

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

June 2019

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.

Production Note:

SIGNATURE OF STUDENT: Signature removed prior to publication.

DATE: 29/06/2019

ACKNOWLEDGEMENTS

First and foremost, I would like to extend my heartfelt gratitude to my principle supervisor Prof. Huu Hao Ngo. His endless guidance, valuable suggestion and constant encouragement make me successfully complete this thesis. From the beginning of my Ph.D. study, his experienced advice and patient assistance help me to adopt to the new environment and improve myself in research and daily life. His conscientious academic spirit and modest, open-minded personality not only guide me through the novel academic research, but also make me to be a better man. Also, heartfelt thanks are extended to my co-supervisor Prof. Wenshan Guo and Dr. Yiwen Liu, whose instructions will always be of great value for my future career and academic research.

Secondly, I would like to thanks to many excellent fellow postgraduate students in our research group including Khan, Dora, Phong, Hang, Loan and Thuy who share their knowledge and selflessly help me during the study. My thanks also go to lab manager Dr. Johir Mohammad for his help in setting up experiments and analysing results. Apart from this, I would like to acknowledge the help and assistance from academic and administration staff from the Faculty of Engineering and Information Technology (FEIT) and Graduate Research School (GRS).

Last but not least, I would like to thank my beloved wife. She makes my life meaningful and delightful, and accompanies me whenever and wherever. Without her unconditional love and tremendous support, I could not complete the Ph.D. study and deliver the final thesis. Thanks a lot for everything she did for me and I love her forever.

TABLE OF CONTENTS

Title page	
Certification of original authorship.....	i
Acknowledgements.....	ii
Table of contents.....	iii
List of tables.....	vii
List of figures	viii
List of abbreviations	xi
List of symbols	xiii
Abstract.....	xvi
CHAPTER 1 Introduction	
1.1 Research background	1-1
1.2 Research motivations and scope	1-4
1.3. Research significance	1-5
1.4 Organization of the report.....	1-5
CHAPTER 2 Literature review	
2.1 Introduction	2-1
2.2 Membrane hybrid system for nutrient recovery	2-3
2.2.1 Membrane-based hybrid system	2-3
A. Forward osmosis	2-3
B. Membrane distillation.....	2-5
C. Electrodialysis	2-6
2.2.2 Bioelectrochemical system.....	2-8
2.3 MBR-based hybrid system	2-14
2.4 Comparison of membrane hybrid systems for nutrient recovery	2-18
2.4.1 Technical feasibility	2-18
2.4.2 Costs involved in the nutrient recovery	2-23
2.5 Future perspectives	2-25
2.6 Conclusion.....	2-28

CHAPTER 3 Experimental investigation

3.1 Introduction	3-1
3.2 Materials	3-1
3.2.1 Synthetic wastewater.....	3-1
3.2.2 Membrane	3-2
3.3 Experimental setup and operating conditions of a double-chamber MFC	3-4
3.4 Analytical methods	3-5
3.4.1 Organics, nutrients, pH, DO and electricity	3-5
3.4.2 Electricity calculation.....	3-7
3.4.3 Characterization of precipitates.....	3-7

CHAPTER 4 Feasibility study on a double chamber microbial fuel cell for nutrient recovery from municipal wastewater

4.1 Introduction	4-1
4.2 Materials and method	4-3
4.2.1. MFC construction	4-3
4.2.2. Microorganisms and synthetic wastewater	4-4
4.2.3. Experimental process	4-4
4.2.4. Analytical method	4-6
4.3 Results and discussions	4-6
4.3.1 Effects of operation mode of anolyte on the nutrient accumulation in the catholyte	4-6
4.3.2 Effects of aeration on the nutrient recovery	4-8
4.3.3 Effects of different separators in the MFC on nutrient recovery	4-13
4.4. Conclusion.....	4-14

CHAPTER 5 Effect of organic loading rate on the recovery of nutrients and energy in a dual-chamber microbial fuel cell

5.1 Introduction	5-1
5.2 Materials and methods	5-4
5.2.1 Experimental setup.....	5-4
5.2.2 Inoculum and experimental operation.....	5-4
5.2.3 Data analysis	5-5
5.3 Results and discussion	5-5

5.3.1 COD removal efficiency	5-5
5.3.2 Electricity generation	5-6
5.3.3 Nutrients recovery	5-11
5.4 Conclusion.....	5-12

CHAPTER 6 Microbial fuel cell for nutrient recovery and electricity generation from municipal wastewater under different ammonium concentrations

6.1 Introduction	6-1
6.2 Materials and methods	6-4
6.2.1 MFC design and setup.....	6-4
6.2.2 MFC operation	6-4
6.2.3 Calculation	6-5
6.2.4 Chemical analysis.....	6-5
6.3 Results and discussion	6-5
6.3.1 Electricity generation	6-5
6.3.2 COD removal	6-8
6.3.3 Nutrient recovery	6-10
6.4 Conclusion.....	6-13

CHAPTER 7 Nutrient recovery using a dual-chamber microbial fuel cell in continuous flow mode under different hydraulic retention time

7.1 Introduction	7-1
7.2 Materials and methods	7-3
7.2.1 MFC preparation	7-3
7.2.2 MFC design and operation	7-4
7.2.3 Calculations.....	7-4
7.3. Results and discussion	7-4
7.3.1 Electricity generation	7-4
7.3.2 COD removal	7-8
7.3.3 Recovery of nutrients	7-10
7.4 Conclusion.....	7-12

CHAPTER 8 Conclusions and recommendations

8.1 Conclusions	8-1
------------------------------	------------

8.2 Recommendations	8-3
References	R-1
Appendix	A-1

LIST OF TABLES

Table 2.1	Main types of membrane hybrid systems for nutrient recovery from wastewater	2-2
Table 2.2	Advantages and disadvantages of various membrane hybrid systems for nutrient recovery	2-18
Table 2.3	Energy analysis of different systems for the N recovery (Kuntke et al., 2012; Maurer et al., 2003; Qin and He, 2014)	2-23
Table 3.1	Characteristics of the synthetic wastewater (displayed in the case of COD: N: P = 300: 5: 1)	3-2
Table 3.2	Technical specifications of CMI-7000 CEM (Inc.)	3-3
Table 5.1	Operational conditions of the double-chamber MFC	5-5
Table 6.1	Composition of artificial municipal wastewater (Ye et al., 2019a)	6-4
Table 6.2	Operational conditions of the dual-chamber MFC	6-5
Table 7.1	Operational conditions of the dual-chamber MFC	7-4

LIST OF FIGURES




Figure 1.1	Mechanism of membrane to concentrate and separate feed water (adapted from Fuchs and Drosig (2010))	1-3
Figure 2.1	Schematic representation of the FO-based hybrid system for the nutrient recovery	2-3
Figure 2.2	Schematic representation of the MD-based hybrid system for the nutrient recovery	2-5
Figure 2.3	Schematic representation of the ED-based hybrid system for the nutrient recovery	2-7
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: Power Supply; membrane: cation-exchange membrane.	2-9
Figure 2.5	Schematic representation of the FO-MD hybrid system for the nutrient recovery	2-13
Figure 2.6	Schematic representation of the MEC-FO hybrid system for the nutrient recovery	2-14
Figure 2.7	Schematic of the OMBR hybrid system for direct nutrient recovery (adapted from Qiu and Ting (2014a))	2-15
Figure 2.8	Schematic of the OMBR-MF hybrid system for direct nutrient recovery (modified from Qiu et al. (2015))	2-15
Figure 3.1	Experimental set-up of MFC	3-5
Figure 3.2	The schematic: a) anode electrode; b) cathode electrode	3-5
Figure 3.3	The analytical instruments used in the experimental investigation: a) TOC analyser; b) pH meter; c) DO meter; d) universal digital meter	3-6
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	4-5

Figure 4.2	Schematic representation of double-chamber MFC for nutrients recovery. CEM represents the cation exchange membrane; represents the anaerobic microorganisms	4-6
Figure 4.3	Ammonium accumulation in the cathode chamber in the: (a) batch mode; (b) self-circulation mode; and (c) single-continuous mode	4-8
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	4-9
Figure 4.5	(a) EDS and (b) SEM image of the precipitates achieved in the cathode chamber in the double-chamber MFC	4-12
Figure 4.6	Removals of NH_4^+ -N and PO_4^{3-} -P using double-chamber MFC with different separators	4-13
Figure 5.1	COD removal efficiency vs operation time at different OLRs (435-870 mgCOD/L·d) in the dual-chamber MFC (daily averages \pm standard deviations)	5-6
Figure 5.2	Electricity generation vs operation time at different OLRs (435-870 mgCOD/L·d) in the dual-chamber MFC (daily averages \pm standard deviations)	5-7
Figure 5.3	Maximum voltage and power density vs OLR	5-9
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 \pm standard deviations)	5-12
Figure 6.1	Energy output of the MFC system as per different influent NH_4^+ -N concentration (5-40 mg/L)	6-6
Figure 6.2	Coulombic efficiency and average powder density as per different influent NH_4^+ -N concentration (5-40 mg/L)	6-8
Figure 6.3	COD removal efficiency of the MFC system as per different influent NH_4^+ -N concentration (5-40 mg/L)	6-9

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)	6-11
Figure 7.1	Power output vs operation time at different HRTs (0.35-0.69 d) in the double-compartment MFC (daily averages \pm standard deviations)	7-5
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 \pm standard deviations)	7-8
Figure 7.3	COD reduction efficiencies vs operation time at different HRTs (0.35-0.69 d) in the double-compartment MFC (daily averages \pm standard deviations)	7-9
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	7-11

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 ₆ H ₁₂ O ₆	Glucose
Ca	Calcium
Ca ²⁺	Ironized calcium
Ca ₅ (OH)(PO ₄) ₃	Hydroxylapatite, HAP
CaCl ₂ ·2H ₂ O	Calcium chloride
CaO	Calcium oxide
C _E	Coulombic efficiency
CH ₄	Methane
CO ₂	Carbon dioxide
CoCl ₂ ·6H ₂ O	Cobalt chloride
CuSO ₄ ·5H ₂ O	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 ₂ O	Water
H ₂ PO ₄ ⁻	Dihydrogen phosphate
H ₂ SO ₄	Sulphuric acid
H ₃ PO ₄	Phosphoric acid
HCl	Hydrogen chloride
HPO ₄ ²⁻	Hydrogen phosphate
I	Current
K	Potassium

K^{+}	Ionized potassium
KCl	Potassium chloride
KH_2PO_4	Potassium dihydrogen phosphate
Mg	Magnesium
Mg^{2+}	Ionized 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
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	Zinc sulphate
ΔCOD	The amount of COD removed

Ph.D. DISSERTATION ABSTRACT

Author: Yuanyao Ye

Date: 30 June 2019

Thesis title: Development of a novel microbial fuel cell for nutrient recovery from synthetic municipal wastewater

Faculty: Faculty of Environmental and Information Technology

School: Civil and Environmental Engineering

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/m² at the OLR of 435 mgCOD/L·d. Higher OLR may disrupt the recovery of PO₄³⁻-P and NH₄⁺-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.