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**Characterizing the Removal of Antibiotics
in Algal Wastewater Treatment Ponds:
A Case Study on Tetracycline in HRAPs**

A thesis presented in partial fulfilment of the requirements for the degree of

Doctor of Philosophy

in

Environmental Engineering

at

Massey University,

Turitea Campus, Palmerston North, New Zealand

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2016

Abstract

Antibiotics are ubiquitous pollutants in wastewater, owing to their usefulness in both animal and human treatment. Antibiotic pollution is a growing concern because of the risk of encouraging antibiotic resistance in wastewater treatment (WWT) systems and downstream of effluent discharge. The aim of this thesis was to investigate the fate of antibiotics in algal WWT ponds, which have unique ecological and environmental characteristics (e.g. presence of algae; diurnal variation in pH, dissolved oxygen, and temperature) compared with conventional biological WWT.

The research in this thesis focused on a case study of the fate of tetracycline (TET, an antibiotic) in high rate algal ponds (HRAP). Indoor lab scale HRAP studies were used to investigate the fate of TET under several operating conditions. Outdoor pilot scale studies (900 L and 180 L HRAPs) under Oceanic and Mediterranean climates were used to validate the lab scale findings. Results showed that high removal (85% to >98%) of TET was possible in the lab and pilot scale HRAPs with HRTs of 4 and 7 days.

Sorption was consistently a low contributor (3-10% removal by sorption) during continuous HRAP studies, based on the amount of TET extracted from biomass. Batch experimentation was used to further distinguish mechanisms of TET removal. The majority of TET removal was caused by photodegradation. Indirect photodegradation of TET was dominant over direct photolysis, with 3-7 times higher photodegradation observed in wastewater effluent than for photodegradation in purified water during batch tests incubated in sunlight. Under dark conditions sorption was the dominant removal mechanism, and biodegradation was negligible in batch tests since aqueous TET removed was recovered ($\pm 10\%$) by extraction of sorbed TET from the biomass.

Irreversible abiotic hydrolysis was not observed during TET removal batch tests in purified (MQ) water.

A kinetic model was developed and used to predict TET removal in the pilot HRAPs, based on parameters derived from batch experiments. The model predictions for aqueous TET concentrations were successfully validated against initial TET pulse tests in the 180 L pilot scale HRAP. However TET removal decreased in subsequent pulse tests in the pilot HRAP, resulting in over-prediction of TET removal by the kinetic model. This decrease in TET removal was associated with decrease in pH, dissolved oxygen concentrations, and biomass settleability, but causal relationships between TET removal and these variables could not be quantified. Until the predictive kinetic model is developed further, this model may serve as a preliminary estimate of TET fate in algal WWT ponds of different design and operation. Future research should also investigate the potential formation and toxicity (including antibiotic efficiency) of TET degradation products, but this was outside the scope of this thesis. Predictions from the model were sensitive to the daily light intensity, suggesting that TET removal would be reduced in the winter months.

Acknowledgements

This doctorate was supported by a Massey University Doctoral Scholarship. I thank Massey University for this provision of funding, and the scholarship administrators for their help.

It was a privilege to work under my supervisors, Prof. Benoit Guieysse (Massey), Prof. Andy Shilton (Massey), and Assoc. Prof. Raúl Muñoz (Valladolid). Their instruction, patience, and engagement with my project were instrumental to my work and their time invested in helping me develop as a researcher is greatly appreciated.

Working at both Massey University and University of Valladolid, there are many other postgraduate students with whom I worked. The friendly work environment in both cities was great to work in. Special thanks go to Cynthia Alcantara, who introduced me to working with HRAPs, Quentin Bechet, who helped with much advice and taught me actinometry techniques early in the PhD, Andrea Hom-Diaz, who worked alongside me for 6 months in NZ in a similar project on antibiotics in HRAPs, Dr. Alma Toledo in Valladolid who taught me the lab systems and helped supervise my projects in Spain, Paul Chambonniere who collected an extra month of tetracycline monitoring data in NZ while I was in Spain, Dimas Garcia who helped by maintaining my HRAP in Spain while I was attending conferences, and Lara Pelaz and Jaime Cortijo, who helped supply my experiments in Spain with primary settled wastewater with their pilot scale primary treatment. Special thanks also go to the postgrad environmental engineering research team: Roland Schaap, Maxence Plouviez, Matt Sells, Aidan Crimp, Ramsay Huang, and Paul Chambonniere; it was a pleasure working in a research team with you, comparing methods and discussing problems, as well as the social relaxation to take a break from studying.

I extend my gratitude to all the wastewater treatment staff at the Palmerston North City Council Totara Rd plant, especially Mike Monaghan, Peter Best, Mike Sahayam, and Elysia Butler for permission to install a pilot HRAP for research, their assistance in facilitating its installation and assisting all the students who worked on the site where they could. I also thank Prof. Fernando Polanco who allowed me to install my pilot HRAP on the roof of his research sheds at University of Valladolid.

I thank the many technical staff also helped me at different stages of my PhD, especially Ann-Marie Jackson, John Edwards, John Sykes, Clive Barber, Anthony Wade, Monica Gay Martin, Araceli Crespo, Julia Good, and Morio Fukuoka. I also thank the administrative staff, especially Glenda Rosomann, Gayle Leader, Dilantha Punchihewa, Trish O'Grady, Michelle Wagner, and Linda Lowe. I acknowledge and appreciate the cleaning staff, who often worked invisibly keeping areas in good order.

I thank my family – my parents John and Robin Norvill and my sisters Elsa and Hannah, for their moral support and encouragement. I also thank my many friends at church, especially Mr. & Mrs. Peez, for their love, care, and spiritual support during my time of doctoral study.

Finally, I acknowledge my Lord and Saviour, Jesus Christ, Who indwells me, for His guidance, protection, and the insight He has granted me into this aspect of His created order. Much of my motivation for this doctoral project comes from a desire to understand His world, being a wise steward of the environment He created, and in order to help people through understanding and minimising hazards from emerging pollutants in wastewater.

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Table of Acronyms

Acronym	Full Name
BOD	Biological Oxygen Demand
CMP	Chloramphenicol (antibiotic)
COD	Chemical Oxygen Demand
CPX	Ciprofloxacin (antibiotic)
HPLC	High Performance Liquid Chromatography
HRAP	High Rate Algal Pond
HRT	Hydraulic Retention Time
IC	Inorganic Carbon
MQ (water)	Milli-Q grade purified water
PAR	Photosynthetically Active Radiation (400-700 nm)
PNCC- WWTP	Palmerston North City Council Totara Rd Wastewater Treatment Plant
RO (water)	Reverse Osmosis grade purified water
SCC mix	Mixture of antibiotics: Sulfanilamide, Ciprofloxacin, and Chloramphenicol
SFL	Sulfanilamide (antibiotic)
SMX	Sulfamethoxazole (antibiotic)
SPE	Solid Phase Extraction
SRT	Solids Retention Time (a.k.a. Sludge Retention Time)
STS mix	Mixture of antibiotics: Sulfanilamide, Tetracycline, and Sulfamethoxazole
TET	Tetracycline (antibiotic)
TN	Total Nitrogen

TOC	Total Organic Carbon
TSS	Total Suspended Solids
UV	Ultraviolet
UVA	Ultraviolet light (320-400 nm)
UVB	Ultraviolet light (290-320 nm)
VSS	Volatile Suspended Solids
WSP	Waste Stabilisation Pond
WW	Wastewater
WWT	Wastewater treatment