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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

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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 (± 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

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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.

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<th>Full Name</th>
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<tr>
<td><strong>BOD</strong></td>
<td>Biological Oxygen Demand</td>
</tr>
<tr>
<td><strong>CMP</strong></td>
<td>Chloramphenicol (antibiotic)</td>
</tr>
<tr>
<td><strong>COD</strong></td>
<td>Chemical Oxygen Demand</td>
</tr>
<tr>
<td><strong>CPX</strong></td>
<td>Ciprofloxacin (antibiotic)</td>
</tr>
<tr>
<td><strong>HPLC</strong></td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td><strong>HRAP</strong></td>
<td>High Rate Algal Pond</td>
</tr>
<tr>
<td><strong>HRT</strong></td>
<td>Hydraulic Retention Time</td>
</tr>
<tr>
<td><strong>IC</strong></td>
<td>Inorganic Carbon</td>
</tr>
<tr>
<td><strong>MQ (water)</strong></td>
<td>Milli-Q grade purified water</td>
</tr>
<tr>
<td><strong>PAR</strong></td>
<td>Photosynthetically Active Radiation (400-700 nm)</td>
</tr>
<tr>
<td><strong>PNCC-WWTP</strong></td>
<td>Palmerston North City Council Totara Rd Wastewater Treatment Plant</td>
</tr>
<tr>
<td><strong>RO (water)</strong></td>
<td>Reverse Osmosis grade purified water</td>
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<tr>
<td><strong>SCC mix</strong></td>
<td>Mixture of antibiotics: Sulfanilamide, Ciprofloxacin, and Chloramphenicol</td>
</tr>
<tr>
<td><strong>SFL</strong></td>
<td>Sulfanilamide (antibiotic)</td>
</tr>
<tr>
<td><strong>SMX</strong></td>
<td>Sulfamethoxazole (antibiotic)</td>
</tr>
<tr>
<td><strong>SPE</strong></td>
<td>Solid Phase Extraction</td>
</tr>
<tr>
<td><strong>SRT</strong></td>
<td>Solids Retention Time (a.k.a. Sludge Retention Time)</td>
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<tr>
<td><strong>STS mix</strong></td>
<td>Mixture of antibiotics: Sulfanilamide, Tetracycline, and Sulfamethoxazole</td>
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<tr>
<td><strong>TET</strong></td>
<td>Tetracycline (antibiotic)</td>
</tr>
<tr>
<td><strong>TN</strong></td>
<td>Total Nitrogen</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
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<tr>
<td>--------------</td>
<td>------------</td>
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<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
</tr>
<tr>
<td>TSS</td>
<td>Total Suspended Solids</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>UVA</td>
<td>Ultraviolet light (320-400 nm)</td>
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<td>UVB</td>
<td>Ultraviolet light (290-320 nm)</td>
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<tr>
<td>VSS</td>
<td>Volatile Suspended Solids</td>
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<td>WSP</td>
<td>Waste Stabilisation Pond</td>
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<td>WW</td>
<td>Wastewater</td>
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<td>WWT</td>
<td>Wastewater treatment</td>
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