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

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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.

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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