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

by Dongle Cheng

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

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Symbol	Description
A^2O	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

Symbol	**Description**
$C_6H_{12}O_6$	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

OH^-	Hydroxyl
PO_4^{3-}-P	Hydrogen phosphate phosphorus
R	Resistor
$ZnSO_4 \cdot 7H_2O$	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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	Dr. Yiwen Liu (Co-supervisor)

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 NH_4^+-N and 32.1% for PO_4^{3-}-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 NH_4^+-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^2/g) and total pore volume (1.14 cm^3/g). SMs are favorable absorbed onto the heterogeneous surfaces of biochar thorough pore-filling and π-π 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.