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DEVELOPMENT OF A NOVEL MICROBIAL FUEL CELL FOR NUTRIENT RECOVERY FROM SYNTHETIC MUNICIPAL WASTEWATER

by Yuanyao Ye

Thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

under the supervision of Prof. Huu Hao Ngo

University of Technology Sydney
Faculty of Engineering and Information Technology

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CERTIFICATION OF ORIGINAL AUTHORSHIP

This research is supported by the Australian Government Research Training Program. I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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LIST OF ABBREVIATIONS

Symbol	**Description**
AEM	Anion-exchange membrane
AnMBRs	Anaerobic membrane bioreactors
AnOMBRs	Anaerobic osmotic membrane bioreactors
BES	Bioelectrochemical system
BMED	Bipolar membrane electrodialysis
CE	Coulombic efficiency
CEM	Cation exchange membrane
COD	Chemical oxygen demand
DI	Distilled
DO	Dissolved oxygen
EBA	Electrochemically active bacteria
ED	Electrodialysis
EDS	Energy dispersive spectroscopy
EMBR	Enhanced biological phosphorus removal
F/M ratio	Food-to-microorganisms ratio
FO	Forward osmosis
HRT	Hydraulic retention time
MBR	Membrane bioreactor
MD	Membrane distillation
MEC	Microbial electrolysis cell
MF	Microfiltration
MFC	Microbial fuel cell
MLSS	Mixed liquor suspended solids
MRC	Microbial recovery cell
NW	Nonwoven
OLR	Organic loading rate
OMBR	Osmotic membrane bioreactor
PAOs	Phosphate accumulating microorganisms
PS	Power supply
RO	Reverse osmosis

SEM	Scanning electron microscopy
SWRO	Seawater reverse osmosis
TOC	Total organic carbon
UF	Ultrafiltration
UTS	University of Technology, Sydney
VFAs	Volatile fatty acids
WHO	World Health Organization Guidelines
WWTPs	Wastewater treatment plants

LIST OF SYMBOLS

Symbol	**Description**
A	Surface area of the anode electrode (in the present case on both sides)
Al	Aluminum
C	Carbon
$C_6H_{12}O_6$	Glucose
Ca	Calcium
Ca^{2+}	Ironized calcium
$Ca_5(OH)(PO_4)_3$	Hydroxylapatite, HAP
$CaCl_2 \cdot 2H_2O$	Calcium chloride
CaO	Calcium oxide
C_E	Coulombic efficiency
CH_4	Methane
CO_2	Carbon dioxide
$CoCl_2 \cdot 6H_2O$	Cobalt chloride
$CuSO_4 \cdot 5H_2O$	Cupric sulphate
e^-	Electron
F	Faraday's constant at 96485 C/mol
Fe	Iron
$FeCl_3$	Ferric chloride anhydrous
$FePO_4$	Ferric phosphate
H^+	Proton
H_2	Hydrogen
H_2O	Water
$H_2PO_4^-$	Dihydrogen phosphate
H_2SO_4	Sulphuric acid
H_3PO_4	Phosphoric acid
HCl	Hydrogen chloride
HPO_4^{2-}	Hydrogen phosphate
I	Current
K	Potassium

K^+	Ironized potassium
KCl	Potassium chloride
KH_2PO_4	Potassium dihydrogen phosphate
Mg	Magnesium
Mg^{2+}	Ironized magnesium
$MgCl_2$	Magnesium dichloride
$MgNH_4PO_4 \cdot 6H_2O$	Struvite, MAP
MgO	Magnesium oxide
$MgSO_4 \cdot 7H_2O$	Magnesium sulphate
N	Nitrogen
N_2	Nitrogen gas
Na	Sodium
$Na_2MoO_4 \cdot 2H_2O$	Sodium molybdate dehydrate
Na_3PO_4	Sodium phosphate
NaCl	Sodium chloride
$NaHCO_3$	Sodium bicarbonate
NaOH	Sodium hydroxide
NH_3	Free ammonia
NH_3 (aq)	Aqueous ammonia
NH_3-N	Ammonia nitrogen
NH_4^+	Ionized ammonia
NH_4^+-N	Ammonium nitrogen
NH_4Cl	Ammonium chloride
NH_4HCO_3	Ammonium bicarbonate
O	Oxygen
O_2	Oxygen gas
OH^-	Hydroxyl
P	Power output
P	Phosphorus
P_A	Powder density
PO_4^{3-}	Hydrogen phosphate
PO_4^{3-}-P	Hydrogen phosphate phosphorus
Pt/C	Platinum on carbon

R	Resistor
R^2	Correlation coefficient
U	Voltage
$ZnSO_4 \cdot 7H_2O$	Zinc sulphate
ΔCOD	The amount of COD removed

Ph.D. DISSERTATION ABSTRACT

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Supervisors:	Prof. Huu Hao Ngo (Principal supervisor) Prof. Wenshan Guo (Alternative supervisor) Dr. Yiwen Liu (Co-supervisor)

Abstract

Microbial fuel cell (MFC) is currently considered as a promising technology for wastewater treatment. This study aims to evaluate the feasibility of a double-chamber MFC to remove nutrients toward their recovery from municipal wastewater. In this scenario, the nutrient recovery can be obtained with the MFC reactor and there is no need of adding chemicals for the pH increase. Besides, energy recovery can also be achieved, which could increase the economic feasibility of this recovery system. Results showed that phosphate ions were not detected in the catholyte when the anode chamber and cathode chamber were not hydraulically connected; in contrast, the accumulation of ammonium was achieved in the cathode chamber under this situation. When anode effluent was used as the influent of the cathode compartment, nutrients can be recovered by chemical precipitation at high pH generated by the MFC itself while supplying aeration in the cathode chamber. Besides, partial phosphate and ammonium were removed by microbial absorption in the anode compartment. It was found that double-chamber MFC with the cation exchange membrane (CEM) as the separator reported the best nutrients removal compared to the forward osmosis membrane and nonwoven acting as the separator. Therefore, the MFC with CEM serving as the separator was utilized in the subsequent experiments.

The impacts of organic loading rate (OLR) (435-870 mgCOD/L·d) on nutrients recovery via the double-chamber MFC for treating domestic wastewater were also evaluated. Experimental results suggested the MFC could successfully treat municipal wastewater with over 90% of organics being removed at a wider range of OLR from 435 to 725 mgCOD/L·d. Besides, the maximum power density achieved in the MFC was 254 mW/m^2 at the OLR of 435 mgCOD/L·d. Higher OLR may disrupt the recovery of PO_4^{3-}-P and NH_4^+-N via the MFC. The same pattern was observed for the coulombic efficiency of the MFC and its highest value was 25.01% at the OLR of 435 mgCOD/L·d.

The dual-chamber MFC was then continuously operated under different influent concentrations of ammonium-nitrogen (5 to 40 mg/L). Experimental results demonstrated that this MFC reactor achieved > 85% of COD removed. Moreover, excess ammonium concentration in the feed solution may compromise the generation of electricity. Simultaneously, the recovery of phosphate achieved in the MFC was not significantly influenced at the wider influent ammonium concentration. In contrast, a high concentration of ammonium may not be beneficial for its recovery.

In addition, the effect of hydraulic retention time (HRT) on the recovery of nutrients by the MFC system was studied. The COD removal rates were relatively stable while varying HRT from 0.35 to 0.69 d, which were over 92%. Similarly, the changes in the recovery rate of nutrients were negligible while increasing the HRT. In contrast, the maximum power generation declined when HRT increased.

Keywords: Domestic wastewater; Microbial fuel cell; Nutrients recovery; Energy recovery; Ammonium concentration effect; Hydraulic retention time; Organic loading rate; Chemical precipitation.

CHAPTER 1

Introduction

1.1 Research background

Phosphorus (P) and nitrogen (N) are essential nutrients for the growth of organisms. Besides, such nutrients have the main responsibility for eutrophication which may seriously impair the quality of water and even cause aquatic life to die (Gao et al., 2018a). Therefore, the discharge of nutrient should be strictly controlled. For this reason, nutrient removal from wastewater is necessary and the concentration of nutrient is required to be below 1-3 mg·N/L and 0.1 mg·P/L respectively at the wastewater treatment in United States and China before they can be released to the environment (Fowler et al., 2013; Liu et al., 2019; Yu et al., 2019a). In wastewater, ammonium and phosphate ions are the main forms of N and P respectively. The former ions are always removed by ammonia stripping and nitrification-denitrification while the removal of the latter is mainly achieved by chemical precipitation and biological uptake (Liu et al., 2017c; Ye et al., 2017; Yin et al., 2017; Zeng et al., 2016). However, nutrient removal does consume a large amount of energy and chemicals. It is reported that an extra 4% electricity is needed for removing N in wastewater treatment plants in the United States (McCarty et al., 2011; Svardal and Kroiss, 2011). Similarly, Xie et al. (2016) recently stated that a sustainable energy supply of 45 MJ/N·kg is used to remove N from wastewater. Nutrient removal may also aggravate global warming due to the emission of 0.9 kg CO_2/m^3 as a consequence of this process (Hall et al., 2011; Rothausen and Conway, 2011).

The explosive growth in the world's population has in turn sparked an increase in the demand for nutrient-based fertilizers, approximately 1.8% per year for food production (Ledezma et al., 2015). However, the current production of fertilizers faces many challenges. Firstly, around 90% of global phosphate demand is utilized for food production (Schröder et al., 2010), but the remaining accessible deposits of phosphate rock will be completely consumed in 30-300 years (Elser and Bennett, 2011). Secondly, no materials can substitute the role of P in the fertilizers production (Ichihashi and Hirooka, 2012). Furthermore, the industrial Haber-Bosch process is employed to produce ammonia for fertilizer production, through which the atmospheric N can be converted into NH_3-N (Fowler et al., 2013). However, the anthropogenic production of NH_3-N exceeds the amount of NH_3-N converted by the natural process (Fowler et al., 2013) and hence disturbs the nature N-cycle. Consequently the environment is subjected to great risks. More importantly, the generation of ammonia from air depletes around

35-50 MJ/kg·N of energy, which accounts for 2% of global energy (Desloover et al., 2012).

As discussed above, nutrient recovery is more valuable than nutrient removal because: i) it can produce nutrient-based fertilizers to ensure food security; ii) it can minimize the environmental footprint of wastewater treatment such as production of much less excess sludge and reduced eutrophication; and iii) N recovery can decrease the consumption of natural resources and save costs associated with N fixation. A wide range of wastewater sources containing rich nutrient such as sewage, urine, and leachate has been utilized for the purposes of nutrient recovery (Gao et al., 2018b; Salehi et al., 2018; Yang et al., 2018; Zhang et al., 2017).

Of all the methods employed in nutrient recovery from wastewater, chemical precipitation is the most widely used due to its high efficiency and stability while the biological nutrient recovery is more attractive (Johansson et al., 2017; Ye et al., 2016b). Chemical precipitation seeks to choose an appropriate precipitator to react with nutrient for precipitates' formation at $pH > 8$ (Romero-Güiza et al., 2015a; Ye et al., 2016b; Zeng et al., 2018). Mg and Ca materials are usually employed as the precipitator to form $MgNH_4PO_4 \cdot 6H_2O$ (struvite) and $Ca_5(OH)(PO_4)_3$ (HAP), respectively. However, Fe and Al materials may not be suitably applied as precipitators because the recovered product tightly binds with phosphate ions, making it difficult for plants to take up phosphate (Petzet and Cornel, 2012). Moreover, the nutrient recovery via chemical precipitation can be economically feasible only if the P concentration in wastewater is over 100 mg/L (Pastor et al., 2010; Ronteltap et al., 2010).

On the other hand, a biological process such as an enhanced biological phosphorus removal (EBPR) system was developed to recover phosphate (Valverde-Pérez et al., 2016). This scenario does highly depend on the phosphate accumulating organisms (PAOs) because phosphate is released from cells to wastewater in an anaerobic state while PAOs can accumulate excessive amounts of polyphosphate in aerobic/anoxic environments (Zhao et al., 2015). In this scenario, the surplus sludge containing rich P is achieved. However, the recovered product (i.e. excess sludge) cannot be applied in agriculture due to the fact it contains heavy metals, toxic matter and pathogens (Schoumans et al., 2015). As for N, the ammonia is normally stripped via air/N_2 out of wastewater at high temperature and pH, after which the volatile ammonia is adsorbed by water and acid solutions to form liquid ammonia or ammonium salts such as ammonium sulphate and ammonium carbonate (Iskander et al., 2016; Kelly and He, 2014; Wu and Modin, 2013).

In the nutrient recovery process, the coexisting heavy metals and toxic substances exert serious effects on nutrient recovery such as impairing the quality of recovered nutrient. For example, Xie et al. (2016) concluded that the recovered struvite crystals were found to have toxic heavy metals contents, in which the arsenic concentration was even greater than 570 mg/kg. As a result of this, the application of such recovered struvite may be forbidden in agriculture due to its low quality and purity. Therefore, it is essential to separate nutrient from the foreign matter to enhance the application potential of recovered nutrient. Since membranes have selective high-rejection for ions, the nutrient can be enriched and separated from foreign substances in the streams (Gerardo et al., 2015). Fig. 1.1 illustrates the membrane separation process for ions from feed solution (Fuchs and Drosg, 2010).

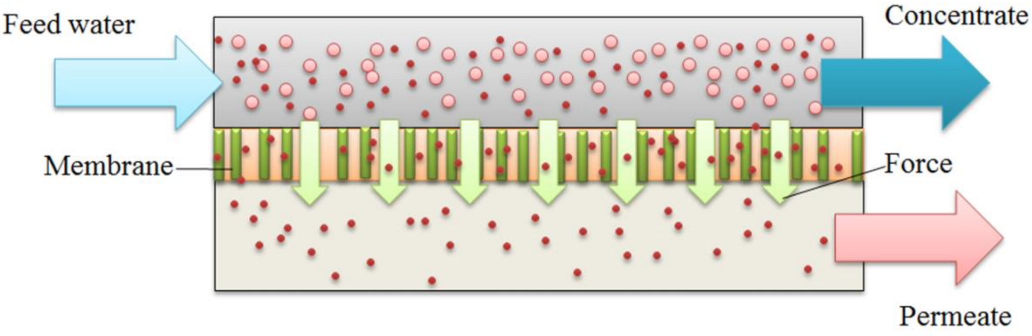

Figure 1.1 Mechanism of membrane to concentrate and separate feed water (adapted from Fuchs and Drosg (2010)).

From Fig. 1.1, it can be seen that a membrane filtration process mainly relies on the pore size of a membrane and water in the feed solution could penetrate the membrane under pressure (Gerardo et al., 2013). The membrane separation technique is a simple physical process, so no chemicals and energy are included in it. For this reason the membrane separation process is more economical than other separation processes in terms of operational and maintenance costs. Currently, some membrane techniques have been integrated with chemical precipitation and biological processes as the membrane hybrid systems for nutrient recovery from wastewater (Ahn et al., 2011; Gerardo et al., 2013; Gong et al., 2017; Ichihashi and Hirooka, 2012; Qiu and Ting, 2014a; Xie et al., 2014b; Zhang et al., 2013b). In such cases the technical and economic feasibility of the nutrient recovery system can be improved.

1.2 Research motivations and scope

Even though the previous studies have pointed out the high potential of microbial fuel cell (MFC) for recovering nutrients in wastewater treatment, studies on the recovery of nutrients via double-chamber MFC are still limited. It is worth noting here that the two-compartment configuration of MFC presents obvious advantages over single- or multi-chamber configuration of MFC. For example, it could enhance the pH elevation which facilitates the nutrients recovered through chemical precipitation and its operation is easier. The possible reason for this is that integrating the anolyte and catholyte in the single-chamber MFC may buffer the pH of electrolyte and thus inhibit the pH elevation of the electrolyte despite the fact that the single-chamber MFC could reduce the overall operating costs to some extent (Ichihashi and Hirooka, 2012; Chen et al., 2015; Damiano et al., 2014; Geng et al., 2018). Therefore, this thesis focuses on the application of a novel double-chamber MFC for recovering nutrient (i.e., phosphate and ammonium) in municipal wastewater treatment. The effects of different operation parameters (e.g., organic loading rate [OLR], influent ammonium concentration and hydraulic retention time [HRT]) on the performance of the MFC system were explored. The long-term goal of this research is to develop and optimize a novel double-compartment MFC for urban wastewater treatment and recovery of nutrients and energy.

The main objectives of this research are as follows:

1) To demonstrate a comprehensive review of current studies on membrane hybrid system for the recovery of nutrients at wastewater treatment;
2) To investigate the feasibility of a novel double-chamber MFC for recovering nutrients in domestic wastewater treatment;
3) To evaluate the effects of OLR on the MFC performance with reference to organic removal, power output and recovery of nutrients;
4) To assess the impacts of influent ammonium concentration on the overall performance of the two-chamber MFC; and
5) To explore the influence of HRT on the recovery of nutrients and energy in the dual-compartment MFC system.

1.3. Research significance

This research can provide a promising and effective way to recover nutrients from domestic wastewater with simultaneous electricity generation through a double-chamber MFC. The feasibility study of the present MFC system presents its high potential for the recovery of nutrients whilst the optimization investigations indicate the possible application of the MFC at full-scale in a wider operation condition in terms of degrading organics, recovering nutrients and generating energy. Thus, the information given in this research will be of significance to further studies regarding the recovery of nutrients in the MFC systems at domestic wastewater treatment.

1.4 Organization of the report

The thesis consisted of eight chapters and each chapter's main contributions are shown as follows:

Chapter 1 briefly presents the significance of nutrient recovery from wastewater and recent challenges in current conventional technologies to realize this objective. The research motivations, scope and significance are highlighted afterward.

Chapter 2 reviews the fundamental aspects of membrane hybrid systems for recovering nutrients in wastewater treatment, including their mechanisms and influencing parameters. Moreover, it also critically discusses the current challenges in nutrient recovery from wastewater through membrane hybrid systems. Finally, possible directions for developing MFC for recovering nutrients are provided.

Chapter 3 demonstrates the detailed materials and methods in this study. Specifically, wastewater composition and membrane material, experimental setup and operation conditions, and analytical methods are explicitly included.

Chapter 4 identifies the potential of the novel double-compartment MFC for the recovery of nutrients in municipal wastewater treatment. This chapter explores the feasibility of recovering nutrients in different operation modes with and without aeration supply in the cathode chamber. It also evaluates the impacts of different separators in the MFC on the recovery rate of nutrients. Besides, the analysis of precipitates obtained in the cathode compartment is present.

Chapter 5 shows the experimental results of the two-chamber MFC performance at various OLRs in terms of organic degradation, energy generation and recovery of nutrients in domestic wastewater treatment. It was found that higher OLRs had negative effects on the energy generation and recovery of nutrients.

Chapter 6 reports the experimental results in the double-compartment MFC at different influent ammonium concentrations in sewage treatment. The performance of the MFC system is assessed with reference to the COD removal, electricity generation and nutrients recovery.

Chapter 7 evaluates the impacts of HRT on the recovery of nutrients and energy and removal of COD in the double-compartment MFC system in urban wastewater treatment.

Chapter 8 summarizes the works and major results of studies in this thesis, draws conclusions, and addresses future perspectives as well.

CHAPTER 2

Literature review

2.1 Introduction

This chapter aims to present a critical and comprehensive review on the current state of the membrane hybrid system for nutrient recovery from wastewater. According to the process of membrane separation, Forward osmosis (FO), membrane distillation (MD) and electrodialysis (ED) are the main membrane technologies that concentrate nutrient in the wastewater treatment (Ahn et al., 2011; Guedes et al., 2016; Xie et al., 2014b; Xie et al., 2016; Zhang et al., 2013b). A bioelectrochemical system (BES) containing a proton-exchange membrane has also attracted attention for its ability to recycle nutrient through a combination of chemical and bioelectrochemical reactions (Deng et al., 2018; Iskander et al., 2016; Kelly and He, 2014). In addition, membrane bioreactor (MBR) is also a promising membrane technique for recovering nutrient (Qiu and Ting, 2014a). The possible reason for this is the nutrient can also be rejected within the bioreactor and the low level of membrane fouling is observed due to the removal of organics. Furthermore the traditional MBRs can: a) reduce the production of surplus sludge, environmental (carbon) footprint and size of equipment; b) improve the quality of effluent due to having a high concentration of suspended solids and long sludge retention time; and c) enhance safety due to no biological sedimentation units (Zanetti et al., 2010). The main types of membrane hybrid systems for nutrient recovery from wastewater are summarized in Table 2.1.

Table 2.1 Main types of membrane hybrid systems for nutrient recovery from wastewater

Membrane hybrid systems	Wastewater source	Performance	Membrane fouling	Overall costs	Reference
FO-based	Swine wastewater	> 93% of ammonium and > 99% of phosphate recovered (struvite)	Cake layer formation	Draw solution Manpower costs Energy consumption of pump and magnetic stirrer	(Wu et al., 2018)
MD-based	Biogas slurry	> 98% of ammonia recovered in 1.0 mol·N/L	Biofouling	Vacuum pressure: 10 kPa Feed temperature: 75 °C	(He et al., 2018)
ED-based	Synthetic manure	78% of ammonium and 75% of phosphate recovered	N/A	Energy consumption: 0.08 kWh/L of hydrolysate treated Current efficiency: low	(Shi et al., 2018)
BES-based	Domestic wastewater	Concentration factors: ammonium (1.5) & phosphate (4.9) (struvite)	Surface fouling and scaling	Energy neutral approach	(Chen et al., 2017)
MBR-based	Municipal wastewater	> 95% of phosphate recovered (calcium phosphate)	Insignificance	Draw solution Additional NaOH	(Qiu and Ting, 2014a)

In this chapter, the mechanisms and processes of membrane hybrid systems for nutrient recovery are introduced. These systems are compared in terms of their technical and economic feasibility. Simultaneously, possible challenges and future direction associated with the application of the membrane hybrid systems for recovering nutrient are discussed.

2.2 Membrane hybrid system for nutrient recovery

2.2.1 Membrane-based hybrid system

A. Forward osmosis

In the FO process, a semipermeable membrane is utilized while the driving force is derived from the osmotic pressure gradient between the feed solution and draw solution. In this scenario, water in the feed side can be transported across the FO membrane to the draw side. Simultaneously, some draw solute may also transfer to the feed side due to reverse salt flux (Roy et al., 2016).

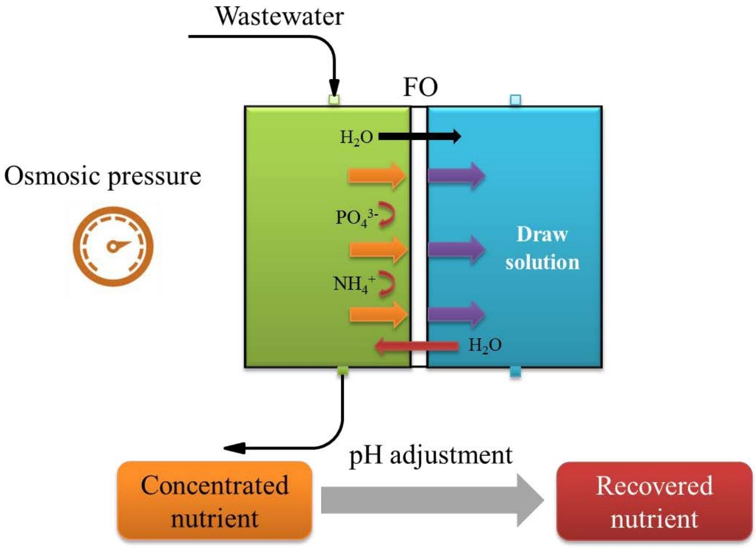

Figure 2.1 Schematic representation of the FO-based hybrid system for the nutrient recovery.

Fig. 2.1 presents the schematic representation of the FO-based hybrid system for the nutrient recovery. It is worth noting that the FO process has been investigated for its ability to enrich nutrient from many wastewater sources such as sewage (Xie et al., 2014b; Xue et al., 2015) and urine (Zhang et al., 2014b). Xue et al. (2015) found the FO process can theoretically concentrate more than ten-fold concentrations of nutrient in the feed solution. Furthermore, phosphate ions are rejected in greater numbers than ammonium ions (Nguyen et al., 2013; Zhang et al., 2014b). The possible reason for this is that the hydrated radiuses of ammonium and phosphate ions are 0.104 and 0.339 nm, respectively (Kiriukhin and Collins, 2002), so phosphate ions are more easily accumulated in the feed side due to larger hydrated radius. The protons coupled diffusion from the feed side to draw side could increase the pH of feed solution (Hancock and Cath, 2009), which is mainly driven by maintaining charge neutrality of the FO process (Xie et al., 2012). The pH of the feed solution may also influence the nutrient retention in the feed side (Xue et al., 2015) since the surface of the FO membrane (i.e. semipermeable membrane) is negatively charged at pH > 7 (Cartinella et al., 2006). In this scenario, ammonium ions are more easily adsorbed on the surface of the membrane and then permeate into the draw side through electrostatic attractions while phosphate ions are pushed and then condensed in the feed side due to electrostatic repulsions. Moreover the species of nutrient is highly affected by pH (Qin et al., 2003):

$$NH_4^+ \rightleftharpoons H^+ + NH_3\ (aq)\ (pK_a = 9.3) \tag{2.1}$$

$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}\ (pK_a = 7.2) \tag{2.2}$$

From Eq. (2.1), NH_4^+ ions are the predominant form of ammonium at pH < 9.3 while NH_3(aq) largely exists at pH > 9.3. According to the Donnan exclusion, NH_3 (aq) is more easily transferred across the charged membrane than NH_4^+ ions (Xue et al., 2015). Thus, more ammonium ions would migrate to the draw side at higher pH and the ammonium retention in the feed side is thereby decreased. By contrast, the increasing pH can result in the higher retention of phosphate ions. This is because HPO_4^{2-} ions are the main form of phosphate ions at pH > 7.2 (Eq. (2.2)), so phosphate ions are more largely pushed to be retained in the feed side at such a pH range. Therefore, a neutral pH around 7 may be the ideal trade-off for improving the overall nutrient retention. Besides, the nutrient enrichment may be influenced by the materials and properties of FO membrane (Xue et al., 2015). For example, the thin-film composite FO membrane synthesized using polyamide had a similarly high negative zeta potential to cation-exchange membranes (Xie et al., 2011; Yip et al., 2010). As a result of this, the ammonium transfer from the feed side to draw side would be enhanced, thus negatively affecting the ammonium enrichment in the feed side.

Ansari et al. (2016) demonstrated an FO-based hybrid system with seawater as the draw solution to recover 92% of phosphate from digested sludge centrate. In the hybrid system, the phosphate and calcium concentrations are elevated due to high rejection rate. Furthermore the pH elevation was observed because of the FO process's inherent property (Hancock and Cath, 2009), which provides favourable conditions for calcium phosphate precipitation. Importantly, the diluted draw solution can be directly discharged to sea, which indicates an energetically favourable hybrid system.

B. Membrane distillation

The MD process is a thermally-driven membrane technique, which can separate gas phase from liquid phase. The possible reason for this is that the use of a microporous and hydrophobic membrane in the MD process can avoid the permeation of liquid substances due to surface tension forces. Generally, the feed solution in the MD process is heated to create the vapour pressure gradient between the feed side and permeate side. In this scenario, the volatile components in the feed solution can be converted to their gaseous forms, after which they are transported across the membrane and then accumulate in the permeate side. Consequently, the volatile compounds such as ammonia can react with the receiving solution for their recovery/removal. The volatile ammonia is usually adsorbed by acids such as HCl and H_2SO_4, for which the ammonium salts are recycled (Ahn et al., 2011) (Fig. 2.2).

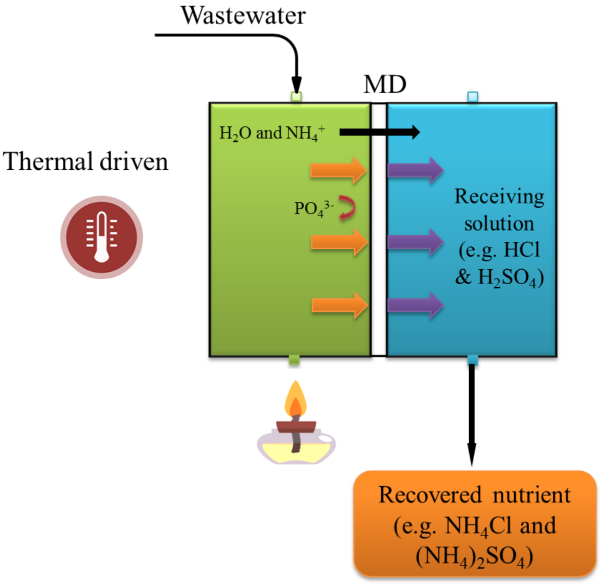

Figure 2.2 Schematic representation of the MD-based hybrid system for the nutrient recovery.

Many authors have utilized the MD process to concentrate nutrient from wastewater (e.g. swine manure) (Thygesen et al., 2014; Zarebska et al., 2014). Normally, phosphate ions are concentrated in the feed solution due to the non-volatility while ammonium ions easily evaporate and thereby accumulate in the permeate side (Zarebska et al., 2014; Zhao et al., 2013). Ammonia mainly presents in the form of volatile ammonia and ammonium ions in the wastewater (Eq. (2.3)). Obviously, the volatile ammonia component is expected to be maximized so that the ammonia enrichment can be enhanced in the MD process:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \quad (2.3)$$

From Eq. (2.3), high pH of the feed solution can increase the amount of volatile ammonia component, so the migration of ammonia to the permeated side is improved as well as its accumulation. However, when pH of the feed solution exceeds a certain value, there is negligible change in the amount of ammonia permeated (Ahn et al., 2011; Qu et al., 2013). The possible explanation for this lies in the mass transfer process being gradually controlled by the resistance caused via the membrane, so the pH is less important for the ammonia permeation (Ding et al., 2006). Furthermore, the high temperature of the feed solution can also enhance the concentrations of volatile ammonia (Ahn et al., 2011; Qu et al., 2013), but the pH is more important for the generation of the volatile ammonia (El-Bourawi et al., 2007). Zhao et al. (2013) also found that excessive feed temperature may result in the membrane fouling, which has detrimental effects on the transfer of volatile ammonia to the permeate side. The possible reason for this is that higher feed temperature may enhance the concentration polarization, which leads to the crystallization of soluble substances near or on the membrane surface and increases the suction force of membrane surface for solute particles. An increase in the feed flow rate could facilitate the volatile ammonia permeate (Qu et al., 2013) due to the increased transport of heat and the mass (El-Bourawi et al., 2007).

Ahn et al. (2011) used the MD process to concentrate ammonia from synthetic wastewater. After that, the volatile ammonia is adsorbed by H_2SO_4 for the formation of ammonium sulphate. The authors highlighted that high pH of the feed solution benefits the ammonia stripping and subsequent ammonia recovery.

C. Electrodialysis

The ED process is conducted in an electrical field with the use of ion-exchange membranes including cation-selective, anion-selective and bipolar membranes. In this scenario, cations and anions are driven by the direct current to the cathode and anode chamber, respectively (Shi et al., 2018). It is worth mentioning that solvent molecules such as water are dissociated into H^+ and OH^-. In the ED process, phosphate ions can be selectively separated from the feed solution and a phosphate-rich stream is thereby produced in the anode chamber while ammonium ions are driven to migrate to the cathode chamber for their enrichment (Fig. 2.3).

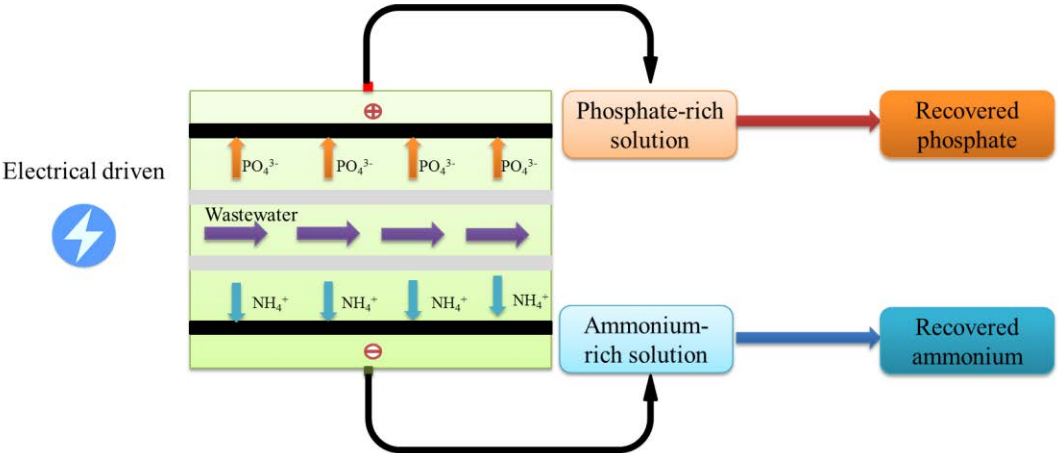

Figure 2.3 Schematic representation of the ED-based hybrid system for the nutrient recovery.

High pH of the feed solution can improve the phosphate enrichment in the ED process (Tran et al., 2014; Tran et al., 2015). This can be explained by the species of phosphate ions at different pH ranges: H_3PO_4 (pH < 2.13), $H_2PO_4^-$ (pH = 2.13-7.20) and HPO_4^{2-} (pH = 7.20-12.33) (Xie et al., 2014b). Obviously, the phosphate ions can more easily migrate to the anode chamber at high pH because of owing more charges. However, the high pH may lead the conversion of ammonium ions into volatile ammonia and hence deteriorate the ammonium accumulation. For this reason, the pH of the feed solution should be kept to avoid the emission of ammonia. Moreover, high current density can enhance the transfer of nutrient across the ion-exchange membrane, which facilitates the nutrient accumulation and recovery (Tran et al., 2014). However, an increase in the voltage may also impair the membrane and reduce its lifetime (Wang et al., 2013a; Zhang et al., 2011b), thus seriously affecting the nutrient enrichment process. Tran et al. (2014) reported that higher influent phosphate concentrations increased the phosphate concentration in the anode chamber and the ED process was able to concentrate phosphate at a wide range of feed phosphate concentration.

Zhang et al. (2013b) proposed an ED-based hybrid system containing an ED process and a struvite reactor to recover phosphate. Their results indicated that the P-rich effluent from the ED process is dosed for the phosphate recovered via struvite with high efficiency (93%). Similarly, Tran et al. (2014) demonstrated that the combination of ED process and chemical precipitation can achieve over 80% of phosphate being recovered by calcium phosphate precipitates. Besides, Shi et al. (2018) developed a bipolar membrane electrodialysis (BMED) system at lab-scale for the nutrient recovery from both synthetic and real pig manure. They found that this system could recover 78% of ammonium and 75% of phosphate ions due to effectively reducing the nutrient loss and enhancing the nutrient enrichment.

2.2.2 Bioelectrochemical system

In the BES, a cation-exchange membrane is normally installed to separate the anode chamber and cathode chamber (Logan et al., 2006). The BES can recover the chemical energy stored in the organic matter and many valuable resources such as nutrient through biological and electrochemical reactions at a wide range of wastewater (Kelly and He, 2014). In this scenario the carbon footprint can also be minimized. Of all the BESs, microbial fuel cell (MFC) and microbial electrolysis cell (MEC) are the most studied. The basic principles of MFC and MEC are shown below (Fig. 2.4):

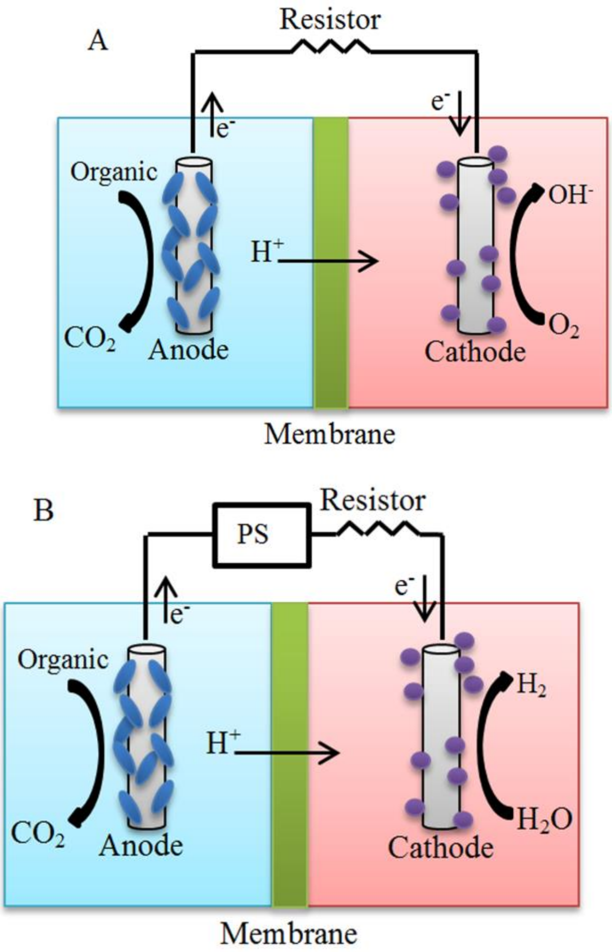

Figure 2.4 Basic principles of MFC and MEC (adapted from Wang and Ren (2013)). (A): MFC with electricity generation; (B): MEC with hydrogen generation and external power supply. ⬮ : Anode Bacterial; ● : Gas (MFC: O_2; MEC: H_2); PS: Powersupply; membrane: cation-exchange membrane.

In the MFC, organic substances are anaerobically oxidated by microorganisms at the anode chamber, during which the electrons are generated and released to the anode with simultaneous production of protons and biogas. Those electrons flow from the anode electrode to cathode electrode along with external electric circuit containing a resistor and electricity is thereby created (Logan et al., 2006). At the same time, protons transfer from the anolyte to catholyte via the cation-exchange membrane while the biogas is collected (Marcus et al., 2011; Rozendal et al., 2006). When an external voltage (> 0.25 V in practice) is applied between the anode electrode and cathode electrode in the MFC, the system is called MEC (Logan et al., 2008). The anode reaction in the MEC and MFC is the same, but the cathode reaction is different as shown below (Logan et al., 2008; Logan et al., 2006):

Cathode reaction in MFC: $2H_2O + O_2 + 4e^- \rightarrow 4OH^-$ (2.4)

Cathode reaction in MEC: $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$ (2.5)

From Eq. (2.4), electrons are oxidized by the terminal electron acceptor such as O_2 derived from air in the MFC, for which hydroxyls are produced. On the other hand, the protons can be reduced for the hydrogen production in the MEC (Eq. (2.5)) since the thermodynamic barrier for proton reduction can be overcome because of the external voltage applied (Zhang and Angelidaki, 2014).

In the MFC, the ammonium ions always transport across the cation-exchange membrane from the anode chamber to cathode chamber by: a) migration driven by electricity; and b) diffusion caused via the ammonium concentration gradient between the anolyte and catholyte (Kuntke et al., 2011). It can be noted here that ammonium diffusion between the anode chamber and cathode chamber will reach an equilibrium because of the dwindling ammonium concentration gradient, but the electricity-driven migration of ammonium from anolyte to catholyte is against the concentration gradient (Cheng et al., 2013). At the cathode chamber, ammonium can be concentrated and converted into ammonia solution at high pH (> 9.5) of the catholyte, after which the ammonia solution is partitioned and stripped either with aeration or N_2 (Kelly and He, 2014). Zhao et al. (2006) observed the pH elevation near the cathode due to the creation of hydroxyls (see Eq. (2.4)). The stripped ammonia can be directly adsorbed by acids such as H_2SO_4 to form ammonium sulphate (Iskander et al., 2016; Wu and Modin, 2013), which can be used to produce fertilizers, food and valuable nitrogen polymers (Matassa et al., 2015). Evidently, ammonia can also be recovered in the form of NH_4HCO_3 if stripped ammonia is mixed with carbon dioxide and water (Qin and He, 2014). Moreover, Kuntke et al. (2011) observed that an increased ammonium concentration in the feed solution had no toxic effects on the MFC performance if the neutral anode pH was kept; in contrary, this may increase the electricity generation and in turn facilitate the ammonium migration.

Similarly, the MEC can also create the ammonium-rich catholyte (Villano et al., 2013). The supply of external power, besides, can enhance ammonium migration and pH elevation of catholyte, thus facilitating ammonium recovery (Wu and Modin, 2013). However, most of the ammonium may accumulate in the catholyte in the absence of aeration due to low stripping effect (Qin et al., 2016). Wu and Modin (2013) used the MEC for ammonium recovery from wastewater, where real and synthetic reject waters are used as the catholyte, respectively. In their study the volatile ammonia is adsorbed by passing through the 2 M HCl solution. The results showed that 94% and 79% of ammonium are recovered from synthetic and real reject water, respectively. This is because real reject water has a higher buffer capacity than synthetic reject water, so the use of real reject water as a catholyte may inhibit pH elevation. Subsequently the efficiency of ammonium recovery is compromised. Simultaneously, 96 ± 6% of hydrogen gas is recycled in the two conditions.

Regarding the P recovery in the BES, the available information is limited. Fischer et al. (2011) used the MFC to extract phosphate bound in $FePO_4$ from digested sewage sludge, after which the P-rich supernatant was dosed with stoichiometric amounts of magnesium and ammonium for the struvite formation. However, this study only utilized MFC to mobilize P from $FePO_4$ with indirect P recovery (Fischer et al., 2011). Currently, the single chamber configuration of BES is mainly studied for direct P recovery. An air-cathode MFC was employed to recover 70-82% of P via struvite precipitation from swine wastewater and the precipitates only occur on the cathode surface (Ichihashi and Hirooka, 2012). The possible explanation is that the oxygen reduction on the cathode tends to increase the localized pH, which contributes to struvite precipitation. Similarly, other authors have employed single-chamber MFC to recycle P from landfill leachate and urine, respectively, both of which achieve high efficiency in P recovery with the phosphate-based precipitates on the surface of the cathode electrode (Damiano et al., 2014; Zang et al., 2012). In addition, a single-chamber MEC can recover 40% of phosphate in the form of struvite at 0.3-0.9 $g/m^2 \cdot h$ and the precipitates also occur on the surface of the cathode (Cusick and Logan, 2012). Undoubtedly, the cathode covered by the struvite may seriously affect the mass transfer of ions and oxygen and the electricity generation is thus inhibited. Nevertheless, Hirooka and Ichihashi (2013) believed that if the precipitates can be moved out of the cathode, the electrode performance can be restored almost to the initial level.

Besides, the feed solution in the anolyte contains a large number of cations such as Mg^{2+}, Ca^{2+} and K^+ which may also have migrational and diffusional flux between the anode and cathode chambers, so the cations competitively affect the nutrient accumulation and recovery (Rozendal et al., 2006). Besides, the transfer of such mineral salts is to maintain the charge neutrality of the system (Logan et al., 2006; Qin et al., 2016). Certainly, the forward and backward diffusion of the cations will reach an equilibrium (Rozendal et al., 2006; Sleutels et al., 2009), but the transport of the cations driven by the electrical field would not be affected by the concentration gradient between the anolyte and catholyte (Rozendal et al., 2006). In the MFC, the transfer of mineral salts to the cathode chamber may increase the catholyte's salinity, so the catholyte resistance is weakened and the electricity generation is thereby enhanced (Qin et al., 2016).

It is worth noting that the combination of different membrane techniques can maximally utilize their advantages for nutrient enrichment and recovery due to double concentration and barrier against nutrient and foreign substances in the feed solution, respectively. In this scenario, the membrane fouling potential can be reduced, which increases the economic feasibility. For instance, Xie et al. (2014b) utilized the FO-MD hybrid system to recover nutrient through struvite precipitation from digested sewage sludge centrate which is derived from a municipal wastewater treatment with biological nutrient removal (Fig. 2.5). In their study, the FO process can concentrate over 90% of ammonium and 97% of orthophosphate and the pH of the feed side is simultaneously elevated due to the diffusion of protons to the draw side (Hancock and Cath, 2009). $MgCl_2$ was used as the draw solution so the reverse draw solute flux can supply additional magnesium ions for the struvite formation. Notably, the MD process was applied to reconcentrate the draw solution and extract fresh water from the centrate, which enhances the hybrid system's economic feasibility. In addition, the FO-MD hybrid system could be utilized for concentrating high-nutrient sludge in the domestic wastewater treatment while using sodium phosphate (Na_3PO_4) as the draw solute (Nguyen et al., 2016). In this scenario, the high-nutrient sludge was enriched, which could also be employed for the nutrient recovery through wet-chemical approach and thermochemical treatment. Simultaneously, the diluted Na_3PO_4 could be recovered by the MD membrane.

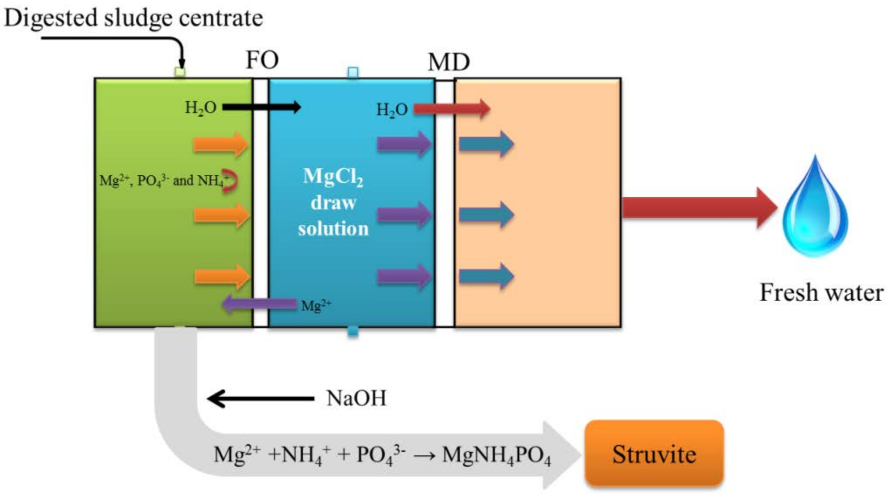

Figure 2.5 Schematic representation of the FO-MD hybrid system for the nutrient recovery.

Additionally, Qin et al. (2016) have recently studied the MEC-FO hybrid system for recovering ammonium and fresh water from landfill leachate (Fig. 2.6). The landfill leachate is firstly treated by the BES; 65.7% and 54.1% of ammonium are recovered in the form of ammonium carbonate in the presence and absence of cathode aeration, respectively. After that, the treated landfill leachate is fed to the FO process while the recovered ammonium (i.e. ammonium carbonate) is utilized as the draw solution, for which the fresh water can be achieved in the FO process. In this study, the BES can be considered as a pre-treatment for the FO process, which removes the organics and partial contaminants with a reduction in the biodegradability of landfill leachate. As a result the problem of FO membrane fouling can be minimized much more effectively.

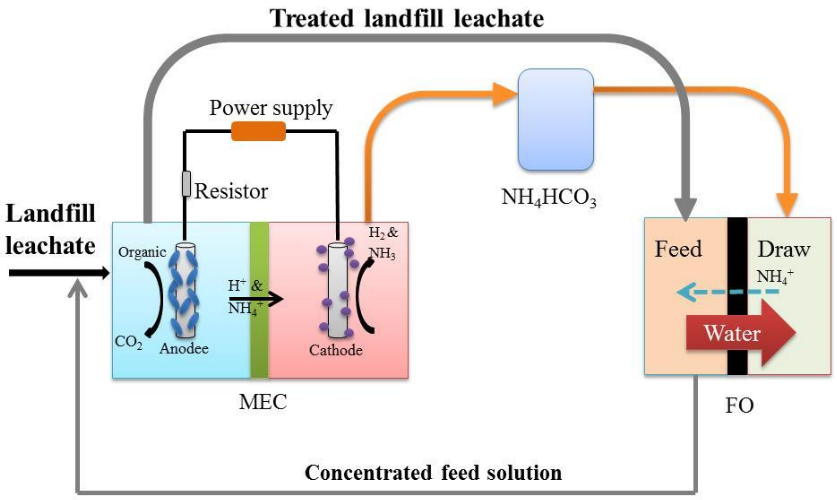

Figure 2.6 Schematic representation of the MEC-FO hybrid system for the nutrient recovery.

2.3 MBR-based hybrid system

The MBR-based hybrid system can remove organics from the feed solution and the membrane fouling potential is thereby decreased, which enhances the efficiency of nutrient recovery. The FO membrane replaces microporous membranes (i.e. microfiltration (MF) or ultrafiltration (UF) membranes) in the conventional MBR to form the osmotic membrane bioreactor (OMBR) (Huang et al., 2015). Compared to the traditional MBR, the OMBR has several advantages including: a) higher rejection rate for most microbes and impurities such as nutrient and mineral salts; b) lower membrane fouling propensity and energy consumption; and c) higher quality of treated wastewater (Achilli et al., 2009; Alturki et al., 2012; Neoh et al., 2016).

Qiu and Ting (2014a) utilized the OMBR-based hybrid system to directly recover nutrient from municipal wastewater with over 90% of nutrient being recovered via struvite precipitation (Fig. 2.7). In this scenario, the FO membrane can highly reject nutrient and mineral salts (e.g. Ca^{2+}, Mg^{2+} and K^+) and thereby enrich them within the bioreactor, so there is no need to add Ca^{2+} and Mg^{2+} for the subsequent nutrient recovery via chemical precipitation. As the draw solute in this study, $MgCl_2$ is used so the reverse draw solute could supplement Mg^{2+} ions to benefit nutrient recovery via struvite precipitation. The salinity of the OMBR-based hybrid system can be controlled at a moderate level due to the nutrient and mineral salts consumed by nutrient recovery. Moreover, due to no need of biological activity in the nutrient recovery process, the selection and enrichment of phosphate accumulating organisms (PAOs) can be avoided while the P-rich surplus sludge production is reduced (Qiu and Ting, 2014a). Notably, the process in this hybrid system is streamlined. This is because once wastewater is fed to the bioreactor, the nutrient is highly rejected by the FO membrane with the mineral salts, after which the nutrient reacts with mineral salts to form precipitates at high pH (> 8). Nearly all the nutrient accumulated within the bioreactor can be recovered except for those that are bioassimilated by the microorganisms.

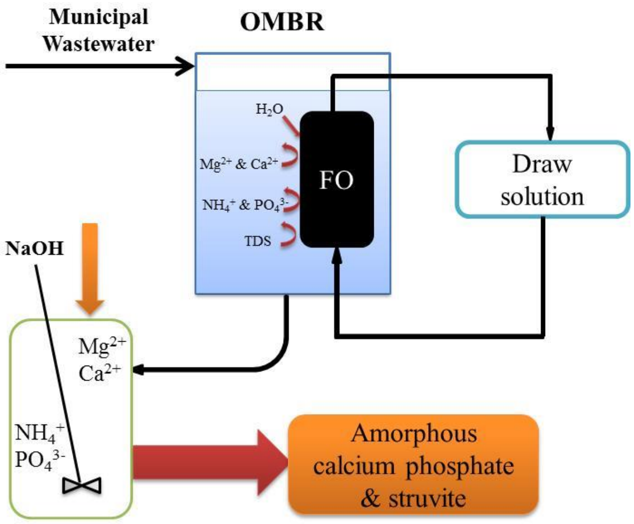

Figure 2.7 Schematic of the OMBR hybrid system for direct nutrient recovery (adapted from Qiu and Ting (2014a)).

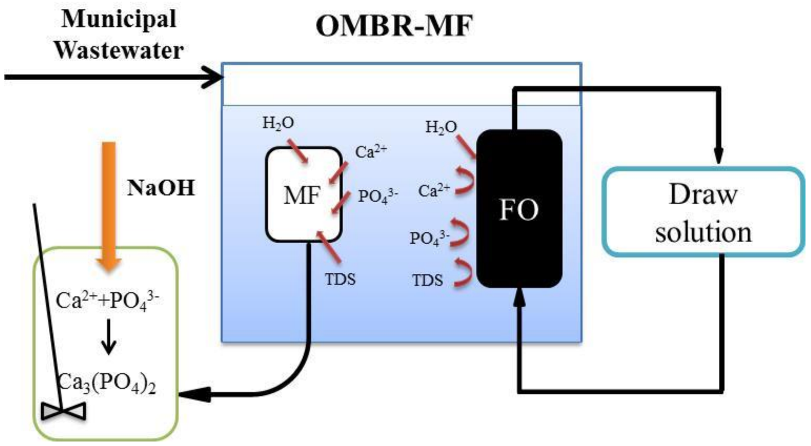

Figure 2.8 Schematic of the OMBR-MF hybrid system for direct nutrient recovery (modified from Qiu et al. (2015)).

Recently, many authors devote to developing the OMBR hybrid system for the nutrient recovery. Based on the OMBR hybrid system, Qiu et al. (2015) added the MF membrane to the system for phosphate recovery, in which MF and FO membranes function in parallel (Fig. 2.8). In this scenario the MF membrane extracts phosphate and mineral salts rejected from the bioreactor, so phosphate can be recovered through calcium phosphate precipitates without the input of Ca^{2+} ions. The results show that the phosphate can be enriched up to 70 mg/L in the bioreactor and 98% of phosphate can be recycled. However, the phosphate and ammonium may react with mineral salts such as Mg^{2+} and Ca^{2+} for the precipitation within the bioreactor if the concentrations of nutrient and mineral salts are high in the feed solution. As a result of this, the amounts of nutrient extracted by the MF membrane for the subsequent recovery may decrease. Increasing MF flow rate may address this issue since this could lower the risk of spontaneous precipitation between nutrient and mineral salts (Qiu et al., 2015). However, Luo et al. (2016) indicated if the MF extraction is conducted at low permeate flux or periodic extraction mode, the economic feasibility of the hybrid system for the P recovery would be improved due to the reduction in the energy consumption and fouling potential of the MF membrane. Moreover, Qiu et al. (2016a) developed a fixed bed biofilm to replace the role of the MF membrane in the OMBR-MF hybrid system, for which the solid/liquid separation to extract the side-stream for controlling salt accumulation and recovering P can be obviated and energy consumption is thereby reduced. In comparison to the OMBR-MF hybrid system, the FO membrane fouling potential is reduced in the OMBR-biofilm hybrid system. The possible reason for this is the separation between biomass and the FO membrane substantially reduces bacteria deposition and colonization. Similarly, Holloway et al. (2015) proposed a new OMBR-based hybrid system, which use a UF membrane in parallel to the FO membrane to form UF-OMBR hybrid system. Compared to the OMBR hybrid system, lower membrane fouling of the FO membrane was observed in the UF-OMBR hybrid system. The possible reason for this is that salts could be drawn by the hybrid system, which maintains low salinity in the activated sludge. Besides, severe membrane fouling associated with the cations may decrease because the concentration of such cations was potentially reduced in the bioreactor. The UF permeate can concentrate more than 50 mg/L phosphate from real municipal wastewater, which is beneficial for the subsequent nutrient recovery. Furthermore, the reverse osmosis (RO) membrane can be employed in the OMBR-based hybrid system to recover fresh water from the draw solution (Luo et al., 2016).

Furthermore, anaerobic MBR (AnMBR) constitutes a promising kind of MBR for nutrient recovery. A possible reason for this is that most of the N and P can be released as ammonium and phosphate, respectively, in the AnMBR permeated wastewater, which would enable subsequent nutrient capture (Jensen et al., 2015). Only partial N and P are removed by biomass growth due to the low biomass yields typical for anaerobic microbes (Smith et al., 2012). Besides, the AnMBR can reduce organic matter and produce energy, thus increasing the technical and economic feasibility of the AnMBR-based hybrid system for recovering nutrient (Ozgun et al., 2013). Jensen (2015) studied nutrient recovery from red meat processing wastewater through AnMBR-based hybrid system and found that 90% of ammonium and 80% of phosphate are recovered. Moreover, pH of the feed solution should be depressed to avoid the loss of nutrient because nitrogen can be converted into gaseous ammonia at high pH (Jensen, 2015). Generally, the biological activity highly depends on the temperature and increases by rising temperature in a certain range (Ozgun et al., 2013). Thus, keeping the temperature at a relatively high level contributes to the enrichment of nutrients that are released by the activity of microorganisms. Ozgun et al. (2013) also suggested that the performance of AnMBR could remain stable at the organic loading rate ranging from 0.5 to 12.5 kg chemical oxygen demand (COD)/m^3 day. This indicates that the AnMBR-based hybrid system could concentrate nutrient over a wide range of wastewater sources due to its tolerance of organic loading rates.

It should be noted here that the anaerobic OMBR (AnOMBR) has more advantages than traditional AnMBR (Chen et al., 2014b), including: a) lower fouling potential due to the FO membrane applied, for which the foulant layers could be compacted and thus decrease water permeation (Lay et al., 2010; Liu et al., 2017a); b) reduce the effluent concentration of dissolved methane; and c) increase the removal/recovery efficiency of P, N and soluble carbon (Martinez-Sosa et al., 2011; Smith et al., 2013; Smith et al., 2012). For this reason, Hou et al. (2017) installed a microbial electrochemical unit into an AnOMBR to form microbial recovery cell (MRC)-AnOMBR system. In this system, the electricity derived from the MRC could extract nutrient and mineral salts from the AnOMBR bulk solution and then drive them to a separated solution for their recovery. Furthermore, 65% of phosphate and 45% of ammonium ions could be recovered with simultaneous excellent removal of organic (>93%). The production of methane was up to 0.19 L CH_4/g COD.

2.4 Comparison of membrane hybrid systems for nutrient recovery

2.4.1 Technical feasibility

Table 2.2 Advantages and disadvantages of various membrane hybrid systems for nutrient recovery.

Membrane hybrid system	Advantages	Disadvantages
FO-based	Low fouling propensity High fouling reversibility High rejection rate for nutrient	Reverse salt flux Organics accumulation Reconcentration of the draw solution
MD-based	High membrane selectivity for ammonia Possibility of the renewable energy utilized Low operating pressure	Membrane wetting Organics accumulation
ED-based	High efficiency for nutrient enrichment	High energy consumption Irreversible membrane fouling Organics accumulation
BES-based	Positive energy balance Low chemical consumption	Accumulation of recovered nutrient on the cathode
OMBR-based	Low energy consumption Low fouling tendency Removal of organic contaminants	Reverse salt flux Reconcentration of the draw solution
AnMBR-based	Low fouling potential Energy recovery	Be sensitive toxicity

As shown in Table 2.2, membrane fouling is a big challenge while applying the membrane hybrid systems for nutrient recovery from wastewater (especially from urine and digested sludge) (Quist-Jensen et al., 2015). The problems encountered are that it may deteriorate the membrane performance, increase energy consumption and consequently reduce economic feasibility.

The membrane fouling resulting from the FO process is readily reversible and thereby easier to clean (Ansari et al., 2017). Another challenge associated with the FO process is that the draw solution is gradually diluted by the permeated water and partial draw solute simultaneously migrates to the feed solution due to the reverse salt flux (Xie et al., 2016). For this reason, the diluted draw solution needs reconcentration if it is expected to be reused; alternatively, a supply of new draw solute is required, but both methods increase operational costs and energy consumption (Achilli et al., 2010). To address this concern, ammonium bicarbonate is a preferred draw solute because it can be easily be recycled through moderate heating (McCutcheon et al., 2005). Furthermore, seawater can be employed as the draw solution if the FO process is applied near a coastal area. The possible reason for this is that: firstly, the transport fees of the draw solution can be obviated; and secondly, there is no need to regenerate the draw solute and the diluted seawater can be directly discharged to the sea. Apart from this, the seawater brine which is a by-product stemmed from the seawater reverse osmosis (SWRO) process can also be used as a draw solution in the FO process because of high osmotic energy (Qiu et al., 2015). After the seawater brine is treated by osmotic dilution, it can be directly returned to the SWRO process without further disposal (Elimelech and Phillip, 2011; Hancock et al., 2012). It should be noted here that coupling FO process with other membrane process such as MD and ED could also reconcentrate the diluted draw solution and simultaneously have the recovery of fresh water (Ansari et al., 2017). In addition, the reverse draw solute flux may not only cause the loss of the draw solute, but also deteriorate the quality of feed solution (Boo et al., 2012; Xie et al., 2014a). Consequently, nutrient recovery is detrimentally affected since the nutrient is rejected and accumulates in the feed side. However, if the Mg-based solution is employed as the draw solution and nutrient is expected to be recovered in the form of struvite, the reverse draw solute flux can supplement Mg^{2+} ions for the struvite formation in the FO-based hybrid system (Xie et al., 2014b). However, the reconcentration of the draw solution is another challenge for the application of FO-based hybrid systems as well as the reverse draw solute flux.

The presence of dissolved organic matters and colloids may result in the membrane wetting in the MD process, for which the feed solution can directly flow through the MD membrane to the permeate side and thus deteriorate the quality of distillate (Gryta et al., 2009; Thygesen et al., 2014; Zarebska et al., 2014). Also, the transfer of heat and mass is blocked because of membrane wetting and the ammonia permeation is detrimentally affected. This despite the fact that 99% of heavy metal such as lead and nearly 100% of antibiotics such as cefotaxime and neutral ciprofloxacin could be rejected in the MD process (Attia et al., 2017; Guo et al., 2018), which facilitate the subsequent ammonia recovery. To address this problem, the wetted MD membrane has to be taken out of the reactor and dried completely, but this must limit the application of the MD-based hybrid system for nutrient recovery. Moreover, some volatile components in permeate streams may seriously hinder nutrient recovery in the MD-based hybrid system. For example, volatile fatty acids can migrate to the permeate side in the MD process, which may contaminate the nutrient-rich permeate streams and impair the quality of recovered nutrient (Xie et al., 2016). Nevertheless, the concentrations of feed solution (especially the salt concentration) have less effect on the quality of penetrating fluid in the MD process compared to other pressure-driven membrane separation processes. The possible reason for this is the driving force in the MD process is derived from the vapour pressure gradient between the feed side and permeate side. Besides, it is more likely for the MD process to utilize the renewable energy sources as a thermally-driven membrane process. The operating pressure of the MD process is lower than that of other pressure-driven membrane techniques. It is notable that the ammonia-rich solution has higher vapour pressure than water, so higher concentrations of ammonia can enhance the vapour pressure gradient between the feed side and permeate side, which improves the ammonia migration to the permeate side (El-Bourawi et al., 2007).

Furthermore, membrane fouling in the ED-based hybrid system may reduce the migration and selectivity of ions (Mondor et al., 2009). It is noted here that the existence of surfactant, protein and negatively charged humic substances can result in the fouling of anion-exchange membrane (Lee et al., 2009; Lindstrand et al., 2000; Watkins and Pfromm, 1999) while the cation-selective membrane deteriorates due to calcium-dominated scaling (Ayala-Bribiesca et al., 2006; Bazinet and Araya-Farias, 2005). Several methods can be conducted to moderate the problem of membrane fouling in the ED process, for instance chemical cleaning with acids or alkalis, reversing the polarity of electrodes regularly and reducing current density (Lee et al., 2002; Mondor et al., 2009; Ruiz et al., 2007). Nevertheless, the lifetime of ion-exchange membranes is long due to the low likelihood of membrane scaling and fouling, and the fact that membrane performance can be improved at higher temperatures (Quist-Jensen et al., 2015). Another issue involved in the ED-based hybrid system for nutrient recovery is that the coexisting ions in wastewater have competitive effects on nutrient fractionation. For example, sulphate and bicarbonate ions are driven by electricity to the anode chamber with phosphate ions. In this scenario, the foreign ions must disturb any further

P recovery and even deteriorate the quality of recovered phosphate. However, the competitive effects are only observed in the initial stage and if the ED-based system operates for a longer time, the impacts can be eliminated (Tran et al., 2015). Moreover, the ED-based hybrid system is highly energy dependent, resulting in high energy consumption. Thus, coupling the ED process with the renewable energy sources could make the ED-based hybrid system more economically feasible.

Compared to the MD- and ED-based hybrid systems for recovering nutrient, the inherent advantages of the FO-based hybrid system include: a) low energy consumption because it utilizes the osmotic driving force derived from the draw solution (Wang et al., 2014b); b) high rejection rate for nutrient in the feed solution; and c) low membrane fouling potential due to the absence of hydraulic pressure applied (Cath et al., 2006; Praveen et al., 2015; Shan and Guo, 2013).

When applying BES to recover nutrient, the organics in the feed solution can be effectively removed and thus lower the membrane fouling potential. The removal of harmful substances such as antibiotics should be highly mentioned because its presence may negatively affect the quality of recovered nutrient and its later use. In the study of Zhou et al. (2018), results showed that nearly all of aureomycin, roxithromycin and norfloxacin could be removed in the MFC and the presence of antibiotics may greatly inhibit the electricity production and thereby have serious impacts on the ammonia migration. Similarly, Xu et al. (2018a) employed MFC for the removal of pharmaceutically active compounds such as pharmaceuticals and endocrine disrupting chemicals which poses a risk to the environment and human health. They observed that the more than 80% of carbamazepine could be removed.

In comparison to the MFC, the MEC can better accelerate ammonium migration from the anode to the cathode chambers due to more electrons being derived from the external high voltage (Sotres et al., 2015; Zhang et al., 2014a). However, the absence of aeration makes it difficult for the ammonia stripping out of the catholyte, for which partial ammonia is accumulated in the catholyte. Another challenge is the external power supply increasing the energy consumption in the MEC. In addition, even though the aeration supply can facilitate ammonia stripping out of the cathode chamber in the MFC, this may also increase the depletion of energy. It is therefore important to develop an appropriate method to push the ammonia out of the catholyte. Nevertheless, in theory recovering ammonium via MFC still has a positive energy balance (Kuntke et al., 2012).

In comparison to the membrane-based hybrid systems (except for the BES-based hybrid system), the MBR-based hybrid system can remove organics such as antibiotics and thus minimize the possibility of membrane fouling (Karaolia et al., 2017; Wang et al., 2018). For example, Raghavan et al. (2018) used the OMBR-based hybrid system for the removal of 12 antibiotics from 5 classes and found that 77.7-99.8% of selected antibiotics can be removed through biodegradation and/or biosorption. More importantly, the removal efficiency of such antibiotics had negligible changes after continuously operating the OMBR for 40 days. Besides, Salinity accumulation in the MBR-based hybrid system may reduce water flux and seriously affect biological activities (Qiu and Ting, 2013; Yap et al., 2012). The possible reason for this is that increasing salinity can change the sludge's surface property such as hydrophobicity and cause the number of extracellular polymeric substances to increase (Qiu and Ting, 2014b). However, the salinity level can be controlled in a manageable range since the nutrient and mineral salts are depleted for the precipitates formation while employing the OMBR-based hybrid system for nutrient recovery. At the same time, membrane fouling can also be moderated in the OMBR-based hybrid system because: firstly, the use of the FO membrane can induce low membrane fouling (Yap et al., 2012); and secondly, osmotic backwashing is applied to remove foulants from the FO membrane's surface (Achilli et al., 2009).

In the AnMBR-based hybrid system, the anaerobic digestion of biosolids can increase the concentrations of dissolved magnesium and phosphate through cell lysis as well as ammonium via protein degradation (Ohlinger et al., 1998; Stuckey, 2012), thus benefiting the nutrient recovery via chemical precipitation. Removing organic substances can decrease membrane fouling potential, but the membrane's sensitivity to toxicity still detrimentally affects the commercial application of AnMBRs at plant-scale (Skouteris et al., 2012). Nevertheless, Huang et al. (2018) found that the AnMBR could be utilized to treat the antibiotics from real pharmaceutical wastewater, in which 73.2 ± 4.3% of amoxicillin and 79.4 ± 4.1% of cefoperazone were removed. The similar findings have been reported by other researchers (Hu et al., 2017; Xiao et al., 2017). It should be noted here that the membrane fouling in the anaerobic reactors such as AnMBRs is more severe than that derived from the aerobic processes (e.g. MBRs) due to containing higher concentrations of foluants.

2.4.2 Costs involved in the nutrient recovery

It was reported that the operational and maintenance costs of nutrient recovery are €2800 and €520 (≈ US$3459.34 and 642.45)/ton·struvite when the initial P concentrations are 50 and 800 mg/L, respectively (Dockhorn, 2009). Similarly, De Vrieze et al. (2016) analysed the operational costs involved in the ammonia recovery in three wastewater treatment plants and found that the costs decreased from €10.70 (≈ US$13.22) to 2.63 (≈ US$3.25)/kg·N when the total ammonia nitrogen concentration in the influent increased from 539 to 2470 mg/L. Both of the findings indicate that the recovering high concentrations of nutrient from wastewater could not only supplement fertilizers production to ensure food security, but also decrease the overall costs involved in the wastewater treatment. This is also the reason to use membrane technology for the nutrient enrichment and subsequent recovery.

Through the energy analysis of the N recovery (See Table 2.3), it could be seen that the ammonium recovery via BES has advantages over the traditional ammonia stripping.

Table 2.3 Energy analysis of different systems for the N recovery (Kuntke et al., 2012; Maurer et al., 2003; Qin and He, 2014)

	MFC	MEC	Conventional NH_3 stripping
Energy consumption (kJg_N^{-1})[a]	18.38	10.93	26.3
Net energy yield (kJg_N^{-1})	-18.38	3.46	-32.5
Ammonium recovery rate ($g_N d^{-1} m^{-2}$)[b]	27.36	3.29	N/A

a The consumption of energy includes external power, aeration and recirculation.

b The rate indicates the N recovery per day per surface area of cation exchange membrane.

For the ammonia recovered by the stripping integrated with adsorption, Desmidt et al. (2015b) found that the market value of ammonium sulphate as the recovered ammonia product was estimated to €1.0 (≈US$1.24)/kg·N. Moreover, it is evident that struvite formation needs alkaline chemicals such as CaO and NaOH for pH adjustment, which accounts for 97% of total chemical costs (Jaffer et al., 2002). However, the formation of struvite in BES does not need pH adjustment because the cathode reaction can cause the pH elevation.

In the OMBR-based hybrid system, the addition of mineral salts for the nutrient recovered by chemical precipitation can be avoided and the costs can be controlled. With reference to the AnMBR-based hybrid system, it can recover energy through methane fermentation and the recovered biogas can be utilized to produce electricity as fuel (Hou et al., 2017). However, hydrogen sulphide existing in the biogas may inhibit application of the methane fermentation due to its corrosivity and toxicity (Weiland, 2010), so the off-gas needs further processing. In contrast, the energy recovered by the BES such as electricity and hydrogen gas can be used directly. In addition, Jensen (2015) reported that the costs for recovering P and N through the AnMBR-based hybrid system are US\$3.50/kg·P and 1.33/kg·N, respectively. Similarly, the production of methane could be achieved up to 0.19 L CH_4/g COD in the nutrient recovery process through the AnOMBR-based hybrid system (Hou et al., 2017).

Renewable energy such as solar energy can be employed to operate the membrane hybrid system for nutrient recovery from wastewater, for which the total costs can be reduced (Zhang et al., 2013c). Zhang et al. (2013c) used solar energy for enhancing the FO-ED membrane hybrid system's sustainability with solar panel prices ranging from €3.32 to 4.92 (≈US\$4.10 to 6.08)/m^3. Moreover, the waste heat energy derived from the power plant can serve as the hybrid system's energy source (Qin and He, 2014; Zhou et al., 2015). In addition, recovering phosphate from wastewater can save €2-3 (≈ US\$2.47-3.71)/kg·P of operational costs compared to phosphate removal (Dockhorn, 2009). Shu et al. (2006) reported that phosphate recovered by struvite can reduce the production of excess sludge and AUD\$1.13 (≈ US\$0.88)/kg·struvite is thereby saved. Similarly, Jeanmaire and Evans (2001) reported that the overall costs in sewage treatment can be reduced by UK 100 pounds (≈ US\$141.72)/ton·P if the process of P recovery is conducted. Moreover, nutrient recovery can produce more fertilizers that can help agriculture. Achat et al. (2014) compared struvite as the recovered nutrient to commercial fertilizers and discovered there is negligible difference between them in terms of fertilization efficiency. This is despite the fact that the market prices of raw phosphate rock and struvite are €0.6-1.2 (≈ US\$0.74-1.48)/kg·P (Desmidt et al., 2015b) and €2.6 (≈ US\$3.21)/kg·P (Dockhorn, 2009), respectively. Hence, the recovered nutrient can be applied as supplementary fertilizers.

2.5 Future perspectives

Wastewater is considered to be the greatest potential source for nutrient recovery because it contains rich nutrient and in large quantities. As nutrient is transferred from a decentralized industry and household to a centralized wastewater treatment plant, the concentration is decreased along this route. The use of membrane technology can enhance the nutrient enrichment, which substantially improves the economic feasibility of nutrient recovery. Besides, membrane process can also separate nutrient from heavy metals and toxic substances and thereby increase the quality and purity of recovered nutrient products. Thus, membrane hybrid system is a promising technology for the nutrient recovery from wastewater. Referring to membrane technology, membrane manufacturing needs more studies that focus on low-cost reduction of potential membrane fouling.

Contaminants in the feed solution such as toxic substances and organic matter need to be removed to decrease the chances of membrane fouling. To remove contaminants from the surface of membrane, back-flushing and chemical clean are necessary, but the system's operational costs may be increased due to consumption of chemicals and energy. It is notable that MBR integrated with FO, MFC, etc., can effectively ameliorate membrane fouling (Hou et al., 2016; Neoh et al., 2016; Ozgun et al., 2013). For example, the membrane fouling in the AnOMBR can be alleviated while applying MFC as the pretreatment (Hou et al., 2016). In this scenario, the MFC could assist the AnOMBR with decreasing the amount of foulants and change the property of the sludge, for which the fouling could be reduced. On the other hand, the electrolyte conductivity can be increased by AnOMBR and the electrochemical reaction kinetics and electricity generation can be thereby enhanced. Similarly, the current density of MEC can be improved through AnOMBR due to the concentrations of organics and solutes in the bulk and increase in the buffer capacity (Hou et al., 2017). In this scenario, the nutrient accumulation for further nutrient recovery could be enhanced as well as the biogas production for recovering energy. It is worth mentioning that the higher selectivity of membranes could improve the performance of BES-AnOMBR hybrid systems (Hou et al., 2017). Moreover, the nutrient recovery could alleviate the migration of the ammonium ions to the draw solutions and decrease the scaling potential caused by phosphate ions in this hybrid system. In addition, the development in the fabrication of membrane can facilitate less likelihood of membrane fouling (Zhang et al., 2014c). For example, the MD membrane with wettability can enhance its anti-fouling ability and thus moderate membrane fouling in the MD process (Liao et al., 2013; Liao et al., 2014; Lin et al., 2014). However, the high costs of membrane construction still constrain improvements in the membrane hybrid system at full-scale (Lin et al., 2011).

Of all the membrane hybrid systems discussed above, the BES- and OMBR-based hybrid systems are the most promising for the nutrient recovery because they can remove organics from the feed solution and thus reduce the membrane fouling potential. For this reason, the technical and economic feasibilities of nutrient recovery are enhanced. It should be noted here that ammonium and energy recovery in the MFC does experience conflict (Kelly and He, 2014). The high current density could facilitate ammonium migration and an increase in the pH of catholyte, but little energy can be recovered. In contrast, if the MFC maximally recovers energy, the electric current may be moderated and ammonium migration is thereby seriously affected. For the purpose of ammonium recovery, MFC should be designed so that ammonium recovery is preferred. Zhang et al. (2013a) have proposed multiple MFC modules consisting of an MFC system which can simultaneously recover ammonium and energy in a separate MFC module.

The phosphate recovery in the BES is obtained by the formation of precipitates on the surface of the cathode, but the recovery mechanism is not clearly understood (Damiano et al., 2014). Precipitates on the cathode may seriously affect the current generation and cathode performance, which inhibits nutrient recovery. Therefore the effects of the phosphate-based precipitates on nutrient recovery should be assessed. Furthermore, how to deal with the cathode covered by the precipitates needs to be investigated. Certainly, a removable cathode can be designed to address this concern. In this scenario, the cathode can be removed from the BES for regeneration while a new cathode should be inserted into the system to ensure it continues to operate. Alternatively, multiple cathode chamber modules can be implemented, and these modules can be replaced for the purposes of regeneration if it is contaminated by the precipitates.

Additionally, the single-chamber BES is the most studied for nutrient recovery, but this configuration may not benefit the increase in pH near the cathode electrode. This may be because the anode and cathode chambers share the same electrolyte and pH of the electrolyte could be buffered through the anode reaction (accumulating protons) and cathode reaction (generating hydroxide ions). However, the double chamber configuration of the BES can well separate the anode reaction (i.e. oxidation) from the cathode reaction (i.e. reduction), for which the purity of the recovered product can be increased (Hamelers et al., 2010). Hence, the future studies should pay more attention to the double-chamber configuration in the BES.

The OMBR-based hybrid system can reject a lot of nutrient and mineral salts with low membrane fouling and energy consumption (Achilli et al., 2009; Alturki et al., 2012; Neoh et al., 2016). In the OMBR-based hybrid system, the FO membrane's performance is affected by a trade-off between water permeability and solute selectivity because of inherent properties (Yip and Elimelech, 2011). If the FO membrane with high water permeability is employed to concentrate nutrient, membrane selectivity may be reduced and the reverse draw solute flux subsequently occurs, which may impair the quality of the feed solution. Simultaneously, partial nutrient may simultaneously permeate into the draw solution, resulting in the loss of nutrient. Certainly, if the draw solution contains the Mg-based solute, the reverse draw solute flux can facilitate nutrient recovery through struvite precipitation due to the supply of Mg^{2+} ions. On the other hand, the FO membrane with high solute selectivity can better enrich the nutrient in the feed side. However, the reverse salt flux of Mg^{2+} ions is inhibited, which reduces struvite precipitation potential. Hence, further studies on membrane permeability-selectivity trade-off are essential. In addition, the reduction in hydraulic retention time (HRT) can also result in a decrease in the process footprint and operational costs because of the shorter processing time with negligible effects on phosphate enrichment and recovery (Qiu et al., 2016b). However, the reduced HRT may rise the system loading rates and thereby increase the membrane fouling potential. As a consequent of this change, the additional costs would occur. Further studies should investigate the optimized HRT with respect to: a) wastewater composition; b) treatment requirements; and c) overall costs at full-scale.

As for the AnMBR-based hybrid system, it can remove organic matter and release phosphate and ammonium ions through the production of energy. Thus, more research on the AnMBR-based hybrid system for nutrient recovery should be conducted.

In most cases, the nutrient is recovered in the form of struvite due to: a) its high application potential in the agriculture as fertilizers; and b) simultaneous recovery of N and P. However, struvite formation is difficult to achieve in real wastewater since it requires large stoichiometric amounts of magnesium, ammonium and phosphate (1: 1: 1). In the BES-based hybrid system for nutrient recovery, precipitates formed on the surface of the cathode are considered to be phosphate-based substances with little struvite (Hao et al., 2013b). However, this does not mean the compounds cannot be applied as fertilizers. Therefore, struvite is not the only choice for nutrient recovery, more choices such as hydroxylapatite can be pursued for direct land application with similar fertilization efficiency as struvite. The quality and composition of the feed water should be analysed because it affects the purity of the recovered product (Le Corre et al., 2009). Another challenge involved in the membrane hybrid system is that struvite formation may occur during the nutrient enrichment process (Xie et al., 2014b). For this reason, low pH should be strictly controlled in the 6.0-6.5 range to avoid spontaneous precipitation of nutrient in the reactor (Qiu et al., 2015; Qiu and Ting, 2014a) before the nutrient is recovered by chemical precipitation.

2.6 Conclusion

Currently, recovering nutrient from wastewater is more valuable than nutrient removal. The possible explanation is that this recovery can provide a supplementary source for fertilizer production, thus easing the burden of increasing demand for food production. Another advantage associated with nutrient recovery is that it can reduce the serious impacts of wastewater treatment on the environment and save costs. Membrane technology can enrich nutrient with high purity, which can improve the economic feasibility of the nutrient recovery process. Considering the membrane fouling as a big challenge for the application of membrane hybrid system to recover nutrient, the integration of membrane technology with biological process such as BES- and OMBR-based hybrid systems may be the most promising technology since this method could effectively remove organics through biological activity and thereby reduce the potential for membrane fouling. In this scenario, the technical and economic feasibility of nutrient recovery is enhanced. Specifically, the inherent advantages of the BES-based hybrid system for nutrient recovery are shown below: i) it can reduce membrane fouling because it removes organics; ii) the pH elevation for nutrient recovery can be achieved by cathode reaction instead of adding alkaline chemicals; and iii) it has a positive energy balance in MFC. It is evident that the OMBR-based hybrid system is preferred to recover nutrient from wastewater due to: a) the low membrane fouling potential caused by the use of the FO membrane and organic removal; b) less energy consumption; and c) high rejection rate for nutrient and mineral salts, and no input of mineral salts is thereby needed for nutrient recovery. However, for the sustainability of nutrient recovery from wastewater in the BES-based hybrid system, the cathode electrode contaminated by the formed precipitates must be properly treated by either replacement or regeneration. Therefore, further researches are needed to focus on the effects of precipitate on the BES-based hybrid system and how to effectively achieve the precipitates. Similarly, the trade-off of FO membrane between water permeability and solute selectivity greatly influence the application of OMBR-based hybrid systems to recover nutrient, which is controlled by the raw materials and preparation process of the FO membrane. Therefore, more studies should be conducted for this. It should be noted here that the activities of microorganism are involved in the BES- and OMBR-based hybrid systems. Hence, how to control the biological stability and reliability is one of the most important issues for the nutrient recovery. To sum up, future research should focus on improving the technical and economic feasibility of the OMBR- and BES-based hybrid systems for recovering nutrient. Moreover, their applications at pilot- and plant-scale need more studies to make these more viable.

CHAPTER 3

Experimental investigation

3.1 Introduction

This chapter provides detailed information about the composition of synthetic wastewater, membrane, experimental setup, operating conditions and analytical methods for the MFC system (Chapter 4-7) in a series of experimental investigations conducted to achieve the objectives of this research outlined in Chapter 1.

3.2 Materials

3.2.1 Synthetic wastewater

In the present study, the synthetic wastewater simulated the domestic wastewater which was processed by the primary treatment including coarse bar screen, fine bar screen, and primary settling tank. In this scenario, the fluctuation can be maximally avoided in the feed solution with a sufficient source of biodegradable organic pollutants provided. In the synthetic wastewater, organics such as glucose and macronutrients including ammonium chloride, potassium dihydrogen phosphate, and trace nutrients are contained (Table 3.1). Furthermore, a stock solution was prepared for 5-days use and stored in a refrigerator at 5 ± 0.5 °C, in which the synthetic wastewater was obtained through diluting the stock solution with distilled water (DI water). The synthetic wastewater was fed continuously and evenly to the treatment system.

Table 3.1 Characteristics of the synthetic wastewater (displayed in the case of COD: N: P = 300: 5: 1)

Compounds	**Chemical formula**	**Molecular weight (g/mol)**	**Concentration (mg/L)**
Organics and nutrients			
Glucose	$C_6H_{12}O_6$	180.0	280
Ammonium chloride	NH_4Cl	53.5	20.25
Potassium phosphate	KH_2PO_4	136.1	4.65
Trace nutrients			
Calcium chloride	$CaCl_2 \cdot 2H_2O$	147.0	0.394
Zinc sulphate	$ZnSO_4 \cdot 7H_2O$	287.5	0.471
Ferric chloride anhydrous	$FeCl_3$	162.2	0.777
Cupric sulphate	$CuSO_4 \cdot 5H_2O$	249.7	0.419
Cobalt chloride	$CoCl_2 \cdot 6H_2O$	237.9	0.45
Sodium molybdate dehydrate	$Na_2MoO_4 \cdot 2H_2O$	242.0	1.35
Magnesium sulphate	$MgSO_4 \cdot 7H_2O$	246.5	5.43
Yeast extract	-	-	32.14
COD	-	-	300
C: N: P			300: 5: 1

3.2.2 Membrane

Cation-exchange membrane (CEM) (CMI-7000) was obtained from Membranes International Incorporated in the USA and used in a specific size for experiments. The technical specifications of such CEM are shown in Table 3.2.

Table 3.2 Technical specifications of CMI-7000 CEM (Inc.)

Functionality	**Strong Acid Cation Exchange Membrane**
Polymer structure	Gel polystyrene cross-linked with divinylbenzene
Functional group	Sulphonic Acid
Ionic form as shipped	Sodium
Color	Brown
Standard size US	48 in × 120 in
Metric	1.22 m × 3.05 m
Functionality	Strong Acid Cation Exchange Membrane
Standard thickness (mils)	18±1
(mm)	0.45±0.025
Electrical resistan (Ohm.cm^2) 0.5 mol/L NaCl	<30
Maximum current density (Ampere/m^2)	<500
Permselectivity (%) 0.1 mol KCl/kg/0.5 mol KCl/kg	94
Total exchange capacity (me$_q$/g)	1.6±0.1
Water permeability (ml/hr/ft^2) @5psi	<3
Mullen burst test strength (psi)	>80
Thermal stability (^{0}C)	90
Chemical stability range (pH)	1-10
Preconditioning procedure	Immerse the membrane in either the application solution or a 5% NaCl solution for 12 h to allow for membrane hydration and expansion.
Storage	Store the membrane at room temperature and low humidity in a sealed airtight container. The storage period should not exceed one year.

3.3 Experimental setup and operating conditions of a double-chamber MFC

A laboratory-scale dual-chamber MFC used in the present study consisted of anode chamber and cathode chamber with a working volume of 350 mL and worked in a temperature-controlled room (Fig. 3.1). In this MFC reactor, a CEM mentioned in Section 3.2.2 was employed in the middle between two chambers, in order to separate them. The chambers and CEM were sandwiched together with silicon gaskets to prevent leakage of anolyte and catholyte. A cylinder-shaped graphite felt served as the anode electrode (Sanye Carbon Co. Ltd., Beijing, China) with a thickness of 6 mm and diameter of 30 mm (see Fig. 3.2a). A carbon-fiber brush (length 30 mm and diameter 30 mm) acted as the cathode electrode (Fig. 3.2b). Apart from this, the seed sludge was taken from Cronulla wastewater treatment plant (Greenhills Beach, New South Wales, Australia) and adopted as the inoculum at the anode compartment. Subsequently, the anaerobic sludge was transferred to the laboratory and then left for 24 h to separate the liquid and solids. After that, the anaerobic sludge was transferred to the anode chamber as the inoculum in the MFC. As for the remaining sludge, it was stored in a fridge at −5 °C to avoid changes in the biological community. Then, the anaerobic sludge with MLSS of 5.0 g/L was added into the anode chamber of double-chamber MFC and cultivated in a sequencing batch mode under room temperature (22 ± 2 °C). During this period, the synthetic municipal wastewater which had a fixed composition (see Table 3.1) was fed to the anode compartment. This process is aimed to make the anaerobic microbes adapted to the new environment. The MFC reactor was used for the experiments until achieving the voltage stabilized. In the continuous mode, the feed solution was pumped to the anode chamber through a peristaltic pump (Model 77202-60, Masterflex, Illinois, United States). Furthermore, the DI water was served as the catholyte of the MFC system.

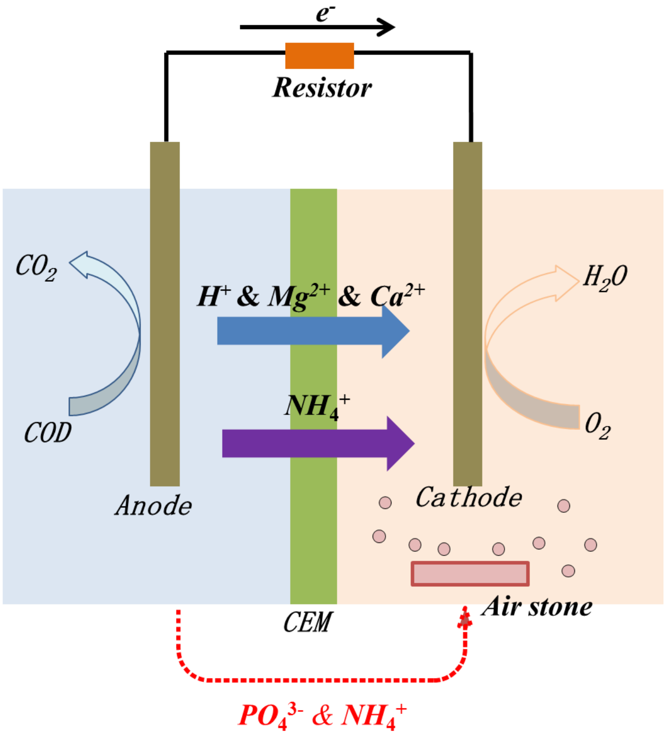

Figure 3.1 Experimental set-up of MFC

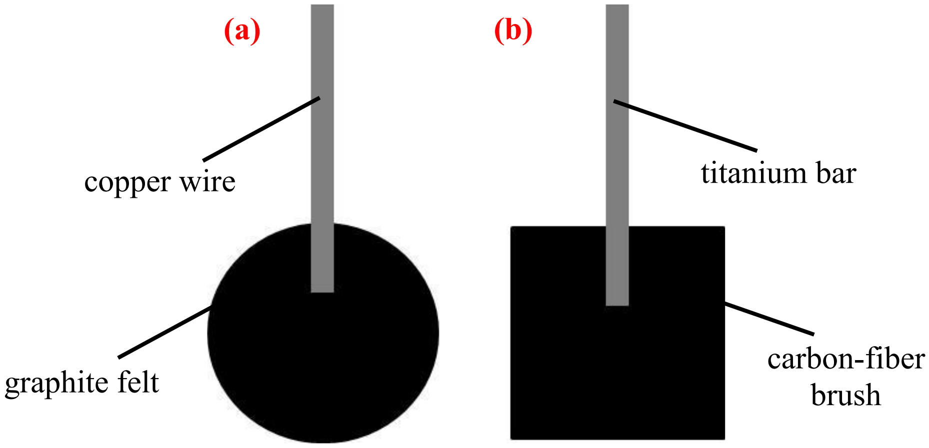

Figure 3.2 The schematic: a) anode electrode; b) cathode electrode

3.4 Analytical methods

For the experimental investigation, all the liquid, gas and sludge samples were tested in duplicate, with an average value and standard deviation for discussion.

3.4.1 Organics, nutrients, pH, DO and electricity

Influent and effluent from the anode compartment and cathode compartment were daily analysed. The liquid samples were required to be filtered through 0.20-µm filters which are made by hydrophilic polytetrafluoroethylene (Merck Millipore, Burlington, USA) to remove fine suspended material and any biomass, and stored in the refrigerator before being analyzed. Total organic carbon (TOC) of the influent and effluent was determined by a TOC analyzer (Analytikjena Multi N/C 2000). Besides, the COD concentrations were measured using test kits (HI93754B-25, Hanna Instruments Australia, Melbourne, Australia). The content of NH_4^+-N and PO_4^{3-}-P was tested via test kits 100683 and114848, respectively (Merck Millipore, Burlington, USA). A pH meter (HI9025, Hanna Instruments, Limena, Italy) was employed to monitor the changes in solution pH. The voltage generation in the MFC system was measured by a universal digital meter (VC86E, Shenzhen City Station Win Technology Co. Ltd., Shenzhen, China). The concentration of dissolved oxygen (DO) was determined by DO meter (Horiba Ltd. Japan, model no. OM-51E). The analytical instruments used were shown in Fig. 3.3.

Figure 3.3 The analytical instruments used in the experimental investigation: a) TOC analyser; b) pH meter; c) DO meter; d) universal digital meter

3.4.2 Electricity calculation

The current (I) generated in the MFC system was calculated according to the Ohm's law, as shown in Eq. (3.1).

$$I = \frac{U}{R} \tag{3.1}$$

where U (mV) is the voltage generated in the MFC reactor; and R (Ω) is the external resistance at 1000.

The power output (P, W) and power density (P_A, W/m^2) are calculated through the following equations:

$$P = UI \tag{3.2}$$

$$P_A = \frac{P}{A} \tag{3.3}$$

where A (cm^2) is the surface area of the anode electrode (in the present case on both sides).

The value of coulombic efficiency (C_E, %) which is linked to the electrons' recovery is given by Eq. (3.4) (Logan, 2008).

$$C_E = \frac{8\int_0^t Idt}{F\Delta CODV} \times 100\% \tag{3.4}$$

where t (d) is the running time of MFC reactor; F (C/mol) is the Faraday's constant at 96485; V (mL) is the effective volume of the anode chamber in the MFC; and ΔCOD (mg/L) is the amount of COD removed in the double-chamber MFC.

3.4.3 Characterization of precipitates

The dried precipitates on the electrodes or in the chambers were scraped off with a plastic sheet. The resulting precipitates were washed by the Milli-Q water for three times to remove soluble chemicals from their surface, which was followed by being dried in an oven at 105 °C. The characterizations of the dried precipitates such as scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were analyzed.

CHAPTER 4

Feasibility study on a double chamber microbial fuel cell for nutrient recovery from municipal wastewater

4.1 Introduction

Phosphorus (P) and nitrogen (N) as nutrients are responsible for several serious environmental problems such as eutrophication in water bodies, especially if both are in quantities in the aquatic environment. In water, P and N exist as phosphate and ammonium ions, respectively. It should be noted that phosphate and ammonium are also essential to plants and crops in agriculture and usually used for direct land application in the form of chemical fertilizers. Phosphate as the nonrenewable resource is mainly derived from natural phosphate-based rocks, but it has been estimated that the global phosphate deposits will completely run out in 30-300 years (Elser and Bennett, 2011). This means the production of phosphate-based fertilizers will end at some point. More importantly, the role of phosphate in the fertilizer production will not be replaced by any other materials (Ichihashi and Hirooka, 2012).

Ammonium utilized for the purposes of fertilizer production is usually achieved through the industrial Haber-Bosch process via the conversion of nitrogen gas in the atmosphere to reactive ammonium (Gong et al., 2017). However, this process is energy-intensive and its excessive application may disturb the natural N-cycle and hence cause problems for the environment and people. For this reason, nutrient recovery is more valuable than nutrient removal because it does not only minimize the pollution risk to receiving waters; also it contributes to sustainable resource management (Nancharaiah et al., 2016; Yan et al., 2018). Currently, the concept of municipal wastewater and its treatment has shifted from a human health concern and environmental hazard to one where it is considered to be an untapped source. Firstly, it contains a large amount of valuable components such as nutrients (phosphate and ammonium ions), heavy metals, fresh water and chemical energy stored in the organics. Secondly, it exists in large quantities (Xue et al., 2015).

Understandably, recovering nutrients from municipal wastewater is a promising research approach with a practical benefit. Several methods including adsorption, chemical precipitation and biological processes have been developed or are still in the development stage for nutrients recovery from municipal wastewater (Iskander et al., 2016; Kelly and He, 2014; Ye et al., 2016a; Ye et al., 2017). For example, biological processes such as an enhanced biological phosphorus removal system can efficiently recover nutrients in the form of excessive sludge. However, the surplus sludge contains toxic substances and pathogens (Ye et al., 2016b), so this method has been banned for direct land application in some European countries such as Switzerland (Schoumans et al., 2015).

Even though the effective recovery of N and P could be obtained via adsorption, the desorption of nutrient-loaded adsorbents may be required to achieve the desired recovered nutrients. As for nutrients recovery through chemical precipitation, this has been deemed one of the most promising methods due to its high stability and efficiency. In this scenario, magnesium and calcium materials are usually utilized as the precipitator. Struvite ($MgNH_4PO_4{\cdot}6H_2O$), which has been employed in stoichiometric precipitation of magnesium, ammonium and phosphate, has proved to be an efficient fertilizer when directly applied in agriculture (Desmidt et al., 2015b; Hao et al., 2013a; Johansson et al., 2017; Kataki et al., 2016; Mitrogiannis et al., 2017). Similarly, calcium can react with phosphate to form hydroxyapatite ($Ca_5[OH][PO_4]_3$, HAP) which also works as an efficient fertilizer supplement. The reaction between nutrient and magnesium/calcium ions could be described as follows:

$$Mg^{2+} + PO_4^{3-} + NH_4^{+} + 6H_2O \rightarrow MgNH_4PO_4{\cdot}6H_2O \downarrow \tag{4.1}$$

$$5Ca^{2+} + 3PO_4^{3-} + 3OH^{-} \rightarrow Ca_5(OH)(PO_4)_3 \downarrow \tag{4.2}$$

The chemical precipitation requires high pH (> 8), for which the pH value is the most important influencing factor. More importantly, the chemicals added to increase the pH could represent a high percentage of the cost of the nutrient recovery process (Barbosa et al., 2016; Huang et al., 2014a; Jaffer et al., 2002).

Microbial fuel cell (MFC) is currently considered a promising technology in the wastewater treatment due to its production of electricity and wastewater purification (Deng et al., 2018; Ortiz-Martínez et al., 2015). Typically, the MFC has an anode chamber and a cathode chamber, respectively, and a cation-exchange membrane (CEM) is installed to separate the two chambers. In the anode chamber, the anaerobic microorganisms are catalysts that convert chemical energy stored in organics directly into electricity (Logan et al., 2006; Yang et al., 2018). MFC can use sewage sludge as a substrate, which is considered a kind of biomass (Abourached et al., 2014; Chen et al., 2013). Recently, nutrients recovery through the MFC process has attracted much attention (Kelly and He, 2014; Nancharaiah et al., 2016; Yan et al., 2018) since the pH value of electrolyte can be raised without adding alkaline chemicals (Colombo et al., 2017; Zhao et al., 2006). In this scenario, the costs of pH adjustment can be reduced. Furthermore, the energy recovered in the MFC may be used for its own operation and maintenance, which indicates that the MFC may be a neutral/positive energy balance system.

The single- and double-chamber MFCs constitute the most common types of MFC. Recently, the single-chamber MFC with an air-cathode electrode and multi-chamber MFC coupled with CEMs and/or anion-exchange membranes (AEMs) have been developed for recovering nutrients from wastewater (Chen et al., 2015; Damiano et al., 2014; Geng et al., 2018; Ichihashi and Hirooka, 2012). For example, Chen et al. (2015) proposed a new MFC that simultaneously uses CEMs and AEMs to recover nutrients and purify wastewater. In their study, wastewater was circulated between the anode and cathode chambers and this particular configuration facilitated nutrient accumulation. According to their findings, the concentrations of ammonium and phosphate ions were condensed to 1.5 and 2.2 of their concentrations, respectively. This caused the removal of > 64% of PO_4^{3-}-P and 96% of NH_4^+-N.

Even though the single-chamber MFC could reduce the overall operating costs to some extent, integrating the anolyte and catholyte may buffer the pH of electrolyte and thus inhibit the pH elevation of the electrolyte. Referring to the multi-chamber MFC, using several chambers may increase the maintenance costs and operation complexity. However, very few articles have studied on nutrient recovery using a conventional double-chamber MFC.

This chapter investigated the feasibility of the conventional double-chamber MFC for nutrient recovery from municipal wastewater. The concentrations of NH_4^+-N, PO_4^{3-}-P and COD along the treatment process and the recovery process were evaluated. Furthermore, the sediment deposits in the cathode chamber were analysed by energy dispersive spectroscopy (EDS) and scanning electron microscopy (SEM). As forward osmosis (FO) membrane is a common membrane technology used for driving ions from one side to another while nonwoven was recently used as the separator in the single-chamber MFC (Yan et al., 2018; Ichihashi and Hirooka, 2012), a new design of double-chamber MFC with the FO membrane or nonwoven as the separator was also evaluated.

4.2 Materials and method

4.2.1 MFC construction

The MFC construction is described in Chapter 3, Section 3.3.

4.2.2 Microorganisms and synthetic wastewater

The microorganisms and synthetic wastewater are described in Chapter 3, Section 3.2.1. Moreover, the concentration of dissolved oxygen (DO) in the anode chamber was controlled at 0.02 ± 0.01 mg/L. All experiments studied in this chapter were conducted using the same synthetic wastewater, in which the measured concentrations of COD, NH_4^+-N and PO_4^{3-}-P were 300 ± 15, 5.0 ± 0.15 and 1.0 ± 0.05 mg/L, respectively.

4.2.3 Experimental process

A bottle containing 1000 mL of the synthetic wastewater was pumped using a peristaltic pump (Model 77202-60, Masterflex, Illinois, United States) into the anode chamber of the double-chamber MFC. The initial pH values of the synthetic wastewater were adjusted to 7.00 ± 0.1 by adding hydrochloric acid (HCl) and sodium hydroxide (NaOH) solutions. The double-chamber MFC was firstly conducted at different operating modes of the anolyte at room temperature (~25 °C), in order to examine the nutrients' accumulation in the catholyte. As shown in Fig. 4.1, the synthetic wastewater in the anode chamber of the MFC functioned in three ways: (a) it was pumped into the anode chamber and kept unchanged for 24 h, and then replaced by the fresh synthetic wastewater (called the batch mode); (b) it was pumped into the anode chamber and then circulated within the anode chamber at a given flow rate of 10 mL/min and then renewed every 24 h (known as the self-circulation mode); and (c) it was pumped to flow through the anode chamber at a fixed flow rate of 0.24 mL/min, which indicated the hydraulic retention time of the anode chamber was 24 h (referred to as the single-continuous mode). In these three modes, the DI water served as the catholyte and the cathode chamber was conducted in the absence of aeration.

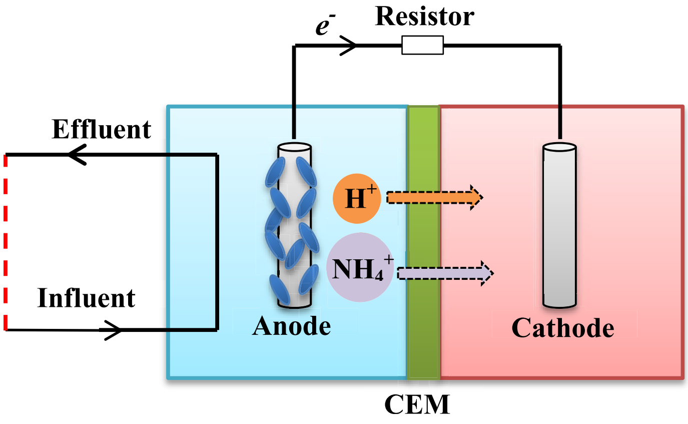

Figure 4.1 Schematic representation of nutrients accumulation using a double-chamber MFC at different operation modes of the anode chamber. In this figure, CEM represents the cation exchange membrane; ⬮ represents the anaerobic microorganisms.

Then the anode chamber was connected to the cathode chamber as described in Fig. 4.2 to explore the performance of nutrient recovery in the cathode chamber. In this scenario, the effluent from the anode chamber was used as the influent for the cathode chamber. Thus, the synthetic wastewater was sequentially treated in two steps in the double-chamber MFC: firstly, treated by anaerobic microorganisms for removing organics and recovering energy in the anode chamber; and secondly, conducted directional ion migration to recover phosphorus and nitrogen in the cathode chamber. In this chapter, the cathode chamber was conducted with and without air supply, respectively, to determine the effects of aeration for catholyte on the nutrient recovery.

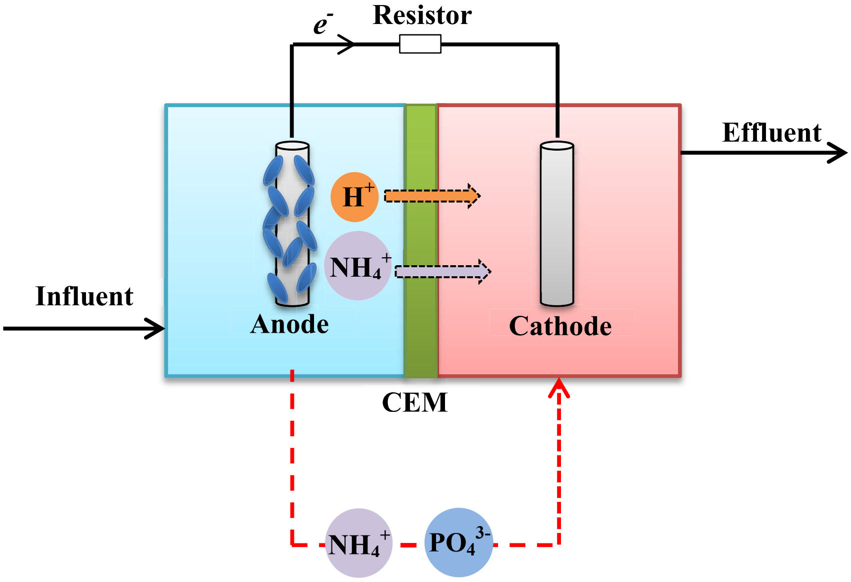

Figure 4.2 Schematic representation of double-chamber MFC for nutrients recovery. CEM represents the cation exchange membrane; ● represents the anaerobic microorganisms.

Alternatively, this process was conducted in the scenario where the FO membrane (Toray Chemical Korea Inc.) and nonwoven with a thickness of 0.75 mm (Dongguan Jia Lianda Nonwoven Co., Ltd. Dongguan, China) were utilized to replace the CEM as the separator of the double-chamber MFC. This experiment was performed while applying aeration in the cathode chamber.

4.2.4 Analytical method

Analytical method is described in Chapter 3, Section 3.4.

4.3 Results and discussions

4.3.1 Effects of operation mode of anolyte on the nutrient accumulation in the catholyte

The effects of operation mode of anolyte on the nutrient accumulation were studied at three conditions as described in Fig. 4.1: (a) batch mode; (b) self-circulation mode; and (c) single-continuous mode. The phosphorus and nitrogen exist as NH_4^+-N and PO_4^{3-}-P, respectively in the synthetic wastewater and their concentrations in the cathode chamber were monitored as a function of operation time (Fig. 4.3). It should be noted here that the initial concentrations of NH_4^+-N and PO_4^{3-}-P in the catholyte (i.e. DI water) were close to zero. From Fig. 4.3, it could be seen that the concentration of NH_4^+-N in the catholyte gradually increased after fresh synthetic wastewater was fed into the anode chamber no matter what the operation modes of the anolyte were. This may be attributed to the pathway of the ammonium transfer across the CEM from the anode chamber to the cathode chamber in the double-chamber MFC. Generally, the ammonium transfer mainly relies on two processes: diffusion and migration. Specifically, diffusion is caused by the ammonium concentration gradient between the anolyte and catholyte while migration is driven by the current field generated by the MFC.

More importantly, the ammonium diffusion depends on the ammonium concentration gradient and may reach equilibrium with decreasing concentration gradient; in contrast, the ammonium migration driven by the electricity is against the concentration gradient. As result of this, the ammonium concentration in the catholyte could gradually increase with running time through the ammonium migration if the MFC could continuously and effectively generate electricity. Specifically, the concentration of NH_4^+-N increased to 5.9, 4.6 and 4.2 mg/L, respectively, after running the double-chamber for 30 d at the self-circulation mode, single-continuous mode and batch mode, respectively. The ammonium transfer across the CEM in the MFC was also observed in other studies (Park et al., 2017; Sotres et al., 2016). The difference in the increase in the ammonium concentrations may be ascribed to the efficiency of energy recovery in the MFC. Results showed that the self-circulation mode of the MFC could generate the maximum voltage of 641.4 mV while the maximum voltages created in the batch and single-continuous modes were 386.4 mV and 591.9 mV, respectively. This indicated that the self-circulation mode better facilitated the effective exposure of anaerobic microorganisms to the synthetic wastewater and thus increased the generation of electrons. In the scenario, more ammonium ions could be driven by current to transfer from the anode chamber to the cathode chamber.

As for the phosphate ions, there was no negligible increase in the phosphate concentration in the catholyte at the three different modes. This is because the phosphate ions as the anions were not allowed to transfer across the CEM.

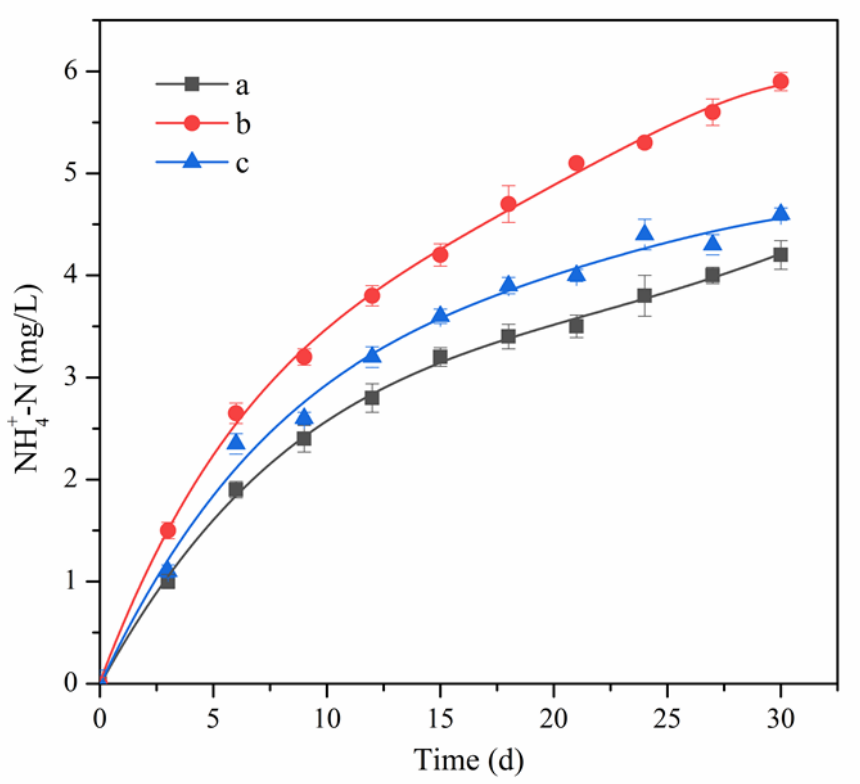

Figure 4.3 Ammonium accumulation in the cathode chamber in the: (a) batch mode; (b) self-circulation mode; and (c) single-continuous mode.

4.3.2 Effects of aeration on the nutrient recovery

As discussed in Section 4.3.1, whatever the operation of the anolyte changed may only lead to the accumulation of ammonium in the catholyte. Thus, the operation mode of MFC was present as described in Fig. 4.2 to investigate the recovery performance and concentrating extent of NH_4^+-N and PO_4^{3-}-P. The synthetic wastewater was pumped to the anode chamber at a given volumetric flow rate of 0.35 mL/min and then treated by the cathode chamber. In this chapter, the cathode chamber was operated under either aeration (oxygen reduction) or no aeration, where the DO concentration in the cathode chamber was controlled at 6.22 ± 0.10 mg/L in the presence of aeration. The changes in the concentrations of NH_4^+-N and PO_4^{3-}-P are plotted in Fig. 4.4.

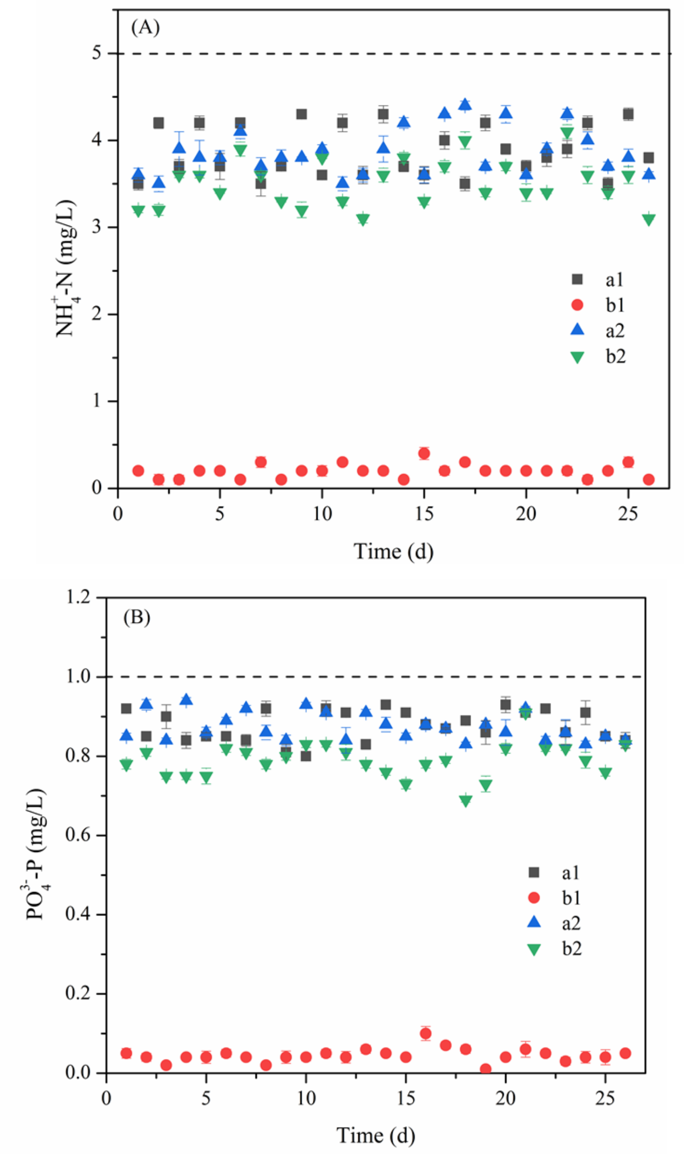

Figure 4.4 Changes in nutrient concentration in the: (a1) anode effluent with aeration supplied in catholyte; (a2) anode effluent without aeration supplied in catholyte; (b1) cathode effluent with aeration supplied in catholyte; (b2) cathode effluent without aeration supplied in catholyte.

As shown in the Fig. 4.4, the concentrations of NH_4^+-N and PO_4^{3-}-P decreased slightly in the anode effluent whether the aeration was supplied in the cathode chamber or not. The reduction in the concentrations of NH_4^+-N and PO_4^{3-}-P ranged from 0.8 to 1.5 mg/L and 0.07 to 0.20 mg/L, respectively. This may be attributed to the biological activity of microorganisms required for their growth. Moreover, this decline indicated that the aeration used in the cathode chamber negligibly influenced the removal behavior of NH_4^+-N and PO_4^{3-}-P in the anode chamber. In contrast, the concentrations of NH_4^+-N and PO_4^{3-}-P in the cathode effluent greatly reduced while supplying aeration in the cathode chamber. The possible reason for this is that most ammonium and phosphate ions were removed by chemical precipitation. In the double-chamber MFC, the electrons generated in the anode chamber transferred along the external circuit to the cathode electrode, and then reacted with oxygen to form the hydroxyl ions. The anode and cathode reactions in this chapter are described in Eqs. (4.3) and (4.4).

$$\text{Anode reaction: } C_6H_{12}O_6 + 6H_2O \rightarrow CO_2 \uparrow + 24H^+ + 24e^- \tag{4.3}$$

$$\text{Cathode reaction: } 2H_2O + O_2 + 4e^- \rightarrow 4OH^- \tag{4.4}$$

From Eq. (4.4), the pH that was localized the cathode electrode increased while aeration was supplied in the cathode chamber. The pH of catholyte ranged from 8.0-8.4 in the presence of aeration in the cathode chamber, which facilitated the ammonium and phosphate precipitating with magnesium and/or calcium ions. By contrast, even though a multi-chamber MFC could efficiently enrich the nutrients (Huang et al., 2014b), additional NaOH is needed to elevate the solution pH in the precipitation process (Chen et al., 2017). Similarly, many other studies also reported that effective nutrient recovery by chemical precipitation needs alkaline condition (Hermassi et al., 2015; Liu et al., 2018).

It could be seen from Fig. 4.4 that the average concentrations of NH_4^+-N and PO_4^{3-}-P decreased to around 0.20 and 0.05 mg/L, respectively. Moreover, the removal of a partial amount of ammonium may be attributed to air stripping. To investigate the effects of air stripping and chemical precipitation on the ammonium removal/recovery was in the process, the anode effluent was collected and performed in two different pathways. Firstly, the pH of anode effluent was increased to 8.1-8.4 using NaOH solution in the absence of aeration. Alternatively, the air stripping was utilized for the anode effluent without the pH elevation. Results suggested that either the pH increase of anode effluent or air stripping for the anode effluent could result in > 97% of NH_4^+-N removed/recovered. This also indicated that the ammonium recovery/removal in the double-chamber MFC was achieved through the combined effects of chemical precipitation and air stripping. In contrast, the changes of the nutrients' concentrations between the anode effluent and cathode effluent were insignificant when the cathode chamber was conducted in the absence of aeration. This is because the pH of catholyte ranged from 7.5 to 7.8 in this scenario and such pH values thereby could not lead to the formation of the nutrient-based precipitates.

In addition, the sediments deposited on the cathode surface and in the catholyte were analyzed by the SEM and EDS after running the double-chamber MFC for 26 d. As shown in the SEM image (Fig. 4.5b), some crystals could be seen. Besides, the EDS was applied to detect the elemental compositions of the precipitates and demonstrated that C, K, Ca, N, O Na, Mg and P were the main elements detected (Fig. 4.5a) and such elemental composites are quite similar to elements of the pure struvite standards (Cusick and Logan, 2012). Many investigations in nutrient recovery via chemical precipitation from wastewater observed an inadequate amount of Mg^{2+} (Wu et al., 2018; Xiao et al., 2018) and additional Mg^{2+} sources are thereby needed such as water-soluble Mg salts and MgO (Huang et al., 2014a; Luo et al., 2018). This undoubtedly increases the overall costs, but the present study achieved the nutrients-based precipitates without magnesium input.

Nevertheless, further research is needed to compare the precipitates achieved in this study to the chemical struvite in terms of the fertilizer's efficacy for crops and plants. Moreover, a small quantity of P observed in the EDS may be attributed to the relatively low phosphate concentration in the influent and short running time.

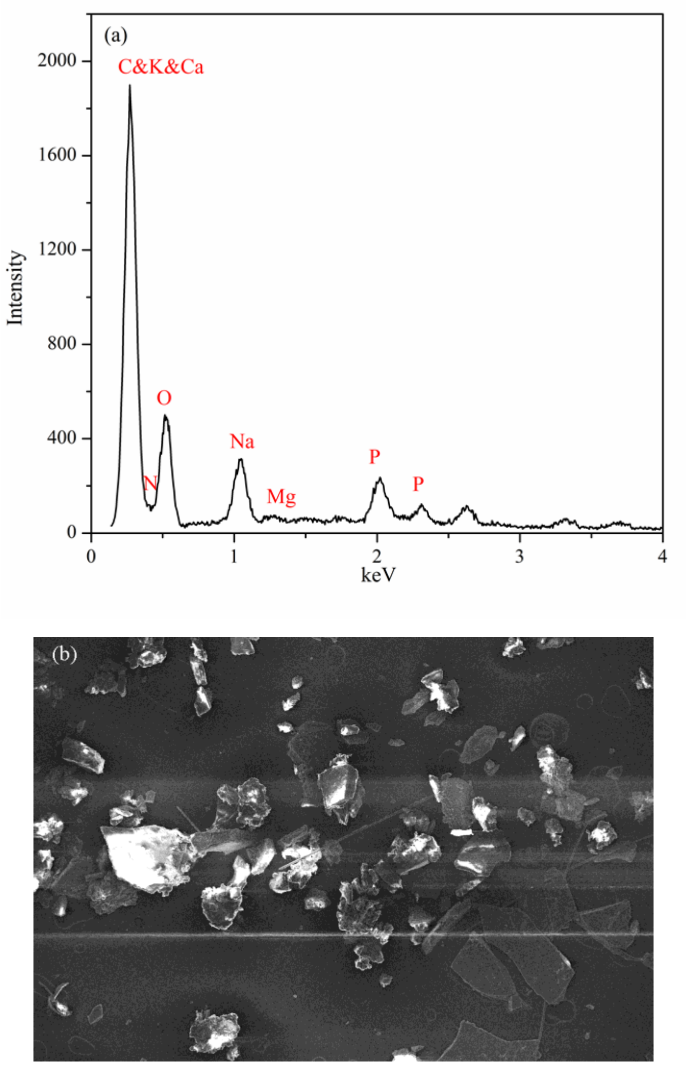

Figure 4.5 (a) EDS and (b) SEM image of the precipitates achieved in the cathode chamber in the double-chamber MFC

In the precipitates, the phosphorus accounts for 2.6% of the total weight of precipitates, leading to the mass balance of PO_4^{3-}-P being studied after running the MFC for 26 d.

Theoretical total mass of PO_4-P in the influent:

1 mg/L×0.35 mL/min×60 min×24×26 (operation period) ×10^{-3}= 13.104 mg

Experimental total mass of PO_4^{3-}-P in the anode effluent:

11.491 mg

Experimental total mass of PO_4^{3-}-P loss in the cathode chamber:

10.902 mg

Theoretical total mass of phosphorus recovered:

417.6 mg (the precipitates weight) ×2.6%= 10.842 mg

According to the analysis, > 94% of phosphorus was recovered in the conventional double-chamber MFC. It could be observed some differences emerged between the experimental loss of PO_4^{3-}-P (10.902 mg) and the theoretical loss (10.842 mg), which may be attributed to the unavoidable loss during the analysis of the precipitates.

4.3.3 Effects of different separators in the MFC on nutrient recovery

As discussed in Section 3.2, the MFC where the CEM was used as the separator could achieve effective nutrients recovery and removal. In the recovery process, the role of CEM was to avoid the direct transfer of anions and facilitate the direct transfer of protons from the anolyte to catholyte, both of which was beneficial to the pH elevation of catholyte and further nutrient recovery by chemical precipitation. In this section, the FO membrane and nonwoven were used to replace the role of CEM in the double-chamber MFC to identify their effects on the nutrient recovery. The new MFC was conducted using the same process as described in Fig. 4.2.

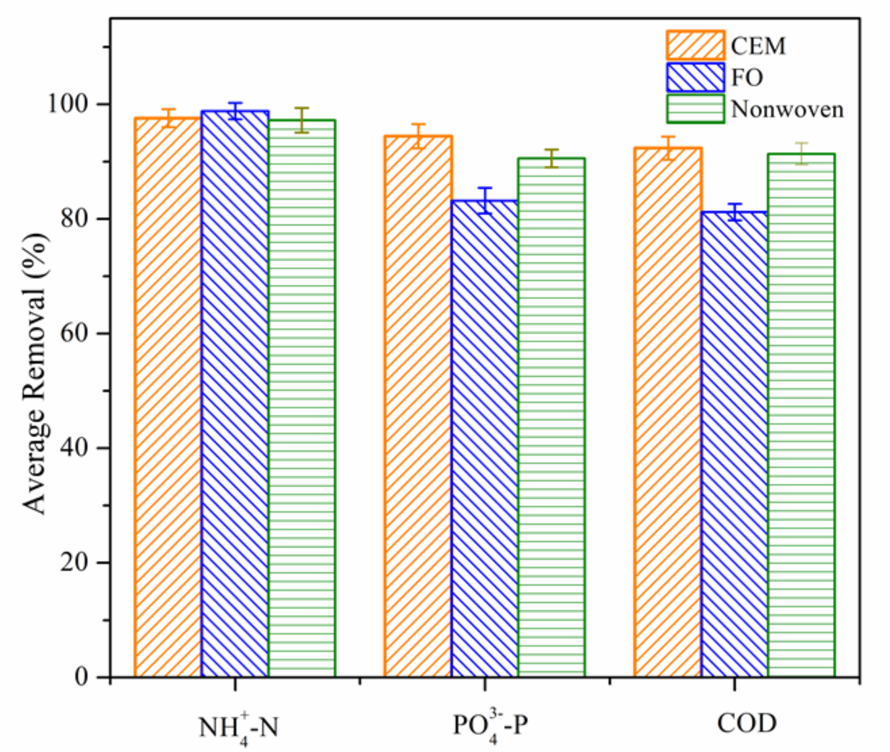

Figure 4.6 Removals of NH_4^+-N and PO_4^{3-}-P using double-chamber MFC with different separators.

As shown in Fig. 4.6, the double-chamber MFC with the CEM as the separator reported the best nutrients removal with >97.58% of NH_4^+-N and > 94.9% of PO_4^{3-}-P removed/recovered, followed by the MFC with the nonwoven and FO membrane, respectively. This is because the transfer of cations across the CEM may facilitate an increase in the pH of catholyte due to maintaining charge neutrality of catholyte. Similarly, the proton consumption for the cathode reaction (i.e. oxygen reduction reaction) plays the same role for increasing pH. Referring to the FO membrane being used as the separator, the MFC could remove 98.81% of NH_4^+-N and 83.18% of PO_4^{3-}-P because pH value of catholyte which was over 8.0 facilitated nutrients recovery through chemical precipitation. Previously, Zhang et al. (2011a) proposed an osmotic MFC with the installment of an FO membrane between the anode and cathode and found that this osmotic MFC could generate higher electrical current than that achieved in a conventional MFC containing CEM, while applying the NaCl solution as a catholyte/draw solution. This may be attributed to the enhanced proton transport with water flux and smaller membrane resistance.

In this chapter, however, the efficiency of phosphate removal achieved in the osmotic MFC was lower than that obtained in the conventional MFC with the CEM as the separator. A possible explanation for this is that some anions in the anolyte diffused to the cathode chamber and thus inhibited the pH elevation of the catholyte. Consequently, the recovery of nutrients via chemical precipitation was weakened. Similarly, the ions in the catholyte and anolyte may also freely transfer across the nonwoven and the pH increase of catholyte was thereby constrained. Nevertheless, the removal efficiency of NH_4^+-N and of PO_4^{3-}-P could reach 97.2% and 90.6%, respectively, while using the nonwoven as the separator of the double-chamber MFC. Similarly, Ichihashi and Hirooka (2012) also used nonwoven as a separator in an air-cathode MFC, which achieved the removal of 70-82% of phosphorus. In addition, the average COD removal efficiencies in the three MFCs with CEM, FO membrane and nonwoven were over 81.19%. Compared to the MFC with FO membrane, the one with CEM and nonwoven as the separator showed higher removal efficiency of COD. The results also indicated that the MFCs with different separators studied above had good performance for the wastewater purification.

4.4 Conclusion

In this chapter, the double-chamber MFC could effectively remove NH_4^+-N and of PO_4^{3-}-P from wastewater for recovery. The MFC could only obtain effective ammonium accumulation in the cathode chamber if the anode chamber was not connected to the cathode chamber. Apart from this, the ammonium transfer from the anolyte to catholyte was mainly driven by the electrical field derived from energy recovery from wastewater, especially in the later running time. Phosphorus and nitrogen were removed by the combined effect of chemical precipitation and microbial absorption while wastewater was sequentially treated by the anode chamber and cathode chamber. Moreover, partial nitrogen was removed through air stripping. Through an analysis of the precipitates formed in the cathode chamber, the main elements in the mixture included phosphorus, nitrogen, magnesium, calcium and hydroxyl compound. When the FO membrane and NW were used as a separator in the double-chamber MFC, the efficiency in removing NH_4^+-N and of PO_4^{3-}-P was inferior to that observed in the conventional MFC.

CHAPTER 5

Effect of organic loading rate on the recovery of nutrients and energy in a dual-chamber microbial fuel cell

5.1 Introduction

Over the last decade, chemical fertilizer production on an industrial-scale has become a worldwide issue, and particularly the issue of supplying nitrogen (N) and phosphorus (P). Phosphate-bearing rocks are always exploited for fertilizer production, but they are expected to peter out in terms of supply within the next 30-300 years (Ye et al., 2017). Furthermore, it is difficult to find substitutes of P in fertilizer production. Thus, the declining deposits of raw P will result in reducing fertilizer-production capacity. On the other hand, the N used for producing fertilizer is obtained through the industrial Haber-Bosch process (Eq. (5.1)):

$$N_2 + 3H_2 \rightarrow 2NH_3 \qquad (5.1)$$

As shown in Eq. (5.1), the process needs additional H_2 which is derived from fossil sources. High temperature and pressure are the key factors in the ammonia production process, and it is in fact an expensive option requiring large amounts of capital. The energy-intensive process can also cause emissions of carbon oxide (CO_2) which act as greenhouse gases which are responsible for global warming. Therefore, both the finite natural resource and climate change is forcing many societies to look for sustainable technologies to recover P and N. Besides the benefits of ensuring food security, the recovery of nutrients can also: firstly, mitigate to some extent the problem of eutrophication in aquatic environments; and secondly, reduce the costs associated with nutrient removal in wastewater treatment.

In recent years, wastewater has been considered a renewable resource because it contains many valuable components such as chemical energy, and nutrients such as PO_4^{3-}-P and NH_4^+-N (Yan et al., 2018). For example, the chemical energy in domestic wastewater is estimated to be at least 13 kJ/gCOD, which is around 9 times higher than the energy used in its treatment (Heidrich et al., 2010). Furthermore, the average energy consumption in conventional wastewater treatment ranges from 0.2 to 0.8 kWh/m^3, which is affected by many factors such as the process type, wastewater source, wastewater quantity and composition, removed pollutants, treatment capacities, regional differences including weather and electricity costs, social and economic characteristics (Callegari et al., 2018; Gu et al., 2017; Li et al., 2017; Xu et al., 2018b; Yu et al., 2019). It was reported that the consumption of electrical energy for wastewater treatment accounts for 3-5% of the total electricity demand in the industrialized countries (Curtis, 2010). Hence, optimizing energy consumption and recovering valuable substances, for instance PO_4^{3-}-P and NH_4^+-N are more important in current wastewater treatment strategies.

Microbial fuel cells (MFCs) constitute a bioelectrochemical system and can sustainably recover electricity and nutrients through the catalysis of electroactive bacteria (Callegari et al., 2018; Ye et al., 2019b). The system can directly convert the chemical energy contained in an organic substrate into electrical energy, during which there is no input of combined heat and power unit. In addition, this technology obviously provides a potentially attractive alternative for treating wastewater compared to the conventional aerobic or anaerobic treatment of wastewater. For instance, the MFC has advantages over the aerobic activated sludge technology due to producing less surplus sludge, faster process kinetics and lower energy input (e.g., aeration supply) in the wastewater treatment (Gil et al., 2003). Furthermore, anaerobic degradation rates in the MFC are faster than those in the traditional anaerobic wastewater treatment. For example, Morris et al. (2009) previously found that the anaerobic biodegradation of diesel range organics was significantly enhanced using an MFC (82% removal efficiency) when compared to the anaerobic treatment (31% removal efficiency). Moreover, the anaerobic degradation rate for phenol was 11.3 ± 0.7 mg/L·d (Franchi et al., 2018) whereas the MFC could achieve the removal rate of phenol at 128.7 ±26.3 mg/L·d (Luo et al., 2009).

An anode compartment and a cathode compartment consist of the conventional MFC, which are separated by a cation exchange membrane (CEM) (Yan et al., 2018). The anode compartment is responsible for the microbial degradation of substrate and generation of electron and proton, while the electrical loop is completed in the cathode chamber equipped with electron acceptors (e.g., O_2) (Eq. (5.2)). Apart from this, the transported protons react with electrons and oxygen (i.e., the electron acceptor) to form water molecules at the cathode (Eq. (5.3)).

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad (5.2)$$

$$2H^+ + 2e^- + O_2 \rightarrow 2H_2O \qquad (5.3)$$

Investigations into the recovery of PO_4^{3-}-P and NH_4^+-N through MFCs from wastewater have been conducted in recent years and the reactor configurations of an MFC include the following versions: single chamber (or air-cathode), dual-chamber, and multi-chamber with different materials of electrodes and separators (Ichihashi and Hirooka, 2012; Yan et al., 2018). So far, the recovery of PO_4^{3-}-P and NH_4^+-N via MFC has mainly been achieved by the formation of nutrients-based precipitates. For example, an air-cathode MFC was developed by Ichihashi and Hirooka (2012) to recover PO_4^{3-}-P and NH_4^+-N from swine wastewater, using a rectangular reactor equipped with a cathode coated by 0.5 mg/cm^2 of Pt/C catalyst. In this scenario, the researchers successfully recovered nutrients via the formation of struvite. However, the amount of phosphate recovered at the cathode was only 27%. The possible reason for this is that the electrolyte was shared by the anolyte (H^+ generation) and catholyte (OH^- generation), thereby impeding the elevation of catholyte pH (Zhao et al., 2006). Consequently, the formation of nutrients-based precipitates at the cathode was seriously compromised in the single-chamber MFC.

Other studies also demonstrated the application of multi-chamber MFC for recovering nutrients, which uses a stack of CEMs and anion-exchange membranes (AEMs) (Chen et al., 2015; Chen et al., 2017). In this scenario, the system can highly concentrate the nutrients from wastewater. Chen et al. (2015) reported that the concentrations of NH_4^+ and PO_4^{3-} were 1.5 and 2.2 times higher than the initial concentration, respectively. However, an input of alkaline chemicals such as NaOH is necessary to offer high pH for nutrients recovery through chemical precipitation. To date, analyses into applying a MFC to recover nutrients are a few (Ichihashi and Hirooka, 2012; Marzorati et al., 2018) whereas studies on recovering nutrients via double-chamber MFCs at laboratory scale are rarer still. Nevertheless, the few available studies still present highly important findings for applications of MFCs, such as explaining the advantages of its application (Ye et al., 2019b). In a recent study, a new dual-chamber MFC was built and then employed for simultaneously recovering PO_4^{3-}-P and NH_4^+-N from domestic wastewater (Ye et al., 2019b). The precipitates formed in the cathode chamber and the analytical results suggested that the characterization of obtained precipitates was similar to the struvite, which suggests the feasibility of the double-chamber MFC for nutrients recovery.

Generally, the MFC's performance is mainly influenced by four processes, these being catalytic reaction of anaerobic bacteria for the substrate, transport of electrons from microorganisms to the anode electrode, transfer of protons from the anode to cathode and the reduction of the electron acceptors in the cathode chamber (Gil et al., 2003; Mardanpour et al., 2017). The organic loading rates (OLRs) are highly relevant to these four processes; for example, Di Lorenzo et al. (2010) found that increasing OLR from 16 to 161 kgCOD/ $m^3 \cdot d$ could decrease the coulombic efficiency from 68 ± 7.2% to 49 ± 2.7% and undermine the maximum current generation. This is because the non-exoelectrogens are more active than the electrochemically active bacteria at higher COD loadings and consequently lower coulombic efficiencies are obtained. In contrast, Aelterman et al. (2008) observed that doubling the OLR resulted in an increase in the current generation at low external resistance (10.5–25 Ω) or during polarization. This contradiction may be attributed to the differences in the electrode materials, carbon sources and other factors that affect the electricity generation. In the present study, the main objective is to evaluate the effects of OLR on the long-term MFC performance for municipal wastewater treatment. A complete assessment of MFC was conducted, including the generation of power, efficiency in removing COD and especially the efficiency in nutrients recovery.

5.2 Materials and methods

5.2.1 Experimental setup

The experimental setup is described in Chapter 3, Section 3.3. Besides, synthetic domestic wastewater used for culturing the inoculum at the anode was prepared employing a specific amount of glucose, which made the corresponding influent COD concentrations range from 300 to 600 mg/L. Other components in it included 0.0046 g KH_2PO_4, 0.02 g NH_4Cl, 0.0054 g $MgSO_4 \cdot 7H_2O$, 0.0004 g $CaCl_2 \cdot 2H_2O$, 0.032 g yeast and 0.61 mL of trace nutrients per litre of distilled water (DI water). The $NaHCO_3$ and H_2SO_4 solutions were employed to adjust the pH of the feed solution to 7.0 ± 0.15 prior to its addition, which is confirmed by a pH meter (hi9025, Hanna Instruments, Limena, Italy). It should be noted here that no assessment of the internal pH control's behavior was conducted in the present study.

5.2.2 Inoculum and experimental operation

The inoculum is described in Chapter 3, Section 3.3. Besides, the MFC was operated under closed circuit and used to treat wastewater at different organic loading rates (OLRs) which were achieved by various influent COD concentrations with a fixed hydraulic retention time (HRT). A diagram of the experimental setup has been provided in another study (Ye et al., 2019b). The MFC's performance was investigated at four different periods and each one lasted for 30 days (Table 5.1).

Table 5.1 Operational conditions of the double-chamber MFC

Parameters	**Experimental period**			
	i	**ii**	**iii**	**iv**
Days	1-30	31-60	61-90	91-120
Flow rate (mL/min)	0.35	0.35	0.35	0.35
HRT (d)	0.69	0.69	0.69	0.69
Influent COD concentration (mg/L)	300	400	500	600
OLR (mgCOD/L·d)	435	580	725	870

5.2.3 Data analysis

Data analysis is described in Chapter 3, Section 3.4.

5.3 Results and discussion

5.3.1 COD removal efficiency

The double-chamber MFC's efficiency in removing COD was explored in the OLR range from 435 to 870 mgCOD/L·d, as shown in Fig. 5.1. According to this figure, it was clearly evident that the COD removal efficiencies were more than 90% when the OLR increased from 435 to 720 mgCOD/L·d. However, if OLR was too high (i.e., 870 mgCOD/L·d) this scenario resulted into COD removal efficiency declining to around 70%. A similar result concerning the impact of OLR on the removal of organics in the MFC was reported in another study (Liu et al., 2016). In contrast, Molognoni et al. (2016) believed that the higher removal efficiency of carbon can be obtained in substrate limiting conditions (OLR < 1000 mgCOD/L·d). This contradiction may be attributed to different species of anaerobic microorganisms being used in the wastewater treatment. Moreover, Tamilarasan et al. (2017) have reported that methanogenic organisms account for COD removal at higher OLR. Excessive organics provide a niche for methanogens, and where the OLR is higher than the maximum electron transfer rate of the MFC results in methanogenesis (He et al., 2005). These findings highlighted the importance of OLR for COD removal in the wastewater treatment because optimized OLR can assist anaerobic microorganisms to effectively utilize the substrate. As well, each change in the OLR may cause a reduction in COD removal efficiency, which may be ascribed to acclimation of anaerobic bacteria at the anode chamber under a new OLR.

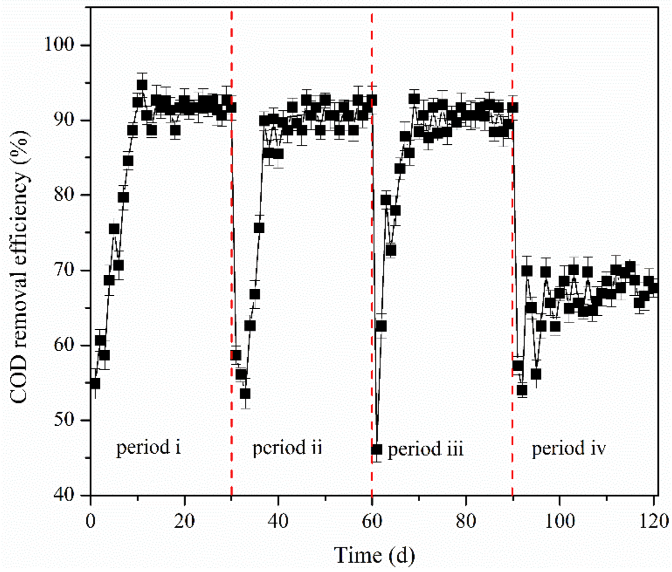

Figure 5.1 COD removal efficiency *vs* operation time at different OLRs (435-870 mgCOD/L·d) in the dual-chamber MFC (daily averages ± standard deviations).

In the dual-compartment MFC, the COD removal was achieved by the combined effects of electrogenic and non-electrogenic microorganisms at the anode chamber for microbial degradation (Logan, 2008). Furthermore, the formation of a biofilm on the surface of the anode electrode could help COD removal and the adsorption of organics to the anode surface (Tamilarasan et al., 2017). There are in fact many factors affecting the COD removal via MFC, such as sources of wastewater and inoculum, MFC configurations and electrode properties, which makes it difficult to compare MFC studies on the subject of COD removal.

5.3.2 Electricity generation

In this section, Fig. 5.2 below depicts the variations in voltage generation at different OLRs (435 to 870 mgCOD/L·d) while applying the dual-compartment MFC to treat municipal wastewater.

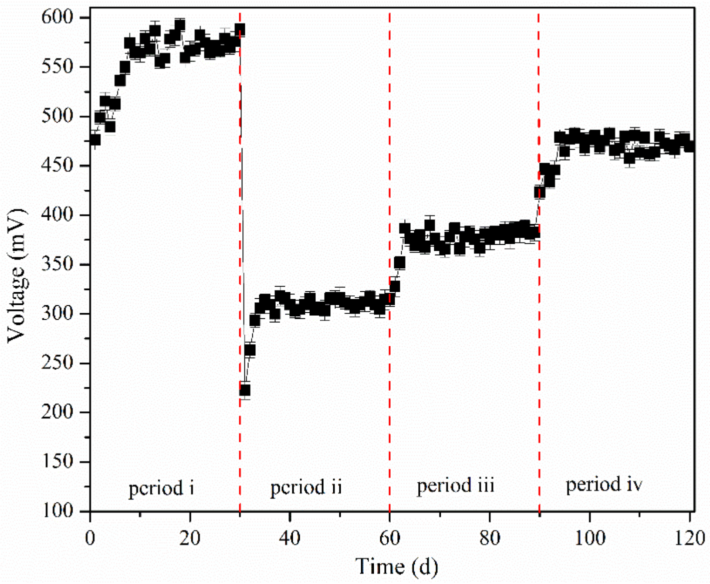

Figure 5.2 Electricity generation *vs* operation time at different OLRs (435-870 mgCOD/L·d) in the dual-chamber MFC (daily averages ± standard deviations).

Overall, the voltage generated by the double-chamber MFC fluctuated at each period. This may be attributed to slight changes in the concentration of feed solution and environment such as room temperature. Generally, the voltage generated in the MFC is related to the concentration of carbon source and their utilization efficiency by the anaerobic microorganisms. During the first period the average electricity generation was more than 550 mV. A possible reason for this is that the operation mode of the double-chamber MFC was under open circuit for 30 days prior to the experiment, during which the biofilm started to form on the anode electrode's surface and thereby made electricity generation possible. It was reported that the substrate can be exploited by inoculum for electricity generation within 24-72 h due to the acclimatization of the inoculum (Tamilarasan et al., 2017). The maximum voltage generated in the double-chamber MFC was 598.9 mV at the OLR of 435 mgCOD/L·d.

Additionally, it could be seen that higher OLR may cause a decline in the amount of electricity being generated in the double-chamber MFC. This may be because low COD concentrations (i.e., OLR) could facilitate electricity production (Hiegemann et al., 2016). Moreover, higher OLR of the anode chamber may lead to a larger risk for membrane fouling, which may detrimentally influence the voltage generation (Elakkiya and Matheswaran, 2013). This had also been detected in the study by Sobieszuk et al. (2017) and they thought that the history of previous OLRs may also strongly influence the electrochemical behavior of the system (del Campo et al., 2013; Sobieszuk et al., 2017). Moreover, He et al. (2015) believed that higher OLR may result in the accumulation of volatile fatty acid (VFA), which may not facilitate the generation of electricity in the dual-component MFC. As discussed in Section 3.1, the activity of methanogenic microorganisms increased due to higher OLR, which in turn weakened the electricity generation-capacity of the electrogenic bacteria. Juang et al. (2011) thought that the MFC could achieve its maximum value of voltage generated at a certain OLR and the value would decrease if the OLR increased.

Nevertheless, it could also be observed that the growth of OLR from 580 to 870 mgCOD/L·d simply increased the voltage generation from 318.2 to 482.6 mV. This is because higher OLRs could evidently offer more substrates (e.g., organic matter) for the electrogenic bacteria, which facilitated the recovery of chemical energy. Some researchers believed there is a relationship between the amount of voltage generated in the MFC and influent COD concentration. For instance, Di Lorenzo et al. (2010) found that a drop in the influent COD concentration of 10-fold led to an around 31%- and 53%-reduction of the current generation and power output, respectively. In a bio-cathode MFC with the tubular membrane, Wang et al. (2014a) reported that the correlation between current and inlet COD concentration (0-3000 mg/L) could be expressed as shown in Eq. (5.8) with correlation coefficient (R^2) of 0.87, in which the y (mA) represents the current whereas the x (mg/L) represents the inlet COD concentration. Similarly, Jia et al. (2016) also proposed the following Eq. (5.9) to present the correlation between voltage (y, V) and COD concentration (500-3000 mg/L) (x, mg/L) with R^2 of 0.94.

$$\mathrm{y} = \frac{0.906x}{267.609+x} \tag{5.8}$$

$$\mathrm{y} = 3 \times 10^{-5}x + 0.2452 \tag{5.9}$$

However, Fig. 5.2 shows that COD removal efficiency may not have a direct relationship with electricity generation. Thus stable COD removal efficiency did not always reflect the stabilization of the voltage due to the nature of the microbial conversion pathways (Sobieszuk et al., 2017). Furthermore the removal of COD was realized by the combined effects of all microbial species present in the anode compartment and affected by their concentrations and balance. By contrast, the electrogenic bacteria’ activity and concentration is the only factor to determine the electricity generation (Sobieszuk et al., 2017; Yu et al., 2015).

For MFCs working in continuous mode, each MFC has a maximum value of voltage generation for different OLRs and the value varies from different MFC configurations. The maximum value of voltage generation obtained in the present chapter and the corresponding value of power density for different OLRs are depicted in Fig. 5.3. It can be seen that the maximum voltage generation was 598.9 mV at the OLR of 435 mgCOD/L·d, which was 1.5 times higher than that reported by Rossi et al. (2018) for treating domestic wastewater via an air-cathode MFC. In comparison to the value reported by Wei et al. (2012), the value present in this study was over 200% higher than their values at different OLRs. This indicated that the electrogenic bacteria cultured in the present chapter had higher utilization efficiency for the substrate when compared to inoculums reported in other studies (Tamilarasan et al., 2017). However, Wang et al. (2010) who used a double-chamber continuous MFC, achieved a voltage of 706 ± 21 mV, which is over 10% higher than our maximum voltage production. This may be ascribed to the inoculation of algae at the cathode chamber. In this scenario, generating the oxygen through the photosynthesis could sustain cathodic oxygen reduction, which improved the MFC reactor's electrochemical performance (Colombo et al., 2017).

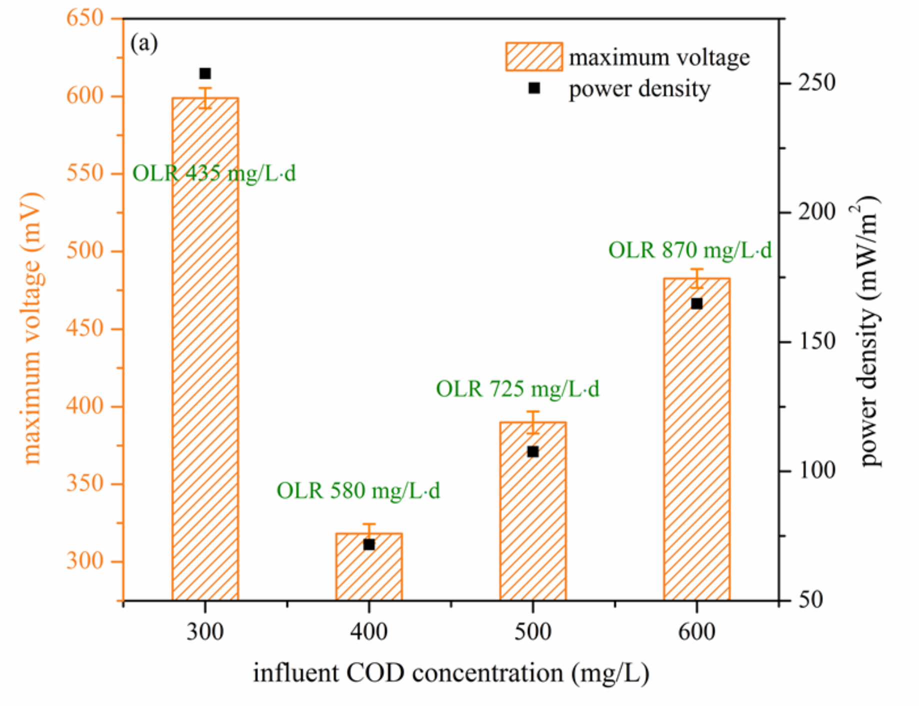

Figure 5.3 Maximum voltage and power density *vs* OLR

While increasing the OLR from 435 to 870 mgCOD/L·d, the power density ranged from 72 to 254 mV/m^2. The low power density achieved in the double-chamber MFC may be attributed to the component of municipal wastewater that served as the feed solution (Yu et al., 2015). Nevertheless, the smaller power density values were often observed in many other studies (Zhou et al., 2013). However, Ichihashi and Hirooka (2012) reported a power density of 2300 mW/m^2 in an air-cathode MFC using a coating of 0.5 mg/cm^2 of Pt/C catalyst on wet-proofed porous carbon paper as the cathode electrode in the treatment of swine wastewater. Notably, the pretreatment of the cathode with catalyst improved the power density. Besides, using a polyester nonwoven cloth as the separator could avoid any danger of membrane fouling, which facilitated the recovery of electricity. Similarly, Chen et al. (2015) obtained a power density of 224 mW/m^2 through the usage of a multi-chamber MFC, using granular activated carbon as the anode electrode.

On the other hand, the coulombic efficiency fell when OLR increased. This is because the anode surface with high saturation may induce side-populations (methanogens, heterotrophs) to compete with electrogenic bacteria for the substrate (Velvizhi and Mohan, 2012), therefore weakening the activity of electrogenic microorganisms. At the OLR of 435 mgCOD/L·d, the maximum coulombic efficiency was around 25%, which was the highest power density reported in the present study. The possible reason for this is that utilizing substrate for methane production was reduced and electroactive bacteria is better in the ascendancy compared to other microbial populations at low OLR (Callegari et al., 2018). Apart from this, the minimum coulombic efficiency was recorded as 2.21% at the OLR of 870 mgCOD/L·d. The maximum value of coulombic efficiency obtained in the present study was lower than that derived from Ichihashi and Hirooka (2012), mainly due to the component of wastewater source and material of the electrode. However, the present MFC showed higher values of coulombic efficiency compared to that reported in other researches (Chen et al., 2015; Colombo et al., 2017; Marzorati et al., 2018). Besides, the MFC at laboratory-scale was continuously fed for 120 d, longer than many other studies on the MFC applications in the wastewater treatment (Chen et al., 2015; Colombo et al., 2017; Ichihashi and Hirooka, 2012; Marzorati et al., 2018).

In addition, energy loss is unavoidable in this chapter and derived from anode overpotential, transport loss, etc. (Puig et al., 2012). The development of electrode material and/or bio-cathode could satisfy an improvement in energy recovery due to reduction in the electrode over-potential (Callegari et al., 2018). As well, the energy losses resulted from membrane ionic transport could be reduced through the application of CEM with lower internal resistance or being less subject to biofouling (Angioni et al., 2016). A more attractive method is to use a membrane-less MFC to curtail the energy losses (Vicari et al., 2018). Nevertheless, the costs and efficiency of such strategies must be taken into account and it should be remembered that the present aim of this dual-chamber MFC is to maximize nutrients recovery rather than electricity recovery.

5.3.3 Nutrients recovery

The effects of OLR on nutrients recovery in the dual-compartment MFC are shown in Fig. 5.4. According to this figure, the removal of NH_4^+-N and PO_4^{3-}-P in the anode effluent was enhanced by increasing the OLR. For example, the average efficiency in removing NH_4^+-N and PO_4^{3-}-P in the anode effluent were 14% and 12.43%, respectively, at the OLR of 435 mgCOD/L·d. It should be noted here that the removal of NH_4^+-N and PO_4^{3-}-P in the anode compartment was obtained by microbial activity for bacterial growth, in which partial NH_4^+-N diffused across the CEM from the anolyte to catholyte for its removal. However, increasing the OLR to 870 mgCOD/L·d resulted in their values growing to 75.13% and 71.5%, respectively. Other studies reported the same results (Kõiv et al., 2016; Liu et al., 2016). The possible reason for this is that the amount of NH_4^+-N and PO_4^{3-}-P used to promote the biomass growth follows a certain organics to nutrients ratio (COD:N:P, in case of biodegradable waste) in the wastewater treatment (Hamza et al., 2019). In this scenario, the growth of OLR may result in increasing the bio-consumption of nutrients. Moreover, it was reported that the amount of nutrients needed for the growth of microorganisms is greater in the high-strength organics wastewater (COD > 4000 mg/L) when compared to the low-strength organics wastewater such as municipal wastewater (Hamza et al., 2018). The decreased concentration of nutrients in the cathode compartment was ascribed to the recovery of nutrients through struvite precipitation (Ye et al., 2019b). However, the enhanced removal of nutrients at the anode chamber may not facilitate the further recovery of NH_4^+-N and PO_4^{3-}-P in the cathode chamber since this could reduce the amount of nutrients being recovered. Specifically, in this scenario, the average recovery rate of NH_4^+-N declined from 85.11% to 24.34% as the OLR increased from 435 to 870 mgCOD/L·d. In the study of Chen et al. (2017), they proposed a multi-chamber MFC to recover nutrients from municipal wastewater with the influent COD of 331 ± 25 mg/L.

However, the recovery efficiency of NH_4^+-N was lower than 20% because most ammonium ions were removed through the nitrification-denitrification process. In the present study, the nitrification and denitrification were absent, which improved the recovery of NH_4^+-N. On the other hand, although around 83.23% of PO_4^{3-}-P could be recovered in the first period, this value fell to 24.4% in the last period. In contrast, Almatouq and Babatunde (2018) found that the growth of influent COD from 500 to 1500 mg/L caused the enhanced recovery of PO_4^{3-}-P since higher COD concentrations resulted in the pH elevation of catholyte and then improve the recovery of PO_4^{3-}-P. The conflict may be attributed to the lower influent COD concentration in the present study, which exerted insignificant impacts on the catholyte pH. Apart from this, the lowest recovery rate of PO_4^{3-}-P (24.4%) was almost the same as the maximum value (27%) obtained in an air-cathode MFC (Ichihashi and Hirooka, 2012), which may be attributed to the limitation of single-compartment configuration as discussed above and other factors such as wastewater sources and separator materials.

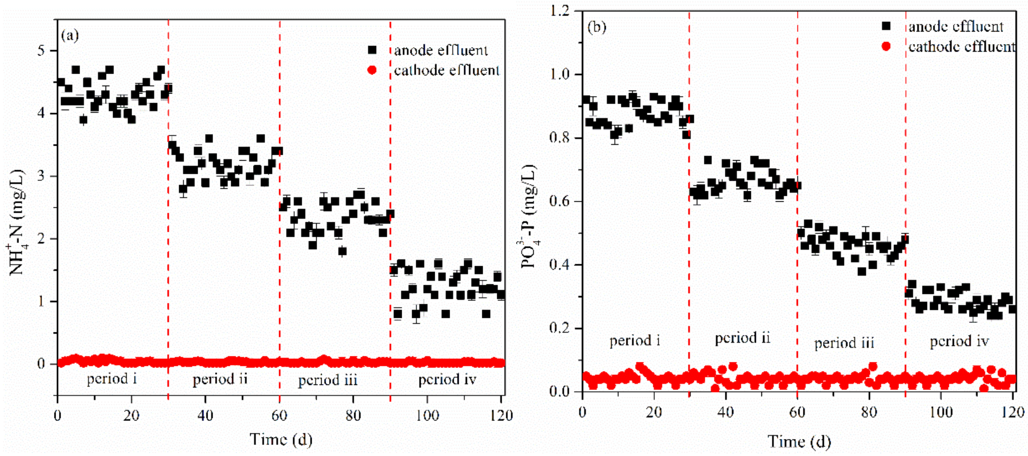

Figure 5.4 Variations in the concentrations of (a) NH_4^+-N and (b) PO_4^{3-}-P in the anode and cathode effluents at different OLRs (435-870 mgCOD/L·d) in the dual-compartment MFC (daily averages ± standard deviations).

5.4 Conclusion

Recovering nutrients from sewage was explored at different OLRs in a double-compartment MFC. The highest voltage generation of 598.9 mV was observed at the OLR of 435 mgCOD/L·d. The recovery efficiency of NH_4^+-N and PO_4^{3-}-P also were decreased with increasing the OLR from 435 to 870 mgCOD/L·d. Conclusively, the dual-chamber MFC could serve as a feasible primary treatment method to recover nutrients and generate electricity from low-strength municipal wastewater. However, the OLR should be optimized if high efficiency in recovering NH_4^+-N and PO_4^{3-}-P, and energy is prioritized.

CHAPTER 6

Microbial fuel cell for nutrient recovery and electricity generation from municipal wastewater under different ammonium concentrations

6.1 Introduction

As essential biological elements and key fertilizer constituents, nitrogen (N) and phosphorus (P) cannot feasibly be substituted. In general, most ammonium-nitrogen used for producing fertilizer is generated by the Haber-Bosch process on an industrial scale, in which the nitrogen gas can be converted into ammonia. However, ammonia production is an energy-intensive and expensive process, during which toxic gas emissions may also be generated and thereby pose risks to the environment (Ye et al., 2018). On the other hand, phosphate-bearing rock is the main source of P, but it is a non-renewable resource and it has been calculated it will be exhausted within 100 years (Li et al., 2018). Given the discussion above, the availability of affordable mineral fertilizers is becoming more challenging (Cordell et al., 2011). In particular, the world's growing population may aggravate the fertilizer supply shortage.

Thus, it is essential to intensively reuse nutrient in fertilizer production, in order to ensure food security. Apart from this, the application of fertilizers in agriculture eventually results in the accumulation of P and N in streams, which may be also attributed to the low utilization efficiency of P and N (Li et al., 2015a). This consequently leads to several serious environmental issues such as eutrophication and red tide. In this scenario, nutrient recovery from wastewater could not only mitigate the environmental footprint, but also create more fertilizer (Ye et al., 2017). Besides, nutrient recovery greatly contributes to the circular economy and has been identified in several programs and national and international objectives (Aho et al., 2015; EUR-Lex, 2015). It can be concluded that looking for effective and efficient methods to recover nutrients for food production in a safe and sustainable manner is hugely important.

In recent years, various nutrient recovery systems have been widely studied and developed in terms of technology, source and application, for example: ammonia stripping from anaerobic digestion (Pedizzi et al., 2017; Serna-Maza et al., 2014), chemical precipitation for simultaneous recovery of N and P from swine wastewater (Huang et al., 2014a; Kataki et al., 2016), and membrane hybrid system for the recovery of nutrients from wastewater (e.g., domestic wastewater and industrial wastewater) (Desloover et al., 2015; Yan et al., 2018). More importantly, these nutrient recovery systems are becoming more competitive when compared to the traditional production technologies of reactive N (Haber-Bosch) and P (phosphate rock mining), especially considering the market value of around € 1.0/kg·N and € 1.9/kg·P (De Vrieze et al., 2016; Desmidt et al., 2015a).

Municipal wastewater exists in large quantities and they contain various pollutants originating from different household sources and activities (e.g., washing, gardening, cleaning and other sanitation-based requirements). For this reason, domestic wastewater is an issue of major concern in many nations around the world. In a conventional municipal sanitation system, urban wastewater is collected and transported to the sewage treatment plants through sewer drainage pipelines. It is possible to reuse treated domestic wastewater for different purposes including irrigation and scenic waterscapes, but the treatment costs are high with 3% of the world's electricity being consumed and producing 5% of global non-carbon dioxide greenhouse gases (Li et al., 2015b).

Consequently, it is essential to optimize energy consumption in the urban wastewater treatment whilst it is suggested that recovering valuable resources such as phosphate and ammonium from sewage can increase the economic feasibility of the treatment system (Pan et al., 2015). The energy optimization and nutrient recovery from domestic wastewater would make the treatment process more sustainable since this: (1) reduces energy requirements; (2) reduces the nutrient load into the natural environment and helps prevent environmental issues from becoming worse; (3) satisfies the increasingly strict government regulations about discharge responsibilities; and (4) generates valuable products and thereby creates another revenue stream. Thus, the selection of cost-effective technologies which are applied to make nutrient recovery possible from domestic wastewater is critical.

Microbial fuel cell (MFC) is a possible technology strategy for realizing this goal. MFC is an example of a bioelectrochemical bioreactor system and has the ability to directly convert organics contained in wastewater into electrical energy. It should be noted here that there is no need of a combined heat and power unit for the power output in the MFC (Hiegemann et al., 2018). A traditional MFC reactor consists of an anode compartment, cathode compartment and separator (often cation-exchange membrane [CEM]). Theoretically, anaerobic microbes in the anode chamber of the MFC could be utilized to catalyze the anode reactions. In this case, the biodegradable chemical oxygen demand (COD) could be transformed into protons and electrons by using electrochemically active bacteria (EAB), which eventually forms an electrical field on the anode (Kim et al., 2015b). Moreover, the generated electrons are transported to the cathode electrode and then reduced by electron acceptor (often air) to complete the electrical loop.

In MFC studies, the systematic wastewater or real wastewater contains a large number of cations which could competitively transfer to the cathode chamber with protons. As a result of this, the transport of cations such as H^+, Na^+, K^+ and Mg^{2+} against a concentration gradient to the cathode chamber could contribute to the high pH that is localized in the cathode electrode (Rozendal et al., 2006). The cathode reaction could also lead to a high pH zone in the cathode chamber in double-chamber MFCs. Subsequently, the combined effects offer a possibility for MFCs to recover ammonium and phosphate through chemical precipitation in wastewater treatment (Ichihashi and Hirooka, 2012; Yan et al., 2018). Furthermore the electricity being generated in the MFC could offset the energy costs in the nutrient recovery system, while the membrane fouling potential of CEM could be reduced. What makes this possible is the current field between the anode compartment and cathode compartment (Wang et al., 2013b).

Recently, many researchers have developed MFC reactors for the recovery of nutrients, including different configurations and sources (Cusick and Logan, 2012; Hirooka and Ichihashi, 2013; Ichihashi and Hirooka, 2012; Qin and He, 2014; Ye et al., 2019b; Zang et al., 2012). It was reported that ammonium ions exert cytotoxic impacts on the microbial community (Hansen et al., 1998; Müller et al., 2006). The possible reason for this is two-fold: (a) the activity of cytosolic enzymes could be detrimentally influenced by un-ionized NH_3; and (b) the hydrophobic NH_3 molecules passively diffuse into the cell and are then converted into the NH_4^+ because of the intracellular pH conditions. Here the ammonium accumulation, in turn, results in the inhibited impacts on the cell by altering intracellular pH conditions (Kadam and Boone, 1996). Apart from this, the bacteria may be dehydrated at high ammonia salt levels due to the changes in the osmic pressure (De Baere et al., 1984). However, only a few relevant studies have been published and evaluated MFCs' ability to inhibit ammonia, including power output and nutrient recovery.

In this chapter, a double-compartment MFC was built as described in another recent study (Ye et al., 2019b), and it proved its ability to recover ammonium and phosphate via chemical precipitation from synthetic municipal wastewater. The possible advantages for the double-chamber configuration to recover nutrients include: firstly, the double-chamber MFC could separate the anolyte and catholyte when compared to the air-cathode MFC, which could facilitate the pH elevation of catholyte and the later nutrient recovery by chemical precipitation; and secondly, multi-compartment MFCs demonstrated greater operational complexity than the double-chamber MFC. The present study aimed to explore the influence of influent ammonium concentrations (5-40 mg·NH_4^+-N/L) on electricity generation, COD removal and recovery of nutrients in the MFC. This investigation was conducted over a long-term operation, in order to verify the resistance of microbes to the presence of ammonium.

6.2 Materials and methods

6.2.1 MFC design and setup

The MFC design and setup are described in Chapter 3, Section 3.3.

6.2.2 MFC operation

The anode compartment and cathode compartment were hydraulically connected, in which the anode effluent served as the influent of the cathode chamber. Fresh anolyte (i.e., synthetic domestic wastewater) was constantly supplied to the anode chamber at 0.35 mL/min through a peristaltic pump (Model 77202-60, Masterflex, Illinois, United States), and its compositions used in this chapter are shown in Table 6.1. The pH of feed solution was adjusted using NaOH and HCl solutions. In addition, the stepwise increasing concentration of NH_4^+–N from 5 to 40 mg/L in the anolyte was obtained by adding ammonium chloride. On the other hand, the distilled (DI) water was utilized as the catholyte with air supply throughout the study, in order to focus solely on anode performance. Further details about the MFC operation are summarized in Table 6.2. Each continuous experiment was conducted in duplicate using parallel columns.

Table 6.1 Composition of artificial municipal wastewater (Ye et al., 2019a).

Parameter	Average ± Std.	Parameter	Average ± Std.
pH	7.00 ± 0.02	COD	300 ± 15 mg/L
NH_4Cl	20-80 ± 1.0 mg/L	KH_2PO_4	4.6 ± 0.5 mg/L
$MgSO_4·7H_2O$	5.4 ± 0.5 mg/L	$CaCl_2·2H_2O$	0.4 ± 0.01 mg/L
Yeast	32 ± 1.0 mg/L	Trace nutrients	0.61 mL

Table 6.2 Operational conditions of the dual-chamber MFC

Parameters	**Experimental period**				
	i	**ii**	**iii**	**iv**	**v**
Days	1-30	31-60	61-90	91-120	121-150
Flow rate (mL/min)	0.35	0.35	0.35	0.35	0.35
Hydraulic retention time (d)	0.69	0.69	0.69	0.69	0.69
Influent NH_4^+–N concentration (mg/L)	5	10	20	30	40
OLR (mgCOD/L·d)	435	435	435	435	435

6.2.3 Calculation

Calculation is described in Chapter 3, Section 3.4.2.

6.2.4 Chemical analysis

Chemical analysis is described in Chapter 3, Section 3.4.1.

6.3 Results and discussion

6.3.1 Electricity generation

The variations in the electricity generation of the dual-compartment MFC were investigated while increasing the influent concentration of NH_4^+–N from 5 to 40 mg/L (see Fig. 6.1). Reportedly, the ammonium could be directly oxidized in the anode compartment of the closed-circuit MFC when the ammonium was the sole substrate (Hussain et al., 2016; Zhan et al., 2012). Electrons could be generated as a result of this. In the present study, however, no evidence was found that electricity generation was enhanced due to the presence of ammonium ions which may act as the electron donor. Certainly, it is possible to operate the MFC in a situation where the ammonium ions served as the only energy source in a closed-circuit, which could identify the potential of direct ammonium oxidization and ammonium acting as the electron donor.

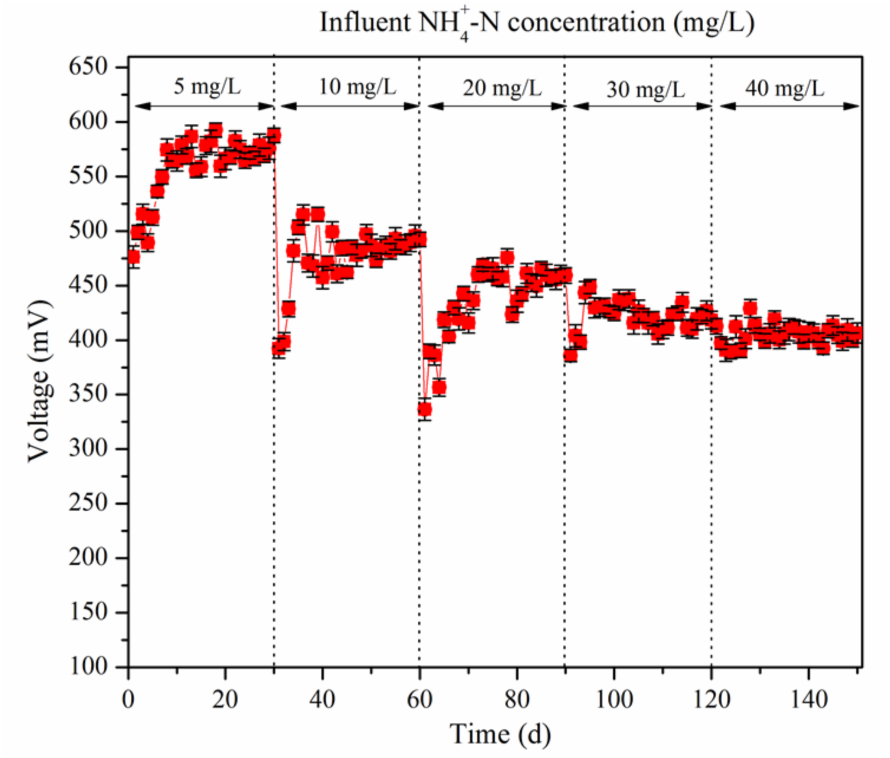

Figure 6.1 Energy output of the MFC system as per different influent NH_4^+–N concentration (5-40 mg/L).

However, this method does not help to conserve methanogenic bacteria and EAB. Also, a certain increase in the amount of ammonium in the anode chamber of MFC could enhance the anolyte's ionic concentration and conductivity, which improved the electron transport and thereby benefited electricity generation in the MFC reactor. However, the conductivity of anolytes does not have a direct relationship with the MFC reactor's generation of electricity (Liu et al., 2017b) since increasing the conductivity of feed water may result in simultaneously elevating diffusion resistance and reduction in ohmic resistance (Nam et al., 2010a). On the other hand, ammonium could also directly serve as a building block for anode-attached microorganisms (Nam et al., 2010b). Based on these methods, the outcomes of ammonium on the power output of MFC are complicated and difficult to quantify.

As shown in Fig. 6.1, the power output exhibited a decline as the feeding ammonium increased from 5 to 40 mg·NH_4^+–N/L, in which the maximum values of 598.9 mV (voltage generation) were obtained at the influent ammonium concentration of 5mg·NH_4^+–N/L. This may be attributed to the ammonium inhibition on the bioactivities of EAB, which detrimentally influenced the electricity generation of the

MFC system. Ammonium inhibition on the power production has also been observed by other researchers in laboratory-scale MFC reactors (Hiegemann et al., 2016; Hiegemann et al., 2018; Kim et al., 2011; Nam et al., 2010b; Tice and Kim, 2014). As an example, the inhibited impacts of ammonium on electricity generation were detected in single-compartment MFCs while increasing the NH_4^+-N concentration over 500 mg/L (Nam et al., 2010b) or 3500 mg/L (Kim et al., 2011). By contrast, Tice and Kim (2014) and Kuntke et al. (2011) did not report the toxic impacts of ammonium on electricity generation even when the NH_4^+-N concentrations were larger than 2500 or 4000 mg/L, respectively. The different conclusions in these publications may be ascribed to the different wastewater sources and inoculum sources.

Interestingly, the inhibited effects of ammonium on the electricity generation gradually weakened with increasing ammonium concentrations. The possible reason for this is that the EAB utilized in the present anode chamber could be generally resistant against high ammonium concentration (Kim et al., 2011; Müller et al., 2006; Nam et al., 2010b). Consequently, the decline in electricity generation could be eased. The low COD concentration of the domestic wastewater leading to maximum electricity generation in the present study was low compared with the results reported in other publications (Xia et al., 2019). However, it suggested the potential for the dual-compartment MFC to produce electricity.

In addition, the power density and coulombic efficiency were analyzed in the present study. As illustrated in Fig. 6.2, the highest point of average power density was 230.17 mW/m^2 at the influent NH_4^+–N concentration of 5 mg/L. It could be seen that the power density decreased by approximately 50% when the NH_4^+–N concentration increased eight-fold to 40 mg /L. This relationship suggests an optimum ammonium nitrogen concentration of 5 mg/L. Besides, the optimum value varied from different studies; for instance, Kim et al. (2011) reported the value was approximately 4000 mg NH_4^+–N /L. Similarly, the coulombic efficiency fell from 25% to 15% while increasing the ammonium nitrogen concentration in the influent from 5 to 40 mg/L in the feed solution. It should be noted here that the reduction in power density and coulombic efficiency of the dual-compartment MFC was weakened at a higher concentration of ammonium nitrogen. This may be attributed to the EAB's ability to generally adapt to the environment with high ammonium concentrations.

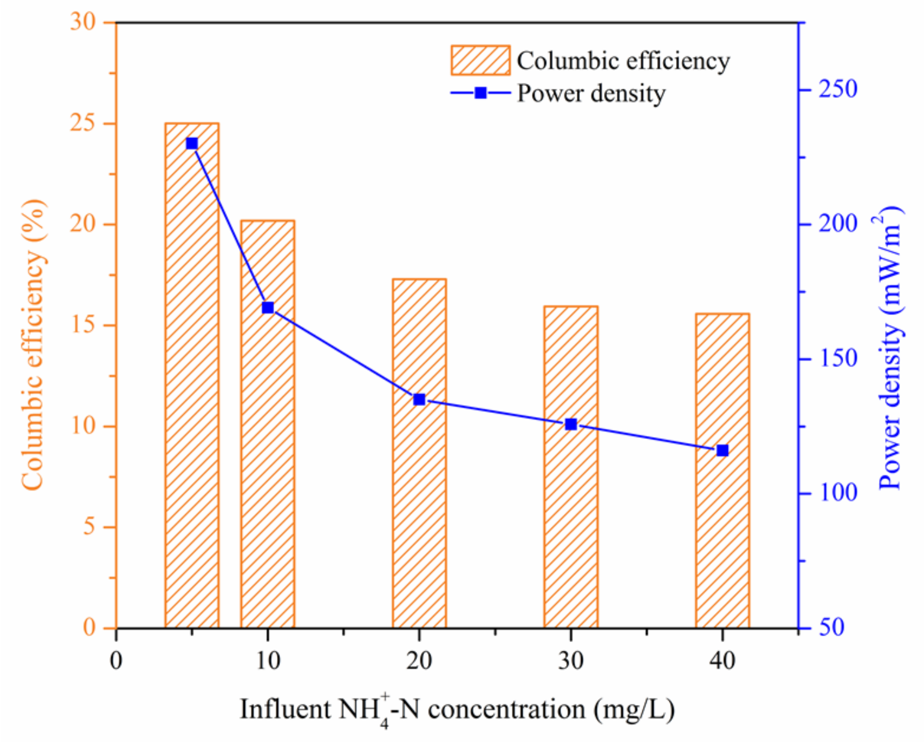

Figure 6.2 Coulombic efficiency and average powder density as per different influent NH_4^+–N concentration (5-40 mg/L).

6.3.2 COD removal

In the experiment, the carbon source of the double-chamber MFC was fixed at 300·CODmg/L. The COD removal efficiency of the MFC as per various feeding ammonium concentrations (5-40 NH_4^+–N·mg/L) was also studied (Fig. 6.3). In this continuous study, the COD removal efficiency in the MFC was calculated based on reactor influent and effluent COD concentrations. As shown in Fig. 6.3, it could be evidently observed that the variations of influent NH_4^+–N concentration made little or insignificant impact on COD reduction, in which the removal efficiencies were almost over 90% during the MFC operation lasting for 150 days. Generally, the COD removal rates in the MFC are influenced by the reactor operation, microbial source and growth at the anode compartment, MFC configurations, wastewater sources and many other factors affecting the COD removal. Interestingly, the microbial communities are also influenced by operational conditions (Zhang et al., 2011c).

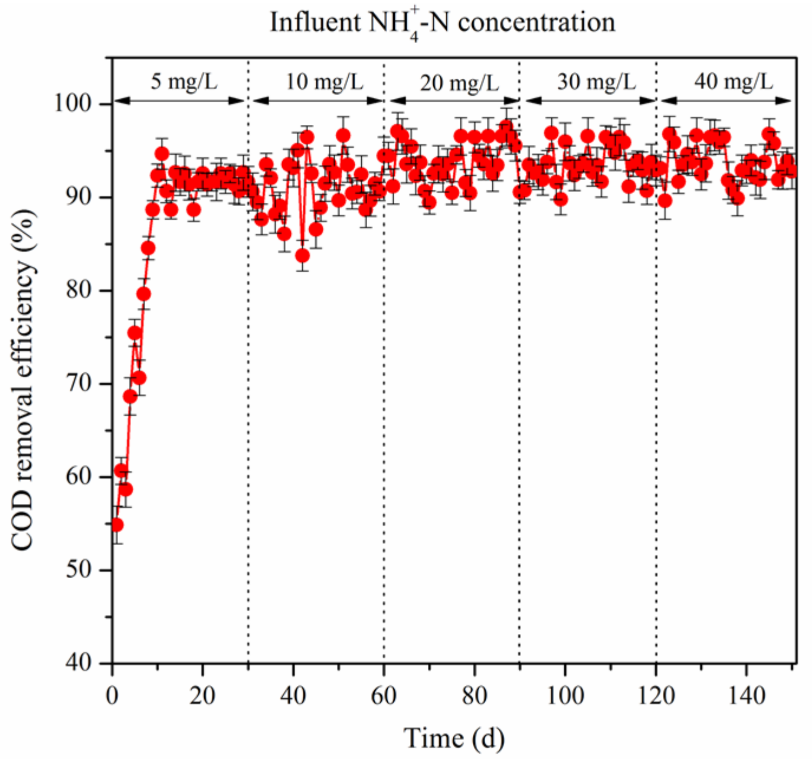

Figure 6.3 COD removal efficiency of the MFC system as per different influent NH_4^+–N concentration (5-40 mg/L).

In the present study, the electrogenic bacterial and non-electrogenic bacterial in the anode chamber may determine the amount of COD removed (Logan, 2008). Moreover, the surface area of the anode electrode could contribute to a reduction in COD since the anode-attached biofilm could simultaneously adsorb and degrade the organics (Tamilarasan et al., 2017). Even though the EAB's activity was detrimentally influenced by increasing the concentration of ammonium nitrogen, it was reported that methanogens that are responsible for the organic removal are more tolerant of elevated ammonia concentrations than EAB (Nam et al., 2010b), which could nonetheless result in effective COD removal. Some authors reported that methanogenesis is negatively influenced by a high ammonium concentration (Chen et al., 2014a; Nettmann et al., 2010; Wilson et al., 2012). Since the ammonium concentrations in the synthetic municipal wastewater were not too high, there was no observation of ammonium inhibition on methanogens.

It is worth noting here that the average removal efficiency of COD increased from 85.56% to 93.70% as the influent ammonium nitrogen concentration varied from 5 to

40 mg/L. Similarly, Tice and Kim (2014) also found that COD removal was still high (> 90%) until the ammonium concentration reached 1000 mg·N/L.

6.3.3 Nutrient recovery

The concentrations of NH_4^+-N and PO_4^{3-}-P in the anode effluent and cathode effluent were examined, respectively. For this part of the experiment, the average removal rates of nutrients in the anode chamber and recovery rates of nutrients in the cathode chamber are depicted in Fig. 6.4.

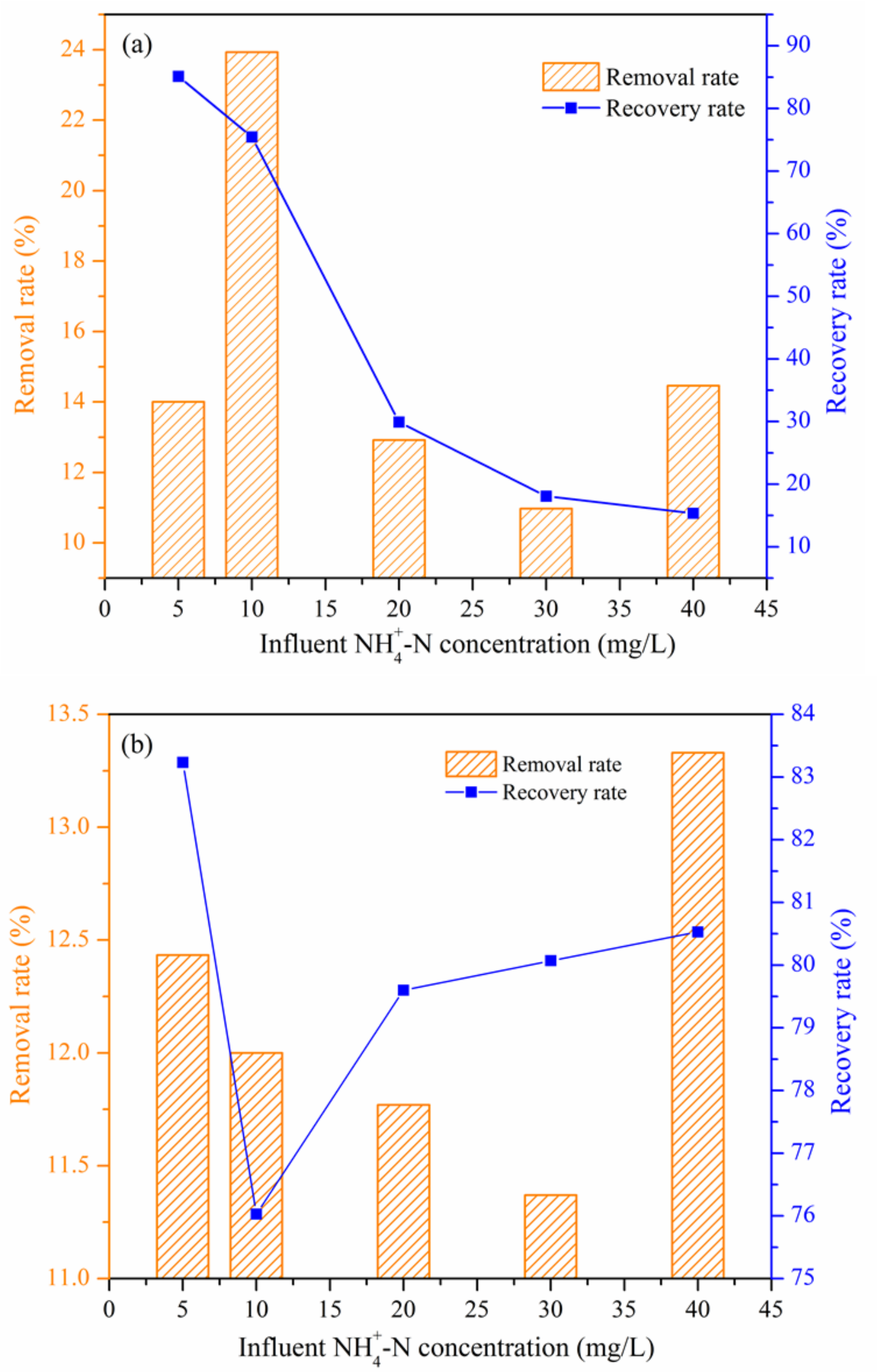

Figure 6.4 Average removal rate in the anode chamber and recovery rate of the double-chamber MFC: (a) NH_4^+-N and (b) PO_4^{3-}-P as per different influent NH_4^+–N concentration (5-40 mg/L).

At the anode chamber of the dual-chamber MFC, the ammonium ions are always removed by the microbial growth and their transport across the CEM to the cathode compartment. The latter pathway offers an opportunity for the continual removal/recovery of ammonium in the double-chamber MFC. It should be noted here that the ammonium transfer to the cathode chamber includes current-driven migration and diffusion caused by the concentration gradient, in which the ammonium migration goes against the concentration gradient. From Fig. 6.4, the average amount of ammonium removed at the anode chamber increased from 0.7 to 5.78 mg/L as the NH_4^+-N concentration varied from 5 to 40 mg/L. Since the electricity generation was detrimentally influenced by higher feeding ammonium concentrations as well as the current-driven migration of ammonium, the possible reason for the enhanced ammonium removal at the anode chamber is that the anaerobic microorganisms gradually adapted to the high ammonium concentrations and took up more ammonium ions for their growth. At the cathode compartment of MFC, on the other hand, several cations such as K^+, Mg^{2+} and Ca^{2+} existing in the feed solution would undoubtedly transfer to the cathode with the ammonium ions.

Compared to other coexisting cations, K^+ ion has the highest mobility, followed by NH_4^+, Ca^{2+}, and Mg^{2+} ions (Faulkner and Bard, 2002). The move rate of NH_4^+ is around 2 times smaller than for H^+. Therefore, H_2O formation and a pH increase at the cathode occurs prior to NH_4^+ transport from the anode to the cathode (Faulkner and Bard, 2002; Kim et al., 2015b). An outcome of this is that it is possible for ammonium ions to be removed by air stripping and/or recovered by chemical precipitation at the cathode compartment. According to another study (Ye et al., 2019b), these two pathways made a combined contribution to the ammonium removal at the cathode chamber. It could be seen from the figure that the average recovery rate of ammonium in the present MFC reactor declined from 85.11% to 15.33% when ammonium concentrations increased. This confirms that the double-compartment MFC could not effectively recover ammonium from ammonium-rich sewage.

As for phosphate ions, the concentration of PO_4^{3-}-P in the solution feeding to the anode chamber of the MFC was 1 mg/L. Either the phosphate removal in the anode chamber or phosphate recovery in the cathode chamber was insignificantly affected by the variations in ammonium concentrations. Specifically, the efficiency in removing phosphate ranged from 11.37% to 13.33% whilst its recovery rate was in the 76.03-83.23% range.

6.4 Conclusion

In the present study, the impacts of ammonium loading rates on the dual-compartment MFC system were explored. This analysis demonstrated that COD removal was negligibly influenced by the feeding ammonium concentration. The MFC system obtained the maximum voltage generation of 598.9 mV and the ammonium inhibition on the electricity generation decreased at higher ammonium concentrations. Furthermore the influent concentration of NH_4^+-N wielded great and negligible impacts on the recovery of ammonium and phosphate ions, respectively. Conclusively, the double-compartment MFC has proven to be useful for recovering nutrients and energy from domestic wastewater under this premise of the acceptable range of NH_4^+-N concentration.

CHAPTER 7

Nutrient recovery using a dual-chamber microbial fuel cell in continuous flow mode under different hydraulic retention time

7.1 Introduction

Nitrogen (N) and phosphorus (P) are un-substitutable micronutrients for living organisms and play a critical role in biological growth. Such nutrients are commonly employed as fertilizers for crops and plants in agriculture. However, the supply of N and P is recently becoming more challenging, especially given the projected increases in food production to satisfy the growing global population and the relevant global fertilizer production, which is required to reach approximately 263 million tons in 2050 (Alexandratos and Bruinsma, 2012). In industry, the Haber Bosch process utilizes the N_2 gas from the atmosphere to produce ammonia for fertilizer production under high pressure and temperature. Obviously, this generation process demands a large input of energy and costs; this results in the emission of toxic gases into the environment. On the other hand, phosphate-based rocks serving as the main source of P are only finite resources and their existing deposits will be exhausted within 50–100 years (Cordell et al., 2011).

Apart from this, applications of nutrients (i.e., N and P) in a full-scale context may eventually cause their accumulation in streams, and a high content of nutrients in the aquatic environment may trigger environmental damage such as eutrophication and red tide. In the global P cycle, human activity has made possible the mobilization of phosphate from phosphate-bearing rocks to the hydrosphere over the last 50 years, and this amount was approximately 500 million tons of P (Cordell et al., 2011). Thus, it is critically important to combine the removal of nutrients with their recovery in waste treatment, which: 1) reduces the need for fertilizer production; 2) curtails the impact of fertilizer production and transportation on climate change; and 3) contributes to a more healthier ecology, and sustainable development (Luo et al., 2018).

In recent years, wastewater management has received increased attention for its efficiency and sustainability (Libralato et al., 2012), which may be attributed to the rapid depletion of materials and energy in the urban metabolism and the resulting energy-water-food nexus (Walker et al., 2014). It is generally accepted that retrieving nutrients (mainly N and P) from wastewater for use in agriculture could contribute to sustainable and better wastewater management (Yan et al., 2018; Ye et al., 2018). Since domestic wastewater contains a large amount of N and P, such a recovery strategy in the treatment system is attractive (Kataki et al., 2016b). Reportedly, the recovery of phosphate from municipal wastewater could theoretically satisfy 15–20% of the world's phosphate demand (Xia et al., 2016).

Chemical precipitation is one of the most popular technologies for recovering nutrients in municipal wastewater treatment and the common final products in this process include hydroxyapatite and struvite, which could be directly used as an eco-friendly slow-release fertilizer. It should be noted here that struvite ($MgNH_4PO_4 \cdot 6H_2O$) precipitation could simultaneously recycle ammonium and phosphate. For this reason, the nutrient recovery through chemical precipitation in domestic wastewater treatment has been widely investigated, in order to assess its feasibility from laboratory-scale to full-scale (De Vrieze et al., 2016; Ye et al., 2017). However, the high cost of chemical inputs may compromise large-scale industrial application of this nutrient recovery system (Romero-Güiza et al., 2015a; Romero-Güiza et al., 2015b). In particular, the addition of alkaline reagents for increasing the pH solution is essential in the chemical precipitation process, which accounts for a large proportion of overall costs in the process, and greatly influences the economic feasibility of the nutrient recovery system during wastewater treatment (Jaffer et al., 2002). Considering this, it is challenging for implementing the proposed objective of nutrient recovery in current conventional systems.

The feasibility of the microbial fuel cell (MFC) system for recovering nutrients from wastewater has been previously reported (Kelly and He, 2014; Lu et al., 2019; Ye et al., 2019b)， in which the obvious advantage of this method refers to the fact that there is no need to add alkaline chemicals for pH elevation in the chemical precipitation process. Initially, the MFC technology can recover the chemical energy contained in the chemical bonds in wastewater treatment. In this scenario, the bio-catalytic capabilities of microbes are utilized to generate a current field (Du et al., 2007), which applies to a range of organic fuel sources in the absence of metal catalysts. In a typical double-chamber MFC, anaerobic bacteria at the anode chamber are employed to oxidize biodegradable substrates, and electrons and protons are thus generated in this process. After that, electrons formed during the anaerobic respiration process transfer to the surface of anode electrode (directly or by mediators) and then to the cathode electrode through the external circuit. Furthermore, the generated protons transport across a cation exchange membrane (CEM) from the anode chamber to the cathode chamber, after which they react with an electron acceptor (e.g., oxygen) and electrons to produce water (or other reduced compounds) (Oliveira et al., 2013). During the cathode reaction, hydroxyl ions localized the cathode electrodes being generated, so the high pH zone of the cathode offers an opportunity for the recovery of nutrients via chemical precipitation.

In general, the MFC performance is governed by many factors such as configurations, electrode materials, inoculum, operation conditions and oxygen supply (Hidalgo et al., 2015; Mardanpour et al., 2017). At the beginning of these MFC studies, the reactors always operate in batch mode, but have now been changed to the continuous mode. The possible reason for this is that the MFC systems are expected to simultaneously generate electricity and purify wastewater, and continuous mode facilitates the further scaling up of MFC reactors.

Hydraulic retention time (HRT) is a key parameter in the design and operation of MFC, and greatly influences the energy requirements, which in turn directly affects the MFC’s performance. It is reported that HRT exerts an important impact on the power output of continuous-flow MFCs because the variations in HRT have a direct effect on the type and quantity of bacteria in the bioreactor (Sharma and Li, 2010; Sobieszuk et al., 2017). Sharma and Li (2010) believed that the optimum HRT is the time that is consistent with the time taken to generate living microbes. Apart from this, the HRT determines the value of shear stress which directly affects the formation of biofilm on a surface (Lecuyer et al., 2011). Thus, the value of HRT should be correctly determined when utilizing MFC systems (Sobieszuk et al., 2017).

In recent years, our group has built a new double-compartment MFC which successfully retrieved nutrients from municipal wastewater (Ye et al., 2019b). Nonetheless there remains a dearth of research examining the potential of this double-chamber MFC for the combined recovery of N and P through chemical precipitation from domestic wastewater without addition of chemicals for pH elevation. In the present study, the main goal is to investigate the individual effects of HRT on the two-chamber MFC reactor working in continuous mode. The efficiency of power output and recovery of nutrients of the MFC system was evaluated.

7.2 Materials and methods

7.2.1 MFC preparation

The MFC preparation (i.e., the synthetic wastewater) is described in Chapter 3, Section 3.2.1.

7.2.2 MFC design and operation

The MFC design is described in Chapter 3, Section 3.3. Moreover, the dual-chamber MFC operated at four different times for a period of 120 days (see Table 7.1). In the present experiments, the volumetric flow rate was changed by the pump (0.35, 0.47, 0.59 and 0.70 mL/min), resulting in different HRTs (0.69, 0.52, 0.41 and 0.35 d). When operating the MFC, electricity generation is the most important parameter for the reactor. The MFC's working condition would be considered as steady when the value of voltage generated remains constant or changes in a negligible range. In each experimental period, the MFC reactor continuously operated until reaching the steady state at the new HRT.

Table 7.1 Operational conditions of the dual-chamber MFC

Parameters	**Experimental period**			
	i	**ii**	**iii**	**iv**
Days	1-30	31-60	61-90	91-120
Flow rate (mL/min)	0.35	0.47	0.59	0.70
HRT (d)	0.69	0.52	0.41	0.35
Influent COD concentration (mg/L)	300	300	300	300
OLR (mgCOD/L·d)	435	580	725	870

7.2.3 Calculations

Calculation is described in Chapter 3, Section 3.4.2.

7.2.4 Analysis

Analysis is described in Chapter 3, Section 3.4.1.

7.3. Results and discussion

7.3.1 Electricity generation

The effects of HRT on the electricity generation of the MFC reactor were evaluated, and the voltage generation in the MFC during the operation period is present in Fig. 7.1. In the anode chamber, the electrically active bacteria (EBA) are responsible for the power output, and their activity and concentration directly affects the energy production. From this figure, at the beginning of the first period (HRT = 0.69 d), the generated voltage increased rapidly, probably due to the change in operation mode from batch to continuous. Subsequently, the voltage became stabilized within nine days and the maximum voltage generated in this period was 598.9 mV. When the HRT was 0.52 d (period II), the maximum voltage fell to 577.6 mV. A further reduction in the HRT resulted in reducing the maximum generated voltage to 564.5 mV at the HRT of 0.41 d (period III). As the HRT decreased to 0.35 d (period V), the maximum voltage was approximately 10% lower than the value obtained at the HRT of 0.41 d.

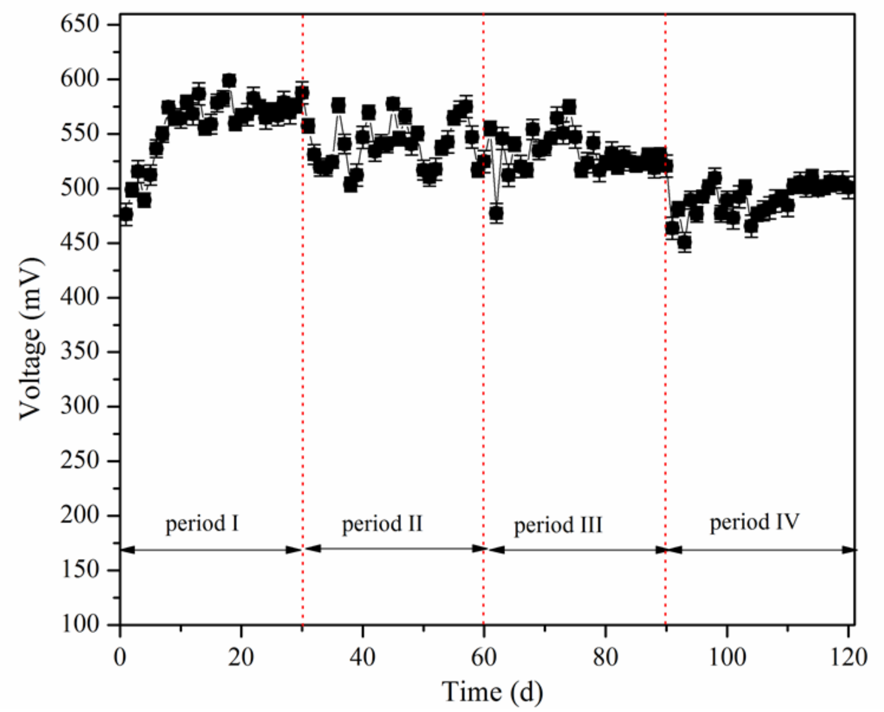

Figure 7.1 Power output *vs* operation time at different HRTs (0.35-0.69 d) in the double-compartment MFC (daily averages ± standard deviations).

Overall, the electricity generation of the MFC reactor revealed a downturn in HRT during the experiments. A possible reason for this is that decreasing HRT may result in: firstly, high flow rates of feed solution which may worsen the mixing conditions (Sobieszuk et al., 2017); and secondly, the loss of anaerobic microbes to some extent in the anode chamber. These two outcomes may greatly influence the concentration of EBA and seriously compromise the growth of the EBA. Moreover, higher HRT could offer longer contact time between the biofilm and substrate in wastewater, which then facilitates the degradation of substrates via EBA to produce and transfer electrons onto the anode surface (Sharma and Li, 2010). Consequently, the power output could be improved. Santos et al. (2017) found that the EBA's activity could be enhanced by increasing HRT, which contributes to the EBA's degradation and transforms the substrate into electricity. Another possible explanation for this is that lower HRT may result in an increase in the OLR correspondingly, and sufficient organics were thus retained in the anode chamber (Ma et al., 2016). In this scenario, the organic biodegradation was enhanced as well as the formation of biofilm attached to the anode electrode. Consequently, the thickness of the biofilm on the anode surface was increased as well as the mass transfer resistance, which inhibited the generation of power. In their analysis, Wei et al. (2012) indicated a dynamic equilibrium existing in the anode chamber, which demonstrated a constant proliferation rate of EBA. For this reason, the voltage would generally become stabilized.

The present results have also been observed in other studies (Li et al., 2013; Rahimnejad et al., 2011; Srikanth et al., 2016). In contrast, a few MFC analyses reported an opposite conclusion in that increasing HRT may adversely influence the voltage generation in MFCs (Akman et al., 2013; Ge et al., 2013; Juang et al., 2012; Wei et al., 2012). This contradiction may be attributed to the MFC configuration and other factors that affect the voltage generation of the MFC reactors. For example, Ge et al. (2013) explored the impacts of HRT on the power output in an osmotic microbial fuel cell fed with domestic wastewater. In their study, decreasing the HRT from 24 h to 6 h caused electricity generation to increase significantly. Apart from this, some researchers thought high HRT may reduce the concentrations of substrate and the cell metabolism at the anode chamber (Liu et al., 2008), which inhibited the MFC reactor's production of energy. A reduced HRT results in more degradation of the substrate used for generating electricity at a unit time in the MFC system, thereby enabling biomass to convert energy (Luo et al., 2017). However, this scenario may require a higher concentration of EBA or stronger biofilm, which could oxidize more organics in a shorter time.

In addition, it is possible that there is an optimum HRT for the electricity generation of each continuously operated MFC reactor, with the optimum values of HRT being specific for different MFC configurations (Rahimnejad et al., 2011). As mentioned above, the maximum generated voltage (598.9 mV) in the present study was observed at the HRT of 0.69 d, which was also optimal for this MFC configuration. In comparison to the study by Akman et al. (2013), the results in this chapter were about

40% higher with reference to the maximum voltage generated at a HRT of 0.5 d. By contrast, this value was around 30% lower than that achieved at the HRT of 0.28 d by Juang et al. (2012) who analyzed a continuous MFC. This may be attributed to the use of neutral red in the anode chamber, which was served as an electron transfer mediator and thereby improved electricity generation.

For generating electricity in the MFC system, how to increase the output power is hugely important. For this reason, the power density is a critical constant in MFC reactors as well as coulombic efficiency. Fig. 7.2 depicts the maximum voltage generated and corresponding power density at each HRT. The maximum power density and coulombic efficiency were 253.84 mW/m^2 and 25.01%, respectively, at the HRT of 0.69 d. In this work, optimizing HRT to generate electricity in the dual chambered continuous MFC was one of the main objectives. For this reason, the HRT of 0.69 d could satisfy this purpose. However, the HRT is expected to be minimized when the effective removal of COD is the main objective of MFCs for wastewater treatment because this could increase the economic feasibility of the MFC system (Chang et al., 2004).

Apart from this, the maximum power density obtained in this chapter was higher than that reported in other studies. For example, Song et al. (2018) operated an up-flow MFC and achieved the maximum power density of 15.41 mW/m^2 at the HRT of 3.0 d. Recently, Yang et al. (2019) found that the modification of the cathode surfaces could accelerate the electron consumption, and thereby improve the power density of a MFC. In their study, the MFC with the mesoporous carbon-modified cathodes could have higher power density compared to that equipped with bare carbon electrons, and the maximum power density could reach 1.179 ± 0.031 W/m^2. The possible explanation for this is that the mesoporous carbon-modified electrode had approximately double the porosity utilization compared to the bare carbon electrode. Similarly, in the study by Luo and He (2016), their results showed that maximum power density of tubular MFCs could rise from 4.29 to 6.50 W/m^3 when the carbon fiber cathode was coated with nickel. It is certain that the power density could be improved by optimizing the\ MFC through changing the operational parameters (e.g., influent COD concentration and solution conductivity).

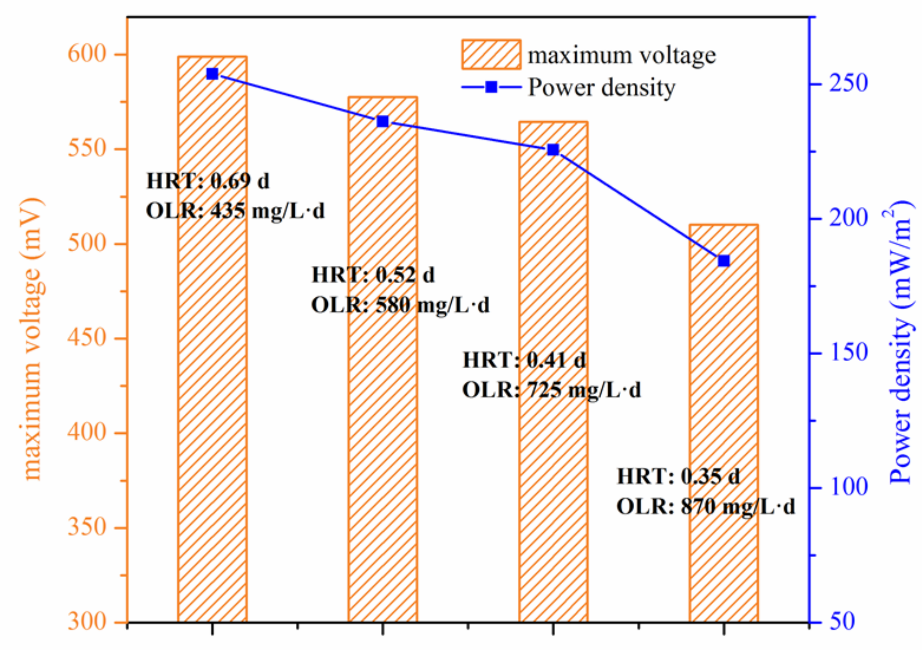

Figure 7.2 Maximum voltage generated and corresponding power density at different HRTs (0.35-0.69 d) in the double-compartment MFC (daily averages ± standard deviations).

7.3.2 COD removal

The performance of this double-chamber MFC with reference to wastewater treatment efficiency was evaluated by the efficiency in removing COD. The COD reduction was tested in the HRT range of 0.35-0.69 d. As shown in Fig. 7.3, the double-chamber MFC reactor effectively removed COD in the HRT range of 0.35-69 d. This may well have been due to the lowest HRT (i.e., 0.35 d), which was still sufficient for the microorganism in the anode chamber to efficiently degrade organic material. Similar results were reported elsewhere (Song et al., 2018; Xie et al., 2018). For instance, Song et al. (2018) observed this phenomenon when they utilized an up-flow MFC coupled constructed wetlands for the removal of sulfadiazine. In this scenario, the removal efficiencies of COD were in the range of 92.4%-94.4% under different HRT conditions.

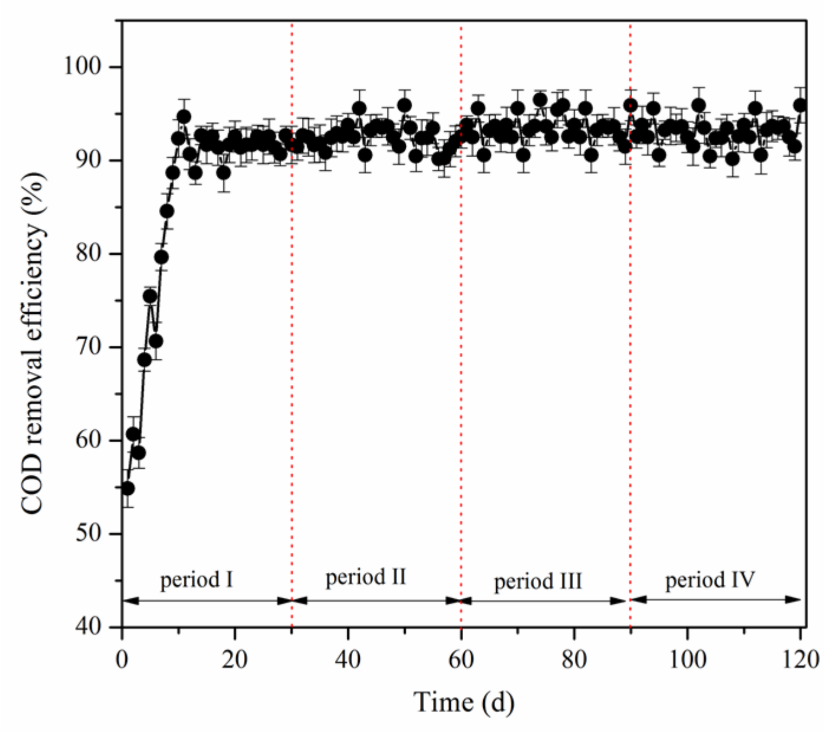

Figure 7.3 COD reduction efficiencies *vs* operation time at different HRTs (0.35-0.69 d) in the double-compartment MFC (daily averages ± standard deviations).

At the MFC reactors, the concentrations of all microbial species at the anode chamber highly determine the removal of COD as well as the balance between the different species of bacteria. Many researchers reported that higher HRT favorably influences the COD degradation (Fazli et al., 2018; Kim et al., 2016; Kim et al., 2015a). A commonly stated explanation for this is that higher HRT results in longer residence time of substrate in the anode chamber, and subsequently anaerobic microbes are allowed to have more contact time to digest the organics, which leads to higher removal efficiencies of COD and better effluent quality (Li et al., 2013). Luo et al. (2017) found that longer HRT could even cause full oxidization of organics in domestic wastewater.

In the study by Ge et al. (2013), they found that the removal efficiencies of COD were approximately 40–60% and 70–80% at the HRT of 10 h and 24 h, respectively, whilst continuously operating an osmotic MFC for domestic wastewater treatment. Similarly, Haavisto et al. (2017) employed a two-chamber up-flow MFC to produce electricity from xylose, in which decreasing the HRT from 3.5 d to 0.17 d resulted in reduced removal of COD from 95% to 78%. In contrast, Akman et al. (2013) reported that increasing HRT from 0.5 to 1.5 d may lead to an increase in the removal of dissolved organic carbon from 38% to 45% in the dual-chamber MFC. Similarly, Li et al. (2013) found that the activity of EBA and organic matter degradation was not inhibited in animal carcass wastewater treatment. This difference in findings may result from the MFC's configuration (Li et al., 2013). Moreover, lowering HRT could increase the quantity of substrate entering the anode compartment, so the total amount of substrate degraded by the microbes (i.e., COD removal efficiency) may be increased (Juang et al., 2012).

7.3.3 Recovery of nutrients

The recovery of nutrients in the double-chamber MFC was assessed at the HRT ranging from 0.35 to 0.69 d and the results are shown in Fig. 7.4. At the anode chamber, the nutrients were mainly removed by microbial activity for their growth. Besides, some ammonium ions may transfer across the CEM from the anode chamber to the cathode chamber to realize its removal at the anode compartment.

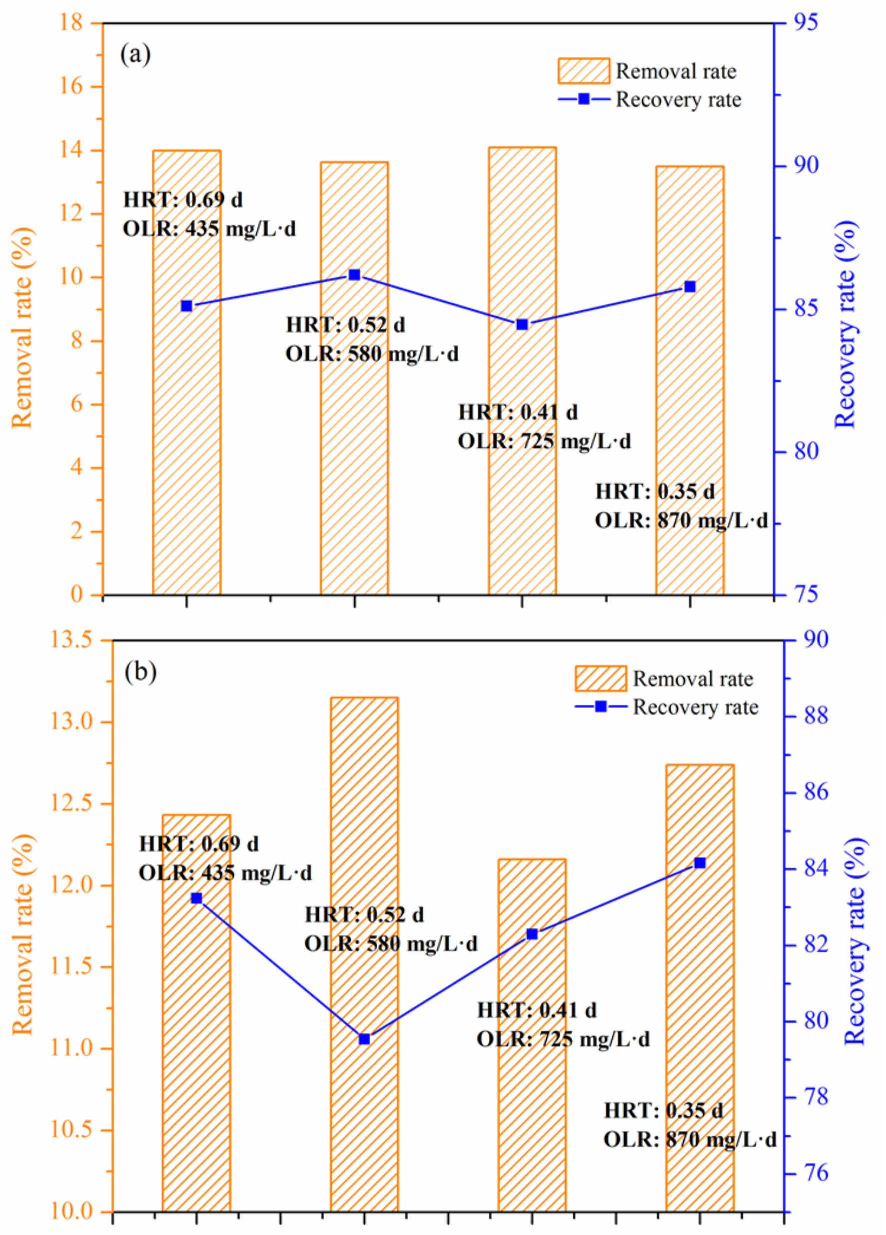

Figure 7.4 Average removal and recovery efficiency of (a) NH_4^+-N and (b) PO_4^{3-}-P in the anode chamber and cathode chamber at different HRTs (0.35-0.69 d) in the double-compartment MFC.

Reportedly, lower HRT resulted in higher OLR, which may cause more bio-consumption of nutrients (Xu et al., 2014; Ye et al., 2019a). However, the analysis of the removal of NH_4^+-N and PO_4^{3-}-P undertaken in the present study shows that the average removal efficiencies of NH_4^+-N and PO_4^{3-}-P at the anode chamber were in the 13%-15% and 12%-14% ranges, respectively. The removals also occurred at different HRTs, which indicated that such HRT ranges wielded an insignificant impact on the removal of ammonium and phosphate (see Fig. 7.4). One possible reason for this is that the enhanced bio-consumption of nutrients at higher OLR resulted from a higher concentration of COD at a unit time whereas changes in the HRT in the present study did not vary the influent COD concentration. Again, the lowest HRT could still offer sufficient contact time for the anaerobic bacteria to take up NH_4^+-N and PO_4^{3-}-P.

Isma et al. (2014) reported that the microbial growth could be improved by decreasing the HRT which leads to a higher F/M ratio, and thus provides more nutrients to the biomass. However, the employment of synthetic domestic wastewater as a substrate in the present study is readily available with sufficient nutrients for the bacterial growth even at low HRT. Apart from this, Liu et al. (2016) documented the significant impacts of HRT on the removal of NH_4^+-N and PO_4^{3-}-P in a photobioreactor system treating acidic wastewater. This may result from different functional microorganisms organized for removing nutrients in the photobioreactor system and MFC system.

On the other hand, at the cathode chamber, the generated electrons and electron acceptor (i.e., O_2) may have the following reaction.

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \qquad (7.3)$$

The pH elevation may result in the recovery of nutrients via chemical precipitation and the reduction in the concentration of NH_4^+-N and PO_4^{3-}-P within the cathode compartment being confirmed. Furthermore, partial NH_4^+-N ions were removed through air stripping in this scenario, in which the ammonium ions were converted into volatile ammonia (Ye et al., 2019b). The changes in the average recovery efficiency of NH_4^+-N and PO_4^{3-}-P at the cathode chamber were negligible.

Furthermore, the experimental results demonstrated that the average recovery efficiencies of NH_4^+-N and PO_4^{3-}-P were approximately 85% and 83% of PO_4^{3-}-P at different HRT conditions. As discussed above, lower HRT could still result in efficient COD removal and effective recovery of nutrients despite the slight inhibition of electricity generation. For this reason, the HRT could be somewhat reduced to increase the economic feasibility of the MFC system, especially if the system's main objective is to recover nutrients and reduce COD concentrations.

7.4 Conclusion

The impacts of HRT (0.35-0.69d) on the dual-chamber MFC's performance were investigated in this research study. Our results demonstrated that the maximum voltage generated was 598.9 mV with a corresponding power density of 253.84 mW/m^2 at HRT = 0.69 d. The effective removal of COD was achieved coupled with the recovery of NH_4^+-N (85%) and PO_4^{3-}-P (83%) proving successful at different HRT conditions. In conclusion, the dual-chamber MFC was feasible for recovering nutrients and producing energy with simultaneous COD reduction in sewage treatment. However, the HRT could be reasonably reduced if the MFC's application to the recovery of nutrients is the major priority.

CHAPTER 8

Conclusions and recommendations

8.1 Conclusions

This PhD thesis aimed at developing a dual-chamber MFC for recovering ammonium and phosphate in domestic wastewater treatment, and optimizing the MFC system through evaluating the impacts of various factors including organic loading rate (OLR), influent ammonium concentration and hydraulic retention time (HRT) on the MFC performance with reference to the electricity generation, COD degradation and recovery of nutrients. The specific conclusions of the research were shown as follows:

1) The double-chamber MFC system has high potential for the recovery of NH_4^+-N and PO_4^{3-}-P in urban wastewater treatment. When the anode compartment and cathode compartment of such MFC reactor were not hydraulically connected, operating MFC for 30 d in either batch mode or continuous mode of anode chamber could only obtain the effective accumulation and latter removal/recovery of ammonium ions. In this case, the highest voltage generation was 641.4 mV. When the MFC was continuously operated at the flow rate of 0.35 mL/min and wastewater was sequentially treated by the anode chamber and cathode chamber, NH_4^+-N and PO_4^{3-}-P could be effectively recovered/removed by the combined effect of chemical precipitation and microbial absorption. In this scenario, the aeration supply was a must to realize this objective. The characteristics analysis of the precipitates achieved in the cathode compartment indicated that elemental composites are quite similar to elements of the pure struvite standards. Compared to the forward osmosis (FO) and nonwoven (NW) serving as the separator of MFC reactor, the utilization of cation exchange membrane (CEM) could obtain higher recovery efficiency of NH_4^+-N and PO_4^{3-}-P and better organic removal.
2) The OLR exerted a significant effect on the MFC performance in terms of power output, COD removal and recovery of nutrients. As the OLR increased from 435 to 725 mgCOD/L·d, the degradation of organics in the MFC system was negligibly influenced with more than 90% of COD removed. However, the COD removal efficiency dropped to approximately 70% at the OLR of 870 mgCOD/L·d. Besides, increased OLR resulted in a downtrend in the electricity generation of MFC reactor, in which the maximum voltage generation was 598.9 mV with corresponding power density of 254 mV/m^2 and coulombic efficiency of 25.01% at the OLR of 435 mgCOD/L·d. This is despite the fact that an

increase in the voltage generation from 318.2 to 482.6 mV as the OLR grew from 580 to 870 mgCOD/L·d, which may be attributed to the more substrates added into the anode chamber at higher OLRs. Furthermore, higher OLR enhanced the removal of nutrients at the anode chamber but compromised the recovery of nutrients in the MFC system. The maximum recovery efficiency of NH_4^+-N and PO_4^{3-}-P were 85.11% and 83.23% at the OLR of 435 mgCOD/L·d, respectively. In conclusion, the OLR should be controlled in a relatively low range if the recovery of nutrients is the main objective of this MFC system.

3) The presence of ammonium ions in domestic wastewater significantly influenced the MFC performance in terms of recovering nutrients and energy and removing COD. Excessive ammonium inhibited the electricity generation of the MFC system: for example, the maximum electricity generation decreased from 598.9 mV to 429.0 mV as the influence ammonium concentration varied from 5 to 40 mg·NH_4^+-N/L. The ammonium inhibition effects declined with increasing the ammonium concentration. Moreover, the changes in the influent ammonium concentration had insignificant influence upon the organic removal with over 85% of COD reduction. As for the recovery of nutrients, high ammonium concentration deteriorated the ammonium recovery in the MFC reactor whilst the efficiency of phosphate recovery was not greatly affected in a wide range of ammonium concentration.
4) The different HRTs made insignificant influent on the recovery of NH_4^+-N and PO_4^{3-}-P in the double-chamber MFC reactor. In this scenario, approximately 85% of NH_4^+-N and 83% of PO_4^{3-}-P were recovered in the HRT range of 0.35 to 0.69 d. Besides, such HRT range could also obtain the efficient degradation of organics with more than 90% of COD removed. In contrast, increased HRT may compromise the energy generation of MFC system. Specifically, the maximum voltage generation decreased from 598.9 mV to 510.3 mV while decreasing the HRT from 0.69 d to 0.35 d. Therefore, an appropriate reduction in HRT could enhance the economic feasibility of the MFC system if the recovery of nutrients is prioritized.

8.2 Recommendations

This Ph.D. thesis has comprehensively investigated the overall performance of two-compartment MFC systems including electricity generation and organic removal, especially the recovery of NH_4^+-N and PO_4^{3-}-P. Nevertheless, further studies on the double-chamber MFC for recovering nutrients should be pursued in future works as summarized below:

1) Future research should consider the analysis of bacterial community with reference to structure and population in the double-chamber MFC system. This may contribute to making effective control for MFC to recover nutrients and generate energy in municipal wastewater treatment.
2) The treatment of real domestic wastewater through the laboratory-scale dual-compartment MFC is recommended to be added in future studies. Since the composition and properties of real wastewater changes over time, such study could examine the feasibility of the practical MFC application for the recovery of nutrients.
3) Pilot- or full-scale of two-chamber MFC systems for recovering nutrients in domestic wastewater treatment should be conducted. This could provide theoretical and technical supports for the commercial application of the MFC systems.
4) CEM is a common separator in the double-chamber MFC reactor, but further research on membrane-less double-chamber MFC are greatly needed because this configuration could decrease the internal resistance of MFC as well as its over cost;
5) As the FO membrane could highly concentrate nutrients, it is important to evaluate the integrated system of the FO process coupled and double compartment MFC for the recovery of nutrients in domestic wastewater treatment.

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Appendix

List of publications

Peer-reviewed journal articles:

1) **Ye, Y.**, Ngo, H.H., Guo, W., Chang, S.W., Nguyen, D.D., Liu, Y., Nghiem, L.D., Zhang, X., Wang, J. 2019. Effect of organic loading rate on the recovery of nutrients and energy in a dual-chamber microbial fuel cell. **Bioresource Technology**, 281, 367-373. (**IF = 5.807,** SJR: Q1)
2) **Ye, Y.**, Jiao, J., Kang, D., Jiang, W., Kang, J., Ngo, H.H., Guo, W., Liu, Y. 2019. The adsorption of phosphate using a magnesia–pullulan composite: kinetics, equilibrium, and column tests. **Environmental Science and Pollution Research**, 1-12. (**IF = 2.800,** SJR: Q2)
3) **Ye, Y.**, Ngo, H.H., Guo, W., Liu, Y., Chang, S.W., Nguyen, D.D., Ren, J., Liu, Y., Zhang, X. 2019. Feasibility study on a double chamber microbial fuel cell for nutrient recovery from municipal wastewater. **Chemical Engineering Journal**, 358, 236-242. (**IF = 6.735,** SJR: Q1)
4) Shi, W., Fu, Y., Jiang, W., **Ye, Y.**, Kang, J., Liu, D., Ren, Y., Li, D., Luo, C., Xu, Z. 2019. Enhanced phosphate removal by zeolite loaded with Mg-Al-La ternary (hydr) oxides from aqueous solutions: Performance and mechanism. **Chemical Engineering Journal**, 357, 33-44. (**IF = 6.735,** SJR: Q1)
5) Tang, Q., Shi, C., Shi, W., Huang, X., **Ye, Y.**, Jiang, W., Kang, J., Liu, D., Ren, Y., Li, D. 2019. Preferable phosphate removal by nano-La(III) hydroxides modified mesoporous rice husk biochars: Role of the host pore structure and point of zero charge. **Science of the Total Environment**, 662, 511-520. (**IF = 4.9,** SJR: Q1)
6) **Ye, Y.**, Liu, W., Jiang, W., Kang, J., Ngo, H.H., Guo, W., Liu, Y. 2018. Defluoridation by magnesia–pullulan: Surface complexation modeling and pH neutralization of treated fluoride water by aluminum. **Journal of the Taiwan Institute of Chemical Engineers**, 93, 625-631. (**IF = 3.849,** SJR: Q1)
7) **Ye, Y.**, Yang, J., Jiang, W., Kang, J., Hu, Y., Ngo, H.H., Guo, W., Liu, Y. 2018. Fluoride removal from water using a magnesia-pullulan composite in a continuous fixed-bed column. **Journal of Environmental Management**, 206, 929-937. (**IF = 4.005,** SJR: Q1)

8) **Ye, Y.**, Ngo, H.H., Guo, W., Liu, Y., Chang, S.W., Nguyen, D.D., Liang, H., Wang, J. 2018. A critical review on ammonium recovery from wastewater for sustainable wastewater management. **Bioresource Technology**, 268, 749-758. (**IF = 5.807,** SJR: Q1)
9) Yan, T.[1], **Ye, Y.**[1], Ma, H., Zhang, Y., Guo, W., Du, B., Wei, Q., Wei, D., Ngo, H.H. 2018. A critical review on membrane hybrid system for nutrient recovery from wastewater. **Chemical Engineering Journal**, 348, 143-156. (**IF = 6.735,** SJR: Q1) [1]Equal First Author.
10) **Ye, Y.**, Ngo, H.H., Guo, W., Liu, Y., Li, J., Liu, Y., Zhang, X., Jia, H. 2017. Insight into chemical phosphate recovery from municipal wastewater. **Science of the Total Environment**, 576, 159-171. (**IF = 4.9,** SJR: Q1)
11) **Ye, Y.**, Ngo, H.H., Guo, W., Liu, Y., Zhang, X., Guo, J., Ni, B.-j., Chang, S.W., Nguyen, D.D. 2016. Insight into biological phosphate recovery from sewage. **Bioresource Technology**, 218, 874-881. (**IF = 5.807,** SJR: Q1)

Contributions to scientific forums

1) **Ye, Y.**, Ngo, H.H., Guo, W., Liu, Y., Chang, S.W., Nguyen, D.D., Ren, J., Liu, Y., Zhang, X. 2018. Feasibility study on a double chamber microbial fuel cell for nutrient recovery from municipal wastewater (Oral presentation). International Bioprocessing Association-International Symposium on Advanced Membrane Bioreactors for Environment Sustainability (IBA-AMBRES 2018). Tianjin, China, 15-18 April 2018
2) **Ye, Y.**, Ngo, H.H., Guo, W., Chang, S.W., Nguyen, D.D., Liu, Y., Ni, B., Zhang, X. 2019. Microbial fuel cell for nutrient recovery and electricity generation from municipal wastewater under different ammonium concentrations (Poster presentation). International Conference on Sustainable Waste Treatment and Management (SWTM-2019). Yangling, China, 6-9 May 2019.

Awards

1) 2016 HDR Students Publication Award from Faculty of Engineering and Information Technology (FEIT), University of Technology, Sydney (UTS) for publishing in high-quality journals.

2) 2017 HDR Students Publication Award from Faculty of Engineering and Information Technology (FEIT), University of Technology, Sydney (UTS) for publishing in high-quality journals.
3) 2019, People’s Choice Award for Poster Presentation in Research Showcase from School of Civil and Environmental Engineering, University of Technology, Sydney (UTS).