

**TREATMENT OF ORGANIC
CONTAMINANTS FROM WATER USING AN
INTEGRATED SORPTION-OXIDATION
SYSTEM**

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**Submitted in fulfilment for the degree of
Doctor of Philosophy**

**Faculty of Engineering
University of Technology, Sydney (UTS)**

Australia

2012

Certificate

I certify that the work in this thesis has not previously been submitted for a degree, nor has it been submitted as part of requirements for a degree. I also certify that this thesis is my own work and it does not contain any material previously published or written by another person except where due acknowledgement is made in the text.

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Abstract

In-situ treatment of chlorophenols using a permeable reactive barrier is still an emerging research area. A novel integrated sorption-oxidation barrier is proposed and systematically investigated in a neutral pH, very poorly buffered water. Intermittent injections of permanganate oxidise dissolved and sorbed chlorophenol as well as the woody sorbent with manganese dioxide formed as a by-product.

Common woody biomass (pine/hardwood) were evaluated as a cost effective sorbent. Chlorophenol uptake on these was relatively low ($3\text{--}8\text{ mg g}^{-1}$) with evidence of sorption hysteresis. Increased sorbent particle size and reactions with the oxidant did not significantly affect sorption. Under dynamic conditions non-equilibrium sorption occurred with higher flow rates.

Oxidation within the porous media was complex with multiple oxidation processes occurring simultaneously. An analytical method was developed to allow the quantification of chlorophenol in the presence of a quenching agent. This allowed the collection of kinetic data for the permanganate oxidation reaction. Oxidation of dissolved chlorophenol by manganese dioxide was found to be minimal. Early time data showed that the oxidation rate of pine (0.06 min^{-1}) was less than for chlorophenol sorbed on pine ($0.07\text{--}0.12\text{ min}^{-1}$) which was much less than for dissolved chlorophenols ($0.4\text{--}1.48\text{ min}^{-1}$). This suggests that the reaction between permanganate and pine materials is kinetically controlled and will dominate only after the oxidation reaction with chlorophenol. The rate of sorbed chlorophenol oxidation decreased with increasing contaminant hydrophobicity. In column studies the oxidation of the pine sorbent was

found to be both pH and residence time dependent. Some evidence of sorbent/column plugging and reduced sorbent oxidant demand due to manganese dioxide precipitation was found at pH 6.15 but not at pH 2.

The research has shown that a novel sorbent-oxidation barrier system that can treat chlorophenol contaminated water is technically feasible. Insights into the key mechanisms that would occur in the system have been given. Further work into operationalizing these processes is still needed.

Acknowledgements

I am especially thankful to my principal supervisor, Dr. Robert McLaughlan, for his guidance, continuous encouragement and support throughout of this study. His valuable ideas and comments helped me to develop my knowledge and skills of doing this research. I would like to thank Professor Saravanmuthu Vigneswaran and my co-supervisor Associate Professor Huu Hao Ngo for their valuable and thoughtful suggestions. Thanks are extended to Associate Professor James Edward Ball for his support and Dr. Shon for encouragement.

I would like to thank my colleagues Lazlo. Othman, Javeed, Than, Wen, Yousef, Ibrahim, Thamer, Johir, Chinu, Sherub and Tahir.

I am grateful for financial support from The CRC for Contamination Assessment and Remediation of the Environment (CARE). I wish to thank the academic and technical staff in the University of Technology Sydney (UTS) to their academic support especially Rami Haddad, David Hooper, Rod Hungerford and Phyllis Agius.

Special thanks to my wife Jinnat Ara for her generosity and help. Thanks to my mother Sufia Begum, daughter Lamia Nureen, son Yusuf Mahdi and all family members.

TABLE OF CONTENTS

ABSTRACT	II
ACKNOWLEDGEMENTS	IV
TABLE OF CONTENTS	V
ABBREVIATIONS	XI
PRINCIPAL NOTATION	XII
LIST OF FIGURES	XIII
LIST OF TABLES	XIX
1 INTRODUCTION	2
1.1 Introduction	2
1.2 Research objectives	4
1.3 Scope of research	5
1.4 Thesis outline	6
1.5 Contribution to knowledge	7
2 LITERATURE REVIEW	11
2.1 Introduction	11
2.2 In-situ treatment technology	11
2.2.1. Permeable reactive barriers/zones	12
2.2.2 In situ chemical oxidation in a reaction zone	18
2.2.3 Sorption-oxidation	23
2.3 Organic matter	27
2.3.1 Chlorophenol contamination in surface and groundwater	28
2.4 Sorption	30
2.4.1 Sorbents	31
2.4.2 Quantifying sorption/desorption	35

2.4.3 Modelling equilibrium sorption	37
2.4.4 Model for kinetic sorption	39
2.4.5 Equilibrium vs. non-equilibrium sorption processes	40
2.4.6 Batch vs. column studies	41
2.5 Chemical oxidation	42
2.5.1 Chemical oxidizing reagents	42
2.5.2 Permanganate	43
2.5.2.1 Permanganate oxidation of chlorophenols	48
2.5.2.2 Permanganate oxidation of woody materials	52
2.5.2.3 Manganese oxides formed as an oxidation by-product	53
2.5.3 Peroxide	53
2.5.4 Sodium persulfate	55
2.5.5 Ozone	57
2.5.6 Oxidation kinetic model	58
2.6 Chemical analysis method	65
2.7 Summary	66
3 EXPERIMENTAL WORK AND METHODOLOGY	69
3.1 Introduction	69
3.2 Composition and types of sorbents	69
3.2.1 Sorbent material preparation	71
3.2.2 Sorbent treated with KMnO_4 for column study	73
3.3 Sorbates	73
3.4 Preparation of solutions	74
3.5 Physical measurements	75
3.5.1 Particle size classification and distribution	75
3.5.2 Physical analysis of GAC and FC	75
3.5.3 Physical analysis of woody materials	75
3.5.4 Bulk density	76
3.5.5 Effective porosity	76
3.5.6 pH measurement	76
3.5.7 Electrical conductivity	76
3.5.8 Zeta potential	77
3.6 Chemical analysis	77
3.6.1 Chlorophenol analysis for oxidation tests	77
3.6.2 Chlorophenol analysis for sorption tests	78

3.6.3 Permanganate analysis	79
3.6.4 Chloride analysis	79
3.6.5 Dissolved organic carbon (DOC) analysis	80
3.6.6 Manganese oxide (MnO ₂) analysis	80
3.7 Experimental methods	80
3.7.1 Chlorophenols in different solvent condition	80
3.7.2 Solid phase extraction procedure	81
3.7.3 Quenching reagent	82
3.7.4 Kinetic method for oxidation of chlorophenols by permanganate	83
3.7.4.1 Fixed KMnO ₄ and CP fixed concentration	83
3.7.4.2 KMnO ₄ and CP varied	84
3.7.5 Spectral study of MnO ₂	85
3.7.6 Batch sorption kinetic procedure	85
3.7.7 Batch sorption equilibrium procedure	86
3.7.8 Batch desorption kinetic procedure	87
3.7.9 Batch desorption equilibrium procedure	87
3.7.10 Fitting isotherms	88
3.7.11 Permanganate oxidation of pine and sorbed-CP	88
3.7.12 Preparation of in-situ MnO ₂ and reaction with CP	90
3.7.13 Column test	90
3.7.14 Column Studies: tracer experiment	93
3.7.15 Column Studies: Breakthrough data processing	94
3.7.16 Column Studies: Leaching test	95
3.7.17 Column Studies: Colloid growth measurements	96
4 METHOD DEVELOPMENT TO QUANTIFY CHLOROPHENOLS DURING PERMANGANATE OXIDATION	98
4.1 Introduction	98
4.2 Results and discussion	99
4.2.1 Spectral analysis for CP	99
4.2.2 Analytical recovery	112
4.2.3 Analysis method development	114
4.2.4 Effect of pH on CP absorbance	114
4.2.5 Effect of quenching agents on CP absorbance	116
4.2.6 Selection of the quenching agent	117
4.2.7 Analysis of 4-CP during oxidation	120
4.2.8 Permanganate decomposition and their spectral studies	121
4.2.8.1 Reactions between KMnO ₄ and 4-CP	121
4.2.8.2 Formation of MnO ₂	122
4.2.8.3 Isosbestic point	123
4.2.9 Chlorophenol kinetics	124

4.3 Conclusion	126
5 KINETIC INVESTIGATIONS OF OXIDATION OF CHLOROPHENOLS BY PERMANGANATE	129
5.1 Introduction	129
5.2 Reaction order	130
5.3 Reactivity of chlorophenols	143
5.4 Effect of water quality	146
5.4.1 Effect of ionic strength	146
5.4.2 Effect of pH	147
5.5 Conclusion	149
6 BATCH CHLOROPHENOL SORPTION-DESORPTION STUDIES	151
6.1 Introduction	151
6.2 Results and discussion	151
6.2.1 Sorption kinetics	151
6.2.2 Analysis of uptake mechanism	157
6.2.3 Equilibrium sorption	160
6.2.3.1 Equilibrium sorption isotherm	160
6.2.3.2 Equilibrium sorption isotherm model	162
6.2.4 Sorption capacity of different sorbents	167
6.2.5 Effect of molecular size and pore structure	169
6.2.6 Effect of benzene ring reactivity	169
6.2.7 Effect of hydrophobicity on sorption	170
6.2.8 Effect of particle size on sorption	171
6.2.9 Desorption	178
6.2.9.1 Desorption kinetics	179
6.2.9.2 Desorption equilibrium	180
6.3 Conclusion	186
7 COLUMN SORPTION STUDY: 2,4-DICHLOROPHENOL	189
7.1 Introduction	189
7.2 Column studies	189
7.3 Effect of flow rate	192

7.4 Effect of particle size	194
7.5 Effect of KMnO ₄ -treatment of pine	195
7.6 Comparison of batch and column sorption capacity	197
7.7 Modelling column 2,4-DCP sorption	199
7.7.1 Thomas model	199
7.7.2 Yoon-Nelson model	201
7.7.3 Yan model	202
7.8 Conclusion	206
8 OXIDATION OF SORBED CHLOROPHENOLS: BATCH AND COLUMN STUDY	209
8.1 Introduction	209
8.2 Stoichiometry	210
8.3 Batch studies	210
8.3.1 Sorption of dissolved CP to pine	210
8.3.2 Oxidation of dissolved CP by dissolved KMnO ₄	211
8.3.3 Oxidation of pine and pine with sorbed CP by dissolved KMnO ₄	211
8.3.4 Desorption of CP from pine	216
8.3.5 Oxidation of CP by in-situ MnO ₂	217
8.3.6 Spectral evidence for KMnO ₄ oxidation	220
8.3.6.1 Reaction between KMnO ₄ and pine/sorbed 2,4-DCP	220
8.3.6.2 MnO ₂ formation	221
8.3.6.3 Isosbestic point	222
8.4 Column studies	223
8.4.1 KMnO ₄ consumption with pine (effect of flow)	225
8.4.2 KMnO ₄ consumption with pine/sorbed-2,4-DCP at flow 5 mL min ⁻¹	227
8.4.3 Evidence of MnO ₂	230
8.4.4 Zeta potential	233
8.4.5 pH change	234
8.4.6 Batch KMnO ₄ consumption at pH ~2	235
8.4.7 Column KMnO ₄ consumption at pH ~2	236
8.5 Conclusion	237
9 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS	239
REFERENCES	251

APPENDICES	270
APPENDIX A	271
APPENDIX B	281
APPENDIX C	284
APPENDIX D	289

Abbreviations

2-CP	: 2-Chlorophenol
3-CP	: 3-Chlorophenol
4-CP	: 4-Chlorophenol
2,4-DCP	: 2,4-Dichlorophenol
2,6-DCP	: 2,6-Dichlorophenol
2,4,6-TCP	: 2,4,6-Trichlorophenol
AOPs	: Advanced Oxidation Processes
BET	: Brunauer-Emmett-Teller
CP	: Chlorophenol
DOC	: Dissolved Organic Carbon
FC	: Filter Coal
GAC	: Granular Activated Carbon
HW	: Hardwood
ISCO	: In-Situ chemical Oxidation
LOD	: Limit of Detection
MDL	: Minimum Detection Limit
NPI	: National Pollutant Inventory
NOD	: Natural Oxidant Demand
PRB	: Permeable Reactive Barrier
PV	: Pore Volume
PVC	: Polyvinyl Chloride

Principal Notation

C_e	: equilibrium concentration (mg L^{-1})
C_o	: initial concentration (mg L^{-1})
D_{ow}	: octanol-water distribution coefficient
K_{ow}	: octanol-water partition coefficient
k_{th}	: Thomas rate constant ($\text{L min}^{-1} \text{mg}^{-1}$)
k_{yn}	: Yoon-Nelson rate constant (min^{-1})
q_t	: amount of sorbate at any time t (mg g^{-1})
q_e	: amount of sorbate at equilibrium (mg g^{-1})
Q	: volumetric flow rate (mL min^{-1})
r^2	: correlation coefficient
k_y	: Yan rate constant ($\text{L min}^{-1} \text{mg}^{-1}$)

LIST OF FIGURES

- Figure 2.1 Groundwater remediation using PRB
- Figure 2.2 Groundwater remediation using horizontal subsurface barriers
- Figure 2.3 Design of the permanganate reactive barrier system
- Figure 2.4 Conceptual design of permanganate-pine barrier (Groundwater)
- Figure 2.5 Conceptual design of permanganate-pine barrier (Subsurface)
- Figure 2.6 Chlorophenol emissions in Australia (Source: www.npi.gov.au)
- Figure 2.7 Breakthrough curves for ideal and non-ideal transport (Source: Brusseau et al., 1997)
- Figure 2.8 Reaction pathways of oxidation of alkenes with permanganate (Lee and Brownridge, 1974)
- Figure 2.9 Structure of selected chlorophenols
- Figure 3.1 Pine wood chips
- Figure 3.2 Hardwood chips
- Figure 3.3 GAC
- Figure 3.4 Filter coal
- Figure 3.5 Particle sizes of woody materials
- Figure 3.6 Sorbent leaching
- Figure 3.7 Solid phase extraction
- Figure 3.8 Chemical reactions of KMnO_4 and chlorophenol
- Figure 3.9 Column setup
- Figure 3.10 Chloride (Cl) breakthrough curve for wood column
- Figure 4.1 UV-visible spectra for 2-CP in water and methanol
- Figure 4.2 UV-visible absorbance for 2-CP in water and methanol
- Figure 4.3 UV-visible spectra for 3-CP in water
- Figure 4.4 UV-visible absorbance for 3-CP in water
- Figure 4.5 UV-visible spectra for 4-CP in water and methanol
- Figure 4.6 UV-visible absorbance for 4-CP in water and methanol
- Figure 4.7 UV-visible spectra for 2,4-DCP in water and methanol
- Figure 4.8 UV-visible absorbance for 2,4-DCP in water and methanol.
- Figure 4.9 UV-visible spectra for 2,6-DCP in water

Figure 4.10 UV-visible absorbance for 2,6-DCP in water

Figure 4.11 UV-visible spectra for 2,4,6-TCP in water and methanol

Figure 4.12 UV-visible absorbance for 2,4,6-TCP in water and methanol.

Figure 4.13 Spectra of 4-CP (~ 0.16 mM) at various pH

Figure 4.14 Spectra of 4-CP (~ 0.16 mM) with quenching agent, pH 5.6, 22 °C

Figure 4.15 Spectra of quenching agent and reagent blank at pH 12

Figure 4.16 Absorption spectra after reaction of 4-CP (~ 0.16 mM) and KMnO_4 (1.5 mM) using quenching agent Na_2SO_3 , pH 12, 22 °C

Figure 4.17 Spectral changes during the oxidation of 4-CP (~ 0.23 mM) with KMnO_4 (~ 0.2 mM) at time intervals of 45 sec, initial pH 5.3, 22 °C. The blue line is the initial KMnO_4 spectrum and the dotted line is the final due to a reaction with CP and MnO_2 is produced

Figure 4.18 A linear relationship between absorbances at two wavelength A_{525} and A_{418}

Figure 4.19 Degradation of chlorophenols by KMnO_4 . $[\text{CP}]_0 \sim 0.16$ mM, Initial KMnO_4 1.5 mM, pH 5.3, 22 °C

Figure 5.1 Degradation of 4-CP under various initial 4-CP concentration with fixed KMnO_4 : $[\text{4-CP}]_0 \sim (0.05\text{--}0.16$ mM), $[\text{MnO}_4^-] \sim 1.5$ mM, $I \sim 0.02$ M, initial pH 7.0 (22 °C)

Figure 5.2 Plot of initial rate $\ln r_0$ versus initial concentration of CP $\ln[\text{CP}]_0$: $[\text{CP}]_0 \sim (0.04\text{--}0.24$ mM), $[\text{MnO}_4^-]_0 \sim 1.2$ for 2-CP, 2,6-DCP and 2,4,6-TCP, ~ 1.5 mM for 3-CP, 4-CP and 2,4-DCP, $I \sim 0.02$ M, Initial pH 7.0 (22 °C)

Figure 5.3 Plot of pseudo-first-order rate constant $\ln k_1$ versus initial concentration of permanganate $\ln[\text{MnO}_4^-]_0$: $[\text{CP}]_0 \sim 0.16$ mM, except 2,4,6-TCP ~0.08 mM, $[\text{MnO}_4^-]_0$ (0.8–3.2 mM), $I \sim 0.02$ M, Initial pH 7.0 (22 °C)

Figure 5.4 Degradation of 4-CP under various concentration of KMnO_4 : $[\text{4-CP}]_0 \sim 0.16$ mM, $[\text{MnO}_4^-] \sim (1.2\text{--}3.2$ mM), $I \sim 0.02$ M, Initial pH 7.0 (22 °C)

Figure 5.5 Oxidation fit curves of 4-CP at various concentration of KMnO_4 : $[\text{4-CP}]_0 \sim 0.16$ mM, $[\text{MnO}_4^-] \sim (1.2\text{--}3.2$ mM), $I \sim 0.02$ M, Initial pH 7.0 (22 °C)

Figure 5.6 Oxidation fit curves of 4-CP at various initial 4-CP concentration with fixed KMnO_4 : $[\text{4-CP}]_0 \sim (0.05\text{--}0.16$ mM), $[\text{MnO}_4^-] \sim 1.5$ mM, $I \sim 0.02$ M, Initial pH 7.0 (22 °C)

Figure 5.7 Conformer of 2-CP

Figure 5.8 Oxidation of 4-CP by KMnO_4 in Milli-Q water and in solution at pH 7.0 with different ionic strength. 4-CP ~ 0.16 mM, $\text{KMnO}_4 \sim 1.5$ mM, I ~ 0.02 – 0.2 M, Initial pH 7.0 (22 °C)

Figure 5.9 Effect of initial pH on 4-CP (~ 0.16 mM) degradation by KMnO_4 (1.5 mM), I ~ 0.02 M (22 °C)

Figure 6.1 Kinetics of sorption of chlorophenols on pine

Figure 6.2 Kinetics of sorption of chlorophenols on HW

Figure 6.3 Kinetics of sorption of chlorophenols on GAC

Figure 6.4 Kinetics of sorption of chlorophenols on FC

Figure 6.5 Chlorophenol uptake onto pine

Figure 6.6 Chlorophenol uptake onto HW

Figure 6.7 Chlorophenol uptake onto GAC

Figure 6.8 Chlorophenol uptake onto FC

Figure 6.9 Equilibrium sorption isotherm for 2-CP onto the sorbents

Figure 6.10 Equilibrium sorption isotherm for 4-CP onto the sorbents

Figure 6.11 Equilibrium sorption isotherm for 2,4-DCP onto the sorbents

Figure 6.12 Prediction of Freundlich equilibrium sorption of chlorophenol onto pine

Figure 6.13 Prediction of Langmuir equilibrium sorption of chlorophenol onto pine

Figure 6.14 Prediction of Freundlich equilibrium sorption of chlorophenol onto HW

Figure 6.15 Prediction of Langmuir equilibrium sorption of chlorophenol onto HW

Figure 6.16 Prediction of Freundlich equilibrium sorption of chlorophenol onto GAC

Figure 6.17 Prediction of Langmuir equilibrium sorption of chlorophenol onto GAC

Figure 6.18 Prediction of Freundlich equilibrium sorption of chlorophenol onto FC

Figure 6.19 Prediction of Langmuir equilibrium sorption of chlorophenol onto FC

Figure 6.20 Sorption capacities at an equilibrium concentration of 70 mg L^{-1} for the chlorophenols using 1.18 mm sorbents

Figure 6.21 Effect of particle size on kinetics of 2-CP by pine

Figure 6.22 Effect of particle size on kinetics of 4-CP by pine

Figure 6.23 Effect of particle size on kinetics of 2,4-DCP by pine

Figure 6.24 Effect of particle size on kinetics of 2-CP by GAC

Figure 6.25 Effect of particle size on kinetics of 4-CP by GAC

Figure 6.26 Effect of particle size on kinetics of 2,4-DCP by GAC

Figure 6.27 Effect of particle size on kinetics of 2-CP by FC

Figure 6.28 Effect of particle size on kinetics of 4-CP by FC

Figure 6.29 Effect of particle size on kinetics of 2,4-DCP by FC

Figure 6.30 Changes of solid phase loading of CP with time during desorption by pine

Figure 6.31 Changes of solid phase loading of CP with time during desorption by HW

Figure 6.32 Sorption-desorption isotherms of 2-CP by pine

Figure 6.33 Sorption-desorption isotherms of 4-CP by pine

Figure 6.34 Sorption-desorption isotherms of 2,4-DCP by pine

Figure 6.35 Sorption-desorption isotherms of 2-CP by HW

Figure 6.36 Sorption-desorption isotherms of 4-CP by HW

Figure 6.37 Sorption-desorption isotherms of 2,4-DCP by HW

Figure 6.38 Desorbed percentages of chlorophenols from pine and HW. These percentages were calculated from the initially sorbed mass and after the 4 desorption cycle.

Figure 7.1 Chloride breakthrough curves for pine column

Figure 7.2 Breakthrough curves for different flow rates under the experimental condition Col-2 (Run-1) and Col-3 (Run-1) (2,4-DCP ~1.84 mM, particle size of pine 4.75 mm)

Figure 7.3 Breakthrough curves for different particle sizes under the experimental condition Col-1 (Run-1) and Col-2 (Run-1) (2,4-DCP ~1.84 mM, flow rate 5 mL min⁻¹)

Figure 7.4 Breakthrough curves for 2,4-DCP sorption with respect to KMnO₄ modified and unmodified pine under the experimental condition Col-3 (Run-1) and Col-4 (Run-2) (2,4-DCP ~1.84 mM, KMnO₄ ~3.8 mM, flow rate 10 mL min⁻¹)

Figure 7.5 Breakthrough curves for 2,4-DCP sorption with respect to KMnO₄ modified and unmodified pine under the experimental condition Col-2 (Run-1) and Col-5 (Run-2) (2,4-DCP ~1.84 mM, KMnO₄ ~3.8 mM, flow rate 5 mL min⁻¹)

Figure 7.6 Effect of flow rate and predicted breakthrough curves of Yan model under the experimental condition Col-2 (Run-1) and Col-3 (Run-1)

Figure 7.7 Effect of particle size and predicted breakthrough curves of Yan model under the experimental condition Col-1 (Run-1) and Col-2 (Run-1)

Figure 7.8 Effect of 2,4-DCP sorption on to unmodified and KMnO_4 -modified pine and predicted breakthrough curves of Yan model under the experimental condition Col-3 (Run-1) and Col-4 (Run-2).

Figure 7.9 Effect of 2,4-DCP sorption on to unmodified and KMnO_4 -modified pine and predicted breakthrough curves of Yan model under the experimental condition Col-2 (Run-1) and Col-5 (Run-2)

Figure 8.1 Consumption of KMnO_4 on pine (1.18 mm) and sorbed CP in pine:
 KMnO_4 (~4 mM), initial pH 6.15, 22 °C

Figure 8.2 The kinetics of oxidation of KMnO_4 with pine and sorbed CP in pine:
Reaction time 0-4 min (inset) and 0-160 min, Pine 1.18 mm, KMnO_4 (~4 mM), initial pH 6.15, 22 °C

Figure 8.3 Oxidation fit curves of CP by in-situ MnO_2 : [CP] ~0.075-0.246 mM, [MnO₂] ~0.034 mM, Initial pH ~5.0, 22 °C

Figure 8.4 Spectral changes during the oxidation of MnO_4^- (~0.1 mM) and 1.5 g of pine (4.75 mm), 22 °C

Figure 8.5 Spectral changes during the oxidation of MnO_4^- (~0.1 mM) and 1.5 g of pine (4.75 mm) sorbed with 2,4-DCP, 22 °C

Figure 8.6 A linear relationship between absorbances at two wavelength A_{525} and A_{418} for pine and KMnO_4 reaction

Figure 8.7 A linear relationship between absorbances at two wavelength A_{525} and A_{418} for sorbed 2,4-DCP and KMnO_4 reaction

Figure 8.8 Chloride breakthrough curves for KMnO_4 pine column

Figure 8.9 KMnO_4 consumptions by pine at different flow rate: Col-4 (Run-1) and Col-5 (Run-1), KMnO_4 ~3.8 mM, Pine 4.75 mm

Figure 8.10 KMnO_4 consumption after 2,4-DCP sorption to pine: Col-5 (run-1) and Col-6 (Run-2), 2,4-DCP ~1.84 mM, KMnO_4 ~3.8 mM, Pine 4.75 mm

Figure 8.11 MnO_2 absorbance for effluent sample under the conditions: Col-5 (Run-1) and Col- 6 (Run-2)

Figure 8.12 MnO_2 on pine

Figure 8.13 MnO_2 particles

Figure 8.14 Zeta potential measurements of colloidal particles under the conditions: Col-5 (Run-1), KMnO_4 ~3.8 mM, Pine 4.75 mm, Flow 5 mL min⁻¹

Figure 8.15 pH measurements for effluent sample under conditions: Col-5 (Run-1),
KMnO₄ ~3.8 mM, Pine 4.75 mm, Flow 5 mL min⁻¹

Figure 8.16 The kinetics of oxidation of KMnO₄ by pine: Pine 4.75 mm, KMnO₄ (~61
mM), pH ~2, 22 °C

Figure 8.17 KMnO₄ consumption by pine: pH ~2, Col-7 (Run-1), KMnO₄ ~63 mM,
Pine 4.75 mm

LIST OF TABLES

- Table 2.1 Reactive materials used in PRBs
- Table 2.2 Comparative study of the proposed pine-permanganate reactive barrier with the other barrier system
- Table 2.3 Chlorophenol sorption on various low-cost sorbents
- Table 2.4 Standard oxidation potential for oxidants used in-situ chemical oxidation.
- Table 2.5 Summary of rate constants for chlorophenol compounds in the KMnO_4 oxidation processes
- Table 3.1 Characteristics of wood used
- Table 3.2 Physical properties of granular activated carbon (GAC) and filter coal (FC)
- Table 3.3 Main physicochemical properties of chlorophenols ([#]Ma et al., 1993; Czaplicka, 2004)
- Table 3.4 Experimental conditions of column sorption experiments at 22 °C
- Table 3.5 Leaching absorbance from pine
- Table 4.1 Spectral and calibration data for 2-CP compounds, initial concentration 0.0063–0.77 mM, 22 °C
- Table 4.2 Spectral and calibration data for 3-CP compounds, initial concentration 0.0078–0.79 mM, 22 °C
- Table 4.3 Spectral and calibration data for 4-CP compounds, initial concentration 0.0076–0.78 mM, 22 °C
- Table 4.4 Spectral and calibration data for 2,4-DCP compounds, initial concentration 0.0062–0.62 mM, 22 °C
- Table 4.5 Spectral and calibration data for 2,6-DCP compounds, initial concentration 0.0067–0.61 mM, 22 °C
- Table 4.6 Spectral and calibration data for 2,4,6-TCP compounds, initial concentration 0.0034–0.52 mM, 22 °C
- Table 4.7 Comparison of absorbance at concentration $\sim 1\text{ mg L}^{-1}$ for chlorophenols
- Table 4.8 Concentration of CP before and after solid phase extraction (SPE)
- Table 4.9 The recovery (%) of CP by extraction with methanol from water solution and identification by UV-visible spectrophotometry
- Table 4.10 Measured maximum absorbance of CP ($\sim 0.16\text{ mM}$) at various pH, 22 °C

Table 4.11 Absorbance of 4-CP (~0.16 mM) with quenching agent, reaction time 20 min, pH 5.6, 22 °C

Table 4.12 Absorbance for various reagents and solutions, pH 12, 22 °C at wavelength range 238–245 nm

Table 4.13 Absorbance for various reagents and solutions, pH 12, 22 °C at wavelength range 292–305 nm

Table 4.14 Rate constants for chlorophenol (~0.16 mM) oxidation by KMnO_4 (1.5 mM), initial pH 5.3, 22 °C

Table 5.1 Reaction order alpha (α) with respect to the [CP]: I ~ 0.02 M, Initial pH 7.0 (22 °C)

Table 5.2 Reaction order beta (β) with respect to $[\text{MnO}_4^-]$: I ~ 0.02 M, Initial pH 7.0 (22 °C)

Table 5.3 Rate constants for the oxidation of chlorophenols (CP) with various concentrations of KMnO_4 : I ~0.02 M, Initial pH 7.0 (22 °C)

Table 5.4 Rate constants for the oxidation of chlorophenols (CP) with fixed concentrations of KMnO_4 solutions: I ~ 0.02 M, Initial pH 7.0 (22 °C)

Table 5.5 Rate constants for 4-CP (~0.16 mM) oxidation by KMnO_4 (1.5 mM): I~0.02–0.2 M, Initial pH 7.0 (22 °C)

Table 5.6 Rate constants for 4-CP (~0.16 mM) oxidation by KMnO_4 (1.5 mM) and at various initial pH (5.5–8.5): I ~0.02 M (22 °C)

Table 6.1 Pseudo-first-order parameters for the sorption of chlorophenols on sorbents

Table 6.2 Pseudo-second-order parameters for the sorption of chlorophenols on sorbents

Table 6.3 Fitted sorption parameters from Freundlich isotherm

Table 6.4 Fitted sorption parameters from Langmuir isotherm

Table 6.5 Best fit Langmuir isotherm parameters of different particle sizes for pine

Table 6.6 Best fit Freundlich isotherm parameters of different particle sizes for pine

Table 6.7 Characteristics of wood particle shape

Table 6.8 Fitted sorption parameters for desorption from Freundlich isotherm.

Table 6.9 Freundlich parameters and hysteresis coefficients for desorption of chlorophenols on pine and hardwood.

Table 7.1 Column characteristics: mass of pine 66 g, mass of glass beads 1665 g

Table 7.2 Column data and parameters obtained at different flow rates, Pine 4.75 mm

- Table 7.3 Column data and parameters obtained at different particle sizes, flow 5 mL min⁻¹, 22 °C
- Table 7.4 Column data and parameters obtained at modified and unmodified pine, 22 °C
- Table 7.5 Examples of batch and column study
- Table 7.6 Predicted parameters from the Thomas model (linear, >0.05 and <0.85) of 2,4-DCP sorption on pine
- Table 7.7 Predicted parameters from the Yoon-Nelson model (linear, >0.25 and <0.85) of 2,4-DCP sorption on pine
- Table 7.8 Predicted parameters from the Yan model (non-linear) of 2,4-DCP sorption on pine
- Table 8.1 Sorption of CP on pine: contact time 3 days, mixing rate 150 rpm, 22 °C
- Table 8.2 Rate constants for chlorophenol (~0.16 mM) oxidation by KMnO₄ (1.5 mM): initial pH 7.0, 22 °C
- Table 8.3 KMnO₄ consumption during oxidation of pine and sorbed-CP after 160 min reaction: KMnO₄ (~4 mM), initial pH 6.15, 22 °C
- Table 8.4 First-order rate constants for pine (1.18 mm) and sorbed CP oxidation by KMnO₄ (~4 mM): initial pH 6.15, 22 °C
- Table 8.5 Desorption of CP from pine
- Table 8.6 Rate constant for CP oxidation by in-situ MnO₂ (~0.034 mM), initial pH ~5.0, 22 °C
- Table 8.7 Column characteristics: pine particle size 4.75 mm, mass of pine 66 g, mass of glass beads 1665 g
- Table 8.8 Column data and parameters obtained at different flow rates
- Table 8.9 Column data and parameters obtained with pine/sorbed CP at flow 5 mL min⁻¹