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Novel Methods for the Removal of Colour from Pulp and Paper Mill Wastewater

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*A thesis submitted in partial fulfilment of the requirements for the
degree of Doctor of Philosophy in Chemistry,
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Abstract

Wastewater produced during pulp and paper manufacture is often highly coloured. Along with a decrease in the aesthetic appeal of the receiving water, the coloured material also reduces the penetration of the sunlight through the water which may decrease photosynthetic rates and affect aquatic productivity. As a result, there is strong pressure from environmental regulators for mills to reduce the colour of these wastewaters. Currently there is no sustainable colour removal technology available to remove this colour, predominantly due to economical restraints.

The current study was undertaken with the aim of assessing novel and environmentally and economically sustainable technologies for the treatment of colour in pulp and paper mill wastewaters.

A New Zealand softwood integrated bleached kraft mill was used for the technology assessment case studies. A synoptic survey of the mill was performed to locate the major sources of wastewater constituents and to select the most appropriate waste streams for application of these technologies. It was found that bleach plant wastewater was a significant source of colour (34 % total mill load), dissolved organic carbon (DOC, 32 %), and soluble chemical oxygen demand (sCOD, 25 %), and was the predominant source of absorbable organic halides (AOX, ~100 %). Given these relative contributions, the concentrated flows arising from this source, and the relative ease of retro-fitting a treatment process at full-scale, this wastewater was selected for remediation. The bleach plant wastewater is discharged in two waste streams, the acidic stream (pH 2) and the alkaline stream (pH 11).

Two systems were investigated as colour removal tools; one chemical, the other biological. Both systems was chosen as suitable for the remediation of bleach plant wastewater (i.e. functioned in the required pH and temperature range), and because they were novel systems which had not been previously considered for removal of colour from wastewater.

The first technology was an advanced oxidative process (AOP) which utilised macrocyclic tetraamide iron(III) complexes. These specially-designed complexes catalytically activate hydrogen peroxide and were developed by Collins *et al.*, at Carnegie Mellon University. The activated complexes had previously been shown to be able to delignify and remove residual colour from kraft pulp. Preliminary trials indicated that these complexes would also have the potential to remove colour from pulp mill wastewaters.

The second technology was an enzymatic treatment that utilised the enzyme cellobiose dehydrogenase (CDH). Although the broader purpose of these enzymes in biological

systems has not been firmly established, previous studies have demonstrated that CDH reactions could reduce quinones. Quinones are highly coloured, lignin-related species produced during the bleaching of pulp that have been hypothesised to contribute a significant proportion of the colour found in bleached kraft mill wastewaters. It was therefore postulated that this enzyme could form the basis of a biological colour treatment for bleached kraft mill wastewaters, with particular focus on colour removal.

Studies were undertaken to assess the effects of substrate concentrations, pH, temperature and time. As the AOP technology functioned best under alkaline conditions, it was selected to remediate the alkaline bleach plant waste stream. Optimal conditions were determined at pH 11, 9 and 7. At pH 11 the optimal conditions were found to be an activator concentration of 2 μM (0.9 mg L^{-1}), a hydrogen peroxide concentration of 26 mM (0.75 g L^{-1}), 40 $^{\circ}\text{C}$ and 4 hours. As the pH decreased to 9, and then 7, more activator and peroxide was required to remove similar levels of colour from the alkaline waste stream. Under optimal conditions, the AOP was able to remove 47 % of the colour from alkaline stage bleaching wastewaters. Additionally, using these conditions the AOP could remove 25 % of the chlorinated organic material (as AOX), however it had no effect on the sCOD of the wastewater.

For the enzymatic treatment two strains of enzyme were assessed. One strain, purified from the soft-rot fungus *Humicola insolens*, preferred alkaline conditions and was used to treat the alkaline stage bleaching wastewater, and the other strain, purified from the white-rot fungus *Phanerochaete chrysosporium*, preferred acid pH and was used to remediate the acid stage wastewater. Conditions required for the enzyme strain that preferred alkaline conditions were 0.01 IU of CDH, 7 mM (2.4 g L^{-1}) of cellobiose, 40 $^{\circ}\text{C}$ and 4 days at pH 7. The enzyme was able to remove 41 % of the colour from the waste stream, however the enzyme treatment had no effect on the chlorinated organic content or the sCOD of the wastewater. Due to a limitation in acidophilic enzyme, optimal conditions were not fully characterised. However, it was found that using 0.1 IU of CDH, 40 $^{\circ}\text{C}$ and 4 days at pH 4.5 resulted in a colour removal from the acid stage bleaching wastewater similar to that achieved for the enzyme strain that preferred alkaline conditions when treating the alkaline stage bleaching wastewater.

An investigation of the structural changes in the wastewater organic material during treatment indicated that the AOP predominantly removed phenolic structures from the wastewater, in addition to structures containing aliphatic double bonds and carbonyl groups. In contrast, CDH solely reduced quinone structures. These findings were supported by studies using model compounds. With AOP treatment there were reaction rate differences for a range of phenolic model compounds with the most reactive compounds being vanillomandelic acid and catechol.

Both technologies were able to remediate wastewater from other sources around the mill, such as the combined whole mill wastewater and the post-secondary treatment system wastewater. Removal efficiencies under optimal conditions were in the range 55 to 65 %. In addition to the removal of colour from wastewater produced during pine processing, both technologies could also remediate wastewater produced during the processing of eucalypt, a hardwood. In this case treatment efficiencies were somewhat lower (33 and 27 % for the AOP and enzyme technologies, respectively) possibly due to the difference in the nature of the chromophores in the hardwood wastewater.

An environmental risk assessment of both technologies was undertaken. The results from this assessment indicated that the AOP treatment did not improve overall biological treatability of the wastewater. The enzyme treatment improved treatability of the wastewater by 92 %, when measured as oxygen uptake of a microbial population. An investigation of the molecular weight distribution found the molecular weight distribution of the wastewater was not altered during treatment with the AOP, however it was altered during enzyme treatment with a preferential decrease in material > 30 000 Dalton. When wastewater which had been pre-treated with the AOP was subjected to biological treatment, the wastewater showed a small colour increase of approximately 15 %, whereas 96 % of the colour removed during enzyme treatment reverted under model aerated lagoon conditions. This finding was consistent with other studies which showed that structures reduced by the enzyme (i.e. quinones) could be oxidised back into their original form. In comparison, the colour removed by the AOP did not revert, suggesting that chromophores altered by the AOP were unable to reform. Microtox™ studies showed that neither the AOP activator, nor the enzyme were toxic to the receiving environment.

An economic study was carried out which found that although the activator is not yet commercially available, the AOP technology could be economically feasible as long as the price of the activator was reasonable. Inventors of the activator estimate that its actual cost would be between USD 100 and 500 per kilogram. Using a worst case scenario of USD 500 per kilogram, it was estimated that if the activator was installed for the remediation of the alkaline bleach plant wastewater at the case study mill it would cost 1 % of the value of the bleached pulp production, and result in a 12 % colour reduction of final wastewater. The economic study found that the enzyme treatment was not feasible (cost relative to value of production was 8 %) due to the high substrate concentrations required.

Overall, the study found that the AOP was a promising colour removal technology for the remediation of the alkaline bleach plant waste stream. Pilot plant trials for wastewater remediation using the AOP technology are expected to commence in the near future.

Acknowledgements

I wish to acknowledge the many individuals who have contributed to this thesis.

My special thanks to my supervisors Dr Trevor Stuthridge (*Forest Research*), Assistant Professor Shawn Mansfield (University of British Columbia, Vancouver) and Associate Professor James Wright (University of Auckland).

Thanks also to Dr Colin Horwitz and Professor Terry Collins, both of Carnegie Mellon University, Pittsburgh, and to Dr Ian Suckling of *Forest Research*.

Funding for this project provided by *Forest Research* and Carter Holt Harvey Tasman is gratefully acknowledged.

The opportunity of working at Carnegie Mellon University, Pittsburgh, and at University of British Columbia, Vancouver was made possible through financial assistance provided by the International Science and Technology (ISAT) Linkages Fund. My attendance at the 8th International Conference on Biotechnology in the Pulp and Paper Industry, Helsinki, Finland was funded by The University of Auckland Graduate Research Fund, the Department of Chemistry, University of Auckland, and *Forest Research*. Sincere thanks to all funding bodies.

My final thanks go to those at *Forest Research*, The University of Auckland, Carnegie Mellon University, The University of British Columbia, Tasman Pulp and Paper Mill, and to friends and family.

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Abbreviations

Units of Measure

M-	mega (10^6)	K_m	Michaelis constant
k-	kilo (10^3)	k_{obs}	rate constant
m-	milli (10^{-3})	L	litres
μ -	micro (10^{-6})	m	metres
n-	nano (10^{-9})	M	molar (mol L^{-1})
%	percentage	m^3	cubic metre
$^{\circ}\text{C}$	degrees Celsius	min(s)	minute(s)
A	absorbance	mol	moles
AU	absorbance units	N	normal solution
amu	atomic mass unit	Pa	Pascal
d	day(s)	ppm	parts per million
Da	Dalton	rpm	revolutions per minute
g	gram(s)	s	second(s)
h	hour(s)	tonne	metric tonne (1 000 kg)
hz	hertz	w/w	weight to weight ratio
k_{cat}	kinetic constant	y	year

IU international units, the amount of enzyme required to produce $1 \mu\text{g}$ product min^{-1}

Pulp and Paper Terminology

ADT	air dried tonne(s)	DOC	dissolved organic carbon
AOP	advanced oxidative process	DTC	dissolved total carbon
AOX	absorbable organic halide	ECF	elemental chlorine free
ASB	aerated stabilisation basin	HRT	hydraulic retention time
BOD	biochemical oxygen demand	IC	inorganic carbon
COD	chemical oxygen demand	MBBR	moving bed biofilm reactor
CPU	chloroplatinate units	MyCoR	mycelial colour removal
CTMP	chemithermomechanical pulp	RBC	rotatory biological contactor
DAF	dissolved air flotation	TC	total carbon
DIC	dissolved inorganic carbon	TMP	thermomechanical pulp
DO	dissolved oxygen	TSS	total suspended solids

NCASI	National Council of the Paper Industry for Air and Stream Improvement
sCOD	soluble chemical oxygen demand

Designation of Bleaching Stages

D	chlorine dioxide
E	alkaline extraction
E _{op}	alkaline extraction in the presence of oxygen and hydrogen peroxide
P _{Fe}	hydrogen peroxide in the presence of iron activator

Techniques and Instruments

ES-MS	electrospray mass spectrometry
GC	gas chromatography
GC-MS	gas chromatography/mass spectrometry
HPLC	high performance liquid chromatography
IR	infra-red spectroscopy
NMR	nuclear magnetic resonance spectroscopy
UV-vis	ultraviolet-visible spectroscopy

Reagents and Materials

APS	aminopropyl silica
AR	analytical grade reagent
BSTFA	N,O,-bis(trimethylsilyl)trifluoroacetamide
CBO	cellobiose oxidase
CBQ	cellobiose:quinone oxidoreductase
CDH	cellobiose dehydrogenase
d _n	deuterated solvent
DCPIP	2,6-dichlorophenol-indophenol
DTMPA	diethylenetriaminepentamethylenephosphonic acid
GF/C	glass-fibre filter disk, grade C
HDPE	high density polyethylene
MtBE	methyl <i>tert</i> -butyl ether
PTFE	polytetrafluoroethylene
THF	tetrahydrofuran
THP	tris(hydroxymethyl)phosphine
THPC	tetrakis(hydroxymethyl)phosphonium chloride
THPO	oxidised THP

VMA vanillic acid

Miscellaneous

°	degree	HMW	high molecular weight
95 % CI	95 % confidence interval	i.e.	that is
α	alpha	LMW	low molecular weight
β	beta	ln	natural log
br	broad	m	multiplet
ca.	circa	max	maximum
dd	doublet of doublets	min	minimum
Δ	change in	MWCO	molecular weight cut-off
$\Delta\epsilon$	ionisation difference	<i>o</i> -	ortho
EC	enzyme commission number	s	singlet
Ed(s)	editor(s)	<i>t</i>	tertiary
equiv.	equivalents	USD	United States dollars
<i>et al.</i>	et alii (and other persons)	UV	ultraviolet light
FAD	flavin adenine dinucleotide	wrt	with respect to
CV	coefficient of variation, calculated by dividing replicate standard deviation by the mean		
δ	delta (or chemical shift wrt NMR)		
ϵ	molecular extinction co-efficient		
EC ₅₀	effective concentration, 50 % response		
λ_{\max}	wavelength of maximum absorbance		
PAD	pulsed amperometric detector		