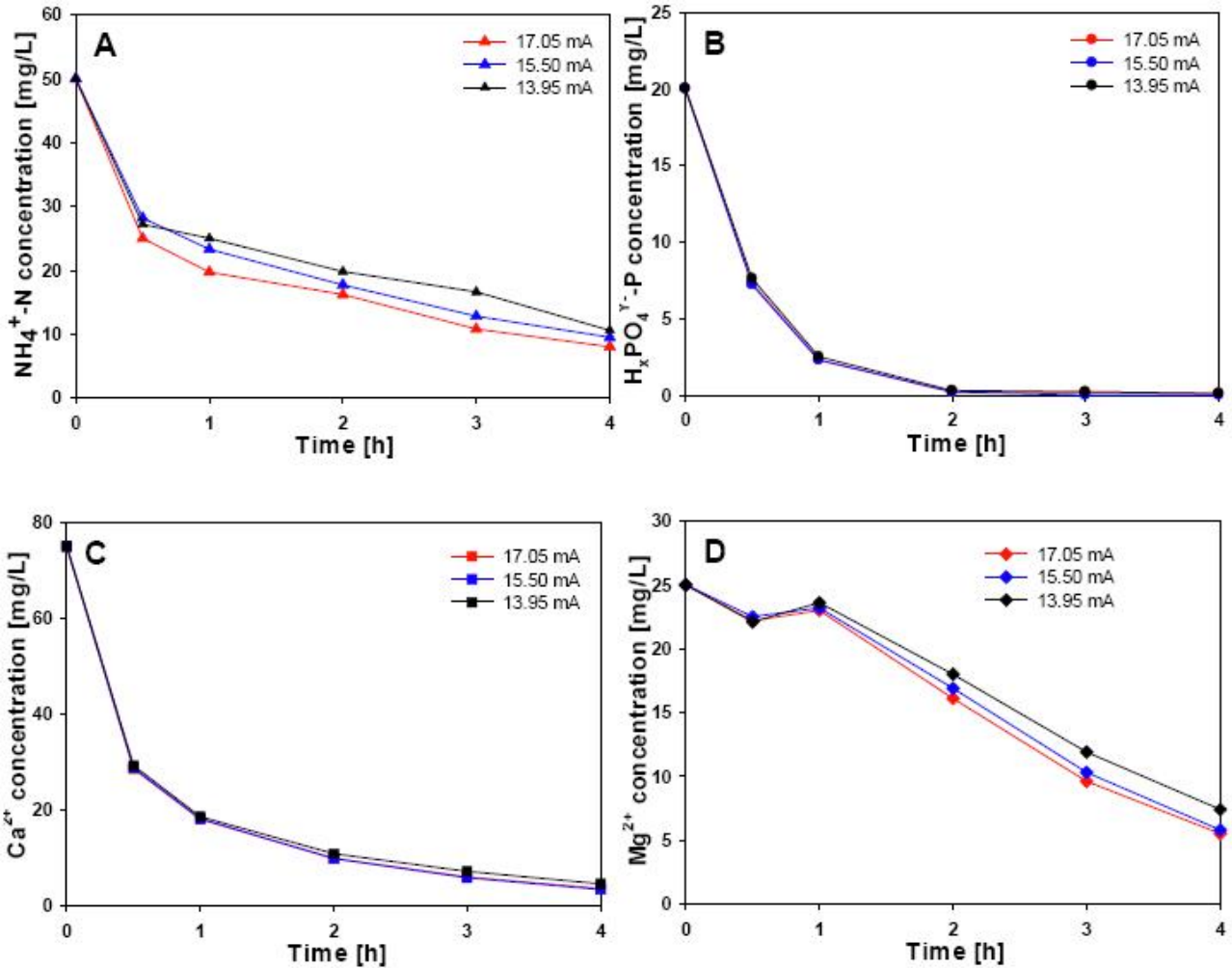


Fig. 3.3. Concentration profile of ions in the dilute compartment of the CEDI cell at 110% of I_{lim} (17.05 mA), I_{lim} (15.50 mA) and 90% of I_{lim} (13.95 mA): (A) $\text{NH}_4^+\text{-N}$, (B) $\text{H}_x\text{PO}_4^{y-}\text{-P}$, (C) Ca^{2+} , (D) Mg^{2+} .

For common strong acid cation exchangers, the selectivity sequence is generally accepted as $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{NH}_4^+ > \text{H}^+$ [31]. The removal efficiencies presented in Fig. 3.4 followed the sequences of $\text{Ca}^{2+} > \text{Mg}^{2+}$ and $\text{Ca}^{2+} > \text{NH}_4^+$; however, the removal efficiency of monovalent NH_4^+ was much higher than that of divalent Mg^{2+} at the beginning the experiment (0 - 2 h). This was likely due to the preferential transport of monovalent NH_4^+ through the CEM under the operation of ED [32,33]. A

possible explanation for the lower removal efficiency of Mg^{2+} rather than Ca^{2+} , may be that the resins had higher affinity for Ca^{2+} and under operation of ED.

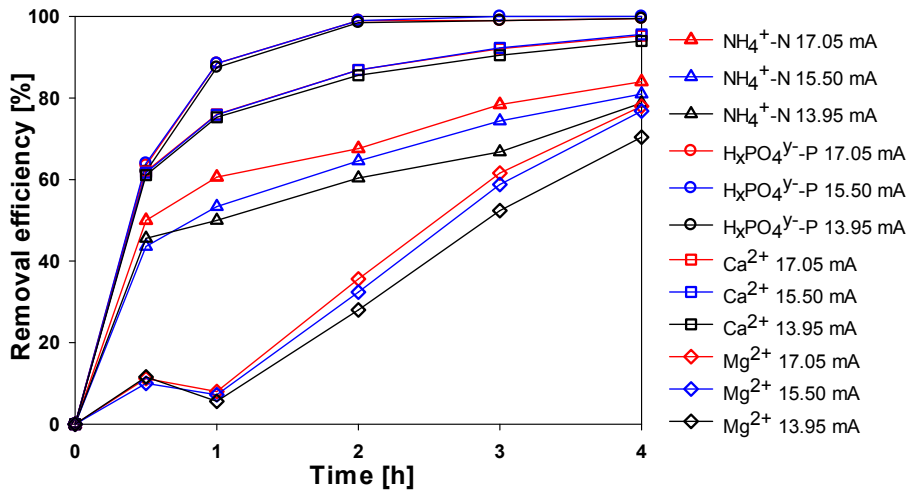


Fig. 3.4. Percent removal of NH_4^+-N , $H_xPO_4^{y-}-P$, Ca^{2+} , and Mg^{2+} in the dilute compartment of the CEDI cell at 110% of I_{lim} (17.05 mA), I_{lim} (15.50 mA) and 90% of I_{lim} (13.95 mA).

A lower removal efficiency of Mg^{2+} rather than Ca^{2+} under operation of ED has also observed [34,35], which might be altered due to the effects of operation conditions, cell design and other types of ions in the solution [36]. As the experiment continued, the removal efficiencies of NH_4^+-N and Mg^{2+} became similar. After 4 h, from 110% I_{lim} to 90% I_{lim} , the removal efficiencies of Ca^{2+} , NH_4^+-N and Mg^{2+} varied from 95.6% to 94.0%, 84.0% to 78.8%, and 78.0% to 70.4%, respectively. More than 98.5% of the phosphate was removed in 2 h and nearly 100% phosphate was removed in 4 h. The high phosphate removal efficiency of Fig. 3.3 indicated the strong potential of the method proposed in this study.

After 3 h, the increased rate of removal efficiencies for ions under the three currents became

diminished, except for Mg^{2+} . Since the removal of Mg^{2+} was not the major objective of this study, 3 h of CEDI operation was recommended for the following energy comparison.

3.3.3 Energy consumption

The voltage curves at 110% of I_{lim} (17.05 mA), I_{lim} (15.50 mA) and 90% of I_{lim} (13.95 mA) were recorded in Fig. 3.5. We can see that the voltage was increased as the input current increased, and the voltage at 110% of I_{lim} (17.05 mA) was much higher than that of I_{lim} (15.50 mA) and 90% of I_{lim} (13.95 mA), which revealed a lower energy efficiency when a current over I_{lim} was applied, in agreement with the discussion in section 3.3.1.

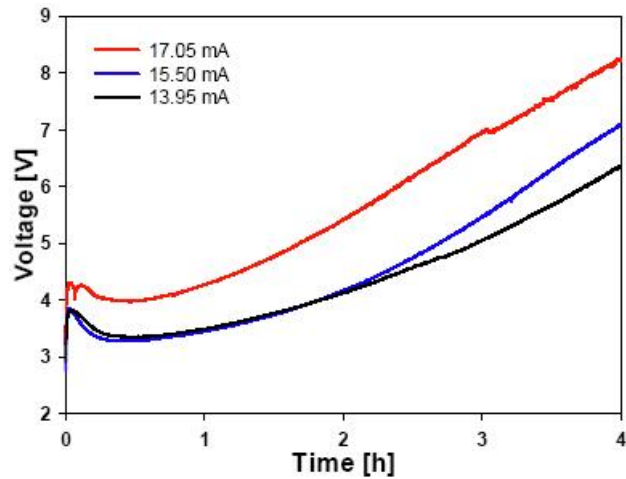


Fig. 3.5. Voltage vs. time at the applied currents of 17.05 mA, 15.50 mA, and 13.95 mA.

The energy consumption of CEDI was evaluated in terms of specific energy consumption (SEC), which was calculated from Eq. (3.2).

$$SEC = \frac{I \int_0^t U dt}{V} \quad (3.2)$$

Where: I is current, U is voltage and V is the volume of the feed water.

The specific energy consumption at currents of 17.05 mA, 15.50 mA, and 13.95 mA over 4 h is depicted in Fig. 3.6. The slopes of three curves were elevated as the operation time was increased, particularly for the curve at 110% of I_{lim} (17.05 mA). The curves at I_{lim} (15.50 mA) and 90% I_{lim} (13.95 mA) were quite close, indicating that CEDI at I_{lim} (15.50 mA) was favorable in terms of energy consumption, as well as removal efficiencies. Higher removal efficiencies were observed at I_{lim} (15.50 mA) rather than at 90% I_{lim} (13.95 mA); hence, it is recommended that CEDI be operated at I_{lim} (15.50 mA).

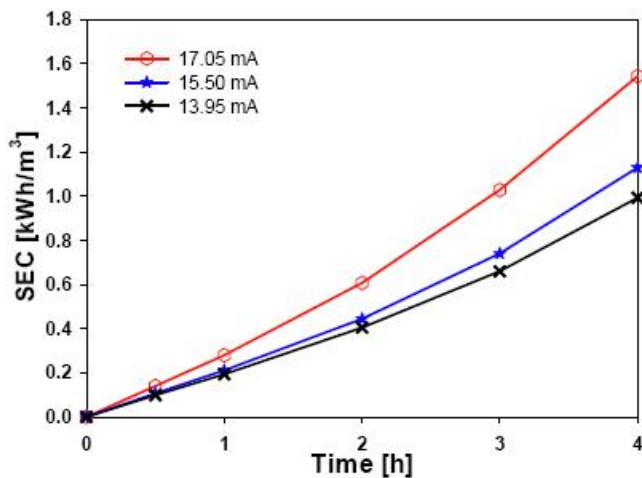


Fig. 3.6. Specific energy consumption vs. time at the applied currents of 17.05 mA, 15.50 mA, and 13.95 mA.

As discussed in section 3.3.2, a three-hour operation duration should be selected. In detail, the specific energy consumption at I_{lim} (15.50 mA) over 3 h was 0.74 kWh/m³ of feed water, which is close to the typical range of energy consumption for pure water production (0.05-0.8 kWh/m³) [19].

3.3.4 pH analysis

Following each experiment, the pH of the solution in each tank of the recirculation line was measured, with the results listed in Table 3.2. We can see that following 4 h of CEDI operation, the pH of the cationic and anionic concentrate compartments were lowered, while the pH in the electrode rinse compartments was increased. The primary reasons for the changes of pH in the solutions might be the combined result of water splitting, which occurred at sites where cationic materials contacted anionic materials in the dilute compartment [37], and the migration of H^+ and OH^- in the EDI cell.

Table 3.2. the pH in the compartments of CEDI at different currents applied over 4 h

pH of the solution	Dilute compartment	Cationic concentrate compartment	Anionic concentrate compartment	Electrode rinse compartments
Initial value	4.96	4.96	4.96	1.07
I = 17.05 mA	4.26	2.03	1.93	1.52
I = 15.50 mA	5.66	2.10	1.98	1.52
I = 13.95 mA	4.02	2.05	1.99	1.59

As illustrated in Scheme 3.1, the rinse solution in the two electrode rinse compartments was circulated in a same close-loop; hence, the H^+ and OH^- produced at anode and cathode would be neutralized. Under the influence of the applied current, the H^+ ions contained in 0.1 M H_2SO_4 (rinse solution) passed through the CEM between electrode rinse compartment and anionic concentrate compartment, and was concentrated in anionic concentrate compartment. As a result, the pH of electrode rinse compartments was increased. Although some of OH^- ions generated from water splitting would pass through the AEM and transfer into anionic concentrate compartment, the results in Table 3.2 reveal that the population of H^+ ions from the electrode rinse compartment exceeded that of OH^- ions from water

splitting thus the pH in the anionic concentrate compartment was decreased. The H⁺ ions resulting from water splitting migrated to the cationic compartment, thus the pH in the cationic concentrate compartment was decreased.

The fluctuation of the pH in the dilute compartment was affected by the equilibrium concentration of the H⁺ and OH⁻ ions in solution. The water dissociation rate at the AEM was larger than that at the CEM [17], while the migration of the H⁺ ions was more rapid than the OH⁻ ions. Therefore, the pH in the dilute compartment might be increased or decreased as the applied current and potential changed at different time intervals. The effect of applied potential, current and characteristics of ion exchange membranes on the fluctuation of pH in dilute compartment will require further investigation.

3.3.5 Experiment repeatability

Since the same EDI cell was previously studied [23] for groundwater treatment, and the repeatability of the EDI cell was well proven, a repeat experiment at I_{lim} (15.50 mA) was conducted to verify the repeatability of the experiments in this study, wherein relative deviation (RD) calculation was used. The results are shown in Table 3.3.

Table 3.3. Relative deviations of tested items in the experiment at 15.50 mA

Time (h)	NH ₄ ⁺ -N	H _x PO ₄ ^{y-} -P	Ca ²⁺	Mg ²⁺
0.5	1.3%	0.7%	0.9%	0.2%
1	2.9%	2.2%	0.8%	0.0%
2	1.7%	0.0%	1.0%	1.8%
3	2.8%	-	1.8%	2.0%
4	2.7%	-	-	1.8%

As discussed in section 3.3.2, the concentrations of $H_xPO_4^{y-}$ -P at 3 h and 4 h were close to zero, which may reach the limits of the measurement method. Any variation from zero would lead the RD to reach as high as 100%, which should not be taken into consideration. This is the same situation for the RD of the Ca^{2+} concentration at 4 h. Hence, these three data are not listed in the table above.

Relative deviations of the items in Table 3.3 were less than 3%. It may thus be concluded that the experiments are repeatable.

3.4 Conclusions

This study investigated the feasibility of using a CEDI system for the simultaneous removal of nutrients (NH_4^+ -N and $H_xPO_4^{y-}$ -P) and hardness ions (Ca^{2+} and Mg^{2+}) from synthetic MWW. An expanded EDI cell was employed to reduce the potential of scaling on ion exchange membranes due to potential precipitation, by separating the cations and anions in different concentrate compartments. On the basis of the results obtained, the CEDI system is recommended to operate at a limiting current of 15.50 mA over 3 h, in terms of the optimization of removal efficiencies and energy consumption. Under this operation condition, efficiencies for the removal of NH_4^+ -N, $H_xPO_4^{y-}$ -P, Ca^{2+} , and Mg^{2+} were 74.4%, 100%, 92.3%, and 58.8%, respectively, and the specific energy consumption was 0.74 kWh/m³ of feed water. The phosphate selective ion exchange resin (Purolite FerrIX™ A33E) exhibited a high removal efficiency in a relative short time for $H_xPO_4^{y-}$ -P, which typically cannot compete with other anions in solution. The results obtained have shown that the CEDI process is very promising for the removal of ionic nutrients and hardness ions from MWW -like wastewater.

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Chapter 4. Freeze concentration for removal of nutrients from synthetic municipal wastewater effluent

4.1 Introduction

Freeze concentration is a physical process in which the impurities in the aqueous solution are rejected from the ice phase during the growth of ice crystals and concentrated in the unfrozen liquid [1]. No chemical and pretreatment are needed for this process and corrosion at low temperature to the treatment facility is attenuated [2]. So far, researches on freeze concentration for wastewater treatment have been reported [3-6].

In the previous studies on the performance of FC, some key parametric factors such as initial impurity concentration [1,5,7-13] and mixing speeds or mixing methods [1,7,9] have been investigated. However, the feed waters that tested in these studies were usually sea water, brackish water or synthetic water with high concentrations of solutes (NaCl and glucose were the two most investigated solutes). Nutrients removal by freeze concentration has also been reported [14-16]. The nutrients concentrations (TN: ~3000-4000 mg/L, TP: ~100-300 mg/L) in these researches were also high as human urine was utilized as feed water. There are few reports on applying FC for the removal of nutrients from effluent with relatively low concentrations, e.g., municipal wastewater treated by anaerobic processes. The objective of this study was to investigate the effectiveness of FC in the removal of nutrients from the wastewater similar to municipal wastewater. Removal efficiencies and concentration ratios of impurities were studied to evaluate the FC performance.

4.2 Materials and methods

4.2.1 Wastewater samples

Synthetic wastewater samples with single compound and multiple compounds were prepared with NH_4Cl , KH_2PO_4 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and glucose to simulate the effluent of anaerobic membrane bioreactors treating municipal wastewater. The glucose was selected to simulate the chemical oxygen demand (COD) in the feed water. KH_2PO_4 (99.0%), $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (99%), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (98%) and $\alpha\text{-D(+)-Glucose}$ (anhydrous), were purchased from Sigma-Aldrich Canada (Oakville, Canada) as analytical grade reagents. NH_4Cl (99.5%) was supplied by ACP (Montreal, Canada). All other chemicals used in the experiments were of reagent grade and used as supplied. Purified water from Thermo Scientific EASYpure II RF (Marietta, United States) was used to prepare the samples.

$\text{H}_x\text{PO}_4^{y-}\text{-P}$ and $\text{NH}_4^+\text{-N}$ were selected to represent the nutrients in the synthetic effluents as organic nitrogen and phosphorous would be mineralized to ammonia and orthophosphate during anaerobic treatment processes [17-19]. COD was selected to simulate the organic impurities in the wastewater. The concentrations ranges of $\text{H}_x\text{PO}_4^{y-}\text{-P}$, $\text{NH}_4^+\text{-N}$ and COD in both single and multiple components feed water were selected according to the effluent quality of anaerobic membrane bioreactors treating municipal wastewater [20,21]. CaCl_2 and MgSO_4 were also added to simulate the inorganic compounds in the effluent of municipal wastewater. The concentrations ranges of Ca^{2+} and Mg^{2+} were determined according to the analysis results of an effluent sample from Thunder Bay Water Pollution Control Plant on June 6, 2015. The details of the wastewater samples prepared are listed in Table 4.1, standard

deviation (SD) is provided for synthetic wastewaters with single impurity and stock solutions were prepared for synthetic wastewaters with multiple impurities.

Table 4.1. Characteristics of synthetic wastewater

Synthetic wastewater with single impurity						
Component	Wastewater 1	Wastewater 2	Wastewater 3	Average pH		
COD ± SD (mg/L)	49.9 ± 0.0	100.5 ± 0.0	151.2 ± 0.0	5.98 ± 0.06		
H _x PO ₄ ^{y-} -P ± SD (mg/L)	4.9 ± 0.1	9.8 ± 0.2	20.2 ± 1.0	5.63 ± 0.14		
NH ₄ ⁺ -N ± SD (mg/L)	10.0 ± 0.0	50.1 ± 0.2	100.7 ± 1.2	5.89 ± 0.11		
Synthetic wastewater with multiple impurities						
	Component concentration					
Wastewater	H_xPO₄^{y-}-P (mg/L)	NH₄⁺-N (mg/L)	COD (mg/L)	Ca²⁺ (mg/L)	Mg²⁺ (mg/L)	pH
A	5.0	10.0	20.0	-	-	5.78
B	5.0	10.0	-	15.0	5.0	5.71
C	20.0	50.0	150.0	-	-	5.55
D	20.0	50.0	-	75.0	25.0	5.41
E	20.0	50.0	150.0	75.0	25.0	5.44

4.2.2 Freezing tests

The freezing apparatus and freezing procedures used by Reynolds (2013) [26] was adopted in the freezing tests. The overall set-up of FC apparatus is depicted in Fig. 4.1. A Thomas Programmable

Ultra-low Refrigerating/Heating circulator (Thomas Scientific, United States) was used to provide power and control the temperature of the freezing bath in which Motomaster Long-life Premixed Antifreeze with a freezing point of $-33.6\text{ }^{\circ}\text{C}$ was filled as a coolant. Two stainless steel beakers (600 mL, diameter: $\sim 85\text{ mm}$) containing feed water were descended into the freezing bath at a constant speed which was controlled by a planetary gearbox. One of the beakers was agitated by an ultrasonic probe. Another beaker was agitated by a mechanical mixer with four horizontal blades. Both ultrasonic probe and mechanical mixer blades were closely maintained above the ice front to reduce the concentration of impurities near the interface of ice/liquid and increase the diffusion from the boundary region through strengthened convective mass transfer [9].

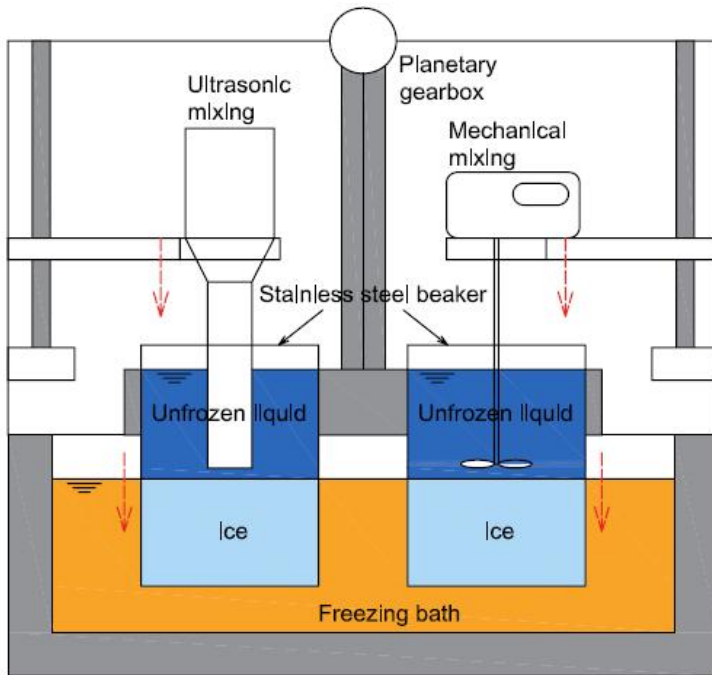


Fig.4.1. Schematic laboratory equipment of progressive freeze concentration with both ultrasonic mixing and mechanical mixing

The temperature of the freezing bath was kept at $-15\text{ }^{\circ}\text{C}$ for all experiments. The two beakers (600 mL) both filled with 400 mL feed water were equally submerged into the freezing bath (from bottom to top) at a controlled velocity along with the vertical rail in the middle of the support panel. As shown in Fig. 4.1, only the portion of the solution in the beaker contacted with the coolant would be frozen to ice. The freezing ratio (ice volume to the initial volume of feed water) was maintained approximately at 80%. It took about 4 to 5 h to achieve a freezing ratio around 80%. No seed ice crystal was introduced in the initial progress of FC in this preliminary study.

Various mixing cycles and speeds were used during FC tests. Mixing cycles for ultrasonic mixing were 1 S/40 S (1 second on/40 second off), 1 S/30 S, and 1 S/20 S with 20% amplitude and mechanical mixing speeds at 100, 200, and 300 RPM were selected. After the experiment, the unfrozen liquid was separated from the ice and the ice was melted at room temperature after the wash step. The effect of different initial impurity concentration in feed water was also examined, as well as the effect of different composition species.

4.2.3 Analytical methods

Original feed water sample, unfrozen liquid and melted ice samples were collected and volumes of the samples were measured using graduated cylinders (250 mL and 100 mL). $\text{H}_x\text{PO}_4^{y-}\text{-P}$ is used to express the possible mixed composition of H_2PO_4^- and HPO_4^{2-} in the solutions. $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, COD and pH in both unfrozen liquid and melted ice were analyzed after each batch of experiment to evaluate the performance of FC. Immediately after the unfrozen liquid was separated from the stainless steel beaker, 10 mL of purified water was injected to wash the surface of ice and area of the beaker contacted with

the unfrozen liquid and then discharged. The small fraction of unfrozen liquid that was washed away was not included in the data analysis. The contamination caused by the residual of unfrozen liquid to the ice sample could be alleviated via the wash step.

The analysis of NH_4^+ -N concentration followed the procedures outlined in the standard method 4500-NH₃ F., (APHA) [27] using a UV-Visible spectrophotometer (Cary 50, Varian, Inc. Australia) with a 4 cm³ quartz cuvette. The concentration of $\text{H}_x\text{PO}_4^{y-}$ -P was monitored using standard method, 4500-P F., (APHA) [27]. The COD was measured using 5220D method as defined in APHA Standard Methods [27] with a HACH DR 2800 spectrophotometer. An Oakton pHTestr[®] 10 pH meter was used to measure the pH of the samples.

4.2.4 Data analysis

Removal efficiency (*Re*) was calculated for the ice samples to show the purification by FC using Eq. (4.1).

$$Re(\%) = \left(1 - \frac{C_i \times V_i}{C_0 \times V_0}\right) \times 100 \quad (4.1)$$

Where: C_0 represents the initial impurity concentration in the feed water and C_i is the impurity concentration in the ice phase. V_i and V_0 is the volume of melted ice and feed water, respectively.

For the unfrozen liquid samples, the impurity concentration was evaluated in forms of concentration ratio C_L/C_0 , where C_L is the impurity concentration in the unfrozen liquid and C_0 is the impurity concentration in the feed water.

Mass balances of the impurities were also checked to assist the data analysis. It was calculated in terms of mass loss, using Eq. (4.2).

$$\text{Mass loss (\%)} = \left(1 - \frac{C_i \times V_i + C_L \times V_L}{C_0 \times V_0}\right) \times 100 \quad (4.2)$$

Where: V_L is the volume of unfrozen liquid.

The experiments in this study lasted 4 -5 h with mixing. Hence the evaporation of the unfrozen liquid may have influence on the results of impurities concentration ratios. Moreover, a small fraction of unfrozen liquid was attached to the ice surface and inner surface of beakers which was then washed away with purified water. This fraction of unfrozen liquid might contain small amount of impurities and was not included in the data analysis, which might also lead to a mass loss of impurities. Other sources such as the error of analytical methods may cause the deviation of the data as well.

Analysis of variance (ANOVA) was carried out to determine whether there was a significant difference between the tested factors discussed in section 4.3. The difference was considered statistically significant at a 95% confidence interval ($p < 0.05$). SigmaPlot 12.0 (Systat Software, Inc., 2011) was used for statistical analysis.

4.3 Results and discussion

4.3.1 Single impurity removal

4.3.1.1 Removal efficiencies

The removal efficiency of COD, $\text{H}_x\text{PO}_4^{y-}$ -P and NH_4^+ -N at the tested ultrasonic mixing circles and

mechanical mixing speeds are depicted in Fig. 4.2. As shown in Fig. 4.2, average removal efficiencies of 100% and 99.9% were achieved for COD and $H_xPO_4^{y-}$ -P. The average removal efficiency of NH_4^+ -N was 96.5%. There were no statistical differences with mixing methods or speeds. The initial feed water impurities concentrations did not influence removal efficiencies either.

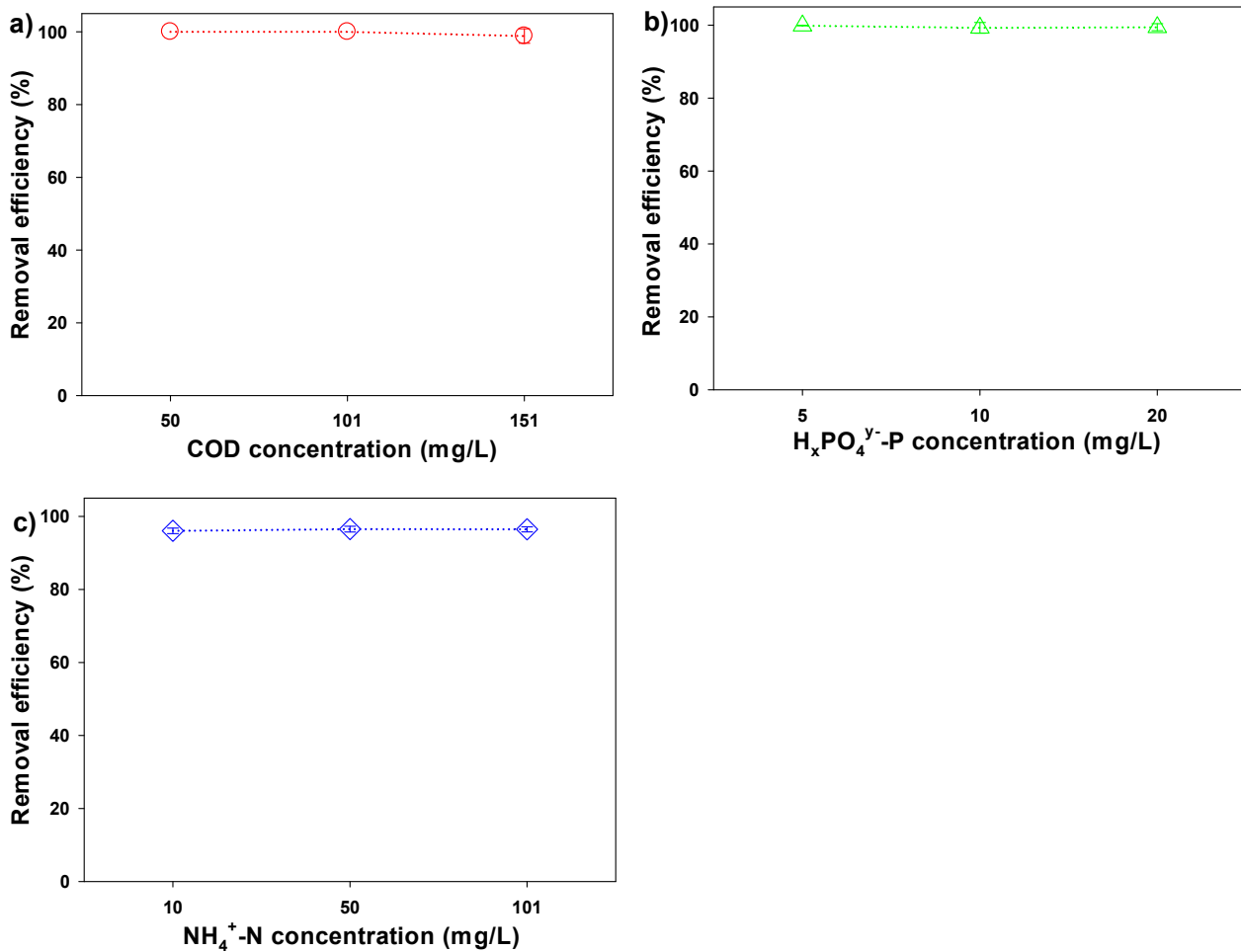


Fig. 4.2. The average removal efficiency of COD a), $H_xPO_4^{y-}$ -P b), and NH_4^+ -N c) in the ice samples

4.3.1.2 Concentrations of impurities in the unfrozen liquid

Fig. 4.3 demonstrates COD causing material, $H_xPO_4^{y-}$ -P and NH_4^+ -N ions concentrated in the unfrozen

liquid versus various initial feed water impurity concentrations. The mean concentration ratios of COD, $H_xPO_4^{y-}$ -P and NH_4^+ -N were 5.94, 5.21 and 4.61, respectively. Initial impurity concentration, mixing methods and speeds (both for mechanical and ultrasonic) did not affect the amount of COD, $H_xPO_4^{y-}$ -P and NH_4^+ -N concentrated in the unfrozen liquid.

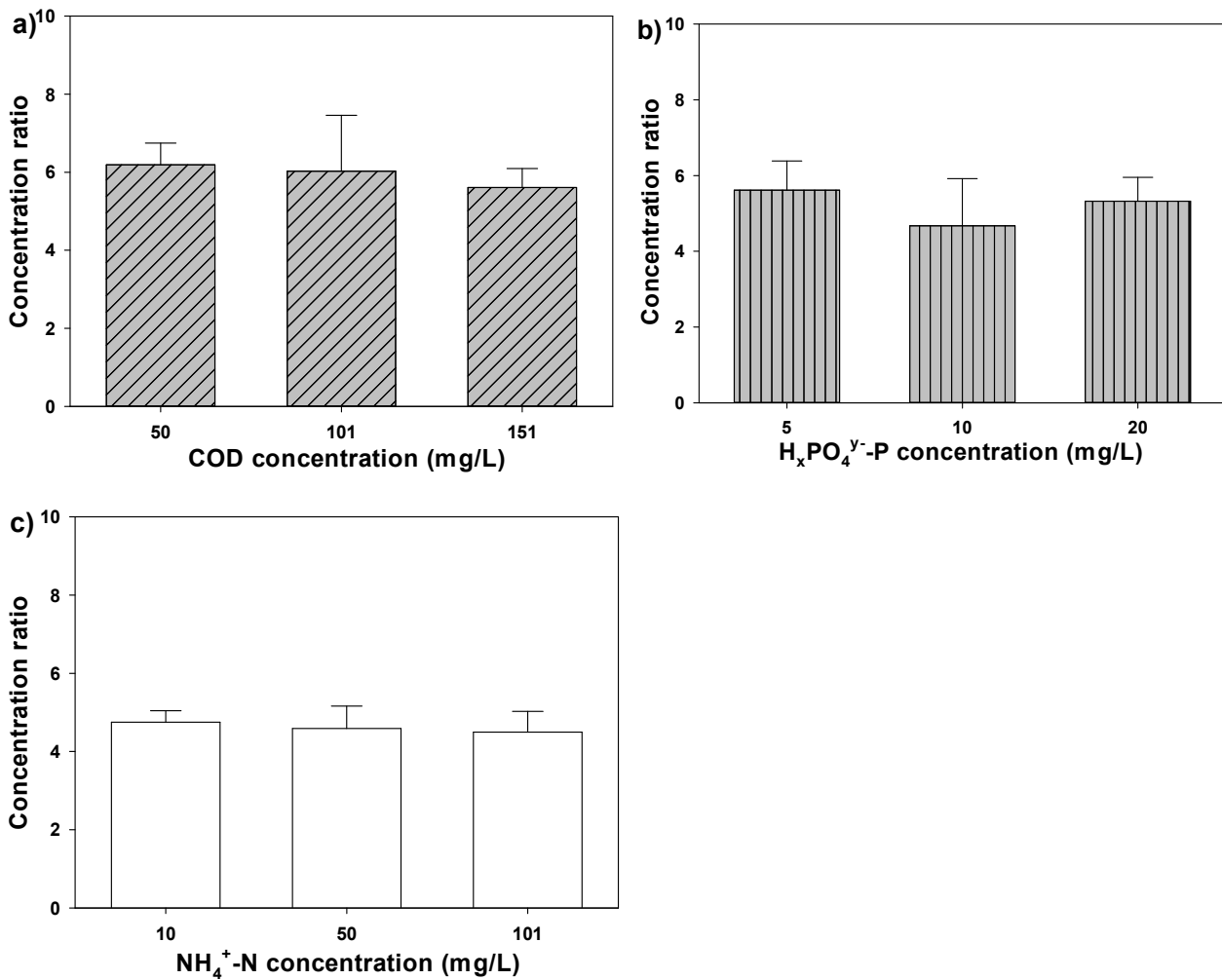


Fig. 4.3. The average concentration ratio of COD a), $H_xPO_4^{y-}$ -P b) and NH_4^+ -N c) obtained under various initial feed water concentrations

The comparisons of the concentrated ratios achieved for COD, $H_xPO_4^{y-}$ -P and NH_4^+ -N in the unfrozen

liquid are illustrated in Fig. 4.4. The highest concentration ratio was achieved for COD causing materials, followed by $H_xPO_4^{y-}$ -P, and the lowest for NH_4^+ -N. This sequence of the concentration ratios of the three impurities was similar to that of the removal efficiencies.

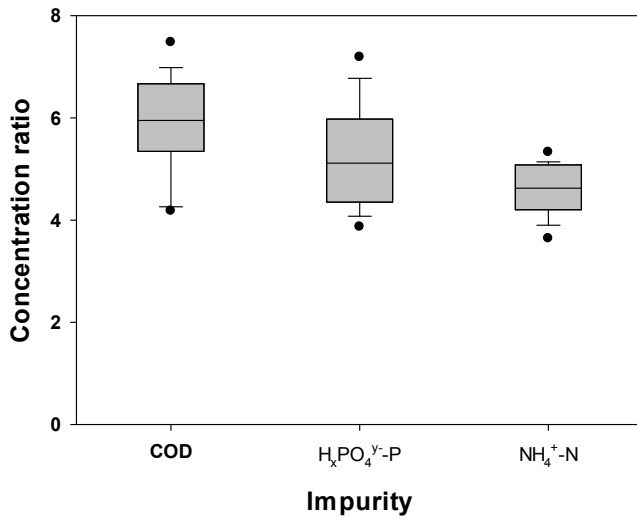


Fig. 4.4. Comparisons of the concentration ratios of COD, $H_xPO_4^{y-}$ -P and NH_4^+ -N

The average mass loss of COD, $H_xPO_4^{y-}$ -P and NH_4^+ -N was 3.0%, 1.6% and 8.7%, respectively. Compared with the mass loss of COD and $H_xPO_4^{y-}$ -P, the higher value of NH_4^+ -N might be caused by additional dilution of the unfrozen liquid samples to fit the measurement limit (0 - 0.6 mg/L) of the employed analytical method (4500-NH₃ F., (APHA)) in this study.

For the three tested single impurities, initial impurity concentration in feed water, mixing methods and speeds were not significant factors both in terms of removal efficiencies and amount of impurities concentrated in the unfrozen liquid during freezing. The possible reasons for the lower removal efficiency and concentration ratios of NH_4^+ -N observed might be the smaller molecular weight of NH_4^+ than those of the COD causing glucose and $H_xPO_4^{y-}$, as solutes of large molecular weight are more

easily separated and concentrated than those of small molecular weight [22], as well as its different chemical characteristics such as molecular structure, size and charge with COD causing glucose and $H_xPO_4^{y-}$ [8,12,13,23], which is further discussed in the following section 4.3.2.1.

4.3.2 Combined impurities removal

4.3.2.1 Removal efficiency

(1) Sample A vs. C

As shown in Fig. 4.5, the average removal efficiencies obtained for $H_xPO_4^{y-}$ -P (99.9%), NH_4^+ -N (96.2%) and COD (100%) in sample A was higher than those in sample C (98.8%, 95.5%, and 98.4%, respectively). The removal efficiencies of $H_xPO_4^{y-}$ -P and COD were significantly affected as the initial impurities concentrations increased ($P = 0.02$ and 0.03 , respectively), whereas the removal efficiency of NH_4^+ -N between sample A and C was not significantly different ($P = 0.22$). At higher concentrations, there were more solutes in the solution. Therefore more chances for them to be caught in the ice structure. Compared with the samples with single impurity, the average removal efficiencies of $H_xPO_4^{y-}$ -P, NH_4^+ -N and COD in sample C were decreased from 99.9% to 98.8%, 96.5% to 95.5%, 100% to 98.4%, respectively, revealing that the addition of other species of impurities also had influence on the removal of each impurity. An increase of initial impurities concentrations in feed water led to a decrease of removal efficiency of each solute were also reported in the researches [12,23,28]. The possible reason for the elevated solutes entrapped in the ice might be due to the change of the dendritic ice structure affected by the change in the viscosity with the addition of the solutes [8].

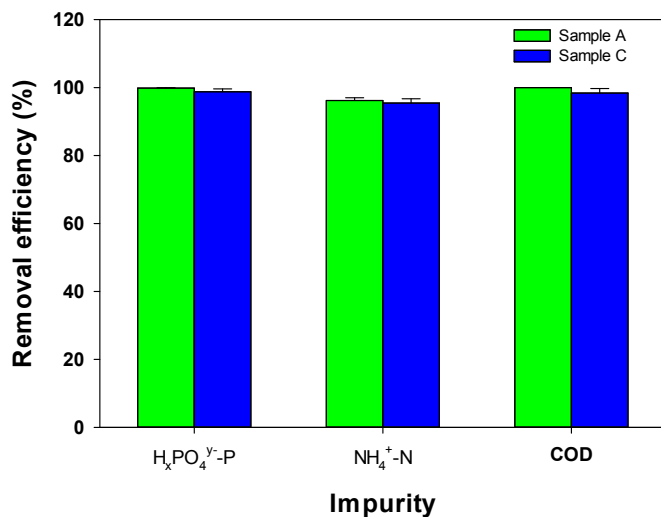


Fig. 4.5. Removal efficiencies of $H_xPO_4^y-P$, NH_4^+-N and COD in sample A and C

(2) Sample B vs. D

As shown in Fig. 4.6, the average removal efficiency of $H_xPO_4^y-P$ was 99.5% for sample B, which was significantly higher than that of 92.7% for sample D ($P = 0.04$), while the average removal efficiency of NH_4^+-N was 95.6% for sample B, which was not significantly higher than that of 92.5% for sample D ($P = 0.08$). A greater decrease of the removal of the two impurities in the sample B and D with the addition of inorganic Ca^{2+} and Mg^{2+} was observed than those in the sample A and C with the addition of organic COD causing glucose. The different extents of decrease in impurity removal efficiency with an increase with different types of impurities and initial concentrations in feed water might be explained in terms of the osmotic pressure of the total system, and the viscosity of the solution when the change in the osmotic pressure was limited, which were considered as the primary determinants of solute removal efficiency and were affected by the coexisting impurities [28]. The chemical characteristics between the coexisting impurities of inorganic Ca^{2+} and Mg^{2+} and organic COD causing

glucose, e.g., molecular structure, size and charge, as well as different concentrations of impurities, might have different influences on the ice-liquid interface structure through the changes in osmotic pressure and viscosity, hence, the impurity removal was differently affected [8,12, 13,23].

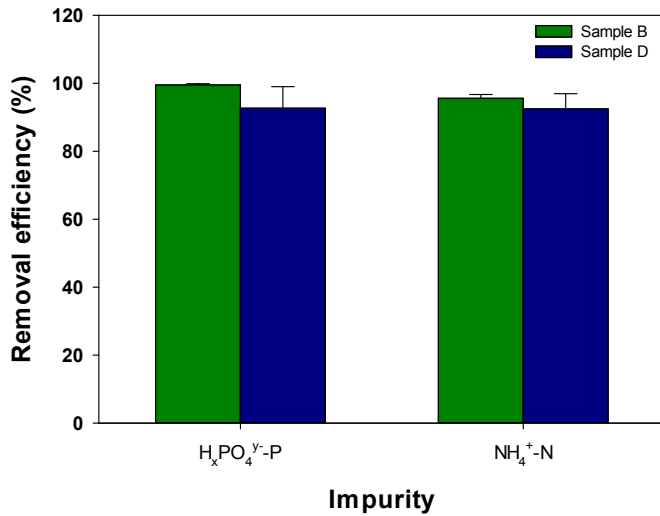


Fig. 4.6. Removal efficiencies of $H_xPO_4^{y-}P$ and NH_4^+-N in sample B and D

(3) Sample E vs. A, B, C and D

The comparison of sample E versus sample A, B, C and D is presented in Fig. 4.7. The average removal levels of $H_xPO_4^{y-}P$, NH_4^+-N and COD in sample E with the most species of impurities at high concentrations were further decreased to 90.6%, 90.2% and 88.2%, respectively. The COD removal efficiency was close to the reported total organic carbon (TOC) removal efficiency of 88.3%, which was investigated with urban wastewater containing 270 mg/L TOC at a freezing ratio of 64% [4].

The results again demonstrated the trend that the removal efficiency of each impurity was decreased as the initial impurities concentrations (both in terms of each impurity concentration and species of

impurities) increased. However, in single impurity system, as discussed in section 4.3.1.1, the initial feed water impurity concentration was not a significant factor on removal efficiency. The reason might be that the change of osmotic pressure and viscosity caused by the increase of single impurity concentration in the tested range were not significantly different.

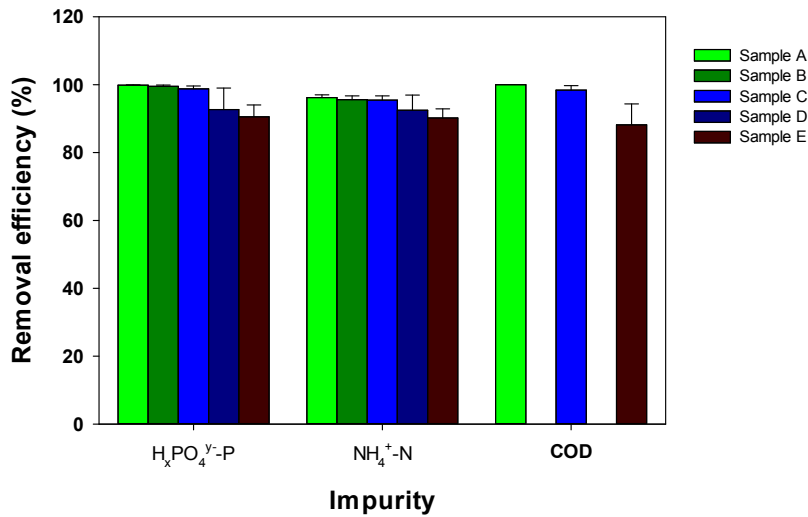


Fig. 4.7. Removal efficiencies of $H_xPO_4^y-P$, NH_4^+-N and COD in sample A, B, C, D and E

4.3.2.2 Concentrations of impurities in the unfrozen liquid

(1) Sample A vs. C

The averaged concentration ratios of $H_xPO_4^y-P$, NH_4^+-N and COD in sample A and C are depicted in Fig. 4.8, which were in the range of 4.51 - 5.35. The concentration ratios in sample C with higher impurities concentrations were lower than those in sample A, similar to the trend of removal efficiencies of the three impurities in sample A and C.

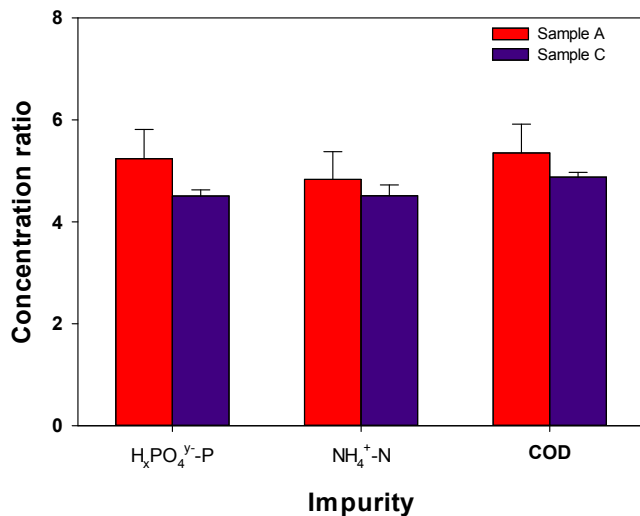


Fig. 4.8. Concentration ratios of $H_xPO_4^{y-}-P$, NH_4^+-N and COD in sample A and C

(2) Sample B vs. D

The level of concentration ratios of $H_xPO_4^{y-}-P$ and NH_4^+-N in sample B and D with the addition of inorganic Ca^{2+} and Mg^{2+} in Fig. 4.9 was similar to that in Fig. 4.8. The results were slightly lower than those in sample A and C with the addition of organic COD causing glucose. The levels in Fig.4.9 ranged from 4.25 to 4.93 and the concentration ratios in sample D with increased impurities concentrations were also significantly lower than the values in sample B ($H_xPO_4^{y-}-P$: $P = 0.003$, NH_4^+-N : $P = 0.008$).

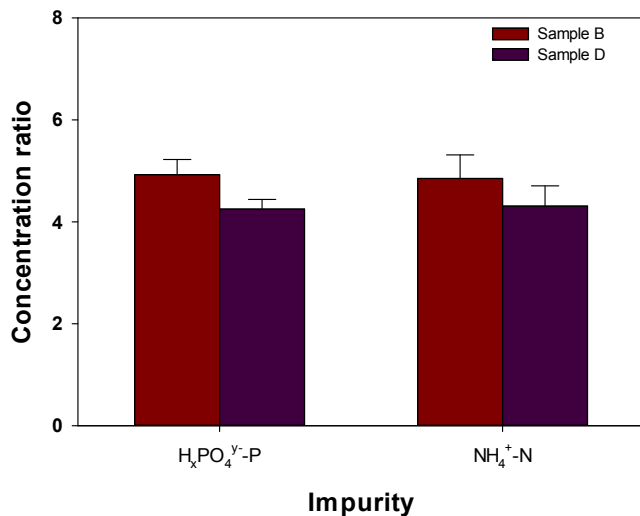


Fig. 4.9. Concentration ratios of $H_xPO_4^{y-}P$ and NH_4^+-N in sample B and D

(3) Sample E vs. A, B, C and D

Similar to the scenario of removal efficiencies in Fig. 4.7, an obvious reduction of concentration ratios of $H_xPO_4^{y-}P$, NH_4^+-N and COD in sample E with the highest initial concentration were observed in the comparison with sample A, B, C and D, which is shown in Fig. 4.10. Specifically, the average concentration ratio of $H_xPO_4^{y-}P$, NH_4^+-N and COD in sample E was 3.85, 4.17 and 4.55, respectively.

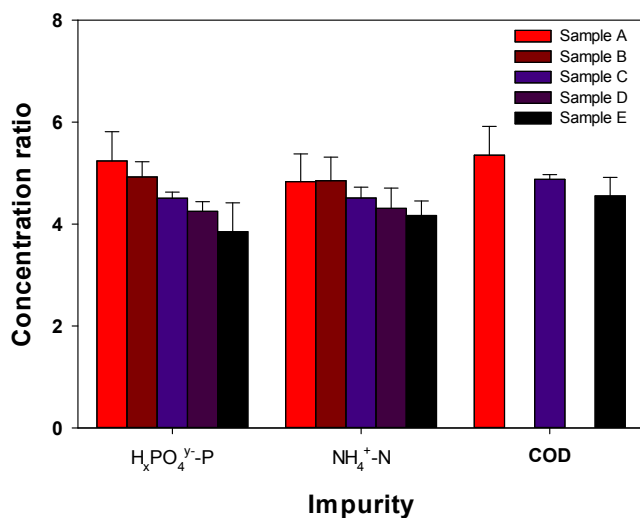


Fig. 4.10. Concentration ratios of $H_xPO_4^{y-}P$, NH_4^+-N and COD in sample A, B, C, D and E

On the basis of the above analysis, it could be concluded that initial impurities concentrations played an important role in the removal efficiencies and concentration ratios which were decreased with higher initial impurities concentrations for multiple impurities system, whereas the initial impurity concentration was not a significant factor on removal efficiencies and concentration ratios in single impurity system. On the other hand, both mixing methods and speeds did not greatly affect the removal efficiencies and concentration ratios for the freeze concentration of multiple impurities, which was similar to the tests with single impurity.

The comparisons of mass loss of $H_xPO_4^{y-}$ -P, NH_4^+ -N and COD in multiple impurities system were also investigated, which are shown in Fig. 4.11. Extreme value and outlier were found for the mass loss of $H_xPO_4^{y-}$ -P, which were not the case for the mass losses of COD and NH_4^+ -N, suggesting that the low mean value of $H_xPO_4^{y-}$ -P concentration ratio might be caused by other factors not considered in section 4.2.4. Software Visual MINTEQ 3.0 (Jon Petter Gustafsson, Sweden, 2012) was then used with estimated concentration ratios of other ions to predict the possible reactions in the unfrozen liquid. The results showed that partial precipitations of $Ca_5(PO_4)_3(OH)$, $CaHPO_4$, $CaHPO_4 \cdot 2H_2O$ might occur for the high concentration sample E when the unfrozen liquid was not completely mixed (ultrasonic mixing cycle of 1 s on 40 s off and mechanical mixing speed of 100 RPM). This might be reason for the unusually low mean value of $H_xPO_4^{y-}$ -P concentration ratio with feed water containing high concentrations of $H_xPO_4^{y-}$ -P and Ca^{2+} .

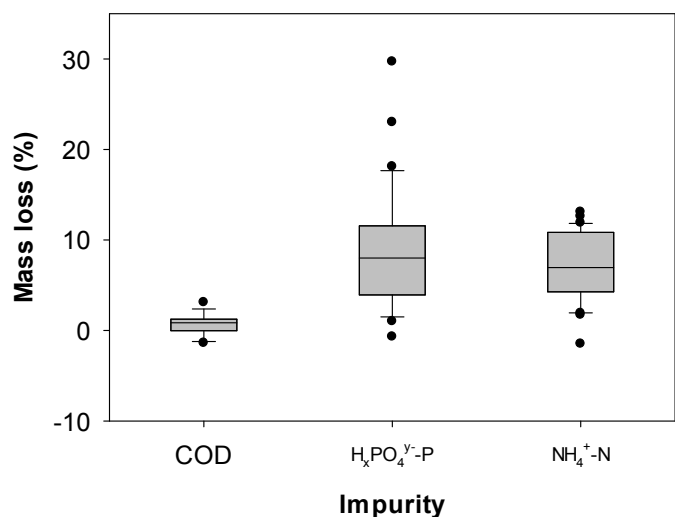


Fig. 4.11. The mass loss of COD, H_xPO₄^{y-}-P and NH₄⁺-N in experiments with multi-component

The pH values of the feed water, the unfrozen liquid and melted ice at different operation conditions were also measured. In general, the average pH value of the unfrozen liquid (single impurity tests: pH = 5.37, multiple impurities tests: pH = 5.13) was slightly lower than that of the melted ice (single impurity tests: pH = 5.95, multiple impurities tests: pH = 5.93). The changes in pH after freezing revealed an imbalance between anion and cation partition to ice which was summarized in [24,25]. The changes in pH is caused by the preferential incorporation of cations/anions over anions/cations to the H⁺/OH⁻ in the ice crystal, e.g., a pH decrease of liquid phase might be caused by the preferential incorporation of NH₄⁺ in the ice phase over Cl⁻, which was dependent on the salt concentration, types of ions, freezing rates, etc. [2, 24,25].

4.4 Conclusions

The experimental results obtained in this study indicated that the FC was efficient to

remove/concentrate the nutrients from synthetic wastewater with components similar to municipal wastewater. High removal efficiencies of COD, $H_xPO_4^{y-}$ -P, and NH_4^+ -N in the feed water with single impurity were 100%, 99.9% and 96.5%, respectively. Furthermore, experiments on single impurities facilitated a better comprehension of FC treatment. Initial impurity concentration, mixing methods and speeds were not significant effects on removal efficiencies and concentration ratios of impurities for the tests with single impurity.

Experiments with five combinations of impurities were also conducted to further study the effects on ultrasonic mixing cycles and mechanical mixing speeds as well as initial impurities concentrations on FC performance. Both mixing methods and speeds had no significant effects on the removal efficiencies of impurities. The removal efficiencies and concentration ratios in the experiments on combined impurities decreased as the concentration of feed water increased both in terms of component concentration and species of solutes. The addition of inorganic Ca^{2+} and Mg^{2+} with the tested concentrations had greater reduction on removal efficiencies and concentration ratios than the addition of organic COD causing glucose. For the sample E with the highest concentration, the average removal efficiency of $H_xPO_4^{y-}$ -P, NH_4^+ -N and COD was 90.6%, 90.2% and 88.2%, respectively. Meanwhile, the concentration ratios of $H_xPO_4^{y-}$ -P, NH_4^+ -N and COD ranged between 3.85 and 4.55. Thus the non-selective FC technique could be considered as a potential alternative for the simultaneous removal of inorganic nutrients and organic impurities from municipal effluent treated by anaerobic membrane bioreactor process without pretreatment and chemical addition.

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Chapter 5. Freeze concentration and electro dialysis for removal of nutrients from synthetic municipal wastewater

5.1 Introduction

In Canada, the temperatures are typically very low during the long winters. This enormous natural cold energy resource might be utilized by freeze concentration for the separation of dissolved solutes from wastewater with the dual benefits of cost saving and lower energy inputs [1,2]. During the freeze concentration process most of the impurities, both soluble organic and inorganic substances, would be rejected from the small dimensions of the ice crystal lattice and concentrated in the unfrozen liquid; thus purified water may be obtained from the ice crystals [3]. No chemicals are required and inexpensive materials may be used for the system with little maintenance, as corrosion is alleviated at low temperatures [4,5]. Therefore, in this study, freeze concentration was proposed as a potential option for the recovery of nutrients from municipal wastewater (MWW) treated by an anaerobic membrane bioreactor (AnMBR). The results of our previous studies showed that high removal efficiencies were achievable for the treated MWW, via one stage freeze concentration. Should higher overall removal efficiencies be required, multi-stage freeze concentration may be considered [6-8]. However, the removal efficiency might be decreased by the increased concentrations of other coexisting inorganic salts in the wastewater [9]. Further steps are required when the salts concentrations in the wastewater are high.

As a mature technology for desalination of brackish water, seawater, and wastewater, electro dialysis

(ED) has been developed and used at industrial scales since 1950s [10], and the high performance of ED in desalination has been widely proven. It comprises a membrane separation process that is based on the forced transport of ionic species through ion selective membranes via the application of an electrical potential difference. The cation exchange membrane (CEM) is only permeable for cations, whereas the anion exchange membrane (AEM) is only permeable for anions. As a result, the ions in the dilute compartment pass through the ion exchange membranes and are transferred to the concentrate compartment, as depicted in the example of Scheme 5.1 [11].

This strategy may provide a suitable solution to address the requirements of high water recovery ratios and small concentrated solution volumes, which is beneficial toward the reduction of wastewater discharges [12]. However, the cost-effectiveness of ED in water desalination is limited to a certain range of ion concentrations in feed water and the requirements of the water product quality, otherwise the investment cost and energy consumption might be very high [12]. More specifically, Mahmoud and Hoadley (2012) pointed out that feed water with low salt concentrations should not be directly treated with ED [13]. Although the feasibility of using electro dialysis reversal (EDR) for direct desalination with raw wastewater [14] and treated MWW [15] have been tested, it is noteworthy that the conductivities or total dissolved solids (TDS) in the two studies were much higher than the values in this study. As an example of conductivities, the averaged value was 3860 $\mu\text{S}/\text{cm}$ [14] and 1924 $\mu\text{S}/\text{cm}$ [15]. It is challenging to modify the ED process for the treatment of wastewater with low salts content, such as the treated MWW in this study.

To overcome the problems of freeze concentration and ED when they are applied on their own, a novel

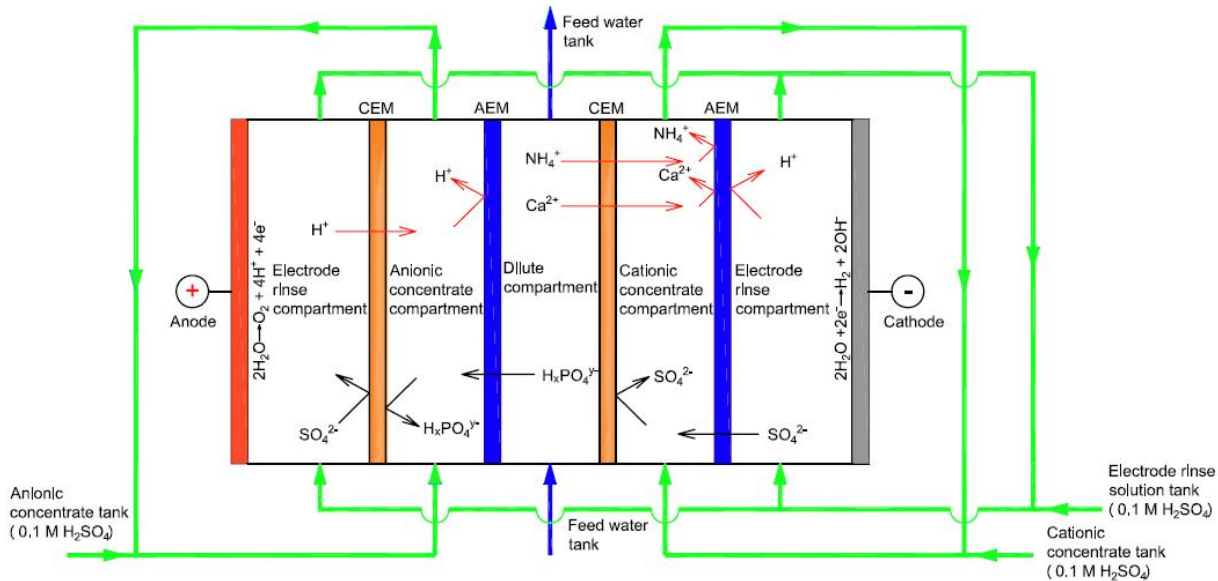
approach was proposed, based on the systematic combinations of these two techniques. We suggested two possible combinations, including the utilization of the freeze concentration as a pre-concentrated process to enhance the performance of ED for treated MWW, and the use of ED for desalination in order to increase the removal efficiency of the freeze concentration. The first combination was studied in this paper. Pre-concentration by freeze concentration might increase the concentration of ionic species in the unfrozen liquid, which was treated by ED, as the feed water; hence, the performance of ED could be improved due to the greatly increased conductivity of the feed water.

In comparison to seawater, brackish water is much more dilute. The feasibility and cost-effectiveness of ED with brackish water having TDS of less than 5000 mg/L was proven [12]. The TDS of freezing concentrated MWW might be controlled in this range via the adjustment of different freezing ratios. Thus, it is theoretically feasible for ED to treat the freezing concentrated MWW. More importantly, freeze concentration significantly reduces the volume of feed water. Taking 80% of the freezing ratio as an example, the volume of the unfrozen liquid is merely 20% of the initial volume. The reduction of the feed water volume, on the other hand, would lower the overall cost and energy input of the ED process. The less volume and higher conductivity of unfrozen liquid might be achieved at a higher freezing ratio. The objective of this paper is to demonstrate the feasibility of the first combination with synthetic MWW. The effects of applied currents on the removal efficiency and energy consumption were examined. The direct feeding of ED with synthetic MWW (namely solution without the preconcentration by freeze concentration), was also conducted to compare the results.

5.2 Experimental

5.2.1 Materials and chemicals

The ion exchange resins of an expanded laboratory electrodeionization (EDI) cell, which were investigated in a previous study [16] were removed, thus an expanded ED cell was formed and studied in this paper. Hence, the materials and dimensions of the ED cell were the same as the EDI cell [16]. Two cation exchange membranes (CMI-7000S) and two anion exchange membranes (AMI-7001S) from Membranes International Inc. were installed. The effective surface area of each membrane was 60 cm² (6 cm x 10 cm). A stainless steel plate (6 cm x 10 cm) was utilized as the cathode, whereas the anode (Ti/Ta₂O₅-IrO₂, 6 cm x 10 cm) was fabricated by our group using an established method published previously [17]. The thicknesses of the dilute compartment, concentrate compartments, and electrode rinse compartments were 10 mm, 10 mm, and 15 mm, respectively. A Voltalab (PGZ 402 Universal Potentiostat) DC was used to provide power to the two electrodes. The configuration of the expanded ED cell is illustrated in Scheme 5.1.



Scheme 5.1. Configuration of the expanded ED cell

The feed water was synthesized using NH_4Cl , KH_2PO_4 , $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and glucose. The NH_4Cl was purchased from ACP, whereas the KH_2PO_4 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ were supplied by Sigma-Aldrich as analytical grade reagents. Anhydrous $\alpha\text{-D}(+)\text{-Glucose}$ was also provided by Sigma-Aldrich. All other chemicals used in the experiment were of reagent grade and used as supplied. Distilled water was employed to prepare the feed water.

A stock solution of feed water was prepared on the basis of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and COD concentrations in the unfrozen liquid of the freeze concentration experiments at an 80% freezing ratio. The Ca^{2+} concentrations in the feed water were roughly estimated due to the lack of analysis results. Following analysis, the concentrations of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, Ca^{2+} , and COD in the feed water are shown in Table 5.1. To ensure that glucose was not naturally decomposed during the storage period, it was introduced to the feed water and completely dissolved just prior to the start of each ED experiment.

The pH of the synthetic feed water was 4.86 and no additional adjustment to the pH was made. The primary rationale for the use of $H_xPO_4^{y-}$ -P in the expression of P was that phosphate ions in this pH range had a mixture of $H_2PO_4^-$ (dominant species) and HPO_4^{2-} , as well as that the pH of the feed water might be decreased by the ED operation, which is indicated in section 5.3.4.

Table 5.1. Main components in the feed water simulating the unfrozen liquid of freeze concentration experiments at an 80% freezing ratio for the treated MWW

Main components	Concentration (mg/L)
NH_4^+ -N	220.0
$H_xPO_4^{y-}$ -P	87.0
Ca^{2+}	260.0
COD	710.0

5.2.2 Sampling and solution analysis

To evaluate the performance of the ED system, the samples were collected periodically from the dilute tank of the recirculation line for the analysis of NH_4^+ -N, $H_xPO_4^{y-}$ -P, and Ca^{2+} . After each experiment, the pH and COD of each circuit were monitored.

An analysis of the NH_4^+ -N concentration in solution was performed by the standard Phenate method (APHA 1999) using a UV-Visible spectrophotometer (Cary 50) with a 4 cm³ quartz cuvette. The concentrations of Ca^{2+} and P were monitored using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) (Varian Vista Pro). The COD was measured as defined in Standard Methods (APHA, 1999) with a HACH DR 2800 spectrophotometer. A VWR[®] SympHony[™] SB20 pH meter was used to measure the pH of the solutions. The current vs. voltage curve and voltage vs. time curve were

recorded using a Voltalab (PGZ 402 Universal Potentiostat).

5.2.3 ED operation

Synthetic wastewater (250 mL), which simulated the solution preconcentrated by freeze concentration for the treated MWW was circulated through the dilute compartment. A 250 mL volume of 0.1 M H₂SO₄ was circulated through the cationic and anionic concentrate compartment separately, with the purpose of increasing the conductivity of the ED cell and lowering the pH of the concentrate solutions to prevent possible precipitation caused by Ca²⁺. A 250 mL volume of 0.1 M H₂SO₄ was also circulated as an electrode rinse solution through the two electrode rinse compartments in all experiments. All four separate circuits were fed by peristaltic pumps with the same constant flow rate (9 mL/min).

The ED system was operated in batch mode. To ensure that no precipitation would be accumulated on the membranes after each experiment, 0.1 M HCl was circulated through the dilute and concentrate compartments as a cleaning solution, followed by distilled water, to remove any residuals in the compartments.

5.3 Results and discussion

5.3.1 Determination of limiting current

In the ED process, differences in the population of transported ions in the solution and via the membranes resulted in the occurrence of concentration polarization at the membrane surfaces [12]. For the ion exchange membranes in the dilute compartment side, a depletion of ions occurred due to the concentration polarization effect. When the ion concentration in the boundary layers at the membrane

surface with the depleted solution approaches zero, the current will attain maximum value in the process, which is defined as the limiting current (I_{lim}) [18]. In this study, the current-voltage (I-V) curve method was investigated for the determination of the limiting current.

The operation conditions for the determination of I_{lim} in the ED cell was the same as described in section 5.2.3. A Voltalab (PGZ 402 Universal Potentiostat) was used to provide current to charge the electrode plates, with increments of 1 mV/s in the range of 0 to 5 V. The determination of I_{lim} is shown in Fig. 5.1.

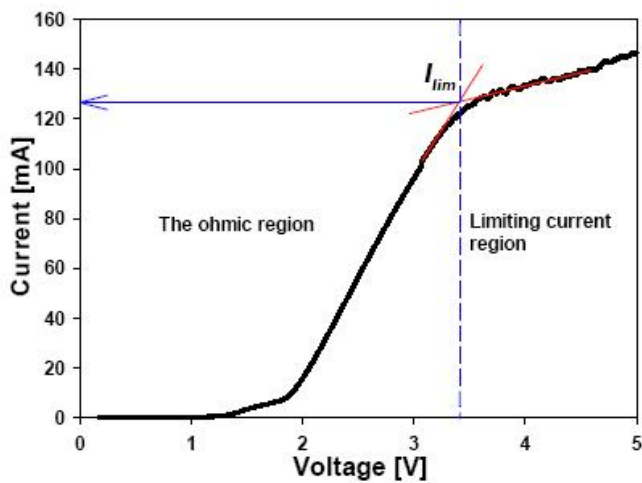


Fig. 5.1. Determination of the limiting current with current-voltage curve of the expanded ED cell at a flow rate of 9 mL/min and a scan rate of 1 mV/s

As shown in Fig.5.1, at the beginning of ED, when the voltage was increased from 0 to 1.3 V, the current observed was close to zero, indicating that the ion exchange membranes and electrodes were charged with the supplied power during this period. The ohmic region (1.3 - 3.4 V) was governed by Ohm's law for the electrolyte and membrane resistance, the current increased linearly with the voltage.

When I_{lim} point was attained (3.4 - 5V, limiting current region), any further increase in the applied voltage led to a small increase in the current, indicating a drastic increase of the cell resistance, which was primarily due to the concentration polarization.

Meanwhile, the water splitting process began. Therefore, the determination of I_{lim} is important for the utilization of current in the ED process, as more energy input is required when ED is operated at a current that exceeds I_{lim} . Typically, ED is operated at current that is below I_{lim} [19,20] in order to reduce energy consumption, and to prevent excessive water splitting while EDI is operated at an overlimiting current. This enhances the continuous electro-regeneration of the resins in situ with the H^+ and OH^- ions produced by water splitting [21]. On the other hand, with recent progress in the research of electroconvection in ED, and the modifications of ion exchange membranes, Nikonenko *et al.* (2014) [22] proposed ED at overlimiting currents to reduce overall costs.

According to Fig. 5.1, the I_{lim} was 126.0 mA. On the basis of the analysis above, experiments at 90% of I_{lim} (113.4 mA), I_{lim} (126.0 mA), and 110% of I_{lim} (138.6 mA) were conducted to investigate the effects of applied currents.

5.3.2 Removal of ammonium, phosphate, and calcium by ED system

(1) Limiting current (126.0 mA)

The experiments at I_{lim} (126.0 mA) were repeated three times, and the standard deviation (S) was calculated using Eq. (5.1).

$$S = \sqrt{\frac{1}{N-1} \sum_{i=1}^N (x_i - \bar{x})^2} \quad (5.1)$$

Where N is the total number of samples, x_i is the value of each data point and \bar{x} is the mean value of the data. The removal of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$ and Ca^{2+} with error bars in the dilute compartment is presented in Fig. 5.2.

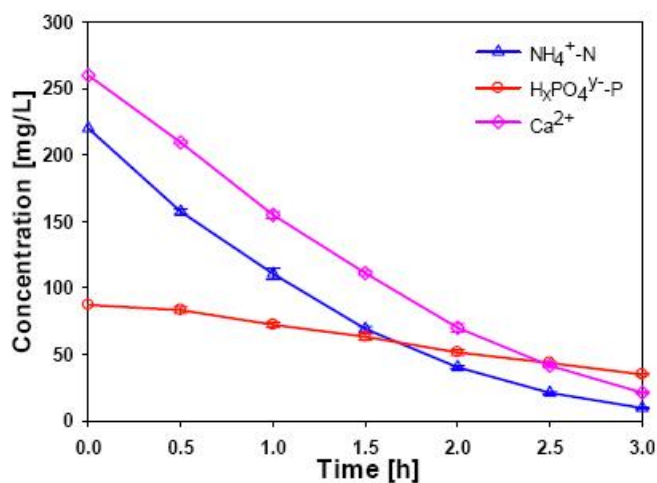


Fig. 5.2. Changes of concentrations of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} in the dilute compartment of the ED cell at 126.0 mA over 3 h

As seen in Fig. 5.2, the removal of $\text{NH}_4^+\text{-N}$ and Ca^{2+} were much more rapid than that of $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and the removal efficiencies of $\text{NH}_4^+\text{-N}$ and Ca^{2+} were higher than that of $\text{H}_x\text{PO}_4^{y-}\text{-P}$. The relatively low removal efficiency of $\text{H}_x\text{PO}_4^{y-}\text{-P}$ may be explained by the larger size and the conversion of H_2PO_4^- to H_3PO_4 , as the pH of the solution in the dilute compartment was decreased under the operation of ED system, which will be discussed in section 5.3.4. The low level of phosphate removal by the ED operation was also observed in other types of wastewater with high salts content; in industrial

wastewater for example [20], and in reverse osmosis concentrates [23].

(2) 90% of I_{lim} (113.4 mA) and 110% of I_{lim} (138.6 mA)

Figs. 5.3A and B show the removal of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} in the dilute compartment of the ED cell at 90% of I_{lim} (113.4 mA), and 110% of I_{lim} (138.6 mA). A similar trend was observed in that $\text{NH}_4^+\text{-N}$ and Ca^{2+} were removed faster with higher efficiencies than $\text{H}_x\text{PO}_4^{y-}\text{-P}$.

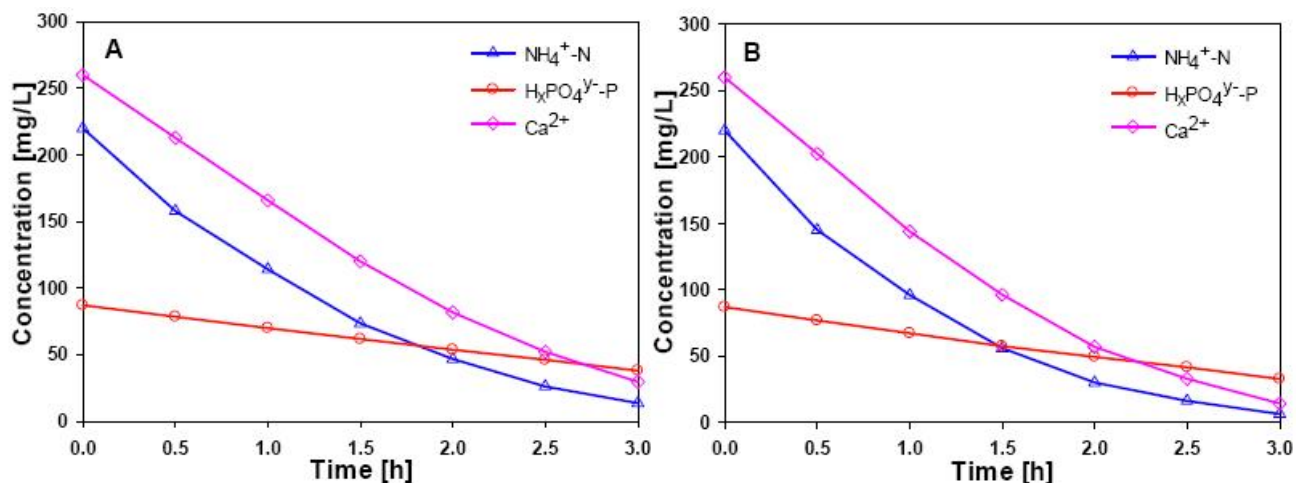


Fig. 5.3. Changes of concentrations of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} in the dilute compartment of the ED cell at current (A) 113.4 mA, (B) 138.6 mA

Fig. 5.4 illustrates a comparison of the removal efficiencies for $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} at a current at 110% of I_{lim} (138.6 mA), I_{lim} (126.0 mA), and 90% of I_{lim} (113.4 mA). According to Fig. 5.4, at the three applied currents, the removal efficiency of $\text{NH}_4^+\text{-N}$ was the highest, followed by Ca^{2+} , and $\text{H}_x\text{PO}_4^{y-}\text{-P}$ as the lowest. The reason that the removal efficiency of $\text{NH}_4^+\text{-N}$ was higher than Ca^{2+} under the operation of ED was primarily due to the fact that monovalent $\text{NH}_4^+\text{-N}$ had preferential transport

through the CEM, while the transport of divalent Ca^{2+} through the CEM was relatively lower [20]. The charges of ions also affect the removal efficiencies as has been demonstrated in previous studies [24,25].

Further, when the applied current was high, the removal efficiencies of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} were increased. This was because the ions were transported under the driving force of a direct current. When the applied current was increased from 113.4 mA to 138.6 mA over 3 h, the removal efficiency of $\text{NH}_4^+\text{-N}$ was increased from 93.9% to 97.1%, and the removal efficiencies of $\text{H}_x\text{PO}_4^{y-}\text{-P}$ and Ca^{2+} were 56.4% - 62.3% and 88.6% - 94.5%, respectively.

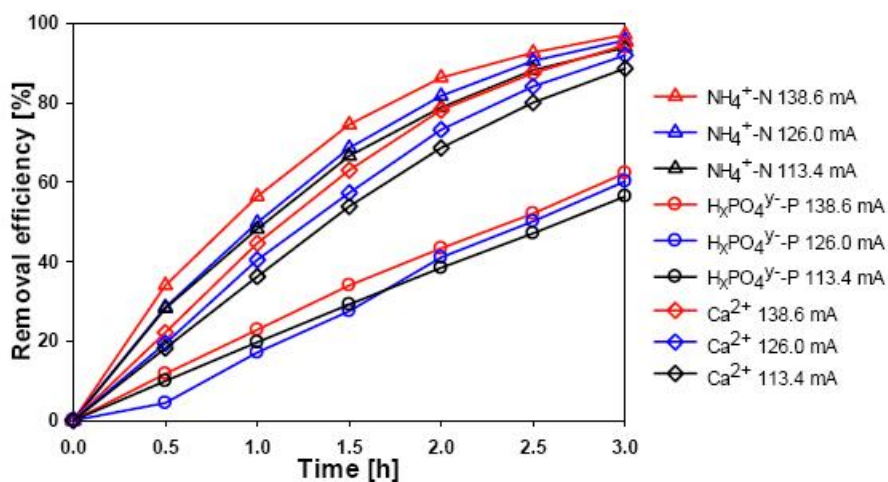


Fig. 5.4. Removal efficiencies of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} in the dilute compartment of the ED cell at currents of 110% of I_{lim} (138.6 mA), I_{lim} (126.0 mA), and 90% of I_{lim} (113.4 mA)

Following each experiment, the COD of the solution in the dilute tank was also analyzed. Minimal COD removal was observed for the ED treatment over 3 h. This was mainly due to the fact that non-ionic glucose was used to simulate the COD in the feed water. Under the operation of ED, the

non-ionic glucose was uncharged and retained in the feed water. Similar extremely low removals of COD in the form of non-ionic species have been reported by Zhang *et al.* (2009) [23].

5.3.3 Energy consumption

The recorded curves of voltage vs. time at a current of 90% of I_{lim} (113.4 mA), I_{lim} (126.0 mA), and 110% of I_{lim} (138.6 mA) are depicted in Fig. 5.5. As can be seen, the voltage was increased as the applied current was increased. The voltage was also elevated when the operation time increased as the conductivity in the dilute compartment declined during the experiment. Moreover, less noise was observed in the curves with higher voltages. This is because higher voltage assists with the reduction of noise and errors in the signal, such that more precise measurements are achievable [26].

An overview of the specific energy consumption (SEC) based on the volume of treated feed water is presented in Fig. 5.6, and was calculated using Eq. (5.2).

$$SEC = \frac{I \int_0^t U dt}{V} \quad (5.2)$$

Where: I is current, U is voltage and V is the volume of the feed water.

It was found that the specific energy consumption increased with the input current. At the conclusion of the experiment at 3 h, the SEC of 90% of I_{lim} (113.4 mA), I_{lim} (126.0 mA), and 110% of I_{lim} (138.6 mA) was 7.88 kWh/m³, 9.52 kWh/m³, and 11.53 kWh/m³, respectively. The obtained values were similar to the range of ~11 kWh/m³ for the desalination of a brackish water through ED [18]. According to a previous study [27], there was higher energy requirement when the salt concentration in the feed water

was increased. The TDS of another investigation by Ali *et al.* [18] was higher than that of the present study, which revealed that the energy consumption obtained in the experiments was relatively higher. This might be explained by the greatly increased resistance due to 20 fold greater distance between the two membranes in the dilute compartment (10 mm) than that of Ali *et al.* [18], which was only 0.5 mm.

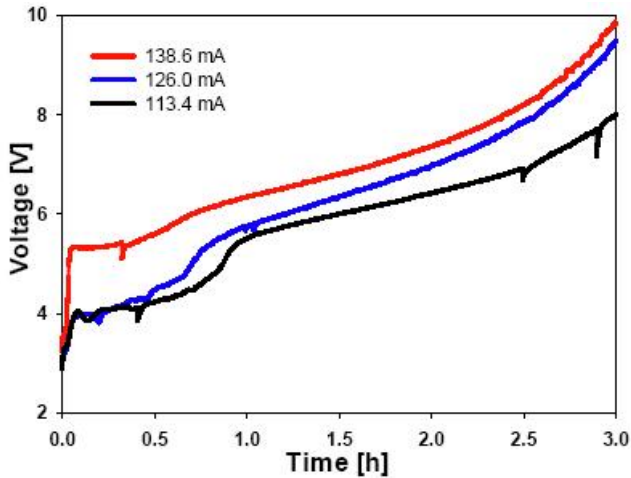


Fig. 5.5. Curves of voltage vs. time at currents of 90% of I_{lim} (113.4 mA), I_{lim} (126.0 mA), and 110% of I_{lim} (138.6 mA)

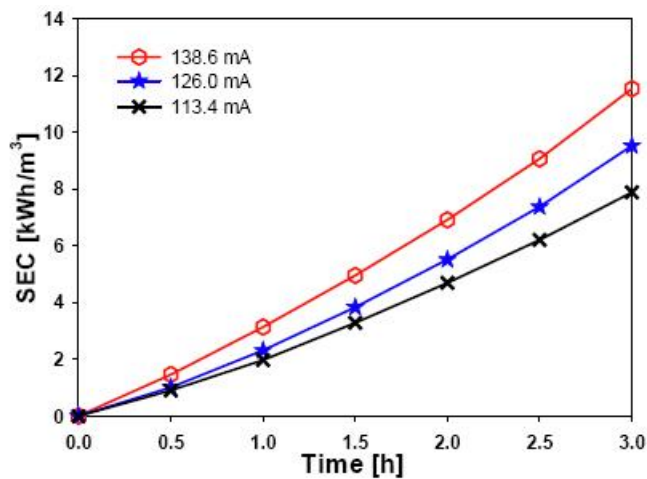


Fig. 5.6. Changes of specific energy consumption during the ED operation at currents of 90% of I_{lim} (113.4 mA), I_{lim} (126.0 mA), and 110% of I_{lim} (138.6 mA) over 3 h.

5.3.4 pH changes

At the conclusion of experiments over 3 h, the pH values in different compartments of the expanded ED cell were measured. The experimental results showed that the increase of current did not have a significant effect on the pH values. For all applied currents, the pH value in the dilute compartment was decreased from 4.86 to ~2.75. The main reason for the drop in pH may have possibly been due to the fact that H⁺ ions, which were contained in 0.1 M H₂SO₄ and circulated within the cationic concentrate compartment, passed through the CEM and were transferred into the dilute compartment, which would in turn make the pH in the cationic concentrate compartment increase from 1.07 to ~1.50. The pH values in the anionic concentrate compartment and electrode rinse compartments changed very little, and no significant variations were observed.

5.3.5 ED experiments for feed water without freeze concentration

To further verify whether the freeze concentration might enhance the performance of ED for the treated MWW, comparison experiments using the treated MWW without freeze concentration as the feed water for ED were conducted. The main components of this synthetic feed water are listed in Table 5.2.

Table 5.2. The main components in the synthetic treated MWW without freeze concentration

Main components	Concentration (mg/L)
NH ₄ ⁺ -N	50.0
H _x PO ₄ ^{y-} -P	20.0
Ca ²⁺	75.0
COD	150.0

The operation conditions were similar to that in section 5.2.3, only the volume of feed water was

increased from 250 mL to 1000 mL. This adjustment was based on the fact that the concentrations of the components in Table 5.1 were approximately four times than that in Table 5.2; thus a four-fold volume of the dilute water was selected to compare the total amount of components removed. The flow rates for all separate circuits were maintained at 9 mL/min.

(1) Operation at limiting current

According to Fig. 5.7, the limiting current for ED with the synthetic treated MWW was determined as 37.3 mA.

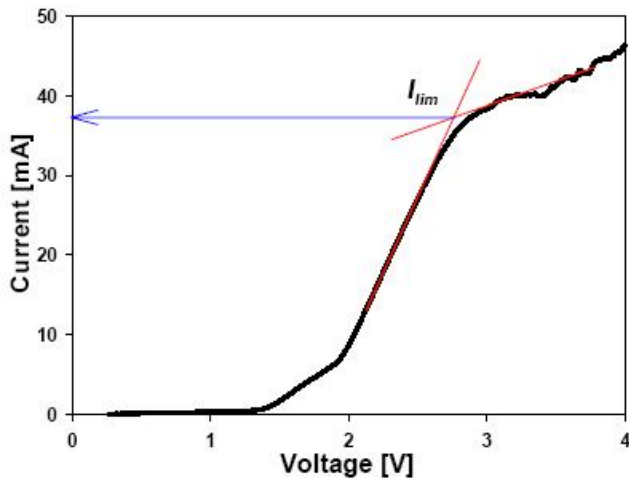


Fig. 5.7. I-V curve for the treated MWW without freeze concentration at a flow rate of 9 mL/min, and a scan rate of 1 mV/s.

The removal of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} in the dilute compartment is shown in Fig. 5.8. The operation time was extended from 3 h to 6 h to further verify the trend. Obviously, no $\text{H}_x\text{PO}_4^{y-}\text{-P}$ removal was observed during the entire experiment. The removal efficiency of $\text{NH}_4^+\text{-N}$ and Ca^{2+} over 3

h was 28.6% and 16.5%. The results indicated that the dilute solution was not suitable for treatment by ED in terms of the removal of $H_xPO_4^{y-}$ -P.

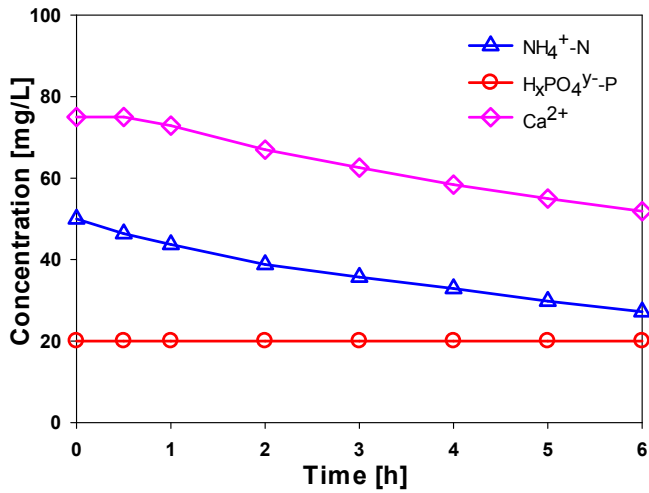


Fig. 5.8. Removal of NH_4^+-N , $H_xPO_4^{y-}$ -P, and Ca^{2+} for the treated MWW without freeze concentration under a current of 37.3 mA

(2) Operation at 126.0 mA

The results in section 5.3.2 revealed that higher removal efficiencies were achieved at increased applied currents. Thus the input current was greatly increased to 126.0 mA in order to learn to what extent the removal of $H_xPO_4^{y-}$ -P might be enhanced. The experiment was intended to run for 6 h; however, the Voltalab (PGZ 402 Universal Potentiostat) stopped automatically at 4.3 h when the voltage exceeded the limit value of 15 V. Hence, data of 4 h is provided in Fig. 5.9. As can be seen in Fig. 5.9, 24.85% of the $H_xPO_4^{y-}$ -P was removed over 3 h. From another aspect, this result suggested that the dilute solution should be concentrated prior to ED treatment as the removal of $H_xPO_4^{y-}$ -P occurred only at a high

current and/or voltage, which were cost-effective for solutions with high salts contents.

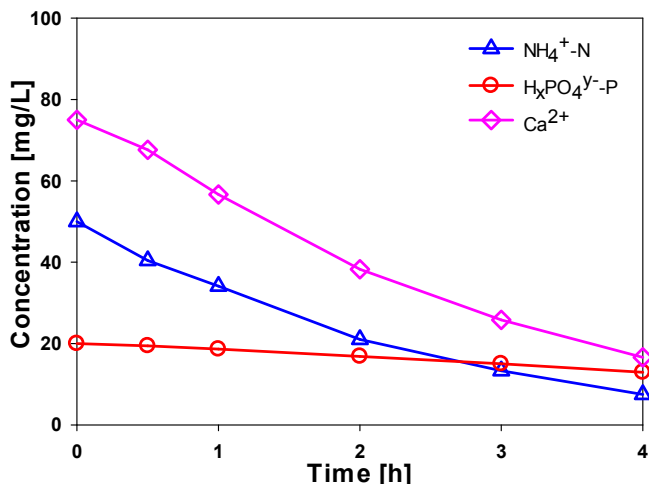


Fig. 5.9. Removal of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} for the treated MWW without freeze concentration at a current of 126.0 mA

5.4 Conclusions

To address the poor performance of ED for the AnMBR effluent treatment of MWW with low salts concentrations, we demonstrated a novel approach using freeze concentration to concentrate the effluent in this study. Synthetic unfrozen liquid at a freezing ratio of 80% for the treated MWW was investigated. An expanded ED cell derived from the expanded EDI cell used in a previous study was utilized to investigate the feasibility of the proposed approach. The experimental results indicated that the pre-concentrated feed water with elevated concentrations of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} may be treated at a current from 113.4 mA to 138.6 mA over 3 h, with removal efficiencies in the range of 93.9% - 97.1%, 56.4% - 62.3%, and 88.6% - 94.5%, respectively. Further comparative experiments

were conducted with the synthetic treated MWW without freeze concentration. The obtained results verified that preconcentration was necessary for the ED process to effectively treat the dilute wastewater, particularly for the removal of $H_xPO_4^{y-}$ -P. Therefore, this approach might be considered as potentially viable to enhance the removal of nutrients for the treatment of MWW.

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Chapter 6. Summary and suggestions for future work

To address the problem of high mineralized nutrients concentrations in the effluent of AnMBRs for MWW treatment, the current M. Sc. Eng. project focused on the use of electrodeionization (EDI), freeze concentration (FC), as well as using FC as a preconcentration step for electrodialysis (ED) for the simultaneous removal of nutrients from synthetic effluent of AnMBRs for MWW treatment. The primary obtained results are summarized below.

6.1 Electrodeionization approach

In Chapter 3, an expanded electrodeionization (EDI) cell packed with mixed resins ((Amberlite[®] 200C Na) and phosphate selective ion exchange resin (Purolite FerrIX[™] A33E)), was investigated for efficacy toward the simultaneous removal of nutrients and other ionized species (such as hardness ions) in the effluent with low energy demand. The effect of the scan rate on limiting current (I_{lim}) determination was studied, and I_{lim} was determined by current vs. voltage plot. Factors of 110% of I_{lim} , I_{lim} and 90% of I_{lim} were applied to the EDI cell. At the recommended I_{lim} over 3 h, the removal efficiency of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, Ca^{2+} and Mg^{2+} , was 74.4%, 100%, 92.3%, and 58.8%, respectively, with a specific energy consumption of 0.74 kWh/m³ of feed wastewater. The results demonstrated that the EDI process is very promising for the removal of ionic nutrients and hardness ions from wastewater similar to municipal wastewater.

6.2 Freeze concentration approach

In Chapter 4, freeze concentration (FC) was investigated for the removal of nutrients from the synthetic municipal wastewater effluent. Synthetic feed water containing the single impurities ($\text{H}_x\text{PO}_4^{y-}\text{-P}$, $\text{NH}_4^+\text{-N}$ and COD causing glucose) and the multiple impurities with different concentrations were tested at various mixing conditions. Without any pretreatment of the feed water and ice seeding, at freezing temperature of $-15\text{ }^\circ\text{C}$ and freezing ratio $\sim 80\%$, the average removal efficiencies of $\text{H}_x\text{PO}_4^{y-}\text{-P}$, $\text{NH}_4^+\text{-N}$ and COD in single impurity tests were 99.9%, 96.5% and 100%, respectively. In multiple impurities tests of same operation conditions, the average removal efficiencies of $\text{H}_x\text{PO}_4^{y-}\text{-P}$, $\text{NH}_4^+\text{-N}$ and COD ranged 99.9% - 90.6%, 96.2% - 90.2%, and 100% - 88.2%, respectively. The ultrasonic mixing cycles and mechanical mixing speeds were not significant effects for the removal efficiencies and concentration ratios of impurities both in single and multiple impurities feed waters. For the effect of initial impurities concentrations on FC performance, the removal efficiencies and concentration ratios in the experiments on combined impurities decreased as the concentration of feed water increased both in terms of component concentration and species of solutes. The experimental results indicated a potential that FC was efficient to remove nutrients from municipal wastewater effluent.

6.3 Approach of using freeze concentration as a preconcentration step for electrodialysis

In Chapter 5, an approach of using freeze concentration (FC) as a preconcentration step for electrodialysis (ED) was investigated for the removal of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} from synthetic municipal wastewater (MWW). Synthetic feed wastewater, simulating the unfrozen liquid of freeze

concentration experiments at an 80% freezing ratio for the effluent of an anaerobic membrane bioreactor in the treatment of MWW was desalinated in an expanded ED cell. A method based on a current vs. voltage curve was employed to determine the limiting current, and the effect of the input current was studied. The removal efficiencies of $\text{NH}_4^+\text{-N}$, $\text{H}_x\text{PO}_4^{y-}\text{-P}$, and Ca^{2+} at a current from 90% to 110% of limiting current over 3 h, ranged from 93.9% - 97.1%, 56.4% - 62.3%, and 88.6% - 94.5%, respectively. Furthermore, experiments with synthetic MWW without FC were carried out to compare the difference. The results revealed that preconcentration was prerequisite for improving the performance of ED for dilute solutions, particularly for the removal of $\text{H}_x\text{PO}_4^{y-}\text{-P}$. FC as a preconcentration step for ED offers a promising approach for the treatment of MWW via ED.

6.4 Suggestions for future work

The feasibility of the proposed three approaches for simultaneous nutrients removal from effluent of AnMBRs for MWW treatment has been proven. However, previous studies typically tested the proposed approaches using synthetic wastewater that contained target impurities, which was not sufficient for practical application. Therefore, actual wastewaters are suggested to be used in future studies. Specific suggestions for future work of the proposed three approaches are listed below.

(1) Electrodeionization approach

Ammonium selective resins should be investigated to enhance the removal of ammonium and ion exchange membranes with higher total exchange capacity should be considered to optimize the performance of EDI.

(2) Freeze concentration approach

More experiments are suggested for systematically quantitative study of pH variance in the ice phase and the unfrozen liquid phase and investigation of whether the FC performance would be affected by the pH of feed water. In addition, from the view point of energy saving, experiments on finding the optimum minimum mixing conditions for wastewater containing relatively low impurities concentrations are suggested. Since ultrasonic mixing cycles and mechanical mixing speeds are not considered as significant effects for the performance of FC with low impurities concentrations wastewater and the initial impurities concentrations of a specific wastewater are given input conditions, the effect of additional operations could be studied if higher removal efficiencies are required, such as ice seeding and partial melting of the ice phase.

(3) Approach of combining freeze concentration and electro dialysis

The improvement of ED cell for wastewater treatment is recommended, as the large distance between the two membranes in the dilute compartment of the ED cell used in this study resulted in the greatly increased resistance and the energy consumption.

(4) The concept of integrated AnMBR and EDI, ED and FC approaches for both bioenergy and nutrients recovery and water reuse should be tested. Efforts should be put in the energy production and consumption and economic analysis of the AnMBR-EDI, ED or FC processes.