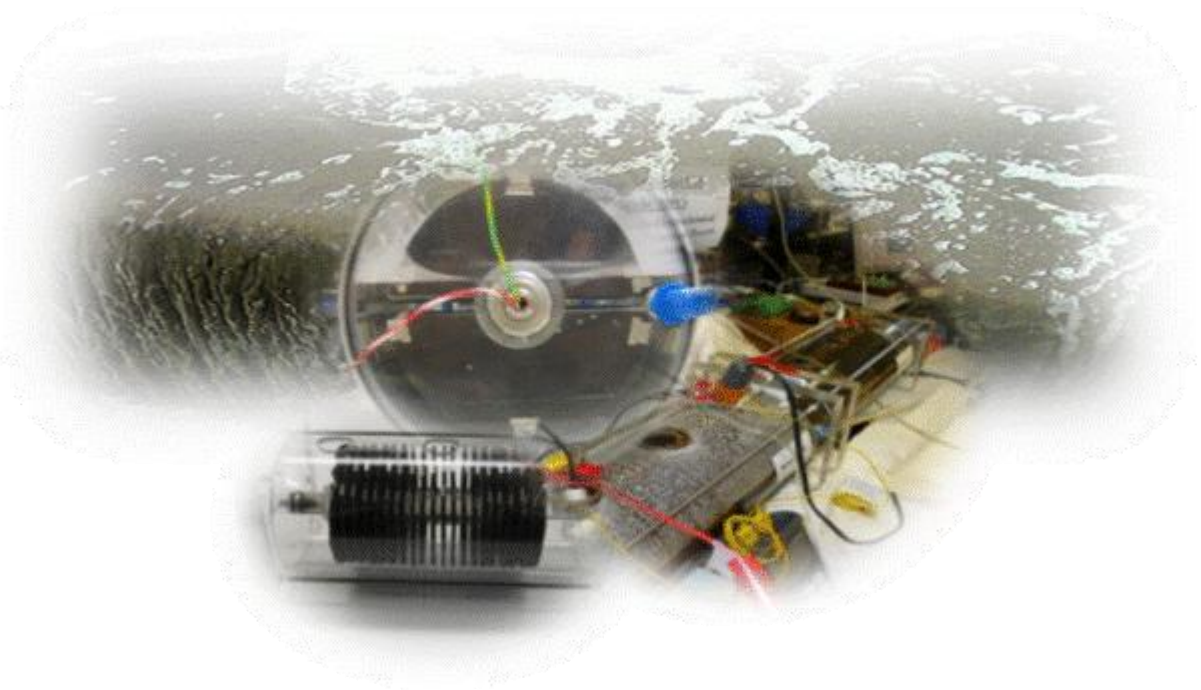
# BIOELECTROCHEMICAL SYSTEMS FOR ENERGY RECOVERY FROM WASTEWATER

KA YU CHENG



# Bioelectrochemical Systems for Energy Recovery from Wastewater

Ka Yu Cheng

BSc (Hons); M.Phil.

A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

in

Environmental Engineering

Faculty of Sustainability, Environmental and Life Sciences

Murdoch University

WA, Australia

November 2009

## Abstract

The global concerns of climate change and energy crisis have provoked research efforts to develop energy-efficient alternatives to conventional activated sludge wastewater treatment processes. Recently, bio-electrochemical systems (BES) such as microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) have emerged as a promising technology for simultaneous energy recovery and wastewater treatment. These systems harness the capacity of microorganisms for the catalysis of electrochemical reaction. In MFCs, chemical energy in the form of organic compounds in wastewater is directly converted into electricity. While in MECs, external electricity is provided to enable more valuable products (e.g. hydrogen) to form at the cathode.

Over the past decade, our knowledge on BES is gaining momentum. However, wastewater treatment using BES has not been successful on an industrial-scale. Many technological bottlenecks still remain unresolved and our understanding of microbe-electrode interactions in BES is incomplete. The overall aim of this thesis is to generate understanding that will be helpful in the development of an energy recovering wastewater treatment process using BESs. The scope of this thesis comprises two themes. The first theme is to study the fundamental aspect of BESs with an emphasis on microbe-anode interactions, the reaction that makes it possible to use organic waste substances as the electron donor for BES. The second theme is to quantify rate limiting steps and to develop practical solutions to overcome the established bottlenecks making room for the development of new technologies of BES for wastewater treatment and related purposes.

Most of the experiments were conducted using a sub-liter scale two-chamber BES equipped with a cation exchange membrane. An electrochemically active biofilm was established at the anode (graphite granules) from an activated sludge inoculum. A synthetic wastewater with acetate as the sole electron donor was used throughout the study. The cathodic electron acceptor was either potassium ferricyanide ($K_3Fe(CN)_6$) or dissolved oxygen. No chemical catalyst (e.g. platinum) was applied to the electrodes. In some experiments, the BES was coupled with a potentiostat to precisely control the biofilm-electrode potential or to perform voltammetric analysis.

The results showed that activated sludge bacteria could readily initiate a highly effective anodophilic biofilm (415 $W \cdot m^{-3}$ after five days with a $Fe(CN)_6^{3+}$ cathode), provided that factors such as electrolyte pH, external resistance and cathodic oxidizing power were not limiting. From the Coulombic efficiency of over 80% the microbial activity could be recorded by online monitoring of the current. This allowed a detailed study of the affinity for the anode of biofilm. In analogy to the well known Michaelis-Menten kinetics, a half-saturation anodic potential ($k_{AP}$) was established at which the microbial metabolic rate reached half its maximum rate. This $k_{AP}$ value was about -455 mV (vs. Ag/AgCl) for our acetate-driven biofilm. A critical anodic potential ($AP_{crit.}$) of about -420 mV (vs. Ag/AgCl) was defined that characterizes both the bacterial saturation by the electron-accepting system and the maximal MFC power output. This information is useful for MFC modeling and optimization.

Although online process control is used for many bioprocesses it is not established for MFC. A new approach was developed that enabled voltammetric studies of the biofilm-anode,

without using potentiostats but by feedback controlling a variable external resistance of the running MFC. This approach could perform the conventional cyclic voltammetry of a MFC without interrupting its operation.

In MFC the anodic reaction is proton liberating while the cathodic reaction is proton consuming. This leads to perhaps the major limitation in MFC operation known as a pH gradient. This limitation was addressed by using a novel operational regime: the intermittent polarity inversion. At electrode potential of -300 mV (vs. Ag/AgCl) the alternating supply of acetate and oxygen to the biofilm resulted in the generation of an anodic and cathodic current of +240 and -80 mA (+1500 and -500 $A \cdot m^{-3}$), respectively. Since the anodic reaction is proton-liberating while the cathodic reaction is proton-consuming, such operational regime prevented the detrimental build-up of a pH gradient enabling a prolonged operation of the MFC without using costly pH control methods (dosing of acid/base or chemical buffers).

The intermittent polarity inversion showed signs of the "anodophilic bacteria" being able to catalyze not only the anodic oxidation of acetate but also the cathodic oxygen reduction. The presence of "anodophilic bacteria" at the cathode could enable a 5-fold increase of power output (from 5.6 to 27 $W \cdot m^{-3}$). This is the first evidence that a BES biofilm can catalyze both the forward and backward electron flow with a single electrode. Based on this finding, a novel scalable, membrane-less BES configuration, termed rotatable bio-electrochemical contactor (RBEC) has been developed.

Similar to rotating biological contactors (RBC), the RBEC consists of a cylindrical water-holding vessel (ca. 3 L) which houses an array of carbon cloth coated discs (electrodes) mounted onto a central horizontal rotatable shaft. Each disc consists of a water-immersed anodic and an air-exposed cathodic half connected via a resistor. No ion-exchange membrane and wastewater recirculation were required as the air-water interface separated anode from cathode. A polarity inversion aiming at overcoming the pH gradient and enable the biofilm to catalyze both the anodic and cathodic reaction could be obtained by merely turning the disc array a half turn.

An electron flow from the submersed half disc to the air exposed half disc established with the moisture film on the air exposed cathode allowing the ionic charge transfer. As with other MFC any measured current could be documented to be linked to COD oxidation. The COD removal caused by the action of the intermittently turning discs was increased by about 30% by merely allowing an electron flow between the anodic and cathodic disc halves. This result suggests that the treatment performance of traditional RBC may be significantly increased by using suitable conductive material as the discs.

By raising the cathodic potential from about -500 to -1200 mV (vs. Ag/AgCl) using a potentiostat the cathodic limitation could be alleviated allowing an increase in electron flow and COD removal rate to 1.32 kg COD $m^{-3}$ $day^{-1}$ (hydraulic retention time 5h). While the COD removal rate was comparable to that of an activated sludge system, the potentiostatically supported RBEC removed COD more energy-efficiently than activated sludge systems (0.47 vs. 0.7-2.0 kWh $kgCOD^{-1}$), even though it was not optimized. The RBEC could also enable electrochemically-driven hydrogen gas or methane gas production when operated as a MEC under fully anaerobic condition.

Overall, this thesis has extended our understanding on how electrochemically active microorganisms behave in BES. Especially, the discovery of the bidirectional microbial electron transfer property may shed light not only on BES development, but also on the context of fundamental microbiology. The new RBEC configuration may widen the functionality or suitability of BES for a large-scale wastewater treatment application. Nevertheless, further process optimization is needed. In particular, the cathodic reaction still remains as the key process bottleneck. Future efforts should thus be oriented towards improving and elucidating in details the mechanisms of the microbe-cathode electron transfers.

## Declaration

I hereby declare that this submission is my own work and that, to the best of my knowledge, it contains no material previously published or written by another person nor material which to a substantial extent has been accepted for the award of any other degree or diploma of the university or other institute of higher learning, except where due acknowledgment has been made in the text.

Ka Yu Cheng

---

(Signature)

## Items derived from this thesis:

1. Patent

   "Wastewater Treatment Process". Australian Provisional Patent (filed in July 2009). Application number 2009903544. (Chapter 7 and 8)

2. Publications

   K. Y. Cheng, R. Cord-Ruwisch and G. Ho. (2007) Limitations of bio-hydrogen production by anaerobic fermentation process: an overview. *American Institute of Physics Conf. Proc.* Vol. 941, 264-269. (Cited in Chapter 1)

   K. Y. Cheng, G. Ho and R. Cord-Ruwisch (2008) Affinity of microbial fuel cell biofilm for the anodic potential. *Environmental Science and Technology.* Vol. 42(10), 3828-3834. (Chapter 3)

   K. Y. Cheng, R. Cord-Ruwisch and G. Ho. (2009) A new approach for in situ cyclic voltammetry of a microbial fuel cell biofilm without using a potentiostat. *Bioelectrochemistry.* Vol. 74, 227-231 (Chapter 4)

   K. Y. Cheng, G. Ho and R. Cord-Ruwisch. (2010) Anodophilic biofilm catalyzes cathodic oxygen reduction. *Environmental Science and Technology.* Vol. 44(1), 518-525. (Chapter 6)

   K. Y. Cheng, G. Ho and R. Cord-Ruwisch. Rotatable bio-electrochemical contactor (RBEC)-A novel wastewater treatment hybrid technology of rotating biological contactor and bioelectrochemical system. To be Submitted. (Chapter 7)

   K. Y. Cheng, G. Ho and R. Cord-Ruwisch. A rotatable bio-electrochemical contactor (RBEC) enables electrochemically driven methanogenesis. To be Submitted. (Chapter 8)

3. Award

   HUBER Technology Prize 2008 (first prize). In IFAT 2008 - 15th International Trade Fair for Water - Sewage - Refuse - Recycling, Munich, Germany. (Part of Chapter 2)

# Acknowledgments

I wish to express my gratitude to a number of individuals. Without their support and help over the past three years, my PhD journey would not be as meaningful and unforgettable as it is.

First of all, my thanks should go to my PhD supervisors who have given me the greatest freedom ever in steering the research direction throughout the thesis. I would like to express my deepest gratitude to each of them:

- Prof. Goen Ho — who has constantly offered me opportunities, supports, guidance, advices and encouragement… Thanks Goen!
- Dr. Ralf Cord-Ruwisch — who has changed my view of dealing with sciences and has offered me his unlimited inspirations on both sciences and philosophies…,. "*Suck & See!*" I am also thankful for the opportunities to participate with his various research and teaching activities, also for his encouragement, coffee and fun times … Thanks Ralf!

Now, I would like to express my immense gratitude to:

- The examiners of this thesis for their valuable expert comments:
  - Prof. Lars Angenent, Department of Biological and Environmental Engineering, Cornell University, USA;
  - Prof. Sang-Eun Oh, Department of Biological Environment, Kangwon National University, South Korea; and
  - Prof. Uwe Schroder, Sustainable Chemistry & Energy Research, Institute of Ecological Chemistry, Technical University-Braunschweig, Germany;
- Murdoch University for offering me the full scholarship and living allowance. Thanks Goen and Ralf again for topping up my scholarship. Without these financial supports I would not be able to thrive through my research journey in such a beautiful and peaceful country.
- Commericialization office of Murdoch Univeristy for funding (Discovers Grant) the works in Chapter 7 and 8 of this thesis. Thanks Dr. Patty Washer and Ms. Sam Dymond of this office for their expert supports on the patent application in the later phase of the thesis.
- My office and laboratory colleagues for their encouragement and precious friendship — Isabella, Davina, Nora, Lee Walker, Wipa, Donny, Mitch, Suwat, Ying, Raj, Liang and Chia …Thanks Mates!
- All technical staff from the university mechanical workshop. Special thank is given to Mr. Fritz Wagen for his brilliant contribution to the design and manufacture of the RBEC reactors. Also, thanks Fritz for showing me your amazing homemade little Jet-engine in your own backyard workshop!

- Mr. John Snowball from the electronic workshop for his excellent assistance on the manufacture of various electronic devices throughout the project. His valuable technical advice is also highly appreciated.

- Dr. Lucy Skillman for her technical assistance with the biofilm analysis and Mr. Gordon for his technical assistance on using the scanning electron microscope.

- Dr. Korneel Rabaey from the Advanced Water Management Centre, The University of Queensland for his kind assistance in manufacturing the high quality bioelectrochemical reactor (and the accessories such as the graphite granules and the cation exchange membrane) used in this thesis and also for his valuable advice on the topic.

- Staff in the School of Environmental Science and the School of Biotechnology and Biological Sciences for creating such a friendly, dynamic and harmonic environment to work in and also for allowing me to use various facilities and equipments.

- Prof. Jonathan Wong (Hong Kong Baptist University), my honors and masters supervisor who has constantly given me encouragement and advice since the first day of my research journey.

Last but not the least; my deepest appreciation are given to my wonderful family: my parents, my brothers (Karson and Kelvin), my wife Suki and her family. – Thanks for your understanding, encouragement in every part, continuous support & love…

Finally I wish to share the joy of completing this work with all of the aforementioned individuals, without their 'source of sustainable energy', completing the thesis alone would be highly "unfeasible"!

Thank You!

Ka Yu

*Bateman - Perth*

*Winter 2009*

# Table of Contents