

**SPECIFIC INTEGRATED BIOCHAR –  
MICROBIAL FUEL CELL  
BIOREACTOR FOR REMOVING  
ANTIBIOTICS FROM SWINE  
WASTEWATER**

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Thesis submitted in fulfilment of the requirements for  
the degree of

**Doctor of Philosophy**

under the supervision of Prof. Huu Hao Ngo

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## **CERTIFICATION OF ORIGINAL AUTHORSHIP**

I, Dongle Cheng declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Civil and Environmental Engineering/Faculty of Engineering and Information Technology at the University of Technology Sydney.

This thesis is wholly my own work unless otherwise referenced or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

This document has not been submitted for qualifications at any other academic institution.

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# TABLE OF CONTENTS

<b>Title page</b>	
<b>Certification of original authorship</b> .....	<b>i</b>
<b>Acknowledgements</b> .....	<b>ii</b>
<b>Table of contents</b> .....	<b>iii</b>
<b>List of tables</b> .....	<b>vii</b>
<b>List of figures</b> .....	<b>viii</b>
<b>List of abbreviations</b> .....	<b>xi</b>
<b>List of symbols</b> .....	<b>xiii</b>
<b>Abstract</b> .....	<b>xvi</b>

## **CHAPTER 1 Introduction**

<b>1.1 Research background</b> .....	<b>1-1</b>
<b>1.2 Research motivations and scope</b> .....	<b>1-4</b>
<b>1.3. Research significance</b> .....	<b>1-5</b>
<b>1.4 Organization of the report</b> .....	<b>1-5</b>

## **CHAPTER 2 Literature review**

<b>2.1 Introduction</b> .....	<b>2-1</b>
<b>2.2 Removal mechanisms of antibiotics during bioprocessing</b> .....	<b>2-2</b>
2.2.1 Removal by sorption .....	2-2
2.2.2 Removal by biodegradation .....	2-3
<b>2.3 Different bioprocesses for removing antibiotics from swine wastewater</b> .....	<b>2-4</b>
2.3.1 Activated sludge (AS) processes.....	2-4
2.3.2 Anaerobic digestion (AD) processes.....	2-9
2.3.3 Constructed wetlands (CWs) .....	2-13
2.3.4 Membrane bioreactor (MBR)-based processes.....	2-18
2.3.5 Bioelectrochemical systems (BESs) .....	2-22
<b>2.4 Comparison of different bioprocesses</b> .....	<b>2-25</b>
<b>2.5 Future perspectives</b> .....	<b>2-29</b>
<b>2.6 Conclusion</b> .....	<b>2-30</b>

## **CHAPTER 3 Experimental investigation**

<b>3.1 Introduction</b> .....	<b>3-1</b>
<b>3.2 Materials</b> .....	<b>3-1</b>
3.2.1 Synthetic wastewater and anaerobic sludge .....	3-1
3.2.2 Targeted antibiotics and organic solvents .....	3-2
<b>3.3 Experimental setup and operating conditions</b> .....	<b>3-2</b>
3.3.1 Batch experiments .....	3-2
3.3.2 MFC system .....	3-3
3.3.3 Biochar-MFC system .....	3-5
<b>3.4 Analytical methods</b> .....	<b>3-6</b>
3.4.1 Antibiotics, organics, nutrients, pH, DO, electricity .....	3-6
3.4.2 Biochar characterization .....	3-7
3.4.3 Data calculation .....	3-7

## **CHAPTER 4 Removal process and mechanism of antibiotics during anaerobic treatment of swine wastewater**

<b>4.1 Introduction</b> .....	<b>4-1</b>
<b>4.2 Materials and method</b> .....	<b>4-2</b>
4.2.1. Materials .....	4-2
4.2.2. Experimental setup and operating conditions .....	4-2
4.2.3. Analytical method .....	4-2
<b>4.3 Results and discussions</b> .....	<b>4-2</b>
4.3.1 Removal of TCs and SMs in anaerobic sludge reactors .....	4-2
4.3.2 Adsorption process of TCs onto anaerobic sludge .....	4-4
4.3.3 Degradation of SMs in anaerobic sludge .....	4-8
<b>4.4. Conclusion</b> .....	<b>4-13</b>

## **CHAPTER 5 Feasibility of microbial fuel cell for removing antibiotics from swine wastewater**

<b>5.1 Introduction</b> .....	<b>5-1</b>
<b>5.2 Materials and methods</b> .....	<b>5-2</b>
5.2.1 MFC construction and inoculation .....	5-2
5.2.2 Experimental design and operation .....	5-2
5.2.3 Data analysis .....	5-2

<b>5.3 Results and discussion .....</b>	<b>5-2</b>
5.3.1 Impacts of SMs on power generation of MFC.....	5-2
5.3.2 Impacts of SMs on COD removal in MFC .....	5-4
5.3.3 Degradation of SMs in MFC.....	5-5
<b>5.4 Conclusion.....</b>	<b>5-7</b>

**CHAPTER 6 Performance of a continuous flow microbial fuel cell for antibiotics removal from swine wastewater**

<b>6.1 Introduction .....</b>	<b>6-1</b>
<b>6.2 Materials and methods .....</b>	<b>6-2</b>
6.2.1 Experimental design and set up .....	6-2
6.2.2 Experimental operation .....	6-3
6.2.3 Analytical methods.....	6-3
<b>6.3 Results and discussion .....</b>	<b>6-3</b>
6.3.1 SMs removal in continuous flow MFC systems .....	6-3
6.3.2 Electricity generation .....	6-8
6.3.3 COD removal .....	6-10
6.3.4 Nutrients removal.....	6-12
<b>6.4 Conclusion.....</b>	<b>6-14</b>

**CHAPTER 7 Antibiotics removal from swine wastewater in microbial fuel cell with a new biochar**

<b>7.1 Introduction .....</b>	<b>7-1</b>
<b>7.2 Materials and methods .....</b>	<b>7-3</b>
7.2.1 Materials.....	7-3
7.2.2 Biochar preparation and modification.....	7-3
7.2.3 Experimental setup and operation .....	7-4
7.2.4 Analytical methods.....	7-4
<b>7.3. Results and discussion .....</b>	<b>7-4</b>
7.3.1 Characterization of biochar .....	7-4
7.3.2 Adsorption behavior of SMs onto biochar .....	7-7
7.3.3 Economic feasibility of the biochar application in the MFC .....	7-9
7.3.4 Removal of SMs in the MFC with the biochar dosage .....	7-9

7.3.5 Performance of the MFC with biochar addition .....	7-11
<b>7.4 Conclusion.....</b>	<b>7-12</b>
 <b>CHAPTER 8 Conclusions and recommendations</b>	
<b>8.1 Conclusions .....</b>	<b>8-1</b>
<b>8.2 Recommendations .....</b>	<b>8-3</b>
 <b>References .....</b>	<b>R-1</b>
 <b>Appendix .....</b>	<b>A-1</b>

## LIST OF TABLES

<b>Table 2.1</b>	Key physical-chemical properties of target antibiotics	2-2
<b>Table 2.2</b>	Removal of target antibiotics during conventional aerobic sludge processes	2-6
<b>Table 2.3</b>	Removal of target antibiotics during conventional anaerobic processes	2-11
<b>Table 2.4</b>	Removal of target antibiotics during constructed wetlands processes	2-14
<b>Table 2.5</b>	Removal of target antibiotics during MBR-based processes	2-19
<b>Table 2.6</b>	Comparison of target antibiotics removal from different bioprocesses	2-26
<b>Table 3.1</b>	Components of the synthetic swine wastewater	3-1
<b>Table 3.2</b>	Batch experiment design for behavior of antibiotics in anaerobic sludge	3-3
<b>Table 4.1</b>	Kinetic and isotherm models and parameters for the adsorption of tetracycline antibiotics onto anaerobic sludge	4-6
<b>Table 4.2</b>	Degradation rate constants ( $k_1$ ) and half-lives ( $t_{1/2}$ ) of the three sulfonamide antibiotics in anaerobic reactor	4-9
<b>Table 5.1</b>	Fitting Results of SMX, SDZ and SMZ degradation in MFC using the first-order kinetic model	5-6
<b>Table 7.1</b>	Physicochemical properties of biochars produced under different conditions	7-4
<b>Table 7.2</b>	Sorption coefficients of SMs onto biochar evaluated by Pseudo second-order and Freundlich models	7-8



## LIST OF FIGURES

<b>Figure 1.1</b>	Pathway of antibiotics from swine farms to the environment	1-2
<b>Figure 1.2</b>	Main structure of this research	1-6
<b>Figure 2.1</b>	Anaerobic digestion process of organic matter	2-10
<b>Figure 2.2</b>	Basic configuration of MFCs: (a) Double chamber; (b) Single chamber.	2-23
<b>Figure 3.1</b>	The schematic of MFC operating under: (a) Self-circulating; (b) Single continual; and (c) Sequential anode-cathode modes	3-4
<b>Figure 4.1</b>	The concentration variation of TCs (a) and SMs (b); and their removal efficiency (c) in the reactor with non-sterile and sterile anaerobic sludge	4-3
<b>Figure 4.2</b>	Adsorption kinetics data and fitted modes of tetracycline (TC) (a), chlortetracycline (CTC) (b) and oxytetracycline (OTC) (c) onto different concentrations of anaerobic sludge	4-5
<b>Figure 4.3</b>	The adsorption isotherms of tetracycline (TC), chlortetracycline (CTC), and oxytetracycline (OTC) onto anaerobic sludge	4-7
<b>Figure 4.4</b>	(a) Removal efficiencies of sulfonamide antibiotics and COD in the anaerobic reactor; (b) First-order biodegradation kinetic model of sulfamethoxazole (SMX), (c) sulfadiazine (SDZ) and (d) sulfamethazine (SMZ).	4-9
<b>Figure 4.5</b>	Removal efficiencies of sulfamethoxazole (SMX), sulfadiazine (SDZ) and sulfamethazine (SMZ) in the anaerobic reactor with different concentrations of COD	4-12
<b>Figure 5.1</b>	The voltage generation under different initial concentrations of SMs in MFC	5-3
<b>Figure 5.2</b>	The removal efficiency of COD in MFC and OC under different SMs concentrations	5-4
<b>Figure 5.3</b>	The concentration change and removal efficiency of SMs in MFC and OC	5-5
<b>Figure 6.1</b>	Removal efficiencies of SMs during the continuous operation of MFC under different scenarios: (a) SMX removal efficiency; (b) SMZ removal efficiency; (c) SDZ removal efficiency	6-5

<b>Figure 6.2</b>	Voltage generation when the MFC is operating under different modes with and without SMs present	6-9
<b>Figure 6.3</b>	COD removal from swine wastewater as MFC operates under different modes with and without SMs present	6-11
<b>Figure 6.4</b>	Nutrients removal efficiencies as the MFC operated under different modes with and without SMs present: (a) $\text{NH}_4^+$ -N removal efficiency; (b) $\text{PO}_4^{3-}$ -P removal efficiency	6-11
<b>Figure 7.1</b>	Characteristics of biochar produced at 400 °C (BC-400), 600 °C (BC-600) and activated by KOH (BC-KOH): (A) FTIR spectrum; (B) Raman spectrum; (C) BET surface area isotherm; (D) SEM-EDS spectrum	7-6
<b>Figure 7.2</b>	The adsorption kinetic (a) and isotherm (b) of SMX, SMZ and SDZ onto biochar	7-8
<b>Figure 7.3</b>	(a) the removal efficiency of SMs in MFC with the addition of different concentrations of biochar; (b) the average removal efficiency of SMs in the anode and cathode chamber of MFC, respectively (500 mg/L of biochar)	7-10
<b>Figure 7.4</b>	(a) the average daily voltage generation and (b) COD and nutrients removal efficiency in MFC with different concentrations of biochar	7-12

## LIST OF ABBREVIATIONS

<b>Symbol</b>	<b>Description</b>
A <sup>2</sup> O	Anaerobic-anoxic-oxic process
AD	Anaerobic digestion
AFMBR	Anaerobic fluidized membrane bioreactor
AnMBRs	Anaerobic membrane bioreactors
A/O	Anaerobic/oxic process
AOB	Ammonia-oxidizing bacteria
ARB	Antibiotic resistant bacteria
ARGs	Antibiotic resistant genes
AS	Activated sludge
ASBR	Anaerobic sequencing batch reactor
BAF	Biological aerated filter
BC	Biochar
BES	Bioelectrochemical systems
BET	Brunauer-Emmett-Teller
BF-MBR	Biofilm MBR
CAP	Chloramphenicol
CEM	Cation-exchange membrane
COD	Chemical oxygen demand
CWs	Constructed wetlands
CSTR	Continuously stirred tank reactor
CTC	Chlortetracycline
DC	Doxycycline
DI water	Deionized water
DIF	Difloxacin
FAO	Food and Agriculture Organization
ECDC	European Centre for Disease Prevention and Control
EDS	Energy dispersive spectrometer
ENR	Enrofloxacin
EPS	Extracellular polymeric substances
ESI+	Electrospray positive ion mode

FTIR	Fourier transform infrared spectrometer
GAC	Granular activated carbon
HRT	Hydraulic retention time
HSF	Horizontal subsurface flow
HSSF-CWs	Horizontal subsurface flow constructed wetlands
MBRs	Membrane bioreactors
MLSS	Mixed liquor suspended solids
MRM	Multiple reaction monitoring
OC	Open-circuit mode
OTC	Oxytetracycline
PAC	Powder activated carbon
PFO	Pseudo-first-order
PSO	Pseudo-second-order
SBR	Sequencing batch reactor
SDZ	Sulfadiazine
SEM	Scanning electron microscopy
SF	Free water surface
SRT	Solids retention time
SF-CWs	Free water surface constructed wetlands
SMs	Sulfonamide antibiotics
SMX	Sulfamethoxazole
SMZ	Sulfamethazine
TC	Tetracycline
TCs	Tetracycline antibiotics
UASB	Up-flow anaerobic sludge blanket
UF	Ultrafiltration
US CDC	United State Centre for Disease Control and Prevention
VFAs	Volatile fatty acids
VSSF-CWs	Vertical subsurface flow constructed wetlands

## LIST OF SYMBOLS

<b>Symbol</b>	<b>Description</b>
$C_6H_{12}O_6$	Glucose
$CaCl_2 \cdot 2H_2O$	Calcium chloride
$CO_2$	Carbon dioxide
$CO$	Carbon monoxide
$CuSO_4 \cdot 5H_2O$	Cupric sulphate
$e^-$	Electron
$FeCl_3$	Ferric chloride anhydrous
$H^+$	Proton
$H_2$	Hydrogen
$H_2O$	Water
$H_2SO_4$	Sulphuric acid
$H_3PO_4$	Phosphoric acid
$K$	Potassium
$K_2CO_3$	Potassium carbonate
$K_2O$	Potassium oxide
$KOH$	Potassium hydroxide
$KH_2PO_4$	Potassium dihydrogen phosphate
$MgSO_4 \cdot 7H_2O$	Magnesium sulphate
$N_2$	Nitrogen gas
$NaN_3$	Sodium azide
$NaHCO_3$	Sodium bicarbonate
$NaOH$	Sodium hydroxide
$NH_3$	Free ammonia
$NH_3-N$	Ammonia nitrogen
$NH_4^+$	Ionized ammonia
$NH_4^+-N$	Ammonium nitrogen
$NH_4Cl$	Ammonium chloride
$NO^{2-}$	Nitrite
$NO^{3-}$	Nitrate
$O_2$	Oxygen gas

$\text{OH}^-$	Hydroxyl
$\text{PO}_4^{3-}\text{-P}$	Hydrogen phosphate phosphorus
R	Resistor
$\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$	Zinc sulphate

## Ph.D. DISSERTATION ABSTRACT

**Author:** Dongle Cheng

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**Thesis title:** Specific integrated biochar - microbial fuel cell bioreactor for removing antibiotics from swine wastewater

**Faculty:** Faculty of Environmental and Information Technology

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### Abstract

Swine wastewater is an important source of antibiotics in the environment due to their large-scale application in swine industry. High levels of antibiotics in swine wastewater have become an increasing global concern considering their potential risks to the environment, human and animal health. The integration of biochar and microbial fuel cell (MFC) is a promising technology for the treatment of swine wastewater containing antibiotics and producing electricity simultaneously. The aim of this study is to investigate the potential of a specific integrated biochar-MFC system to treat swine wastewater containing antibiotics. In this scenario, it is necessary to identify the removal process and mechanism of antibiotics in the anaerobic sludge that used in the anode chamber of MFC. Through a series of batch experiments, the results indicated that the removal of tetracycline antibiotics (TCs) in the anaerobic sludge contributed to the

biosorption of sludge, while biodegradation was responsible for the removal of sulfonamide antibiotics (SMs). The adsorption data of TCs in anaerobic sludge fitted well with the pseudo-second order kinetic and the Freundlich isotherm modes, which suggested a heterogeneous chemisorption process. Cometabolism was the main mechanism for the biodegradation of SMs and the process fitted well with the first-order kinetic model. Microbial activity in the anaerobic sludge might be curtailed due to the presence of high concentrations of SMs.

The performance of a double-chamber MFC for treating swine wastewater with the addition of different concentrations of SMs was investigated under the anode self-circulation operating condition of MFC. It is observed that chemical oxygen demand (COD) could be effectively removed (>95%) and almost not affected by the presence of SMs in MFC. A stable output of voltage was also observed. The removal efficiency of sulfamethoxazole (SMX), sulfadiazine (SDZ), and sulfamethazine (SMZ) in the MFC was in the range of 99.46% to 99.53%, 13.39% to 66.91% and 32.84% to 67.21%, respectively, which were higher than those in a traditional anaerobic reactor with 97.45% - 98.89% for SMX, 11.96% - 31.24% for SDZ and 23.85% - 33.49% for SMZ. The biodegradation process of SMs in MFC was fitted to the first-order kinetic model. Hence, MFC revealed strong resistance to antibiotic toxicity and high potential for the treatment of swine wastewater containing antibiotics.

For industrial application of the MFC in the treatment of swine wastewater containing antibiotics, the MFC was conducted in continuous operating modes under different conditions. Voltage can also be successfully generated during the continual operation with the maximum value of ~550 mv. Effective removal of COD can be achieved in both single continuous (>80%) and sequential anode-cathode (> 90%) operating modes. Nutrients can also be removed in the cathode chamber of the MFC with the maximum removal efficiency of 66.62% for  $\text{NH}_4^+\text{-N}$  and 32.1% for  $\text{PO}_4^{3-}\text{-P}$ . The removal efficiency of SMs under the sequential anode-cathode operating mode of MFC was around 49.35% - 59.37% for SMX, 16.75% - 19.45% for SMZ and 13.98% - 16.31% for SDZ, respectively. The inhibition of SMs to pollutants' remove in both chambers of MFC was observed after SMs exposure, suggesting that SMs exert toxic effects on the microorganisms. Moreover, a positive correlation was found between the higher  $\text{NH}_4^+\text{-N}$  concentration used in this study and the removal efficiency of SMs in the cathode chamber. Results suggest that it is feasible to use the continuous anode-cathode MFC to treat swine wastewater with antibiotics, while the removal efficiency of antibiotics required to be



further improved.

The addition of biochar into the MFC is a promising method for enhancing the removal of antibiotics in continuous flow MFC. Biochar adsorption is an effective method for the removal of antibiotics from wastewater with advantages of low cost, easy production and environmentally friendly. A new pomelo peel derived biochar was developed in this study. The biochar activated by KOH displayed a large surface area (2457.37 m<sup>2</sup>/g) and total pore volume (1.14 cm<sup>3</sup>/g). SMs are favorable absorbed onto the heterogeneous surfaces of biochar thorough pore-filling and  $\pi$ - $\pi$  electron donor–acceptor (EDA) interaction. The biochar's addition to a certain concentration (500 mg/L) could enhance the removal efficiency of SMX, SDZ and SMZ to 82.44% - 88.15%, 53.40% - 77.53% and 61.12% - 80.68%, respectively. Moreover, the electricity production and COD removal were increased by increasing the concentration of biochar. The improved performance of MFC could be due to the role of porous biochar as an adsorbent and biocarrier of the growth of microorganisms.

**Keywords:** Swine wastewater; Antibiotics; Adsorption; Biodegradation; Microbial fuel cell; Electricity generation, Organic removal; Nutrients removal.