Development of contaminant removal material suitable for implementation in cold regions

Junchao Ma

Submitted in total fulfilment of the requirements of the degree of Doctor of Philosophy

Supervisors:
Dr Kathryn A. Mumford
Professor Geoffrey W. Stevens

March, 2018

Department of Chemical and Biomolecular Engineering
University of Melbourne
Abstract

Natural factors and anthropogenic activities result in hydrocarbon and heavy metal contaminants being commonly present at scientific research stations in Antarctica and other cold regions. Due to existing quarantine regulations, slow reaction kinetics at low temperatures and potentially detrimental freeze-thaw cycling, there are currently limited proven methods for soil or water remediation in these cold climates. Among these, permeable reactive barriers (PRBs) have shown great promise for passive water treatment and are being developed as a standalone or supporting technique for remediation activities. Currently, many researchers are focusing on the development of more effective composite materials to be implemented in PRBs.

In this thesis, natural zeolite was selected and modified with Diphenyldichlorosilane (DPDSCI) to increase its ability to adsorb hydrocarbons, and evaluated for its potential application in permeable reactive barriers tasked with fuel removal. Batch and column sorption tests confirmed that the modified zeolite was able to capture hydrocarbons and be subsequently regenerated multiple times with minimal change in adsorption efficiency. The Langmuir isotherm and advection-dispersion-reaction solute transport equation (ADRE) predicted the adsorption process of DPDSCI modified zeolite well for batch and column tests, respectively.

To enhance in-situ bioremediation, zeolite was conditioned into an ammonium form prior to surface modification to determine whether the DPDSCI modified ammonium exchanged zeolite was able to simultaneously adsorb hydrocarbons and release nutrients. This was successfully verified in both batch and column tests. The material was shown to be capable of regeneration in batch and column tests without reduction in hydrocarbon adsorption and nutrient release ability. Additionally, field tests indicated that the material presented good nutrient release, hydrocarbon adsorption capacity and had successfully promoted microbial growth on the material surface thereby enhancing the biodegradation process.

Overall, the DPDSCI modified ammonium exchanged zeolite compared well to GAC. It provided reversible hydrocarbon adsorption, provided a stable nutrient source, and provided a robust surface for micro-organism growth and biodegradation activities. Therefore, it is regarded as a potential material for use in PRBs in the future.
Declaration

I declare here that this thesis titled “Development of contaminant removal material suitable for implementation in cold regions” has not been previously submitted to any other institution or university for a higher degree.

I certify that this thesis comprises only my original work and all the information and literature used in this thesis have been accurately cited. The contributions of others have been appropriately acknowledged.

Junchao Ma

Junchao Ma
Acknowledgements

I would firstly thank Dr Kathryn Mumford for her meticulous care for my entire PhD study. Without her guidance, I cannot find my research object so quickly and without her support, I cannot achieve so many works smoothly and cannot experience an Antarctic trip. And thanks for her kindly help, my English writing skills are greatly enhanced and thereby have one paper published and two papers submitted. I would also like to express my appreciation to Professor Geoffrey Stevens for his time in correcting my experimental design, answering my puzzles raised from experiments, and providing me comments about published works.

For laboratory works, I would especially thanks Dr Tom Statham and Dr Benjamin Freidman. It was Tom that help me familiar with the lab facilities and all requirements for a lab user. And Ben gave me a lot of support in experiment implements and minimizing the experimental errors. Besides that, he also provided me many tips for surviving in Antarctica and conducting a field test. Meanwhile, I would appreciate Dr Kezia Kezia and Sam Law for their help in HPLC test and Wen Li for her help in ICP test. And I would also want to thank my team mates, Jack Churchill, for helping me quickly adapt to Antarctic life and achieve my field test successfully and Becca McQuillan, for her help in lab work and pleasant talks. I would also acknowledge Dr Yong Wang and Dr Qiang Sun for their help in computer modelling, Dr Lydia Ong for her help in SEM testing, and Justin Fox for the column equipment modification. And I want to thank Tabitha Cesnak and Dr Michelle De Silva for their assistance with administration, conference organization and quarantine accreditation.

For field tests, I would extend my big thank to Australian Antarctic Division, especially the kindly staffs from Department of the Environment and Energy: Tim Spedding, Dr Lauren Wise, Greg Hince, Dr Dan Wilkins, Dr Rebecca McWatters, Bianca Sfiligoj, Deborah Terry. Without your kindly help, I cannot achieve my field test successfully and also enjoy the Antarctic life. I would also acknowledge the financial support from Chinese Scholarship Council, University of Melbourne scholarship, the Particulate Fluids Processing Centre, Australian Antarctic Science project, Clive Pratt Scholarship.

Finally, I would like to thank my parents for supporting me study here and travel around, and my lovely friends for understanding and supporting me across the past three and half years.

Everyone mentioned above all plays a crucial role in my PhD study. Without all of you, I do not think I can survive from the frustrate moments and obtain this achievement.
Publications arising from this thesis

Journal articles


Conference presentation/poster

Oral presentation: 10th World Congress of Chemical Engineering, Barcelona, Spain, October 2017

Poster presentation: Society of Environmental Toxicology and Chemistry, Hobart, Australia, October 2016
# Table of Contents

Abstract .................................................................................................................................................... i  
Declaration .............................................................................................................................................. ii  
Acknowledgements ................................................................................................................................ iii  
Publications arising from this thesis ...................................................................................................... iv  
Table of Contents .................................................................................................................................... v  
List of Abbreviations .............................................................................................................................. xi  
List of Symbol ....................................................................................................................................... xiii  
List of Figures ........................................................................................................................................ xv  
List of Tables ....................................................................................................................................... xviii  

Chapter 1 Introduction ........................................................................................................................... 1  
1.1 Research introduction ................................................................................................................... 2  
1.2 Research aims ............................................................................................................................... 3  
1.3 Research objectives ...................................................................................................................... 3  

Chapter 2 Background and Literature review ......................................................................................... 6  
2.1 Permeable reactive barriers (PRBs) .............................................................................................. 7  
2.1.1 Development of PRBs ............................................................................................................. 7  
2.1.2 Application in Antarctica ........................................................................................................ 8  
2.2 Contaminant sorption material .................................................................................................. 11  
2.2.1 Zeolite .................................................................................................................................. 12  
2.2.2 Coating material ................................................................................................................... 12  
2.3 Factors that influence the adsorption ability .............................................................................. 16  
2.3.1 pH ......................................................................................................................................... 16  
2.3.2 Temperature ........................................................................................................................ 16  
2.3.3 Groundwater constituents ................................................................................................... 17  
2.3.4 Flow rates ............................................................................................................................. 17  
2.3.5 Other factors ........................................................................................................................ 17  
2.4 Regeneration methods ................................................................................................................... 18  
2.5 Research Required ...................................................................................................................... 18
### Chapter 3 Experimental materials and methods

#### 3.1 Chemical reagents

#### 3.2 Experimental materials

#### 3.3 Hydrocarbon source

- **3.3.1** Laboratory tests (Toluene)
- **3.3.2** Field tests (Total Petroleum Hydrocarbons)

#### 3.4 Analytical techniques

- **3.4.1** Electrical Conductivity
- **3.4.2** Fourier Transform-Infrared Spectroscopy
- **3.4.3** High Performance Liquid Chromatography
- **3.4.4** Inductively Coupled Plasma-Optical Emission Spectrometry
- **3.4.5** pH
- **3.4.6** Scanning Electron Microscopy
- **3.4.7** Sieving
- **3.4.8** Thermogravimetric Analysis
- **3.4.9** Ultraviolet-Visible Spectroscopy

#### 3.5 Experimental design

- **3.5.1** Surface modification by DPDSCI
- **3.5.2** Batch equilibrium study
- **3.5.3** Batch regeneration study
- **3.5.4** Column study
- **3.5.5** Column regeneration study

### Chapter 4 Batch studies of DPDSCI coated zeolite

#### 4.1 Introduction

#### 4.2 Materials and Methods

- **4.2.1** Natural zeolite and its surface modification process
- **4.2.2** Surface characterization
- **4.2.3** Equilibrium tests
- **4.2.4** Regeneration tests

#### 4.3 Modelling

- **4.3.1** Adsorption isotherms
- **4.3.2** Adsorption thermodynamics

#### 4.4 Results and Discussion
4.4.1 Thermogravimetric analysis ................................................................. 34
4.4.2 FT-IR analysis ........................................................................................ 35
4.4.3 Adsorption behaviour of sorbent material .............................................. 36
4.4.4 Adsorption thermodynamics ................................................................. 39
4.4.5 Regeneration test ................................................................................... 40
4.5 Conclusions ............................................................................................. 41

Chapter 5 Column studies of DPDSCI coated zeolite ........................................ 43
5.1 Introduction ............................................................................................ 44
5.2 Materials and Methods ........................................................................... 44
  5.2.1 Columns and materials ......................................................................... 44
  5.2.2 Toluene adsorption column tests ......................................................... 44
  5.2.3 Regeneration tests ................................................................................ 44
  5.2.4 Reactive transport modelling ............................................................... 45
  5.2.5 Axial dispersion tests ........................................................................... 45
5.3 Modelling ............................................................................................... 45
  5.3.1 Flow characteristics ............................................................................ 45
  5.3.2 Reactive transport in the column .......................................................... 47
5.4 Results and Discussion ........................................................................... 49
  5.4.1 Adsorption performance ..................................................................... 49
  5.4.2 Regeneration test ................................................................................ 49
  5.4.3 Axial dispersion coefficient ................................................................. 51
  5.4.4 Reactive transport modelling ............................................................... 54
5.5 Conclusions ........................................................................................... 56

Chapter 6 Batch studies of DPDSCI coated ammonium exchanged zeolite .................. 58
6.1 Introduction ............................................................................................ 59
6.2 Materials and Methods ........................................................................... 59
  6.2.1 Raw materials .................................................................................... 59
  6.2.2 Surface modification ......................................................................... 59
  6.2.3 Equilibrium tests ................................................................................ 59
  6.2.4 Regeneration tests .............................................................................. 60
6.3 Modelling ............................................................................................... 60
6.4 Results and Discussion ........................................................................... 60
Appendix 8.11 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the inlet of AZ column (D).
# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AAD</td>
<td>Australian Antarctic Division</td>
</tr>
<tr>
<td>AAT</td>
<td>Australian Antarctic Territory</td>
</tr>
<tr>
<td>ADE</td>
<td>Advection-Dispersion Equation</td>
</tr>
<tr>
<td>ADRE</td>
<td>Advection-Dispersion-Reaction Solute Transport Equation</td>
</tr>
<tr>
<td>ALS</td>
<td>Australian Laboratory Services</td>
</tr>
<tr>
<td>AST</td>
<td>Analytical Services Tasmania</td>
</tr>
<tr>
<td>ATK</td>
<td>Aviation Turbine Kerosene</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy</td>
</tr>
<tr>
<td>AZ</td>
<td>Ammonium Exchange Zeolite</td>
</tr>
<tr>
<td>BDTDA</td>
<td>Benzyltetradecylammoniumchloride</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller theory</td>
</tr>
<tr>
<td>BTEX</td>
<td>Benzene, Toluene, Ethylbenzene and Xylene</td>
</tr>
<tr>
<td>C18</td>
<td>Octadecyltrichlorosilane</td>
</tr>
<tr>
<td>CPB</td>
<td>Cetylpyridinium Bromide</td>
</tr>
<tr>
<td>CTAB</td>
<td>Hexadecyltrimethylammonium Bromide</td>
</tr>
<tr>
<td>CWTP</td>
<td>Contaminated Wastewater Treatment Plant</td>
</tr>
<tr>
<td>DAZ</td>
<td>DPDSCI Coated Ammonium Exchange Zeolite</td>
</tr>
<tr>
<td>DPDSCI</td>
<td>Diphenyldichlorosilane</td>
</tr>
<tr>
<td>DTG</td>
<td>Differential Curves of Thermogravimetric Analysis</td>
</tr>
<tr>
<td>DZ</td>
<td>DPDSCI Coated Zeolite</td>
</tr>
<tr>
<td>EC</td>
<td>Electrical Conductivity</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EPS</td>
<td>Extracellular Polymeric Substances</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FIA</td>
<td>Flow Injection Analysis</td>
</tr>
<tr>
<td>FT-IR</td>
<td>Fourier Transform-Infrared Spectroscopy</td>
</tr>
<tr>
<td>GAC</td>
<td>Granular Activated Carbon</td>
</tr>
<tr>
<td>GC</td>
<td>Gas Chromatography</td>
</tr>
<tr>
<td>HDTMA</td>
<td>Hexadecyltrimethylammonium Bromide</td>
</tr>
<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
</tr>
<tr>
<td>IC</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td>ICP-AES</td>
<td>Inductively Coupled Plasma-Atomic Emission Spectroscopy</td>
</tr>
</tbody>
</table>
ICP-OES: Inductively Coupled Plasma-Optical Emission Spectrometry

MPH: Main Power House

ODMBA: Octadecyldimethylbenzylammonium

PRBs: Permeable Reactive Barriers

SAB: Special Antarctic Blend diesel

SMZ: Surface Modified Zeolite

TGA: Thermogravimetric Analysis

TPH: Total Petroleum Hydrocarbons

SDBAC: Stearyldimethylbenzylammoniumchloride

SEM: Scanning Electron Microscopy

UV-Vis: Ultraviolet Visible Spectrophotometer

ZVI: Zero-Valent Iron
List of Symbol

$C$: Tracer Concentration in Bulk Solution in Column Test (mg/L)

$C_e$: Concentration of Contaminants in Solution at Equilibrium in Langmuir Equation (µmol/L)

$C_m$: Concentration of Contaminants in Material Surface at Equilibrium in Freundlich Equation (µmol/g)

$C_0$: Initial Tracer Concentration in Column Test (mg/L)

$C_s$: Concentration of Contaminants in Solution at Equilibrium in Freundlich Equation (µmol/L)

$d$: Particle Diameter (m)

$D_l$: Axial Dispersion Coefficient (m$^2$/s)

$f_{oc}$: Sorbent’s Fractional Organic Carbon Content

$\Delta G^0$: Standard Gibbs Free Energy (kJ/mol)

$\Delta H^0$: Standard Enthalpy Change (kJ/mol)

$K$: Equilibrium Adsorption Coefficient in Gibbs Free Energy Function

$K_0$: Linear Constant in Langmuir Equation (L/µmol)

$K_f$: Freundlich Constant in Freundlich Equation

$K_l$: Langmuir Constant in Langmuir Equation (L/µmol)

$K_{oc}$: Organic Carbon-Based Partition Coefficient

$n$: Material Porosity

$n_f$: Freundlich Constant in Freundlich Equation

$\rho$: Water Density (kg/m$^3$)

$\rho_b$: Bulk Density of Test Column (kg/m$^3$)

$Pe'$: Modified Péclet Number

$PV$: A Single Pore Volume

$q$: Toluene Concentration on Adsorption Materials in Column Test (mg/g)

$q_e$: Adsorption Capacity at Equilibrium in Langmuir Equation (µmol/g)

$q_{max}$: Langmuir Constant in Langmuir Equation (µmol/g)

$R$: Molar Gas Constant in Gibbs Free Energy Function

$R^2$: Coefficient of Determination

$Re'$: Modified Reynolds Number

$\Delta S^0$: Standard Entropy Change (kJ/mol)

$Sc$: Schmidt Number

$S_v$: Specific Surface Area Per Unit Volume

$T$: Absolute Temperature in Gibbs Free Energy Function
\( \mu \): Water Viscosity (Pa·s)

\( U_0 \): Superficial Fluid Velocity in Column Test (m/s)

\( \bar{v} \): Average Pore Velocity in Column Test (m/s)

\( x \): Distance Taken Along the Flow Line in Column Test (m)
List of Figures

Chapter 2
Figure 2.1 The location of new Casey station and fuel spill site near the main power house, Windmill Islands, East Antarctica (Mumford et al., 2013).................................................................................................................................9
Figure 2.2 Reaction process for the surface modification of silanol groups on zeolite with chlorosilane...15

Chapter 3
Figure 3.1 Petroleum hydrocarbons in the range of C1 to C40 (Freidman, 2016).................................23
Figure 3.2 The 45ml glass vials used in batch test. It contained certain amount of reactive material and 40ml of solution..................................................................................................................................................27
Figure 3.3 The system used to conduct column tests. ..............................................................................29

Chapter 4
Figure 4.1 Thermoanalytical data of raw zeolite and DPDSCL-zeolite ..................................................35
Figure 4.2 FT-IR spectra of raw zeolite and DPDSCL-zeolite ..................................................................36
Figure 4.3 Toluene adsorption isotherms on DPDSCL-zeolite at 20°C and 4°C.................................37
Figure 4.4 Freundlich, Langmuir and Linear isotherms for toluene adsorption on DPDSCL-zeolite at 20°C (a) and 4°C (b) ........................................................................................................................................38
Figure 4.5 Regeneration test for toluene uptake onto DPDSCL-zeolite ..................................................41

Chapter 5
Figure 5.1 The schematic diagram of column design..............................................................................46
Figure 5.2 The toluene adsorption curves of unamended zeolite and fresh DPDSCL-zeolite at 20°C and 4°C. Initial toluene concentration (C0) is 0.5 mmol/L and the flow rate is 11.24 PV/h.............................49
Figure 5.3 The regeneration tests of DPDSCL-zeolite at 20°C. Initial toluene concentration (C0) is 0.5 mmol/L and the flow rate is 11.24 PV/h. ..................................................................................................................50
Figure 5.4 The regeneration tests of DPDSCL-zeolite at 4°C. Initial toluene concentration (C0) is 0.5 mmol/L and the flow rate is 11.24 PV/h..............................................................................................................51
Figure 5.5 The effect of flow rate on axial dispersion at 20°C. The lines present the CXTFIT model fit. ...52
Figure 5.6 The effect of flow rate on axial dispersion at 4°C. The lines present the CXTFIT model fit....53
Figure 5.7 The relationship between modified Reynolds number (Re1) and axial dispersion coefficient (D1) of full packed column.........................................................................................................................54
Figure 5.8 The observed and fitted toluene adsorption curves of DPDSCL-zeolite at 20°C under various flow rates. .......................................................................................................................................55
Figure 5.9 The observed and fitted toluene adsorption curves of DPDSCL-zeolite at 4°C under various flow rates. ........................................................................................................................................56

Chapter 6
Figure 6.1 Ammonium release of DAZ at different initial concentration of potassium and toluene........61
Figure 6.2 Toluene adsorption of DAZ at different initial concentration of potassium and toluene ....62
Figure 6.3 Toluene adsorption isotherm of DZ and DAZ in 0 mmol/L potassium chloride solution ......64
Figure 6.4 Freundlich, Langmuir and Linear isotherms for toluene adsorption on DAZ in various potassium chloride solutions........................................................................................................................................64
Figure 6.5 Langmuir (a,b) and Freundlich (c,d) parameters for toluene adsorption on DAZ in various potassium chloride solutions........................................................................................................65
Figure 6.6 Langmuir isotherm fitted curves for toluene adsorption on DAZ in various potassium chloride
Chapter 7

Figure 7. 1 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 1.65 PV/h. The reactive material was ammonium regenerated DAZ.

Figure 7. 2 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 2.59 PV/h. The reactive material was ammonium regenerated DAZ.

Figure 7. 3 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 3.03 PV/h. The reactive material was ammonium regenerated DAZ.

Figure 7. 4 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene and the flow rate was 1.63 PV/h. The reactive material was ammonium regenerated DAZ.

Figure 7. 5 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene and the flow rate was 2.50 PV/h. The reactive material was fresh DAZ.

Figure 7. 6 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene and the flow rate was 3.10 PV/h. The reactive material was fresh DAZ.

Figure 7. 7 pH change in the column test under various flow rates. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene.

Figure 7. 8 pH change in the column test under various flow rates. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene.

Figure 7. 9 EC change in the column test under various flow rates. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene.

Figure 7. 10 EC change in the column test under various flow rates. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene.

Figure 7. 11 The toluene adsorption curves of fresh DAZ at 20°C under various flow rates. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene.

Figure 7. 12 The toluene adsorption curves of fresh DAZ at 20°C under various flow rates. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene.

Figure 7. 13 The observed and fitted toluene adsorption curves of DAZ at 20°C under various flow rates (influent toluene concentration was 0.5mmol/L).

Figure 7. 14 The observed and fitted toluene adsorption curves of DAZ at 20°C under various flow rates (influent toluene concentration was 1mmol/L).

Figure 7. 15 Ion exchange during regeneration process. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 3.03PV/h.

Figure 7. 16 Toluene concentration change during regeneration process. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 3.03PV/h.

Chapter 8
Figure 8.1 The diagram of column installation in the field test .................................................................89
Figure 8.2 The temperature of influent in field test..................................................................................91
Figure 8.3 The pH and EC of influent in field test......................................................................................92
Figure 8.4 The average potassium concentration in the influent and effluent of AZ and DAZ columns ....93
Figure 8.5 The average sodium concentration in the influent and effluent of AZ and DAZ columns ..........94
Figure 8.6 The average calcium concentration in the influent and effluent of AZ and DAZ columns ........95
Figure 8.7 The average magnesium concentration in the influent and effluent of AZ and DAZ columns....96
Figure 8.8 The equivalent sorb/release amount of cation on the surface of DAZ. Equivalent amount (meq/L) = ion concentration (mmol/L) × its electric charge .................................................................97
Figure 8.9 The equivalent sorb/release amount of cation on the surface of AZ. Equivalent amount (meq/L) = ion concentration (mmol/L) × its electric charge .......................................................................................97
Figure 8.10 The average chloride concentration in the influent and effluent of AZ and DAZ columns ....98
Figure 8.11 The average sulphate concentration in the influent and effluent of AZ and DAZ columns .....99
Figure 8.12 The average ammonia concentration in the influent and effluent of AZ and DAZ columns ...100
Figure 8.13 The average nitrate concentration in the influent and effluent of AZ and DAZ columns ....101
Figure 8.14 The average nitrite concentration in the influent and effluent of AZ and DAZ columns ....101
Figure 8.15 The total kjeldahl nitrogen concentration in the influent and effluent of AZ and DAZ columns ..........................................................................................................................................102
Figure 8.16 The average dissolved reactive phosphorus concentration in the influent and effluent of AZ and DAZ columns ........................................................................................................103
Figure 8.17 The average C_{10-13} concentration in influent and effluent of AZ and DAZ columns.........104
Figure 8.18 SEM micrograph of cell attachment on the surface of reactive material (a. sample from AZ column; b. sample from DAZ column) .........................................................................................109
Figure 8.19 SEM micrograph of cell morphology on the surface of DAZ (a. EPS from single bacteria; b. crystals produced from bacteria activity) .........................................................................................109
List of Tables

Chapter 2

Table 2.1 Previous research on modified zeolite and synthesized zeolite .................................................................14

Chapter 3

Table 3.1 Chemical reagents used in this thesis ..............................................................................................................21
Table 3.2 Operating conditions and sample introductions settings of ICP-OES ..................................................................24
Table 3.3 Reagents preparation and their mixture ration with sample in salicylate method ............................................26

Chapter 4

Table 4.1 Freundlich, Langmuir and Linear parameters for toluene adsorption on DPDSCI-zeolite at 20°C and 4°C ..............................................................................................................................................39
Table 4.2 Adsorption thermodynamics parameters for toluene adsorption on DPDSCI-zeolite under Langmuir isotherms at 20°C and 4°C ..................................................................................................................40

Chapter 5

Table 5.1 The flow parameters of axial dispersion test at both 20°C and 4°C .....................................................................53
Table 5.2 Summary of experimental conditions, breakthrough point (C/C_0=0.10) and saturation point (C/C_0=0.99) of column experiments, toluene adsorption capacity at both batch and column test after calculation ..............................................................................................................................................56

Chapter 7

Table 7.1 Summary of initial conditions, breakthrough point (C/C_0=0.10) and saturation point (C/C_0=0.99) of the column tests and toluene adsorption capacity at different conditions after calculation. .........................................................83

Chapter 8

Table 8.1 The total cation exchange amount of DAZ and AZ after 450PV ..........................................................................98
Table 8.2 The hydrocarbon components extracted from the surface of reactive materials in AZ and DAZ columns ............................................................................................................................................................107
Table 8.3 The ratio of hydrocarbon components for reactive materials in different columns (the blank cell means the at least one of the components was not detected) .................................................................................108
Chapter 1
Introduction
1.1 Research introduction

Geographically isolated from other continents, Antarctica is often described as a mysterious place. The appearance of permanent ice and long distance from public attention has mislead people that this continent is the last great wilderness untouched and undisturbed by humans. However, just like other continents, Antarctica has not escaped from the impact of local and global human activities and not all areas are set in idyllic beauty (Huiskes et al., 2006). Anthropogenic activities in exploring polar areas require energy, which is typically produced via the combustion of fuel. This has led to accidental oil spills, polluting the air, snow, waterways, soil and biota (Bargagli, 2008). Pollutants produced on other continents have also impacted on the remote polar environment, as some pesticides have been found in biotic and abiotic matrices in Antarctica and Southern Ocean (Bargagli, 2008).

The major contaminants presented at Casey Station, Australian Antarctic Territory (AAT) are heavy metals and petroleum hydrocarbons (Bargagli, 2008). These are primarily a result of the abandonment of the waste such as batteries and fuel drums in addition to on-going accidental spills (Aislabie et al., 2004; Tin et al., 2008). Previous studies have indicated that heavy metal contaminants of concern are predominantly copper, lead, zinc, iron, cadmium, antimony and arsenic, as well as localized hotspots of silver, while the major hydrocarbon pollutants are un-degraded Special Antarctica Blend diesel, Bergen distillate with lubrication oil and Aviation Turbine Kerosene (Mumford et al., 2013; Snape et al., 2001).

The typical characteristics of the contamination and complicated environmental conditions in the Antarctic (Filler et al., 2006) lends itself to the use of permeable reactive barriers (PRBs) to treat petroleum-contaminated and heavy-metal-laden sites in Antarctic (Mumford et al., 2013; Snape et al., 2001). A major task at this stage of development is to improve the performance and extend the longevity of reactive material used in PRBs (Erto et al., 2014; Santonastaso et al., 2015). One example PRB located at Casey Station contains: ammonium amended zeolite, granular activated carbon (GAC) and natural zeolite (Mumford et al., 2013). The ammonium amended zeolite is used to supply a controlled release of nutrient cations for biodegradation processes, the GAC is used to adsorb hydrocarbons, whilst natural zeolite is used to adsorb excess nutrients (Mumford et al., 2013). This allocation aims to combine hydrocarbon adsorption and biodegradation.

Even though GAC has been proven to have the best efficiency in removing hydrocarbon contaminants, it possesses poor mechanical strength and may fracture when undergoing freeze thaw cycling in Antarctic environments (Arora et al., 2011b; Hornig et al., 2008), and has been shown to
undergo irreversible hydrocarbon adsorption (Freidman et al., 2017a; Freidman et al., 2017b; Mumford et al., 2015), whereby captured hydrocarbons are not easily accessible to the microbial communities for biodegradation. Considering the drawbacks of GAC, it is necessary to develop an alternative and appropriate reactive material used in in-situ PRBs.

1.2 Research aims

Considering the requirements of reactive material applied in PRBs installed in cold regions and the extreme environmental conditions on site, it is necessary to develop a material that possesses hydrocarbon adsorption, nutrient release ability and provides a substrate for microbial growth. Additionally, it needs to possess a rigid structure that is resistant to extreme weather conditions experienced in polar climates. Furthermore, the adsorption of hydrocarbons should be reversible such that hydrocarbons adsorbed should, when appropriate, be accessible for contaminant degrading microorganisms.

1.3 Research objectives

This thesis builds on the previous work of Mumford (2008) (Mumford, 2008), Arora (2010&2011) (Arora et al., 2011b, 2011c), and Statham (2014) (Statham, 2014) who investigated the performance of reactive materials in the Permeable Reactive Barriers installed in Casey station, Antarctica and the methods to improve the efficiency of reactive material in cold temperatures. Based on the adsorption mechanisms of raw reactive materials and the factors that influence the biodegradation process, it is important to develop a composite material that possesses both hydrocarbon adsorption and biodegradation promotion capacity.

Based on a literature review in Chapter 2, diphenyldichlorosilane (DPDSCI) was selected as a coating to modify natural zeolite and ammonium amended zeolite. Its performance in hydrocarbon adsorption and nutrient release under various environmental conditions was investigated. Laboratory studies and filed test were conducted in this work.

The thesis structure is as follows:

Chapter 2

This chapter introduced the development of PRBs in temperate regions and its application at Casey station, Australian Antarctic Territory, Windmill Islands, East Antarctica for soil water and surface water remediation. Considering the extreme environmental conditions, the base material selected
was zeolite. Zeolites are a commercially available material often applied in PRBs. The material is described in detail, in addition to the modification methods that are sometimes used to alter its physical and chemical characteristics. Additionally, the environment factors that may impact the material behavior are discussed. To extend the operational life of the material, several regeneration methods are provided.

Chapter 3

This chapter detailed the modification procedure, the experimental design, the chemical and analytical methods used.

Chapter 4

This chapter presented the results of the batch study of DPDSCI modified zeolite, including the modification process, surface characterization, toluene adsorption tests at 20°C and 4°C and regeneration tests. To evaluate the performance of modified zeolite, the adsorption isotherms and thermodynamics were also investigated. The results indicated that surface modification increased the toluene adsorption capacity of the material in batch scale and water was sufficient for toluene removal.

Chapter 5

This chapter presented a column study of DPDSCI modified zeolite, including axial dispersion tests, toluene adsorption tests, regeneration tests and reactive transport modelling tests for 20°C and 4°C. To explore the adsorption mechanism, computer modelling (CXTFIT and MATLAB) was used to calculate the axial dispersion coefficient, maximum adsorption capacity and the adsorption curves. These models fit the data well and indicates the modification enhanced the adsorption ability of the zeolite.

Chapter 6

This chapter presented the results of the batch study of DPDSCI modified ammonium exchanged zeolite. It includes toluene adsorption, ammonium release, and regeneration tests at 20°C and 4°C. It proves the possibility of combining the hydrocarbon adsorption and biodegradation together with this reactive material.

Chapter 7
This chapter presented the results of column study of DPDSCI modified ammonium exchanged zeolite. Adsorption and regeneration tests at different influent concentrations and flow rates showed that this material possessed a stable toluene adsorption and nutrient release capacity over 3 regeneration cycles.

**Chapter 8**

This chapter presented the field study of DPDSCI modified ammonium exchanged zeolite. Small scale adsorption tests were conducted over 5 days at Casey station. The preliminary results indicated that the hydrocarbon adsorption was enhanced and the biodegradation was promoted on this material.

**Chapter 9**

This chapter presented a comprehensive summary of the laboratory and field tests and provided recommendations for the future research.
Chapter 2
Background and Literature review
2.1 Permeable reactive barriers (PRBs)

2.1.1 Development of PRBs

Worldwide there are many reports of serious groundwater pollution resulting from accidental spills, improper disposal of chemicals, poor agricultural practices and mining activities (Thiruvenkatachari et al., 2008). In attempts to clean-up contaminated water and restore contaminated sites back to near pristine conditions, scientists began to develop technologies such as the pump-and-treat method in the 1980s (Thiruvenkatachari et al., 2008). In the last decade, permeable reactive barriers (PRBs), filled with reactive materials to intercept and remove contamination from water has become one of the most promising remediation technologies (Obiri-Nyarko et al., 2014).

2.1.1.1 Installation of PRBs

There are two designs frequently used in field applications: Continuous or Funnel-and-Gate PRBs (Gavaskar, 1999). Continuous PRBs use a single reactive gate placed across the front of polluted plumes, whilst the funnel-and-gate system contains a permeable gate installed between two impermeable walls which lead the contaminated plume towards the reactive zone (Thiruvenkatachari et al., 2008). The specific installation depends on the hydrogeological characteristics of the contaminated site and the cost of reactive materials (Gavaskar, 1999).

2.1.1.2 Working mechanism

Mechanisms utilized by PRBs to remove contaminants from water may be characterized by the following categories (Roehl et al., 2005): 1) Physical or chemical adsorption of the contaminants within reactive zone; 2) Precipitation using chemical or microbial triggers; 3) Decomposition via chemical or biological means.

2.1.1.3 Advantages of PRBs

Compared with traditional pump-and-treat system for groundwater remediation, PRBs have the following advantages (Thiruvenkatachari et al., 2008): 1) The contaminants can be degraded or immobilized in situ hence potentially reducing the operating costs; 2) The potential for cross media pollution is decreased, as the contaminants do not leave the reactive zone of the PRBs; 3) Seldom continuous energy is required, rather periodic replacement or rejuvenation of reactive materials is necessary; 4) less technical and regulatory requirements as compared to more active processes such as pump and treat.

Although PRBs have a longer service life and lower operational cost, the long-term stability of
reactive materials, filter clogging, adsorption and diffusion variability, and channel formation are still the main limitations to PRBs technologies and require further development (Filler et al., 2006).

2.1.2 Application in Antarctica
2.1.2.1 Environmental conditions in Antarctica

Casey station is located on a coastal, ice-free rock and gravel peninsula in the Windmill Islands, East Antarctica (Fig.2.1) (Mumford et al., 2013). The ground is frozen in winter and during the summer period, surface soils thaw to the permafrost and a large volume of meltwater is produced (Deprez et al., 1999). The average wind speed is 18km/h in summer and 31km/h in winter (Deprez et al., 1999), whilst the mean temperature is +2.9°C and -19.2°C in the summer and winter respectively (Deprez et al., 1999). The average annual water-equivalent precipitation is 210 mm, and has only undergone slight variation over the past 14 years (from 150 mm to 350 mm) and the flow rate of meltwater in the MPH fuel spill site is around 13 to 26 m³/d in the summer season (Mumford et al., 2013). The maximum depth of soil is 1m and beneath this is the weathered rock/permafrost (Mumford et al., 2013). The annual temperature of Antarctic soil ranges from -15 to -40 °C dependent on the area and soil depth (Aislabie et al., 2004; Campbell et al., 1987) and the pH value of sediment is around 6-9 (Deprez et al., 1999). Due to the environmental conditions in Antarctica, the soil moisture content within the active layer is quite low and ranges from 0.5% by weight at the soil surface to 10% immediately above the permafrost layer (Campbell et al., 1994). There are also abundant biota living in this area, such as mosses, lichens, seals, penguins and a range of other birds (Tin et al., 2008).
2.1.2.2 Contaminants in Antarctica

The long-time abandonment of waste such as batteries, fuel drums, in addition to accidental spills or the discharge of liquid effluent (Aislabie et al., 2004; Tin et al., 2008), results in contaminants such as heavy metals and petroleum hydrocarbons existing at a number of Antarctic sites (Bargagli, 2008). Previous field investigations reported that heavy metal contaminants of concern are primarily copper, lead, zinc, iron, cadmium, antimony and arsenic, as well as localized hotspots of silver, while the major hydrocarbon pollutants are Special Antarctic Blend diesel, Bergen distillate with little amounts of lubrication oil and Aviation Turbine Kerosene (Mumford et al., 2013; Snape et al., 2001).

2.1.2.3 Development of PRBs in Antarctica

Hydrocarbon contaminant concentrations in soil or groundwater quickly accumulate and exceed the background levels and the Environmental Investigation Guideline Levels, largely due to the low metabolism rate of hydrocarbons in the Antarctic environmental conditions (Aislabie et al., 2004). Beginning in 1994, scientists have taken action to clean up these pollutants in Casey station (Deprez et al., 1999). After the post-clean-up action in Thala Valley during 1995-1996, Snape et al (Snape et
al., 2001) found this extraction and removal method caused unintended contaminant migration. Not all contaminants were removed successfully from the site and some concentrations were found to be even higher compared to before the extraction. Therefore, a more efficient technology, PRBs was introduced in this site for the restoration after the investigation of contaminant dispersal process and site specific conditions.

2.1.2.4 Installation of PRBs

Typically, installation of PRBs in cold regions such as Casey station is very different to those constructed in the temperate regions throughout the world due to the extremely low temperatures and seasonal freeze-thaw cycles in subsurface water (Mumford et al., 2013). One example PRB constructed at Casey Station is in a the Funnel-and-Gate design, possessing five modified cage pallets, along with heat trace, thick Styrofoam insulation, temperature sensors and stainless steel multi-ports (Mumford et al., 2013). The whole system was placed on a thick concrete pad so that the plumes can horizontally flow across each treatment cell (Mumford et al., 2013).

The reactive materials in this PRB have three functions: nutrient delivery, hydrocarbon sorption and removal of excess nutrient (Mumford et al., 2013). To achieve this, normally three zones are applied. The first zone is for nutrient delivery and ZeoPro™, ammonium Australian zeolite are used for this purpose. The second zone uses Granulated Activated Carbon (GAC) plus Raw St. Cloud zeolite, ZeoPro™ and sodium Australian zeolite to achieve hydrocarbon sorption process. The last zone contains sodium-activated clinoptilolite zeolite to remove the exceed nutrient cations.

2.1.2.5 Preliminary results of PRBs installed in Casey station

Through several years’ field trials, expected results were achieved (Mumford et al., 2015; Mumford et al., 2013; Mumford et al., 2014). Data showed that the wings of this PRB successfully guided water flow from the spill site area passing through the cages (Mumford et al., 2013). The nutrient delivery material successfully released the ammonia and phosphate into the melt water flowing to the hydrocarbon adsorption zone and the sodium pre-treated zeolite in the last zone captured the excess ammonium (Mumford et al., 2013). The migrating hydrocarbons were captured and degraded within the reactive zone, as the fuel contained within the reactive material was more degraded than the that remaining in the soil at the field site (Mumford et al., 2015). This indicates the degradation level in PRBs is gradually promoted. The overall performance of this PRB indicated it is an appropriate method to treat contaminants in cold regions, however there is a need to further investigation and improve their treatment efficiency and extend their long-term stability.
2.1.2.6 Future developments

Although this PRB has performed well, improvements have been identified. 4 years after installation, the GAC were found to have disintegrated when its particle size was compared to fresh media, whilst media sampled from other cages, including zeolite and sand, presented no significant difference (Mumford et al., 2014). This indicates that when considering material to be used in the hydrocarbon capture zone, there may be benefits forthcoming if a more robust material was used to ensure the reactive zone maintained permeability. Additionally, not all barrier cages achieved same level of contaminant degradation. Results indicated that the cage containing GAC and MaxBac as the major adsorption materials possessed the lowest treatment effectiveness even though the total microbial count was higher, whilst the other cells, such as zeopro, zeolite and sand, delivered lower nutrient concentrations but exhibited higher degradation rates (Mumford et al., 2015). The possible reason given was that the high nutrient levels and irreversible hydrocarbon adsorption by GAC promoted the total heterotroph numbers opposed to fuel degrading populations (Mumford et al., 2015).

Considering the limitations in the current application, it is necessary to develop an appropriate material suitable in this system. The required characteristics of this material should include good but reversible hydrocarbon adsorption ability, and stable nutrient release ability.

2.2 Contaminant sorption material

Through extensive investigation on the materials that widely applied for water remediation, activated carbon (Hashim et al., 2011; Obiri-Nyarko et al., 2014; Thiruvenkatachari et al., 2008), zeolites (clinoptilolite) (Hashim et al., 2011; Obiri-Nyarko et al., 2014; Thiruvenkatachari et al., 2008), iron sorbents (ZVI/pyrite) (Hashim et al., 2011; Obiri-Nyarko et al., 2014; Thiruvenkatachari et al., 2008), graphene (Wang et al., 2013), multi-walled carbon nanotubes (Liu et al., 2013; Xiao et al., 2014; Yu et al., 2014), diatomite (Aivalioti et al., 2012), present good adsorption capacity towards hydrocarbons and heavy metals.

Among these commercially used materials, coarse-grained and thereby free-draining materials are preferred, as in the previous trench tests, the water presented in trails contained with fine-grained materials would freeze rather than drain freely and that would not permeable (Snape et al., 2001). Additionally, as large quantities are required for use in typical PRB design, the material need to be cheap and easy accessible. An excellent material that meet these criteria are zeolites.
2.2.1 Zeolite

As a well-known inorganic adsorbent of aluminosilicate family, natural zeolite possesses a highly microporous surface and rigid three dimensional structure, containing alkali, and alkaline earth metals in its frameworks (Torabian et al., 2010). Due to its unique structural characteristics, natural zeolite is commonly used to capture cations through ion exchange, with limited applications for anions and organic adsorption (Mahabadi et al., 2007). The cation selectivity for clinoptilolite is as followed: Cs⁺ > Rb⁺ > K⁺ > NH₄⁺ > Ba²⁺ > Sr²⁺ > Na⁺ > Ca²⁺ > Fe³⁺ > Al³⁺ > Mg²⁺ > Li⁺ (Cooney et al., 1999).

Therefore, even though zeolites have a low affinity for hydrocarbon separation, they are often used a nutrient in promoting PRB performance (Mumford et al., 2013). Normally in contaminated sites, there are inadequate concentrations of available nutrients (especially N and P) to support the growth of degrading bacteria (Hatzinger et al., 2015). The application of ammonium amended zeolite can continuously provide sufficient nutrient concentrations for microorganism activities, which greatly enhance the cultivation of degrading bacteria, and thereby indirectly extend the longevity of PRB as the PRB life is not limited by material saturation (Mumford et al., 2015).

Though zeolite possesses many merits, further improvement in its adsorption of hydrocarbons would be beneficial. To achieve this, surface modification on natural zeolite is introduced.

2.2.2 Coating material

To enhance the adsorption capacity of natural zeolite towards hydrocarbons, two conventional methods are typically used. Cationic surfactant and chlorosilane modifications, these are introduced here.

2.2.2.1 Cationic surfactants

Like many other natural materials, the permanent negative charges on the surface of zeolite would easily balance with the exchangeable cations, resulting high cation exchange capacity but poor anion or organic attraction (Wang et al., 2010). Therefore, to improve the hydrophobicity of the zeolite surface, cationic surfactants, such as hexadecyltrimethylammonium bromide (HDTMA), cetylpyridinium bromide (CPB), have been used (Obiri-Nyarko et al., 2014).

The main functional groups in these surfactants are hydrophilic and positively charged head groups and hydrophobic tails (Chutia et al., 2009; Leyva-Ramos et al., 2008; Wang et al., 2010; Zeng et al., 2010). After the modification process, these functional groups are attached to the external surface of zeolite via electrostatic forces (Haggerty et al., 1994; Wang et al., 2010). As a result, the charge of the
“new” external zeolite surface is reduced or reversed, leading to anions or non-polar organics being adsorbed on this surfactant coating (Leyva-Ramos et al., 2008; Wang et al., 2010).

Previous studies have confirmed the performance of surfactant modified zeolite in removing anions such as chromate, arsenate, antimonite, phosphate and nitrate (Chutia et al., 2009; Hrenovic et al., 2008; Leyva-Ramos et al., 2008; Schick et al., 2010; Wingenfelder et al., 2006). As for the removal of hydrocarbons, good results have been obtained when compared to natural zeolite (Bowman, 2003; Ghiaci et al., 2004; Kuleyin, 2007; Li et al., 2000; Michael Ranck et al., 2005). The summary of previous research is presented in Table 2.1.
<table>
<thead>
<tr>
<th>Base material</th>
<th>Modification material</th>
<th>Target</th>
<th>Linear $K_d$ (L/kg)</th>
<th>Langmuir $q_m$ (mg/g)</th>
<th>Freundlich $K_f$ (mg$^{1-n}$g$^{-1}$L$^n$)</th>
<th>Calculated capacity (Using Langmuir parameter $q_m$) (µmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinoptilite</td>
<td>Diphenyldichlorosilane (DPDSCI)</td>
<td>Toluene</td>
<td>0.02</td>
<td>5.16</td>
<td></td>
<td>(Huttenloch et al., 2001)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Xylene</td>
<td>0.05</td>
<td>8.90</td>
<td></td>
<td>(Huttenloch et al., 2001)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Naphthalene</td>
<td>0.15</td>
<td>22.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Octadecyltrichlorosilane (C18)</td>
<td>Naphthalene</td>
<td>17.30</td>
<td></td>
<td></td>
<td>(Northcott et al., 2010a)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Xylene</td>
<td>9.70</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hexadecyltrimethylammonium (HDTMA)</td>
<td>Benzene</td>
<td>79.21</td>
<td>16.61</td>
<td>0.39</td>
<td>212.95</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
<td>43.25</td>
<td>11.35</td>
<td>0.17</td>
<td>120.74</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aniline</td>
<td>0.13</td>
<td></td>
<td>1.25</td>
<td>(Ghiaci et al., 2004)</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Nitrobenzene</td>
<td>0.13</td>
<td></td>
<td>0.06</td>
<td>98.86</td>
<td>(Kuleyin, 2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chlorophenol</td>
<td>12.71</td>
<td>0.06</td>
<td></td>
<td>(Kuleyin, 2007)</td>
<td>(Kuleyin, 2007)</td>
</tr>
<tr>
<td></td>
<td>n-Cetylpyridinium bromide (CPB)</td>
<td>Benzene</td>
<td>103.4</td>
<td>23.07</td>
<td>0.36</td>
<td>295.77</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
<td>47.41</td>
<td>11.88</td>
<td>0.22</td>
<td>126.38</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Benzyltetradecyl ammonium chloride (BDTDA)</td>
<td>Phenol</td>
<td>1.30</td>
<td>0.05</td>
<td></td>
<td>13.81</td>
<td>(Kuleyin, 2007)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Chlorophenol</td>
<td>6.41</td>
<td>0.77</td>
<td></td>
<td>49.86</td>
<td>(Kuleyin, 2007)</td>
</tr>
<tr>
<td></td>
<td>Stearyldimethylbenzylammonium chloride (SDBAC)</td>
<td>Atrazine</td>
<td>0.43</td>
<td></td>
<td>2.00</td>
<td>(Lemic et al., 2006)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lindane</td>
<td>0.99</td>
<td></td>
<td>3.40</td>
<td>(Lemic et al., 2006)</td>
<td>(Lemic et al., 2006)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Diazinone</td>
<td>1.35</td>
<td></td>
<td>4.40</td>
<td>(Lemic et al., 2006)</td>
<td>(Lemic et al., 2006)</td>
</tr>
<tr>
<td></td>
<td>Octadecyldimethyl benzyl ammonium (ODMBA)</td>
<td>Ochratoxin A</td>
<td>3.41</td>
<td></td>
<td>8.45</td>
<td>(Daković et al., 2003)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Fumonisin B$_1$</td>
<td>7.35</td>
<td></td>
<td>10.18</td>
<td>(Daković et al., 2007)</td>
<td>(Daković et al., 2007)</td>
</tr>
<tr>
<td>Synthetic zeolite</td>
<td>Octylmethyldichlorosilane</td>
<td>Toluene</td>
<td>215.60</td>
<td>2340</td>
<td></td>
<td>(Song et al., 2005)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hexadecyltrimethylammonium (HDTMA)</td>
<td>Benzene</td>
<td>48.53</td>
<td>7.74</td>
<td>0.40</td>
<td>99.26</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Toluene</td>
<td>48.66</td>
<td>9.33</td>
<td>0.39</td>
<td>101.43</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
<td>29.02</td>
<td>7.42</td>
<td>0.15</td>
<td>78.96</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>n-Cetylpyridinium bromide (CPB)</td>
<td>Benzene</td>
<td>82.46</td>
<td>14.95</td>
<td>0.39</td>
<td>191.67</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Toluene</td>
<td>80.51</td>
<td>16.44</td>
<td>0.48</td>
<td>178.70</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Phenol</td>
<td>34.23</td>
<td>9.425</td>
<td>0.14</td>
<td>100.27</td>
<td>(Ghiaci et al., 2004)</td>
</tr>
<tr>
<td></td>
<td>Hexadecyltrimethylammonium bromide (CTAB)</td>
<td>TPH</td>
<td>92.30%</td>
<td></td>
<td></td>
<td>(Saremnia et al., 2016)</td>
<td></td>
</tr>
</tbody>
</table>
Despite this promising performance, cationic surfactants like HDTMA or CPB still face many challenges, such as the loss of the surface coating after rapid sorption/regeneration cycles and the disintegration of zeolite particle itself (Michael Ranck et al., 2005; Wang et al., 2010). The potential desorption of HDTMA from zeolite surface would result in the potential formation of toxic unbound HDTMA molecules in aqueous solution, which has been reported to be toxic to bacteria (Hrenovic et al., 2008). As these drawbacks would reduce the long-term stability of reactive material, therefore, this modification is not considered in this thesis.

2.2.2.2 Chlorosilane

To change the surface characteristics of mineral based adsorption materials from hydrophilic to lipophilic, the silanol groups on the mineral surface may be altered via a series of reactions. Among these, modification by chlorosilane is frequently applied.

Chlorosilane is a reactive chemical compound with up to three nonpolar aliphatic or aromatic groups which can be grafted covalently to the silanol groups on the surface of mineral adsorbents (Huttenloch et al., 2001). This treatment will provide a stable chemical linkage between chlorosilane and the mineral, which greatly reduces the potential loss of the hydrophobic coating in later applications as compared to the modification with cationic surfactants (Northcott et al., 2010a).

The basic silanization process for the surface modification of zeolite is shown in Figure 2.2. In the presence of pyridine and elevated temperatures, the chlorine on the chlorosilane compound has a high affinity to the hydrogen of hydroxyl groups on the zeolite surface. This results in the combination of H$^+$ and Cl$^-$ from the two compounds and the formation of a stable Si-O-Si-C bond, leading to chlorosilane being covalently grafted to the zeolite surface. The more hydroxyl groups on the zeolite surface, the more chlorosilane molecules with phenyl groups that may be attached, leading to a better adsorption capacity towards organic contaminants.

![Figure 2.2 Reaction process for the surface modification of silanol groups on zeolite with chlorosilane](image-url)
Previous researchers have shown that the octadecyltrichlorosilane modified natural zeolite possesses a high capacity for the removal of dissolved o-xylene and naphthalene from water (Northcott et al., 2010a). In addition to the use of zeolites as base materials, the grafting of chlorosilane onto GAC to enhance 2,4-dichlorophenol removal has also been investigated and better adsorption performance was obtained (Yang et al., 2010).

Key to the use of chlorosilane modified materials is the selection of the most efficient chlorosilane to enhance sorption of specific components. In previous work, chlorosilane components containing phenyl headgroups, such as diphenylchlorosilane have exhibited superior affinity for aromatic compounds when compared to other chlorosilanes, i.e. trimethylchlorosilane, tert-butyl(dimethyl)chlorosilane, dimethyloctadecylchlorosilane, and therefore can be viewed as potential coating material to enhance the hydrocarbon capture ability of natural zeolite (Huttenloch et al., 2001). Meanwhile, there are few studies investigating the potential desorption of chlorosilane from adsorption materials and its toxicity to the environment. Further research on this topic is required.

2.3 Factors that influence the adsorption ability

2.3.1 pH

Previous studies have shown that suitable pH values for natural zeolite to remove metal components is between 3 and 11 (Misaelides et al., 1995), meanwhile this range is also suitable for the behavior of surface modified zeolite (Li et al., 1998; Northcott et al., 2010a). PH has not been observed to fluctuate dramatically in soil and groundwaters in cold regions but remains stable at around 9 (Freidman, 2016). Therefore, it is anticipated that the performance of the modified zeolite would not be impacted by the pH of environment if it was applied on site.

2.3.2 Temperature

As the temperature in temperate regions does not change dramatically, thereby it would not take into the consideration that might impact the performance of reactive material. However, previous studies (Arora et al., 2011a; Arora et al., 2011b, 2011c; Hornig et al., 2008; Woinarski et al., 2003) have shown that extremely cold temperatures characteristic of Antarctica may influence the capacity of materials to remove contaminants and the reaction kinetics of adsorbents in PRBs, when compared with their performance in normal temperature. In column testing (Hornig et al., 2008), the adsorption capacity of granular active carbon towards hydrocarbons (naphthalene, o-xylene,
toluene) is also reduced when the temperature drops from 20°C to 4°C. Therefore, temperature should be considered when investigating the performance of the materials in batch and column tests.

2.3.3 Groundwater constituents

If there are abundant dissolved substances in the groundwater besides the target contaminants, the efficiency of reactive materials in PRBs may be influenced (Obiri-Nyarko et al., 2014; Woinarski et al., 2003). The presence of inorganic species, such as Ca^{2+}, Mg^{2+}, SO_{4}^{2-} and CO_{3}^{2-} in the aquifer may compete with the pollutants for the binding sites on zeolite whilst the natural organic matter may take adsorption sites on activated carbon or modified zeolite (Misaelides, 2011; Wang et al., 2010). A naphthalene adsorption test (Hornig et al., 2008) has shown that ionic strength only presents only a small influence on the naphthalene adsorption capacity of GAC and surfactant modified zeolite when exposed to a solution containing 1.0M CaCl_{2} (Li et al., 1998). Some inorganic (Na’, K’) ions can be beneficial to the degradation performance on the nutrient release zeolite (Freidman et al., 2016b). Overall, for the modified zeolite used in this thesis, the influence of simple ions and ionic strength is investigated.

2.3.4 Flow rates

The hydrology of contaminated sites changes continuously, and as such the flow rate of groundwater is not always stable (Farhadian et al., 2008; Meckenstock et al., 2015). Previous works have shown that flowrates influence the adsorption performance of sorbents in column systems (Richard et al., 2010; Schick et al., 2011; Wang et al., 2011; Woinarski et al., 2006). Hence in this thesis, the influence of flow rates is taken into consideration when conducting column studies.

2.3.5 Other factors

Besides the environmental factors mentioned, different surface modifications may also influence the surface characteristics of adsorbents and thereby affect the adsorption behavior. For example, the inner pore structure of mineral adsorption materials might be filled or blocked after modification by coating materials, influencing the contaminant adsorption efficiency (Lu et al., 2008; Mallard et al., 2015; Northcott et al., 2007; Yu et al., 2014). Meanwhile the coating materials might be lost or damaged during application, which would also influence the performance of reactive materials (Michael Ranck et al., 2005; Wang et al., 2010). Therefore, the influence of surface coating towards adsorption behavior and the potential loss of surface coating during the test are investigated in this work.
2.4 Regeneration methods

To extend the life of PRBs, the ability to regenerate the reactive material is an important consideration (Altare et al., 2007). Typically, there are two types of methods that may be implemented to regenerate the reactive material: physicochemical and biological methods (Altare et al., 2007; Bowman, 2003; Misaelides, 2011; Nooten et al., 2010).

Previous studies have shown that octadecyltrichlorosilane modified zeolite can be used, regenerated and reused at least three times through washing with distilled water without significant reduction in hydrocarbon adsorption efficiency (Northcott et al., 2010a). Air sparging, wet-air oxidation and electrochemical methods have been proven efficient in removing pollutants from surfactant modified zeolite, activated carbon, clay in columns and PRB systems (Altare et al., 2007; Hansen et al., 1994; Yeung et al., 2011). The main advantages of using physical treatment methods are that they are efficient and more easily controlled as compared to biological systems. The main disadvantages are that they are generally more expensive and require extra manual work (Altare et al., 2007).

To reduce the cost of regeneration processes, biological methods are being developed (Nooten et al., 2010). These methods are typically cheaper, as bacteria can colonize on the surface of some sorbents, without significant effort or intervention (Misaelides, 2011; Nooten et al., 2010). However, there are limitations: 1) due to the poor environmental conditions in contaminated sites (Meckenstock et al., 2015), the number of degrading populations is generally low initially and there may be a considerable lag time, hence the regeneration efficiency at the early stages would be low (Misaelides, 2011); 2) inadequate nutrient or food sources may be present in the contaminated site (Farhadian et al., 2008), and therefore the microorganisms may exhibit low activity, or even a dormant status (Kieft et al., 1997) and regeneration efficiency may not be improved in short-term.

To maintain a net positive benefit of physicochemical and biological methods, there may be benefits in combining these two methods together, which is the focus of this thesis.

2.5 Research Required

This chapter reviews the development of PRBs in temperate and cold climates. The general mechanism, advantages and disadvantages of PRBs are introduced. For the PRBs installed at the MPH fuel spill site at Casey station, the extreme environmental conditions, target contaminants, preliminary installation, achievements and further development directions are presented.

Materials commonly used in water remediation are reviewed. Upon consideration of the factors
impacting on PRB performance, including regeneration, natural zeolite conditioned into ammonium form and easily modified by chlorosilane is selected for further investigation in batch and column trials.

The coating material, chlorosilane (diphenyldichlorosilane) was selected to modify natural zeolite. It has been shown that the two phenyl groups of this molecule have a high affinity for aromatic hydrocarbons. Additionally, the link between the coating and base material is a covalent bond and as such has an increased stability as compared to the electrostatic bond that cationic surfactants are attached by.

The environmental elements that may impact the performance of sorbents are also reviewed. Among them, temperature, flow rates, solution ionic strength and surface modification sequence are identified as important and are further investigated in this thesis.

Overall, the performance of modified zeolite and modified ammonium exchanged zeolite is assessed in both batch and column trials under different conditions and the behavior of modified ammonium exchanged zeolite is determined in field tests.
Chapter 3
Experimental materials and methods
3.1 Chemical reagents

Except where otherwise stated, the chemicals used were all analytical grade and used without further purification. Details regarding the chemicals used are listed in Table 3.1. All experimental and standard solutions were prepared with Milli-Q water (Millipore, resistivity > 18 MΩ/cm). Distilled water (Millipore, resistivity > 15 MQ/cm) was used for all cleaning procedures.

<table>
<thead>
<tr>
<th>Chemical reagents used in this thesis</th>
<th>Chemical</th>
<th>Formula</th>
<th>Supplier</th>
<th>Purity</th>
<th>Use</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>CH₃CN</td>
<td>Merck</td>
<td>99.9%</td>
<td>HPLC carrier</td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>(CH₃)₂CO</td>
<td>Chem-Supply</td>
<td>99.8%</td>
<td>Material washing</td>
<td></td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>NH₄Cl</td>
<td>Chem-Supply</td>
<td>99.5%</td>
<td>Conditioning of natural zeolite</td>
<td></td>
</tr>
<tr>
<td>Diphenyldichlorosilane (DPDSCI)</td>
<td>(C₆H₅)₂SiCl₂</td>
<td>Sigma-Aldrich</td>
<td>97.0%</td>
<td>Reagent in surface modification of natural zeolite</td>
<td></td>
</tr>
<tr>
<td>Electrical conductivity buffer</td>
<td>-</td>
<td>Crison</td>
<td>-</td>
<td>EC probe calibration</td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>C₂H₅OH</td>
<td>Chem-Supply</td>
<td>99.5%</td>
<td>Cleaning</td>
<td></td>
</tr>
<tr>
<td>Glutaraldehyde</td>
<td>C₅H₈O₂</td>
<td>Merck</td>
<td>25%</td>
<td>Microscopy</td>
<td></td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>Chem-Supply</td>
<td>99.7%</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Potassium chloride</td>
<td>KCl</td>
<td>Chem-Supply</td>
<td>99.0%</td>
<td>Reagent in ion exchange test</td>
<td></td>
</tr>
<tr>
<td>Potassium sodium tartrate</td>
<td>C₆H₁₀KNa·4H₂O</td>
<td>Chem-Supply</td>
<td>99.0%</td>
<td>Analysis of ammonium</td>
<td></td>
</tr>
<tr>
<td>pH buffer</td>
<td>pH 4,7,10</td>
<td>Chem-Supply</td>
<td>-</td>
<td>pH probe calibration</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>C₅H₅N</td>
<td>Ajax</td>
<td>99.0%</td>
<td>Organic solvent and buffer for surface modification of natural zeolite</td>
<td></td>
</tr>
<tr>
<td>Sodium citrate</td>
<td>C₆H₁₀Na₂·2H₂O</td>
<td>VWR Chemicals</td>
<td>100%</td>
<td>Analysis of ammonium</td>
<td></td>
</tr>
<tr>
<td>Sodium Chloride</td>
<td>NaCl</td>
<td>Chem-Supply</td>
<td>99.7%</td>
<td>Reagent in axial dispersion test</td>
<td></td>
</tr>
<tr>
<td>Sodium dichlorocyanurate</td>
<td>C₆H₅O₂Cl₂Na·2H₂O</td>
<td>Sigma-Aldrich</td>
<td>98.0%</td>
<td>Analysis of ammonium</td>
<td></td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Chem-Supply</td>
<td>97.0%</td>
<td>pH adjustment</td>
<td></td>
</tr>
<tr>
<td>Sodium nitroprusside</td>
<td>Na₂[Fe(CN)₅NO]-2H₂O</td>
<td>Sigma-Aldrich</td>
<td>99.0%</td>
<td>Analysis of ammonium</td>
<td></td>
</tr>
<tr>
<td>Sodium salicylate</td>
<td>C₇H₅NaO₃</td>
<td>Sigma-Aldrich</td>
<td>99.5%</td>
<td>Analysis of ammonium</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>Merck</td>
<td>99.9%</td>
<td>Hydrocarbon source</td>
<td></td>
</tr>
</tbody>
</table>

3.2 Experimental materials

The raw material used in this thesis was natural zeolite (Castle Mountain Zeolite, Quirindi, N.S.W., Australia)(Mumford et al., 2013). Before use, it was sieved with an 8×16 US mesh sieve (2.36-0.85mm) and BET surface area measured (18.01 m²/g) (Freidman et al., 2016b). Energy Dispersive Spectroscopy (EDS) Microanalysis of the natural zeolite indicated that it had the following
composition (% atomic weight): O-66.99; Al-6.99; Si-24.85; Fe-0.16; Na-0.8; K-0.11; Ca-0.21; N-0.00; Mg-0.02; S-0.00; P-0.01 (Freidman et al., 2016b).

Before surface modification, the natural zeolite was washed with 20 (w/w) % hydrochloric acid in a batch for 24 hours to remove impurities. Following this, it was rinsed with distilled water until the effluent reached a pH of 5. The resulting material was dried at 105°C for 24 hours.

The ammonium exchanged zeolite was prepared by contacting approximately 50g of Milli-Q water washed natural zeolite with 2mol/L ammonium chloride solution in a glass conical flask and shaken at 100rpm for 120h. The ammonium chloride solution was replaced every 24 hours to ensure the zeolite was converted into a near homo-ionic state (Woinarski et al., 2003). After that, the material was washed by distilled water and dried at 105°C for 24 hours.

In the column tests, inert ballotini glass beads (Potters Industries Inc.) were used to hold the reactive material in place. Before use in the glass columns, the beads were sieved with a 25×35 US mesh sieve and washed with distilled water.

3.3 Hydrocarbon source

3.3.1 Laboratory tests (Toluene)

BTEX (Benzene, Toluene, Ethylbenzene and Xylene) are typical aromatic hydrocarbons commonly found in contaminated sites. Therefore, they are often used in laboratory experiments to represent fuel components (Hornig et al., 2008). In this thesis, toluene was selected from BTEX to evaluate the hydrocarbon sorption properties of the materials developed. This selection was based on its relatively high water solubility (515mg/L), and therefore its ability to provide wide concentration range for experimental analysis and model development (Hornig et al., 2008).

3.3.2 Field tests (Total Petroleum Hydrocarbons)

In the field application, contaminated water was pumped from a contaminated site and used as influent for the experiments. According to previous investigations (Mumford et al., 2013; Snape et al., 2001), this water may contain un-degraded Special Antarctica Blend (SAB) diesel, Bergen distillate, lubrication oil and Aviation Turbine Kerosene (ATK). The specific carbon numbers of interest are listed in Figure 3.1. As a variety of petroleum products are likely present, Total Petroleum Hydrocarbons (TPH) will be used to evaluate the sum of hydrocarbon contaminants on site.
3.4 Analytical techniques

3.4.1 Electrical Conductivity

Electrical Conductivity (EC) of liquid samples were measured using an EC (Crison GLP 31) probe. Before use, the probe was calibrated at 0.147 mS/cm, 1.413 mS/cm and 12.88 mS/cm using EC standard solutions.

3.4.2 Fourier Transform-Infrared Spectroscopy

Fourier transform-infrared spectroscopy (FT-IR) was used to identify the reactive functional groups on the surface of materials. This work was conducted by Attenuated Total Reflectance-Fourier Transform Infrared Spectroscopy (ATR-FTIR) (Frontier™, Perkin Elmer Inc., USA). Before analysis, the material was milled into smaller particle size with a mortar and pestle. The sample to be analysed...
was placed on a crystal plate and secured by an electronic force gauge. The analysis range was 500-4000 cm\(^{-1}\) in absorbance mode.

3.4.3 High Performance Liquid Chromatography

High performance liquid chromatography (HPLC) (LC-20A prominence, Shimadzu & Agilent 1200) was used to measure concentrations of toluene in solution. This analysis was performed using a C18 column (Agilent, 3.5µm size, 4.6x75mm) under the following conditions: an acetonitrile and water mixture with a ratio of 60:40 v/v at a flow rate of 0.8ml/min as the mobile phase; sample injection volume 50µL, isocratic elution mode, 10 min run time. Detection was performed at a wavelength of 220nm and 254nm. The autosampler was conditioned at 10°C to avoid sample evaporation, and the column temperature was 30°C. Toluene concentration was evaluated against standards prepared over the range between 20 to 100 mg/L (Appendix 3.1 and Appendix 3.2). Toluene peak retention time is observed at 3.3-3.4 min.

3.4.4 Inductively Coupled Plasma-Optical Emission Spectrometry

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) (Varian 720-ES, Varian Inc.) was used to detect the concentration of potassium (K\(^+\)) in the solution. The operating conditions for the analysis is in Table 3.2. A calibration curve was prepared for each sample run (Appendix 3.3).

<table>
<thead>
<tr>
<th>Conditions used</th>
<th>Sample introduction settings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power (kW)</td>
<td>1.20</td>
</tr>
<tr>
<td>Plasma flow (L/min)</td>
<td>15.0</td>
</tr>
<tr>
<td>Auxiliary flow (L/min)</td>
<td>2.25</td>
</tr>
<tr>
<td>Nebulizer flow (L/min)</td>
<td>0.75</td>
</tr>
<tr>
<td>Replicate read time (s)</td>
<td>1.00</td>
</tr>
<tr>
<td>Instr stabilization delay (s)</td>
<td>15</td>
</tr>
</tbody>
</table>

3.4.5 pH

The pH of the liquid samples was measured using a pH probe and a meter (Eutech Instruments CyberScan pH 11). Before use, the probe was calibrated at pH 4, 7 and 10 using pH standard solutions.
3.4.6 Scanning Electron Microscopy

Environmental Scanning Electron Microscopy (ESEM) (QUANTA CRYO SEM, FEI Company, USA) was used to investigate the surface morphology of the solid samples. Samples obtained from the field tests required pre-treatment due to the potential presence of biofilm on the surface of the materials. These samples were fixed in 2.5% glutaraldehyde in 1M phosphate buffer solution for 4 hours, then dehydrated in 10, 30, 50, 70, 90, 100, 100, 100% acetone for 30 minutes at each concentration. The repeated dehydration at 100% acetone was to ensure the complete removal of water from the samples. The dehydrated samples were then dried in a fumehood and sputter coated with gold (Dynavac SC100) for 2.5 minutes before imaging.

3.4.7 Sieving

The 8×16 US (2.36-0.85mm) mesh sieves (Endecotts) were used for sieving to ensure all materials had similar particle size.

3.4.8 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) measurements were performed using a TGA/SDTA851e (Mettler Toledo) to determine the change in mass of the materials with temperature. This information was used to interpret the physical and chemical properties of the samples. In this evaluation, the starting temperature was 25°C and samples were heated in an oxygen atmosphere until a temperature of 900°C was reached at a heating rate of 10°C /min.

3.4.9 Ultraviolet-Visible Spectroscopy

An Ultraviolet Visible (UV-Vis) Spectrophotometer (Cary 3000, Agilent) was used to detect the concentration of total ammonium (total NH₄⁺) in solution. The salicylate method was used and followed a previous study (Laskov et al., 2007). Before analysis, a number of reagents needed to be prepared. The composition of the reagents and their mixing ratios are shown in Table 3.3. The total NH₄⁺ was detected at a wavelength of 660nm and appropriate baseline correction and calibration standards (Appendix 3.4) were used to ensure result accuracy.
### Table 3.3 Reagents preparation and their mixture ration with sample in salicylate method.

<table>
<thead>
<tr>
<th>Step</th>
<th>Reagent A</th>
<th>Reagent B</th>
<th>Reagent C</th>
<th>Reagent D</th>
<th>Reagent E</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>Dissolve 8.25 g of C₆H₄O₆KNa·4H₂O in 125 ml Milli-Q water.</td>
<td>Dissolve 2.5 g of NaOH in 50 ml Milli-Q water.</td>
<td>Dissolve 0.05 g of Na₂[Fe(CN)₅NO]·2H₂O in 50 ml Milli-Q water.</td>
<td>Dissolve 0.4 g of C₃N₃O₃Cl₂Na·2H₂O in 100 ml Milli-Q water.</td>
<td>2:1 v/v mixture of Reagent B and C. Stable for 4 hours.</td>
</tr>
<tr>
<td>Step 2</td>
<td>Add 6 g of C₆H₅O₇Na₃·2H₂O and adjust volume to 250 ml with Milli-Q water.</td>
<td>Add 8 g of C₆H₅NaO₃ and adjust volume to 100 ml with Milli-Q water.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step 3</td>
<td>Adjust pH of the solution (~8.4) to 5.2 using HCl.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Step 4</td>
<td>Mix Reagent A (2mL) + Reagent E (1.2mL) + Sample (2mL) + Reagent D (0.8mL) and after 60 minutes of reaction time, the blue-green indophenol dye can be measured by UV-Vis.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### 3.5 Experimental design

#### 3.5.1 Surface modification by DPDSCI

Prior to surface modification, the natural zeolite was washed with 20 (w/w) % hydrochloric acid in a batch for 24 h to remove impurities and then rinsed by distilled water until the effluent reached a pH of 5. The resulting material was dried at 105 °C for 24 h.

Ten grams of dried zeolite was weighed and placed into a two-necked flask with 40 mL pyridine and 92 mmol diphenyldichlorosilane (DPDSCI). The mixed solution was heated under nitrogen atmosphere at 80 °C for 48 h in a temperature controlled heating bath. This design ensured that the reaction was conducted in an anhydrous condition, preventing the hydrolysis of chlorosilane. Following this, the modified material was filtered and washed with acetone and distilled water, and subsequently dried at 105 °C.

#### 3.5.2 Batch equilibrium study

Batch equilibrium experiments were conducted in a series of 45ml glass vials and capped with a Teflon lined septa cap (Figure 3.2). The same amount of reactive material (0.3g) and 40ml of varying
concentrations of toluene in Milli-Q water were added to each vial. A blank was also used to ensure the initial concentrations were accurate. Then these vials were placed into an incubator (TLM-590, Thermoline Scientific) and shaken at 120 rpm at temperature ranging from 4°C to 20°C and times from 24h to 72h. The temperature and experimental time were different in different tests. Following shaking, solution was removed using glass pipette and analysed. Batch tests were conducted duplicate and sampled triplicate.

*Figure 3.2* The 45ml glass vials used in batch test. It contained certain amount of reactive material and 40ml of solution.

3.5.3 Batch regeneration study

To determine whether solvent or water can wash the toluene from the surface of DPDSCI coated zeolite, methanol, acetone and hot water were used to wash the used material for 6 hours as a batch. Following washing, the excess solvent was removed by drying in a vacuum oven at 60 °C for 24 h. The material collected after single adsorption test and first washing cycle was termed 1st regenerated. After conducting the adsorption test on the 1st regenerated sample, the material was collected again and the washing cycle repeated. This material was called 2nd regenerated. The 1st and 2nd regenerated sample and fresh sample (0.5g) were used in the toluene adsorption tests, with 1mmol/L toluene solution and under 20 °C for 24 h. The adsorption test was conducted in the same manner as that described in Section 3.5.2.
To examine whether the DPDSCI coated ammonium exchanged zeolite had the ability to continuously adsorb hydrocarbons and release nutrients, the used material was collected after equilibrium tests and washed by 2mol/L ammonium chloride for 120h at 120rpm and 20°C conditions. The conditioning procedure was the same as that described in Section 3.2. The material after one washing cycle was termed 1st regenerated. Following regeneration, this material then underwent batch equilibrium test using 1mol/L KCl and 1mmol/L toluene solution. Following this, the material underwent the same washing cycle and was termed 2nd regenerated. This was repeated once more and final material was termed 3rd regenerated.

3.5.4 Column study

The column tests were conducted in a vertical glass column with a height and inner diameter of 129 mm and 28 mm respectively (Figure 3.3). The wall thickness of glass column was 2mm. The end of the column was capped with an acrylic plastic cap and inside this cap there were several Teflon pads to protect the glass column. Tygon tube (Masterflex Tygon Fuel & Lubricant tubing (F-4040-A), L/S 14, 50 ft) was used at the bottom and top of the system to deliver the influent and effluent. Between the tube and the material, there was a Nylon mesh (200μm) to avoid the material blocking the tube. Influent was introduced to this system in an up flow direction at different pump speeds depending on the flowrate required. The effluent was collected at the end of column for analysis. To ensure the temperature was consistent, the tests were conducted in an incubator (TLM-590, Thermoline Scientific) at temperatures ranging from 4°C to 20°C. The volume of adsorbents in adsorption test and reactive transport modelling test were approximately 20mL and 80mL, respectively.
3.5.5 Column regeneration study

Regeneration tests were conducted to detect whether the material could be used multiple times without significant decrease in hydrocarbon adsorption ability. After the column was saturated with toluene, the influent was replaced with water until all the toluene was ejected. The column after the first washing cycle was termed 1st regenerated. This column was then saturated again with toluene, and subsequently washed and termed 2nd regenerated. This was repeated once more and the final material termed 3rd regenerated. Tests were conducted at both 4°C and 20°C and sampled in triplicate.
Chapter 4
Batch studies of DPDSCI coated zeolite
4.1 Introduction

Zeolite was modified by diphenyldichlorosilane (DPDSCI) and characterized for its potential application in PRBs tasked with fuel removal. Characterization was completed to compare the material structure before and after the modification process. Batch adsorption tests were performed at both 20°C and 4°C to detect hydrocarbon capture performance at various temperatures and regeneration experiments were conducted to determine material longevity. Adsorption isotherms and thermodynamics were studied to determine the mechanism of hydrocarbon capture.

4.2 Materials and Methods

4.2.1 Natural zeolite and its surface modification process

The raw zeolite material used was natural clinoptilolite zeolite. It was modified by DPDSCI following the method described in Section 3.5.1.

4.2.2 Surface characterization

The DPDSCI modified and unamended zeolite were analysed using Fourier Transform-Infrared Spectroscopy (FT-IR) and Thermogravimetric Analysis (TGA) to determine whether the surface modification was successful. These techniques were introduced in Section 3.4.

4.2.3 Equilibrium tests

Batch equilibrium experiments were conducted following the method described in Section 3.5.2. 300mg of unamended zeolite or DPDSCI coated zeolite and 40 mL of toluene solution was added to each vial. The toluene solution was varied from 0.1 mmol/L to 1.5 mmol/L. These tests were conducted under 20 °C and 4 °C for 24 hours. Preliminary studies confirmed that 24 h was sufficient for equilibrium to be achieved by both zeolite materials at temperate and low temperature conditions (Hornig et al., 2008; Li et al., 2000; Li et al., 1998). After shaking, 4 mL of solution was taken and the concentration of toluene was determined by HPLC. Each test was conducted in duplicate and sampled in triplicate.

4.2.4 Regeneration tests

A regeneration test was conducted to detect whether the material could be used multiple times without significant decrease in hydrocarbon adsorption ability. The detailed procedure was discussed in Section 3.5.3.
4.3 Modelling

4.3.1 Adsorption isotherms

The Langmuir, Freundlich and Linear isotherms were used to analyse the toluene adsorption behaviours by modified zeolite at both 20 °C and 4 °C (Arora et al., 2011b).

4.3.1.1 Langmuir adsorption equations

The Langmuir model is more likely to be relevant for monolayer and homogeneous surface adsorption processes. The specific equation is represented as (Chatterjee et al., 2010; Chern et al., 2002; Northcott et al., 2010a):

\[ q_e = \frac{q_{max}K_lC_e}{1+K_lC_e} \] (4.1)

where \( C_e \) is the concentration of contaminants in solution at equilibrium (µmol/L), \( q_e \) is the adsorption capacity at equilibrium (µmol/g). \( q_{max} \), the Langmuir constant, is related to the maximum adsorption capacity (µmol/g) of the adsorbent and \( K_l \) is a constant, similar to equilibrium constant (L/µmol). The Langmuir equation can be re-arranged as follows:

\[ \frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_l} \] (4.2)

4.3.1.2 Freundlich adsorption equations

Freundlich type isotherms have been used to describe many adsorption systems, and has been found applicable whether the surface is homogeneous or not (Hornig et al., 2008). The equation may be represented as follows:

\[ C_m = K_f \cdot C_s^n \] (4.3)

It may be linearized to give the following:

\[ logC_m = logK_f + n \cdot logC_s \] (4.4)

where \( C_m \) (µmol/g) and \( C_s \) (µmol/L) respectively represent the concentration of contaminants in material surface and solution at equilibrium. The terms \( K_f \) and \( n \) are constants for the given system.

4.3.1.3 Linear adsorption equations

Although both Langmuir and Freundlich isotherms are commonly applied to describe the behaviour
of many sorption systems, linear isotherms are more often used to describe hydrocarbon sorption, especially at narrow concentration ranges and low concentration levels (Northcott et al., 2010a). This isotherm implies that sorption is not dependent on the initial hydrocarbon concentration of the aqueous solutions. The linear sorption behavior may be described by the following equation:

$$C_m = K_d \cdot C_s$$  \hspace{1cm} (4.5)

In this form, $C_m$ and $C_s$ have similar meanings to the Freundlich adsorption equations, while the $K_d$ (L/µmol) is the distribution coefficient. To reflect the dominant influence of solid-phase organic carbon on the sorption of organic solutes, the distribution coefficient is often normalized by the following equation:

$$K_{OC} = \frac{K_d}{f_{OC}}$$  \hspace{1cm} (4.6)

where $f_{OC}$ is the sorbent's fractional organic carbon content, and the resulting parameter $K_{OC}$ is the so-called organic carbon-based partition coefficient.

4.3.2 Adsorption thermodynamics

The Gibbs free energy function shows how the equilibrium constant is related to temperature. The standard Gibbs free energy can be calculated from the standard enthalpy change and standard entropy change.

$$\Delta G^0 = \Delta H^0 - T \Delta S^0$$  \hspace{1cm} (4.7)

where $\Delta G^0$(kJ/mol) is the Gibbs free energy for a specific temperature and pressure. $\Delta H^0$(kJ/mol) is the standard enthalpy change and $\Delta S^0$(kJ/mol) is the entropy change.

At equilibrium, $K$ is related to the standard free energy change via equation 4.8:

$$\Delta G^0 = -RTlnK$$  \hspace{1cm} (4.8)

where $K$ is the equilibrium adsorption coefficient and $T$ is the absolute temperature in Kelvin. $R$ represents the molar gas constant, which is 8.314 J/(mol K).

The enthalpy change ($\Delta H^0$) can thus be obtained from the variation of $K$ with temperature by combination of equation (4.7) and (4.8) and it is assumed that $\Delta S^0$ is independent of temperature (Kuleyin, 2007).
\[ \ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \]  

(4.9)

4.4 Results and Discussion

4.4.1 Thermogravimetric analysis

The results of the thermogravimetric analysis for the modified and unamended zeolite are presented in Figure 4.1. This figure shows the weight loss curves (TG) and the corresponding differential curves (DTG) of the materials, which indicates the endothermic and exothermic reactions happening when heating the samples to 900°C. As shown, the modified zeolite presented different mass change steps and peak temperatures compared with the raw zeolite.

According to the peaks for the DTG Natural Zeolite curve, the mass loss of untreated zeolite mainly occurs between 25-200°C, which is the temperature of water evaporation (Bish et al., 1989). However, this dehydration process is not significant for modified zeolite as there is only a slight weight loss and no apparent DTG peak appears before 200°C. From 200-800°C, the modified zeolite begins to lose weight (8-9%) due to the volatilization of the phenyl groups of the chlorosilane on the zeolite surface (Huttenloch et al., 2001). In DTG curves of modified zeolite, it is shown that during these endothermic and exothermic reactions, there are two distinct steps occurring at 260°C and 560°C respectively. It is possible that these represent the breaking of two different sets of covalent bonds between the chlorosilane and zeolite surface, which requires a different energy (Huttenloch et al., 2001). During the modification process, the DPDSCI may form a double bond to two adjacent surface silanol groups or a single bond to one surface silanol group or to an organosilanol group after two successive synthetic processes (Ogawa et al., 1998). As the double bonds require more energy to break, some mass loss may occur at a higher temperature (Huttenloch et al., 2001).
4.4.2 FT-IR analysis

The FT-IR spectrum of the raw zeolite and DPDSCI modified zeolite is presented in Figure 4.2. As shown, significant changes happen on the surface of the zeolite after modification. It has been reported previously that the characteristic peaks of zeolite are between 500-1200 cm\(^{-1}\) and specifically, in the 830-1110 cm\(^{-1}\) is silicon-oxygen stretching (Northcott et al., 2010a). This can be observed from both zeolite materials. However, the DPDSCI coated zeolite shows a more apparent peak, indicating the modification is successful and silane has been grafted to the zeolite surface. Further evidence is in the bond range of 1450-1650 cm\(^{-1}\), where DPDSCI coated zeolite presents multi-characteristic peaks of benzene (Silverstein et al., 2014). In addition, the modified zeolite does not show any apparent peaks in 3003-3077 cm\(^{-1}\), which suggests that there is no pyridine on the surface of zeolite (Silverstein et al., 2014).
4.4.3 Adsorption behaviour of sorbent material

The adsorption performance of DPDSCI coated zeolite and natural zeolite at various toluene concentrations at 20°C and 4°C are shown in Figure 4.3. For both temperatures, the adsorption of toluene by modified zeolite follows the traditional isotherm shape.

At 20°C, the behavior of modified and unamended zeolite is very different. At low toluene concentrations (below 200µmol/L), an average of 17% of the toluene present was absorbed by DPDSCI coated zeolite while less than 1% is captured by natural zeolite. This demonstrates the modification of the zeolite surface improves the toluene adsorption ability of zeolite.

Compared with the performance at 20°C at low toluene concentrations (below 200µmol/L), only 8.7% of toluene is captured by modified zeolite at 4°C. The reduced adsorption performance of the material at low temperatures continues across all toluene concentration ranges, therefore it may be concluded that the adsorption is temperature dependent. A similar temperature dependence for toluene sorption onto HDTMA modified zeolite has been previously reported (Hornig et al., 2008).
The fitting of Freundlich, Langmuir and Linear isotherms for toluene adsorption on DPDSCI coated zeolite at 20°C and 4°C are presented in Figure 4.4. As shown, the linear model does not fit the experimental data well while the Langmuir isotherm presents the best fit across the entire concentration range investigated, with the highest coefficient of determination ($R^2$ in Table 4.1). This indicates that the adsorption on the DPDSCI coated zeolite is a monolayer and homogenous surface adsorption process (Kuleyin, 2007).

According to the equation of Langmuir isotherm, the maximum toluene uptake is 8.85 µmol/g at 20°C and 6.74 µmol/g at 4°C. The maximum capacity of this material at 20°C is of a similar order of magnitude to that found previously (Huttenloch et al., 2001). However, when compared to the performance of octylmethyl dichlorosilane modified synthetic zeolite (Song et al., 2005), the capacity for toluene is not as high. The reason for this might be that there are more effective hydroxyl groups on the surface of synthetic zeolite compared to a natural zeolite, which increases the chlorosilane loading on the particle, thus improving the adsorption capacity. Also, the maximum capacity of this material is less than that of cationic surfactant modified synthetic zeolite (Ghiaci et al., 2004). It is likely that the different bonding process during surface modification results in the different capacities. As chlorosilane requires specific bonding sites for attachment, it is limited by available sites, whereas as the surfactant is held by electrostatic attraction there is more scope for attachment.
Figure 4. Freundlich, Langmuir and Linear isotherms for toluene adsorption on DPDSCI-zeolite at 20°C (a) and 4°C (b)
Table 4.1 Freundlich, Langmuir and Linear parameters for toluene adsorption on DPDSCI-zeolite at 20°C and 4°C

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Parameters</th>
<th>20°C</th>
<th>4°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Freundlich</td>
<td>n_f</td>
<td>0.4307</td>
<td>0.4725</td>
</tr>
<tr>
<td></td>
<td>K_f (µmol^{1-n_f} g^{-1} L^n_f)</td>
<td>0.3289</td>
<td>0.1887</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.9702</td>
<td>0.9806</td>
</tr>
<tr>
<td>Langmuir</td>
<td>q_{max} (µmol/g)</td>
<td>8.850</td>
<td>6.739</td>
</tr>
<tr>
<td></td>
<td>K_L (L/µmol)</td>
<td>0.0026</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.9751</td>
<td>0.9953</td>
</tr>
<tr>
<td>Linear</td>
<td>K_d (L/g)</td>
<td>6.803</td>
<td>5.344</td>
</tr>
<tr>
<td></td>
<td>Log K_OC</td>
<td>1.903</td>
<td>1.798</td>
</tr>
<tr>
<td></td>
<td>R^2</td>
<td>0.1934</td>
<td>0.083</td>
</tr>
</tbody>
</table>

4.4.4 Adsorption thermodynamics

The free energy and enthalpy change of toluene adsorption of DPDSCI coated zeolite are shown in Table 4.2. As the K_f in Freundlich isotherm does not have any physical meaning (Northcott et al., 2010b), it is not used in this analysis. In the Langmuir and linear isotherms, the constant K may be used to reflect the equilibrium constant (Northcott et al., 2010a; Woinarski et al., 2003), as the Langmuir isotherm fitted the data best, it was used in this analysis following the application of Equations 4.7-4.9 to examine the enthalpy and free energy.

The negative number for the free energy (∆G) in Table 4.2 indicates the sorption process occurs spontaneously, which is typically the nature of adsorption processes (Kuleyin, 2007). This process was found to be endothermic as the enthalpy change (∆H) of this process is positive. This inference also fits the trend presented in Figure 4.3, as temperature is increased and toluene adsorption is increased. As the enthalpy change is approximately 1.206kJ/mol, it indicates that intermolecular interactions during the adsorption process are mainly Van der Waals interactions (4-9kJ/mol) with some hydrophobic bonding (4kJ/mol) and charge transfer, which occurs between aromatic moieties (π-π electron stacking interactions) (Von Oepen et al., 1991). The low equilibrium enthalpy means there is a small temperature influence (Hamaker et al., 1972), suggesting the adsorption capacity of this material would not be significantly affected by the cold temperature. It also shows weaker bonds (Ten Hulscher et al., 1996), indicating the strength of toluene adsorption is not very strong and the hydrocarbon on the modified zeolite surface might be easily utilized by microbes when compared with GAC (∆H of GAC can range from 5.80 to 44.99 KJ/mol based on different adsorption capacity) (Qiu et al., 2012; Zhang et al., 1991), which is an important foundation for future biodegradation.
processes.

Table 4.2: Adsorption thermodynamics parameters for toluene adsorption on DPDSCI-zeolite under Langmuir isotherms at 20°C and 4°C

<table>
<thead>
<tr>
<th>Isotherms</th>
<th>Parameters</th>
<th>20°C</th>
<th>4°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>ΔG (kJ/mol)</td>
<td>-19.15</td>
<td>-18.04</td>
</tr>
<tr>
<td></td>
<td>ΔH (kJ/mol)</td>
<td></td>
<td>1.206</td>
</tr>
<tr>
<td></td>
<td>ΔS (J/mol)</td>
<td></td>
<td>69.45</td>
</tr>
</tbody>
</table>

4.4.5 Regeneration test

The results of the regeneration test for toluene sorption onto DPDSCI coated zeolite are shown in Figure 4.5. For the first regeneration, there is a significant difference (around 20%) between the adsorption observed for the fresh sample and washed samples. Among them, methanol washed samples presented the best performance. For the second regeneration, the sorption capacity of both acetone and methanol washed samples reduced further, while that of hot water washed samples were stable. Therefore, the DPDSCI coated zeolite has the potential to be used and regenerated with a tolerable reduction in performance. Regeneration with water is also a more environmentally friendly option as compared to the other solvents trialed.
According to the results from the TGA and FT-IR measurements, the chlorosilane, diphenyldichlorosilane was successfully coated on to the surface of a natural zeolite without change to the internal porous structure. Batch adsorption tests showed a good capacity in adsorbing toluene by DPDSCI coated zeolite, compared with the raw material. The adsorption study demonstrated that the Langmuir isotherm fitted the adsorption best, indicating its monolayer and homogeneous character. The thermodynamic calculation showed the sorption process was spontaneous and endothermic. Based on the enthalpy change of adsorption, the intermolecular interactions between hydrocarbon and DPDSCI coated zeolite were mainly Van der Waals interactions with some enhancement of hydrophobic bonding and π-π electron stacking interactions. The results from regeneration test also demonstrated this modified zeolite can be used several times with a tolerable reduction in performance.

Therefore, this modified zeolite has the advantages of good adsorption capacity with less adsorption strength, good regenerated ability and less temperature dependency. Compared with the drawbacks

---

**Figure 4.5** Regeneration test for toluene uptake onto DPDSCI-zeolite

### 4.5 Conclusions

According to the results from the TGA and FT-IR measurements, the chlorosilane, diphenyldichlorosilane was successfully coated on to the surface of a natural zeolite without change to the internal porous structure. Batch adsorption tests showed a good capacity in adsorbing toluene by DPDSCI coated zeolite, compared with the raw material. The adsorption study demonstrated that the Langmuir isotherm fitted the adsorption best, indicating its monolayer and homogeneous character. The thermodynamic calculation showed the sorption process was spontaneous and endothermic. Based on the enthalpy change of adsorption, the intermolecular interactions between hydrocarbon and DPDSCI coated zeolite were mainly Van der Waals interactions with some enhancement of hydrophobic bonding and π-π electron stacking interactions. The results from regeneration test also demonstrated this modified zeolite can be used several times with a tolerable reduction in performance.

Therefore, this modified zeolite has the advantages of good adsorption capacity with less adsorption strength, good regenerated ability and less temperature dependency. Compared with the drawbacks
of GAC, the irreversible adsorption which is hard to combine with bioremediation and unstable mechanism in the freeze-thaw cycles, this modified zeolite is more suitable as fill material for the future application in PRBs in cold regions.
Chapter 5
Column studies of DPDSCI coated zeolite
5.1 Introduction

Chapter 4 showed that the adsorption of toluene was improved when the surface of natural zeolite was modified with DPDSCI. In this chapter, the adsorption behavior and long-term stability of DPDSCI coated zeolite was investigated in a column study by testing the toluene adsorption performance and material regeneration at various temperatures. Computer modelling (CXTFIT and MATLAB) was adapted to explore the adsorption mechanism, including the calculation of the axial dispersion coefficient and maximum adsorption capacity.

5.2 Materials and Methods

5.2.1 Columns and materials

The natural and modified zeolite, and inert ballotini glass beads used in the column study were detailed in Section 3.2.

5.2.2 Toluene adsorption column tests

The system used in this column study was detailed in Section 3.5.4. For the adsorption test, the materials were packed as follows: 32mm height of glass beads at the base, followed by 32mm of DPDSCI coated zeolite and then 62mm of glass beads at the top (equivalent to the volume of 20mL, 20mL, and 40mL, respectively). All materials were separated by Nylon mesh (200µm). The influent was 0.5 mmol/L toluene solution and the pump speed was 93.31 mL/h (equivalent to flow rate of 11.24 PV/h).

A single pore volume (PV) is defined as the volume of toluene solution present in the section containing modified zeolite in the column per unit time. This term is commonly used in column studies (Altare et al., 2007; Arora et al., 2011c; Michael Ranck et al., 2005). The effluent was collected at the end of the column and analysis conducted via HPLC. Tests were conducted at both 4°C and 20°C in duplicate and sampled in triplicate.

5.2.3 Regeneration tests

The Regeneration tests were well presented in Section 3.5.5. The material was packed via the same method as for the toluene adsorption test.
5.2.4 Reactive transport modelling

To develop models that describe the material performance, the entire glass column was packed with DPDSCI coated zeolite. The column was pre-saturated with Milli-Q water and agitated such that no air bubbles were present. 0.5 mmol/L toluene solution was used as influent and introduced to the saturated column at time zero in an up flow direction at various flow rates. The pump speeds were set 50.47, 76.62, 93.31 ml/h respectively (equivalent to flow rates of 1.52, 2.31 and 2.81 PV/h). The effluent was collected at the column outlet and HPLC analysis conducted to determine the toluene concentration. Tests were conducted at both 4°C and 20°C and sampled in triplicate.

5.2.5 Axial dispersion tests

Using a similar method to that previously described (Arora et al., 2011c), axial dispersion tests were conducted by running 8.6 mmol/L NaCl solution through the saturated column (using the same configuration as the reactive transport modelling test) in an up flow direction at a known flow rate. This was continued until the effluent concentration was the same as influent, after which it was replaced with a deionized water feed which was denoted time zero. The flow rates investigated were 1.52, 2.31 and 2.81 PV/h. The effluent samples were collected every 2 minutes and the Na⁺ concentration was determined via conductivity (Section 3.4.1). Tests were conducted duplicate at both 4°C and 20°C.

5.3 Modelling

5.3.1 Flow characteristics

Several parameters are used to describe the flow characteristics through a column, including the axial dispersion coefficient, Reynolds and Pécelt numbers.

5.3.1.1 Axial dispersion coefficient $D_i$

In a saturated, homogeneous, isotropic media system with steady-state uniform flow, the advection-dispersion equation (ADE) for the transport of a non-reactive solute in the axial (x-axis) direction (Figure 5.1) (Arora et al., 2011c) can be expressed as:

$$\frac{\partial C}{\partial t} = D_i \frac{\partial ^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x}$$  \hspace{1cm} (5.1)

where $C$ is the tracer concentration in bulk solution (mg/L), $D_i$ is the axial dispersion coefficient (m²/s), $x$ is the distance taken along the flow line (m), $\bar{v}$ is the average pore velocity (m/s), which is
the real average speed of the solution passing through a porous medium (Holdich, 2002).

Figure 5.1 The schematic diagram of column design

Inverse modelling (Figure 5.1) was carried out to determine the required parameters by fitting a solution of the ADE (Equation 5.1) to the axial dispersion test results. With the continuous tracer input into a semi-infinite length column with an initial solute concentration: \( C(x, 0) = 0 \) at \( x \geq 0 \), the boundary conditions are: \( C(0, t) = C_0 \) at \( t \geq 0 \), and \( \frac{dc}{dt}|_{x=\infty} = 0 \) at \( t \geq 0 \).

\[
\frac{C}{C_0} = \frac{1}{2} \left[ \text{erfc} \left( \frac{x-\bar{v}t}{2\sqrt{D_k}t} \right) + \exp \left( \frac{-\bar{v}x}{D_k} \right) \text{erfc} \left( \frac{x+\bar{v}t}{2\sqrt{D_k}t} \right) \right] 
\]  

(5.2)

where \( \text{erfc} \) is the complimentary error function. The parameters \( D_k \) and \( \bar{v} \) were determined by Equation 5.2 using the computer program CXTFIT (Arora et al., 2011c). CXTFIT code was developed by the U.S. Agriculture Department for determining contaminant transport parameters in laboratory column tests and model non-reactive and reactive transport of solutes through porous media. The
example of CXTFIT code was presented in Appendix 5.1.

5.3.1.2 Reynolds number

The Reynolds number is a dimensionless parameter that represents the ratio of inertial to viscous forces of the flow. The conventional Reynolds number is used to distinguish laminar flow and turbulent flow. For fluid flow in porous media, energy losses from the fluid due to viscous forces influence the prediction of flow type (Holdich, 2002). Therefore, the modified Reynolds number ($Re'$) (Holdich, 2002) is used to determine flow characteristics within in porous media as follows:

\[
Re' = \frac{\rho U_0}{(1-n)S_v \mu}
\]

\[
S_v = \frac{6}{d}
\]

where $\rho$ and $\mu$ are water density (kg/m$^3$) and viscosity (Pa·s), $U_0$ is superficial fluid velocity in the column (m/s), and $n$ is the material porosity. $S_v$ is specific surface area per unit volume which is determined by $d$, the particle diameter (m). After modification, typical packed bed Reynolds numbers (Holdich, 2002) are updated to: Laminar flow ($R_{e'} \leq 0.01$); Transitional flow ($0.01 < R_{e'} \leq 2$); Turbulent flow ($2 < R_{e'}$).

5.3.1.3 Péclet number

The Péclet number represents the relative effect of advective solute transport compared to dispersive transport. The modified Péclet number ($Pe'$) for flow in porous media is:

\[
Pe' = Re' \times Sc = \frac{U_0}{(1-n)S_vD_l}
\]

\[
Sc = \frac{\mu}{\rho D_l}
\]

where $Sc$ is the Schmidt number, which represents the characteristics of simultaneous momentum and mass diffusion convection processes.

At relatively high Péclet numbers, advection dominates the transport process whereas diffusion/dispersion dominate the transport process at relatively low Péclet numbers (Shackelford, 1994).

5.3.2 Reactive transport in the column

The loss or gain of solute within an elemental volume of porous media can occur from chemical
reactions that take place within the pore water or because of transfer of solute to or from the solid phase (Freeze et al., 1979). The loss of solute from solution due to adsorption can be described by including an additional term in Equation 5.1 to describe the effect of the rate of change in solute concentration in the solid phase. This is known as the advection-dispersion-reaction solute transport equation (ADRE) (Arora et al., 2011c):

$$\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} - \frac{\rho_b}{n} \frac{\partial q}{\partial t} \tag{5.7}$$

where $\rho_b$ is the bulk density of the DPDSCI coated zeolite column and $q$ is the toluene concentration on adsorption materials (mg/g). The term $\frac{\rho_b}{n} \frac{\partial q}{\partial t}$ is the rate of change in solution concentration due to sorption processes.

Using results obtained from Section 4.4.3, the Langmuir sorption isotherm is used to describe the relationship between the fluid and solid phase solute concentration for the toluene-modified zeolite material system. Therefore in this study, the ‘$q$’ in Equation 5.7 is equal to $q_e$ in Langmuir model:

$$q_e = \frac{q_{max} K_l C_e}{1 + K_l C_e} \tag{5.8}$$

where $C_e$ is the concentration of contaminants in solution at equilibrium (mg/L), $q_e$ is the adsorption capacity at equilibrium (mg/g), $q_{max}$ is the maximum adsorption capacity (mg/g) of the adsorbent and $K_l$ is the equilibrium constant (L/mg). Langmuir equations for toluene sorption on DPDSCI coated zeolite in column test modelling are converted from the results obtained in Section 4.4.3 as:

$$q = 0.02289 C_e / (1 + 0.028 C_e)$$

$$q = 0.01694 C_e / (1 + 0.027 C_e)$$

at 20°C and 4°C respectively.

MATLAB, a general mathematical computer program, is used to solve the partial differential equations mentioned. The initial concentration is: $C(x, 0) = 0$ at $x \geq 0$, the boundary conditions are: $C(0, t) = C_0$ at $t \geq 0$, and $\frac{dc}{dt}{|_{x=\infty}} = 0$ at $t \geq 0$. The example of MATLAB code was shown in Appendix 5.2.
5.4 Results and Discussion

5.4.1 Adsorption performance

The adsorption of toluene onto DPDSCI coated zeolite at 20°C and 4°C, and natural zeolite at 20°C are presented in Figure 5.2. It can be observed that the chlorosilane coating improved the toluene adsorption ability of the natural zeolite. Natural zeolite adsorbed minimal quantities of toluene (less than 5% of the toluene present was removed), while DPDSCI coated zeolite showed distinct capture ability before 30 PV of influent had been injected, adsorbing 60% of toluene at the early stages. Meanwhile, temperature did not significantly impact the adsorption performance at the investigated flowrates. This reiterates the results obtained from batch study (Section 4.4.3). Furthermore, the trend of toluene adsorption whereby the concentration sharply increases, before stabilizing and becoming saturated, is similar to that of SMZ (Michael Ranck et al., 2005). From this, it may be speculated that if other hydrocarbons sorb onto SMZ well, they may also sorb well onto DPDSCI coated zeolite. Overall, the adsorption tests proved that this modified zeolite could be used for hydrocarbon capture over a wide temperature range.

![Figure 5.2](image)

Figure 5.2 The toluene adsorption curves of unamended zeolite and fresh DPDSCI-zeolite at 20°C and 4°C. Initial toluene concentration (C₀) is 0.5 mmol/L and the flow rate is 11.24 PV/h.

5.4.2 Regeneration test

The results of long term stability tests of DPDSCI coated zeolite at the temperatures investigated are
shown on Figure 5.3 (20°C) and Figure 5.4 (4°C). Though slight difference may exist at the initial period, the whole adsorption trend is similar for all regeneration tests at both temperatures. This indicates that there is no significant reduction in the sorption capacity of DPDSCI coated zeolite after repeated adsorption and washing processes. Similar phenomena was found in the investigation of the regeneration of SMZ when contacting with BTEX (Michael Ranck et al., 2005). The positive outcomes of these tests indicate that this material may be promising in field applications. With biotechnology increasingly used in the remediation of hydrocarbon contaminated sites (De Jesus et al., 2015), continuous adsorption and elution of contaminants on the surface of materials is of benefit when combined with biofilm technology (Freidman et al., 2016b). The contaminants adsorbed to the surface of this material can be regarded as a food source for microbial communities (Freidman et al., 2016b). Due to the release of hydrocarbons from the material, the food source may be rapidly provided and sufficient carbon would benefit microbial breeding and contaminant removal (Mumford et al., 2015).

Figure 5.3 The regeneration tests of DPDSCI-zeolite at 20°C. Initial toluene concentration ($C_0$) is 0.5 mmol/L and the flow rate is 11.24 PV/h.
5.4.3 Axial dispersion coefficient

The axial dispersion tests were used to understand the flow characteristics within the packed column. The effluent concentration trends in Figure 5.5 and Figure 5.6, show that at higher flowrates contaminant breakthrough occurs earlier. The corresponding axial dispersion coefficient under different flow rates and temperatures mimicked this result by being larger at high flow rates (Table 5.1). Upon comparison of the curves presented in Figure 5.5 and Figure 5.6, the time at which the Na\(^+\) concentration began decreasing, and the time that water fully saturated the column under 4°C were only slightly slower than that at 20°C, indicating temperature has little influence on the axial dispersion process.

The calculated modified Reynolds numbers, refer from Table 5.1, are generally between 0.006 to 0.03, indicating that transitional flow occurs in the packed column (Holdich, 2002). Meanwhile, the modified Péclet number (Table 5.1) shows relatively low numbers (around 0.01 to 0.02), indicating diffusion, especially molecular diffusion dominate the whole solute transport process (Shackelford, 1994; Yu et al., 1999). It is also observed that the modified Péclet numbers show little dependence on modified Reynolds numbers, which is consisted with other studies regarding liquids dispersion through packed beds (Edwards et al., 1968).
The relationship between the modified Reynolds number and the axial dispersion coefficient of the full packed column is shown in Figure 5.7. It can be observed that at the same temperatures, the modified Reynolds number has a linear correlation with the axial dispersion coefficient for all flow rates. At different temperatures, the curves have similar slopes ($1.2 \times 10^{-4}$ and $1.3 \times 10^{-4}$), but different intercepts ($9.3 \times 10^{-7}$ and $3.7 \times 10^{-7}$). It may be speculated that for a given column, temperature may slightly affect the intercept of regression equation between $R_e'$ and $D_l$. Meanwhile, packed column design, including column parameters, material characteristics, may influence the slope of the regression. This may be proven via the comparison with the results of other column test. Arora investigated the adsorption performance of GAC in the same column conditions at both 20°C and 4°C (Arora et al., 2011c). Based on her data, the relationships between modified Reynolds number and axial dispersion coefficient at 20°C and 4°C were $D_l = 1.1 \times 10^{-5}R_e' + 1.8 \times 10^{-6}$ and $D_l = 1.5 \times 10^{-5}R_e' - 3.2 \times 10^{-8}$, respectively. The different intercepts result from the influence of temperature. The different magnitude of regression slope between DPDSCI-zeolite and GAC column is due to the different materials characteristics.

![Figure 5.5](image.png)

**Figure 5.5** The effect of flow rate on axial dispersion at 20°C. The lines present the CXTFIT model fit.
Figure 5.6 The effect of flow rate on axial dispersion at 4°C. The lines present the CXTFIT model fit.

Table 5.1 The flow parameters of axial dispersion test at both 20°C and 4°C

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Pump Flow rate</th>
<th>D_i</th>
<th>R'e</th>
<th>P'o</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C)</td>
<td>(PV/h)</td>
<td>(m²/s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>1.52</td>
<td>8.12×10⁻⁷</td>
<td>0.0130</td>
<td>0.0161</td>
</tr>
<tr>
<td></td>
<td>2.31</td>
<td>1.40×10⁻⁶</td>
<td>0.0209</td>
<td>0.0151</td>
</tr>
<tr>
<td></td>
<td>2.81</td>
<td>2.56×10⁻⁶</td>
<td>0.0296</td>
<td>0.0116</td>
</tr>
<tr>
<td>4</td>
<td>1.52</td>
<td>4.61×10⁻⁷</td>
<td>0.0060</td>
<td>0.0203</td>
</tr>
<tr>
<td></td>
<td>2.31</td>
<td>7.95×10⁻⁷</td>
<td>0.0095</td>
<td>0.0189</td>
</tr>
<tr>
<td></td>
<td>2.81</td>
<td>1.39×10⁻⁶</td>
<td>0.0130</td>
<td>0.0147</td>
</tr>
</tbody>
</table>
5.4.4 Reactive transport modelling

To explore the mechanism of toluene adsorption, a theoretical model (ADRE) was applied to simulate and predict the transport process. As previously discussed, the Langmuir isotherm was used to predict toluene adsorption onto DPDSCI coated zeolite. As shown in Figure 5.8 and Figure 5.9, the predicted curves are in good agreement with the experimental data.

The comparison of Langmuir parameters in batch and column tests are shown in Table 5.2. The equilibrium constant ($K_l$) and maximum adsorption capacity ($q_{max}$) calculated from column data were found to be larger than those observed from batch experiments at both 20°C and 4°C, indicating even greater adsorption occurs in laboratory columns. Similar discrepancies have been found previously including in the work of Simpson and Bowman, 2009 and Woinarski et al., 2006 (Simpson et al., 2009; Woinarski et al., 2006).

At 20°C, the adsorption performance of DPDSCI coated zeolite under various flow rates are presented in Figure 5.8. At lower flow rates, later breakthrough occurs, which is consistent with the
data presented in Table 5.2. The reason might be at room temperature, the breakthrough curve for a given adsorbent with same column parameters mainly depends on the contact time, which is dominated by the fluid superficial velocity (Wang et al., 2011). With slower influent passing, the functional groups on sorbents surface may have more opportunity to interact with toluene in the water, which extends the time to reach breakthrough and saturation points (Richard et al., 2010; Schick et al., 2011). At 4°C, the flowrate does not have a great influence on the adsorption curves, as they are very close to one another (Figure 5.9). This may be because the maximum adsorption capacity is lower at lower temperature (Ma et al., 2018) (Table 5.2) and so, the capacity is obtained faster at all flowrates investigated. Similar behavior has also been observed for the adsorption of copper by Na-clinoptilolite (Woinarski et al., 2006).

Through the evaluation of toluene adsorption onto DPDSCI coated zeolite, it could be concluded that: 1) in temperate climate, the performance of the adsorption material may be impacted by environmental factors such flow rate, while in cold regions this seems to have less influence; 2) the ADRE equation could adequately predict the performance of DPDSCI coated zeolite under various temperature and flow rate conditions, which could be applied in the future to simulate the toluene or hydrocarbon adsorption process by this material in the field. This observation has also been reported for other sorbents on other aromatic pollutants (Richard et al., 2010).

![Figure 5.8](image)

**Figure 5.8** The observed and fitted toluene adsorption curves of DPDSCI-zeolite at 20°C under various flow rates.
Figure 5.9 The observed and fitted toluene adsorption curves of DPDSCL-zeolite at 4°C under various flow rates.

Table 5.2 Summary of experimental conditions, breakthrough point \((C/C_0=0.10)\) and saturation point \((C/C_0=0.99)\) of column experiments, toluene adsorption capacity at both batch and column test after calculation

<table>
<thead>
<tr>
<th>Temperature (^{\circ}\text{C})</th>
<th>Flow rate ((\text{PV/h}))</th>
<th>Breakthrough point ((\text{PV}))</th>
<th>Saturation point ((\text{PV}))</th>
<th>(K_i) ((10^{-2} \text{ L/mg}))</th>
<th>(q_{\text{max}}) ((10^{-1} \text{ mg/g}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>1.52</td>
<td>2.90</td>
<td>11.92</td>
<td>2.81</td>
<td>6.55</td>
</tr>
<tr>
<td></td>
<td>2.31</td>
<td>2.09</td>
<td>8.82</td>
<td>6.55</td>
<td>16.58</td>
</tr>
<tr>
<td></td>
<td>2.81</td>
<td>1.27</td>
<td>6.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>1.52</td>
<td>1.99</td>
<td>7.18</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.31</td>
<td>1.74</td>
<td>6.62</td>
<td>7.75</td>
<td>7.06</td>
</tr>
<tr>
<td></td>
<td>2.81</td>
<td>1.55</td>
<td>6.50</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.5 Conclusions

The toluene adsorption efficiency, longevity and mechanism of the DPDSCL coated zeolite in a packed
column was studied by measuring both inlet and exit concentrations of toluene as a function of injected volume and fitting the results to ADRE. According to the adsorption and regeneration tests, the adsorption capacity and long term stability of DPDSCI coated zeolite were not impacted by temperature or flow rate compared with unamended zeolite. These characteristics make it a promising material for future remediation of hydrocarbon contaminated sites at various temperatures. To investigate the adsorption and transport mechanism, axial dispersion tests and reactive transport modelling were conducted. The modified Reynolds number and modified Péclet number were obtained from axial dispersion tests. These showed that transitional flow occurred during the adsorption process and diffusion may dominate the flow. The good agreement between experiment data and modelling prediction indicates the ADRE equation with Langmuir equilibrium isotherm could simulate the toluene adsorption on DPDSCI coated zeolite well. The maximum capacity calculated from the modelling of column tests results exceeds that determined in batch experiments.

Overall, the column tests of DPDSCI coated zeolite prove this material could be suitable used in the remediation of hydrocarbon contaminants sites even at cold temperature for a long period. Performance modelling shows that the behaviour of this material could be adequately predicted at various temperatures and flow rate conditions.
Chapter 6
Batch studies of DPDSCI coated ammonium exchanged zeolite
6.1 Introduction

Comparing with the performance of unamended zeolite with DPDSCI coated zeolite (DZ), the latter is shown to be effective for toluene adsorption and exhibited long-term stability and regeneration ability at both 20°C and 4°C. To enhance the biodegradation process in PRBs, DPDSCI coated ammonium exchange zeolite (DAZ) was selected for further investigation primarily as to see whether it possesses both reversible hydrocarbon adsorption and nutrient release abilities. To investigate this, batch tests were conducted by immersing this material into different concentrations of toluene and potassium chloride solutions. The potassium chloride was selected to test ammonium release ability of DAZ as for this type of zeolite, it presents similar affinity towards potassium, compared with ammonium.

6.2 Materials and Methods

6.2.1 Raw materials

The raw zeolite material used was natural clinoptilolite zeolite. Details were provided in Section 3.2.

6.2.2 Surface modification

Before surface modification by DPDSCI, the natural zeolite was firstly conditioned into the ammonium form (AZ) using the method described in Section 3.2. Following this, the material was coated with DPDSCI. The detailed process was presented in Section 3.5.1.

6.2.3 Equilibrium tests

To determine the hydrocarbon adsorption and nutrient release ability of DAZ, batch tests were conducted in solutions of toluene and potassium chloride (KCl). The initial KCl concentration varied from 0 mmol/L to 1200 mmol/L and for a given KCl concentration, different amounts of toluene were added (nominal concentrations of 0 mmol/L, 0.5 mmol/L, 1 mmol/L, 1.5 mmol/L and 2.5 mmol/L).

40mL of the mixed solution and consistent masses of DAZ (0.3g) were used to conduct batch equilibrium tests. The detailed procedure was presented in Section 3.5.2. The experimental temperature was 20°C and the shaking period was 72 hours. Previous studies have proven that 72 hours is sufficient for ion exchange equilibrium and hydrocarbon adsorption equilibrium to be achieved by modified zeolite (Torabian et al., 2010; Woinarski et al., 2003).

After shaking, 4mL solution was taken by glass pipette from each vial to test the toluene
concentration by HPLC. 5mL of solution was then extracted using a plastic springe from the same sample vial and filtered by Millex syringe-driven filter unit (filter paper pore size 0.22µm). The sample was diluted by 20 and 200 times to detect total ammonium concentration by Visible Spectrophotometer and potassium concentration by Inductively Coupled Plasma. In addition, 10ml solution was taken from each vial to test the pH and EC of initial and final solutions. Each test was conducted in duplicate and sampled in triplicate.

6.2.4 Regeneration tests

Regeneration tests were conducted to examine whether the material developed had the ability to continuously adsorb hydrocarbons and release nutrients. The detailed process of ammonium reloading and toluene washing was presented in 3.5.2.

6.3 Modelling

Modelling of the adsorption experiments used the Langmuir and Freundlich isotherms. These isotherms were previously applied to describe the toluene adsorbed on the surface of DZ in batch experiments (Section 4.3).

6.4 Results and Discussion

6.4.1 Nutrient release performance

The ammonium release performance of DAZ in various potassium and toluene concentrations is shown in Figure 6.1. As shown, when potassium concentration increased from 0 to 200 mmol/L, the ammonium released from DAZ also increased. At 200 mmol/L of potassium concentration, the ammonium release from 0.3g DAZ reaches a maximum. From this the maximum ammonium release capacity of this material was found to be 0.8 mmol/g, which is slightly lower than natural ammonium exchange zeolite (0.989 mmol/g) (Freidman et al., 2016b). This may be due to the loss of ammonium during surface modification with DPDSCI. Here, the hydrochloric acid produced may displace the ammonium cations in DAZ (Huttenloch et al., 2001). Regardless, the ammonium release capacity of DAZ is still much higher than that of Octadecyltrichlorosilane (C18) modified ammonium exchanged zeolite (0.3 mmol/g) (Northcott et al., 2010a). The difference may be due to the variation in the modification sequence. For DAZ, the ammonium exchange process was undertaken before the chlorosilane modification, while for C18 modified ammonium zeolite, the ion exchange occurred after. Generally, after chlorosilane modification, the material surface would become hydrophobic (Huttenloch et al., 2001). This make it difficult for material to interact with ammonium cations
dissolved in the aqueous phase, resulting in a reduced ammonium loading. Furthermore, surface modification by chlorosilane may clog zeolite pores (Mallard et al., 2015) and reduce its mesoporosity (Yu et al., 2015).

Besides the influence of initial potassium concentration, the toluene concentration seemed to have no effect on the ammonium release from DAZ. Similar results have been found previously (Freidman et al., 2016a).

![Figure 6.1 Ammonium release of DAZ at different initial concentration of potassium and toluene](image)

6.4.2 Hydrocarbon adsorption behaviour

The toluene adsorption performance under various initial concentrations of potassium and toluene are presented in Figure 6.2. At low concentrations (600-700µmol/L), the amount of toluene adsorbed reduced slightly when potassium chloride was added into solution, compared with the blank (same toluene concentration without any potassium chloride, triangle data point). With initial toluene concentrations increasing from 1000 µmol/L to 1500 µmol/L, the variation between the amount of toluene absorbed in pure and saline solutions decreased. This indicates the presence of salt negatively influenced the adsorption performance of DAZ. No similar studies have been conducted previously, however the increased salt reduces the solubility of toluene in solution, changing the
distribution coefficient. As for the influence of different potassium concentration, no significant difference is observed from Figure 6.2.

![Figure 6.2 Toluene adsorption of DAZ at different initial concentration of potassium and toluene](image)

6.4.3 Adsorption isotherms analysis

The Figure 6.3 shows the fitted Langmuir isotherm for toluene adsorption onto DPDSCI coated zeolite (Section 4.4.3) and the experimental data points of toluene adsorption onto DAZ with 0mmol/L KCl. It can be observed that there is no significant variation between the result of DAZ batch test (without potassium chloride added) and DZ batch test (Section 4.4.3). This indicates that DAZ had a similar toluene adsorption capacity (9.355 µmol/g, calculated from the data of DAZ in Figure 6.3) with DZ when there is no salt present in solution. This confirms that the presence of ammonium does not negatively impact the ability of the coating to adsorb toluene.

As the amount of toluene adsorbed by DAZ under various initial potassium concentrations were different, three isotherms (Freundlich, Langmuir and Linear) were trialed to determine which exhibited the best fit by comparing the coefficient of determination ($R^2$). As shown in Figure 6.4,
similar to previous work, the Langmuir isotherm exhibited the best fit, with the highest coefficient of determination \( R^2=0.9999 \), compared with Freundlich and Linear isotherms \( R^2=0.9973 \) and \( R^2=0.9545 \) respectively. This indicates that regardless the additional ion exchange process, the toluene adsorption on the DAZ still follows the monolayer and homogenous surface adsorption process.

Freundlich and Langmuir parameters presented interesting trends (Figure 6.5). When there was no KCl in the solution, the value of \( q_{\text{max}} \) (Figure 6.5a) and \( K_l \) (Figure 6.5b) in the Langmuir isotherm were similar to the maximum adsorption capacity and equilibrium constant in DZ batch test (Section 4.4.3), which was 8.850 µmol/g and 0.0026 L/ µmol respectively. With the initial potassium concentration increasing from 0 to 200 mmol/L, \( q_{\text{max}} \) presented a sharp increase while \( K_l \) showed a rapid decrease. This indicates that the toluene uptake process of DAZ was strongly affected when ions were present in solution. Similar conclusions were also drawn previously for the adsorption of pesticides on montmorillonite (Delle Site, 2001). Following this, the \( q_{\text{max}} \) and \( K_l \) results obtained from 200 to 1200 mmol/L initial potassium concentrations remained stable at 20.864 ± 3.602 µmol/g and 0.000344 ± 0.0000660 L/ µmol respectively. The maximum adsorption capacity of DAZ was enhanced when salt was added to the aqueous phase. Previous studies have shown that the toluene solubility decreases from 5.6 mmol/L to 3.3 mmo/L when potassium concentration increases from 0 to 1 mol/L (Sada et al., 1975). The decreasing solubility will cause the toluene to adsorb strongly on to the hydrophobic surface of DAZ (Delle Site, 2001), resulting the enhanced adsorption capacity. As for \( n_f \) (Figure 6.5c) and \( K_f \) (Figure 6.5d), the parameters of Freundlich isotherm, both showed similar decreasing trend: a rapid drop when initial potassium concentration was within 200 mmol/L, and afterward, both parameters reached their extreme value regardless the initial potassium concentration change.

Using the corresponding Langmuir parameters under each initial potassium concentrations, several fitted curves are presented on Figure 6.6. It can be observed that when potassium chloride is added to the solution, the extent of toluene adsorption decreases, indicating that the maximum adsorption capacity gradually increases. This changing process is consisted with the explanations of Figure 6.5.
Figure 6.3 Toluene adsorption isotherm of DZ and DAZ in 0 mmol/L potassium chloride solution

Figure 6.4 Freundlich, Langmuir and Linear isotherms for toluene adsorption on DAZ in various potassium chloride solutions
Figure 6.5 Langmuir (a,b) and Freundlich (c,d) parameters for toluene adsorption on DAZ in various potassium chloride solutions

Figure 6.6 Langmuir isotherm fitted curves for toluene adsorption on DAZ in various potassium chloride solutions based on the data from Figure 6.2
6.4.4 EC and pH change

The EC and pH of the solutions before and after the 72 hours testing period are presented in Figure 6.7. These solutions contained different concentrations of potassium chloride, and no toluene. There is no significant difference between the results obtained from initial and equilibrated solutions for both EC and pH.

The influence of toluene concentration on solution EC and pH is shown in Figure 6.8 and 6.9. The pH results were all located near the dotted line (slope=1). This indicates that the change of toluene concentrations in aqueous phase did not have a significant impact on the pH of solutions. As for the EC of the solutions, there was no difference between the initial and final solutions.

*Figure 6.7* The pH and EC of initial and final solutions under different concentrations of potassium chloride solutions (without toluene)
Figure 6.8 The pH of initial and final solutions under different concentration of toluene and potassium chloride blending solutions

Figure 6.9 The EC of initial and final solutions under different concentration of toluene and potassium chloride blending solutions
6.4.5 Regeneration test

The results of long term stability tests for DAZ are presented in Figures 6.10 and 6.11. After each ammonium regeneration procedure, the maximum ammonium capacity increased to the same amount as for unmodified ammonium zeolite (Freidman et al., 2016b). The possible reason may be because the ammonium conditioning process occurred prior the surface modification. During the surface modification process, some ammonium may be replaced by the hydrogen generated. After the adsorption test, the rapid washing processes by ammonium chloride helps to reload the ammonium back to the surface of material, thereby increasing the ammonium present. This indicates that in future applications, the material may be effectively regenerated and reused for nutrient release. As for toluene adsorption capacity, it can be observed that the amount of toluene adsorbed decreased after the first regeneration, however, for later regenerations it increased and in fact exceeded the initial uptake. The variation may be due to the experimental error. This illustrates that this material possesses good long-term stability for toluene adsorption as the DPDSCI is covalently bonded to the surface of zeolite and it would not be easily washed off in the salt solution.

Figure 6.10 Regeneration test for ammonium release on DAZ
6.5 Conclusions

The combined performance of hydrocarbon adsorption and nutrient release of DPDSCI coated ammonium exchange zeolite were investigated under different concentrations of toluene and potassium chloride solutions. Results showed that the change of toluene concentration had a slight impact on the nutrient release ability of the material and the initial release capacity was 0.8 mmol/g, which was not significantly different to the performance of ammonium exchanged zeolite previously developed. Different concentrations of potassium chloride in the aqueous phase influenced the availability of toluene and consequently affected the adsorption on to the material. The Langmuir isotherm exhibited the best fit to the experimental data, proving the adsorption mechanism was the same as chlorosilane coated zeolite. The adsorption isotherm parameters of Langmuir isotherm, $q_{\text{max}}$ increased from 9.355 µmol/g to an ultimate status (20.864 µmol/g) when potassium chloride concentration increased from 0 to 200 mmol/L, while $K_l$ presented an opposite trend. The EC and pH results showed that the conductivity and acidity of solutions were not affected by the different potassium chloride concentrations while they were slightly influenced by toluene concentration. The regeneration test showed this material can be utilized, washed and reused at least three times.

Overall, the good toluene adsorption, nutrient release and regeneration ability of chlorosilane coated...
ammonium zeolite makes it a promising material for use in PRBs to enhance in-situ bioremediation processes.
Chapter 7
Column studies of DPDSCI coated ammonium exchanged zeolite
7.1 Introduction

Chapter 6 showed that DAZ possess a good toluene adsorption capacity, nutrient release and ability to be regenerated. Hence, this material is tested in a dynamic system to assess its potential performance in situ. In these column tests, the continuous toluene adsorption and nutrient release performance, regeneration behavior, EC and pH change were examined at different influent concentrations and various flow rates at 20°C. Computer modelling was used to explore the adsorption mechanism, including the calculation of maximum adsorption capacity.

7.2 Materials and Methods

7.2.1 Columns and materials

The natural and modified ammonium exchanged zeolite were prepared using the same method presented in Section 6.2.2.

7.2.2 Toluene adsorption and Nutrient release tests

Columns tests were conducted in the system described in Section 3.5.3. The column was pre-saturated with MilliQ water and then reactive media was added under agitation such that no air bubbles remained. The influent contained various concentrations of potassium chloride and toluene (5mmol/L KCl + 0.5mmol/L Toluene and 5mmol/L KCl + 1mmol/L Toluene). The pump speeds were set at 2.5, 3.5, 4.5 rpm respectively (equivalent to flow rates of 1.65, 2.59 and 3.03 PV/h). The effluent samples were collected at the end of the column and then together with influent samples tested for toluene, total ammonium and potassium concentration by HPLC, UV and ICP respectively using the same methods described in Section 6.2.3. The pH and EC change during the process was also examined. Tests were conducted at 20°C and sampled in triplicate.

7.2.3 Regeneration tests

To detect whether the material could be used multiple times without significant decrease in hydrocarbon adsorption and nutrient release ability, regeneration tests were also conducted using the method described in Section 3.5.3. After the column material was contacted with toluene solution for 24 hours, the influent was replaced with water for another 24 hours. This 24 hour period was termed a ‘washing cycle’. The column after the first washing cycle was termed 1st regenerated. This column was then contacted with toluene solution again, and subsequently washed which was termed 2nd regenerated. The influent was 5mmol/L KCl and 0.5 mmol/L toluene solution and the flow rate was 3.03PV/h. Tests were conducted at 20°C and sampled in triplicate.
7.3 Modelling

The advection-dispersion-reaction solute transport equation was used to predict the toluene adsorption performance in column tests, similar to Chapter 5. The detailed equations used were presented in Section 5.3.2 and the example of MATLAB code was presented in Appendix 5.2.

7.4 Results and Discussion

7.4.1 Nutrient release performance

The ion exchange performance of the material at different initial conditions are presented in Figures 7.1 to 7.6. The potassium concentration in the influent was stable in each test, except for the slight increase observed in Figure 7.6. Whilst flowing through the column, the potassium in the aqueous phase is exchanged with ammonium present in the zeolite. As the initial potassium concentration in solution was quite low, the modified ammonium zeolite took up the majority of the potassium cations present and therefore the potassium concentration in effluent was low and stable during the test period.

Results for the flowrates varying from 1.65 to 3.03 PV/h are presented in Figures 7.1 to 7.4. As shown, in these tests the ammonium concentration in the effluent reduced from 17 mmol/L to 4.5 mmol/L in the beginning 5 pore volumes, and then remained stable until the end of the test time. Meanwhile, opposite trends were observed in the Figures 7.5 and 7.6. In these tests, the ammonium concentration in aqueous phase increased from 2 mmol/L to 4 mmol/L after 5 pore volumes of influent, before stabilizing. The different performances observed may be due to the reactive materials in the column. The DAZ used in the tests presented in Figure 7.5 and 7.6 were freshly manufactured, while the DAZ in the others were used and washed by ammonium chloride solution using the method in Section 3.2. According to the results presented in Section 6.4.5, regeneration process would not negatively change the ammonium release and toluene adsorption ability of DAZ.

As shown, the ammonium release ability of DAZ was stable under different initial toluene concentrations and various flow rates for at least 200 pore volume passed. This indicates that this material can continuously provide nutrients for biofilm growth if applied in situ. Previous studies have also shown that the total NH₃ release of ammonium amended zeolite in flow cells may remain after 6500 BV at 23°C and 9000BV at 4°C (Freidman et al., 2016a).
Figure 7.1 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 1.65 PV/h. The reactive material was ammonium regenerated DAZ.

Figure 7.2 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 2.59 PV/h. The reactive material was ammonium regenerated DAZ.
Figure 7. 3 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 3.03 PV/h. The reactive material was ammonium regenerated DAZ.

Figure 7. 4 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene and the flow rate was 1.63 PV/h. The reactive material was ammonium regenerated DAZ.
Figure 7.5 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5 mmol/L KCl and 1 mmol/L Toluene and the flow rate was 2.50 PV/h. The reactive material was fresh DAZ.

Figure 7.6 Nutrient concentrations present in effluent water samples. The initial influent concentration was 5 mmol/L KCl and 1 mmol/L Toluene and the flow rate was 3.10 PV/h. The reactive material was fresh DAZ.
7.4.2 EC and pH change

The change in EC and pH during the column tests are presented in Figures 7.7 to 7.10. The pH of the effluent (Figure 7.7) of the 5 mmol/L KCl and 0.5 mmol/L toluene at flowrates varying from 1.65 PV/h to 3.03 PV/h, fluctuated around 6.0. Similar results were found for the pH of the effluent of 5 mmol/L KCl and 1 mmol/L toluene when flowrate was 1.63 PV/h (Figure 7.8) and the pH was 5.4 under the flowrate of 2.50 and 3.10 PV/h (Figure 7.8). These pH values are suitable for the bioremediation processes (Das et al., 2011). It is postulated that the pH is lower for the flowrate of 2.50 and 3.10 PV/h due to it being fresh DAZ as opposed to regenerated material. As shown in the batch test presented in Section 6.4.5, the regenerated material exhibited higher ammonium content, which might reduce the H⁺ concentration on the surface of material, resulting in a higher observed pH in these tests.

As for the EC of the effluent, two trends were also observed from Figure 7.9 and 7.10. The EC of the effluent of 5 mmol/L KCl and 0.5 mmol/L toluene solution decreased from 4600 to 770 ms/cm at beginning 10 PV passing through and then stabilized around 770 ms/cm, regardless the change of flowrate. Similar trend was found in the effluent of 5 mmol/L KCl and 1 mmol/L toluene solution when the flowrate was 1.63 PV/h, while the rest two flowrates of same initial solution, the EC showed opposite trend, increasing from 500 to 800 ms/cm at beginning 10 PV passing through and then stabilized around 770 ms/cm. The variation of EC results may be also because of the reactive materials in the column.
Figure 7.7 pH change in the column test under various flow rates. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene.

Figure 7.8 pH change in the column test under various flow rates. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene.
**Figure 7.9** EC change in the column test under various flow rates. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene.

**Figure 7.10** EC change in the column test under various flow rates. The initial influent concentration was 5mmol/L KCl and 1 mmol/L Toluene.
7.4.3 Toluene adsorption behaviour

The toluene adsorption performance of the material under various initial concentrations and flow rates are presented in Figures 7.11 and 7.12. Regardless the initial concentration and flow rate, the toluene was rapidly adsorbed by DAZ until 20 PV passed. Following this, the column reached saturation whereby the toluene concentration in the effluent and influent was almost the same.

For the same influent composition, the faster flowrates resulted in the shorter breakthrough times. At lower flowrates, the contact time between the toluene and DAZ is increased, allowing a higher proportion of toluene to be adsorbed, thereby extending the breakthrough time (Richard et al., 2010; Schick et al., 2011; Wang et al., 2011). The initial concentration was not observed to influence the breakthrough time in these tests.

Figure 7.11 The toluene adsorption curves of fresh DAZ at 20°C under various flow rates. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene.
7.4.4 Reactive transport modelling

The model developed in Section 5.3 was used to predict the toluene adsorption performance of DAZ. The experimental results and their predictions are presented in Figure 7.13 and 7.14. It can be observed that there is deviation between the predicted and experimental data, with the regression coefficients of 0.97 and 0.99 for the different initial conditions. The observed variation may be due to the presence of potassium. According to results from the batch tests (Section 6.4.3), potassium would impact the toluene adsorption behavior. Here, the toluene adsorption capacity used in Equation 8 (Section 5.3.2) was that obtained from the batch tests where the potassium concentration was 4.91 mmol/L. However, as discussed in Section 5.4.4, the capacity of the material for toluene in columns is different to that in batch tests. This difference would result in the deviation observed.

Table 7.1 summarized the adsorption capacity along with the breakthrough and saturation point. For the same initial conditions, higher flow rates, and an earlier breakthrough time occurred, which was consistent with experimental observation. When comparing the effluent of toluene concentrations, higher concentrations seemed to have little impact on the breakthrough time. The maximum
adsorption capacity calculated was larger in the column test than in the batch work (1.387 mg/g). Similar trends were also observed for the DZ. In the same initial condition, K_l was lower when the flowrate was faster. This might because different flowrates would lead to different amount of potassium ion presented in the solution, resulting to the different toluene solubility and therefore influencing the adsorption process.

Figure 7.13 The observed and fitted toluene adsorption curves of DAZ at 20°C under various flow rates (influent toluene concentration was 0.5mmol/L)
Figure 7.14 The observed and fitted toluene adsorption curves of DAZ at 20°C under various flow rates (influent toluene concentration was 1mmol/L)

Table 7.1 Summary of initial conditions, breakthrough point (C/C₀=0.10) and saturation point (C/C₀=0.99) of the column tests and toluene adsorption capacity at different conditions after calculation.

<table>
<thead>
<tr>
<th>Initial conditions</th>
<th>Flow rate (PV/h)</th>
<th>Breakthrough point (PV)</th>
<th>Saturation point (PV)</th>
<th>Ki (10⁻² L/mg)</th>
<th>q_max (mg/g)</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>5mmol/L KCl +</td>
<td>1.65</td>
<td>2.95</td>
<td>20.65</td>
<td>4.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.59</td>
<td>2.20</td>
<td>18.08</td>
<td>3.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5mmol/L Toluene</td>
<td>3.03</td>
<td>1.55</td>
<td>17.52</td>
<td>2.52</td>
<td>1.661</td>
<td>0.9792</td>
</tr>
<tr>
<td>5mmol/L KCl +</td>
<td>1.63</td>
<td>2.91</td>
<td>19.98</td>
<td>4.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.50</td>
<td>2.13</td>
<td>17.04</td>
<td>3.24</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1mmol/L Toluene</td>
<td>3.10</td>
<td>1.43</td>
<td>16.49</td>
<td>2.52</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.4.5 Regeneration test

The long-term stability of DAZ under the same initial conditions (5mmol/L KCl and 0.5 mmol/L Toluene blended solution; 3.03PV/h flow rate) is presented in Figures 7.15 to 7.17. Upon comparison of the potassium and ammonium concentration in the influent and effluent of fresh, 1st water
regenerated and 2nd water regenerated DAZ (Figure 5.15), no significant difference may be observed. This indicates that the material would maintain a stable nutrient release for at least 2 regeneration cycles. As Milli-Q water is used to wash the material, no ion exchange would occur and no ammonium would be released during the flushing period.

As for the hydrocarbon adsorption and desorption process (Figure 7.16), toluene adsorbed onto the surface of DAZ can be easily washed off, and reloaded. This reversibility of hydrocarbon adsorption indicates that it would be accessible to microbial biofilms.

Upon comparison of the toluene adsorption performance of fresh and water washed DAZ in a column system (Figure 7.17), a slight difference in hydrocarbon adsorption may be observed. Similar results may also be found in the regeneration tests of DZ (Section 5.4.2) and SMZ (Michael Ranck et al., 2005).

Overall, the positive outcomes indicate the DAZ column can be used, washed and reused at least twice without significant reduction in nutrient release and hydrocarbon adsorption capacity.

![Figure 7.15](image)

Figure 7.15 Ion exchange during regeneration process. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 3.03PV/h.
Figure 7.16 Toluene concentration change during regeneration process. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 3.03PV/h.

Figure 7.17 Toluene adsorption performance among 1st, 2nd and 3rd regenerated DAZ. The initial influent concentration was 5mmol/L KCl and 0.5 mmol/L Toluene and the flow rate was 3.03PV/h.
7.5 Conclusions

The nutrient release and hydrocarbon adsorption performance of DAZ in column tests are presented. Under different toluene concentrations and flow rates, DAZ exhibited stable ammonium release without being impacted by a change in influent properties, such as flowrate or composition. For the same initial condition (same potassium and toluene concentrations), the toluene adsorption process of the column was only influenced by the aqueous flowrate. At constant flowrates, the toluene adsorption process presented little difference when the initial toluene concentration was changed.

The advection-dispersion-reaction solute transport model was used to simulate the toluene adsorption process when ion exchange was occurring. The regression coefficients between experimental data and predicted results shown the fitting was not as good as the modelling of DZ, but still within 97%. The variation may be due to the presence of potassium. The calculated maximum toluene adsorption capacity was larger than that in batch work. Similar trend was also found for the DZ. The regeneration tests shown the DAZ column can be used, washed and reused for at least twice without significant reduction in ammonium release and toluene adsorption capacity.

Overall, the column test of DAZ had proven stable ammonium release and toluene adsorption in a larger scale test. This characteristic will greatly enhance the in-situ bioremediation process as it can provide a long-term nutrient source, adsorb and store the hydrocarbon on the surface as a food source, thereby solving two main factors that limit the growth of bacteria. Furthermore, the rigid physical structure of the modified zeolite can resist the extreme environmental conditions in remote regions, such as Antarctica.
Chapter 8
Field application of DPDSCI coated ammonium zeolite
8.1 Introduction

Chapter 6 and 7 demonstrated that DAZ possessed stable ammonium release and toluene adsorption capacity, along with long-term stability for both batch and column tests. Here, the material is tested under complex field conditions.

8.2 Materials and Methods

8.2.1 Columns and materials

The column configuration was similar to the column study presented in Section 3.5.3 (Figure 8.1). Contaminated water was pumped through the columns at a rate of 2.5 ml/min (equivalent to 4.52 PV/h). Columns A to D contained different reactive materials (A-C were DAZ whilst D was AZ). The field test was conducted over 5 days. Fresh feed water was collected each day from the Contaminated Wastewater Treatment Plant (CWTP) and its temperature, EC and pH were recorded. The effluent of each column was collected every morning and afternoon for Total Petroleum Hydrocarbon (TPH), ions (K⁺, Na⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻) and nutrient (NH₄⁺, NO₃⁻, NO₂⁻, organic nitrogen, total Kjeldahl nitrogen, dissolved reactive phosphorus) analysis. To detect the influence of volatile hydrocarbons, influent samples were also collected twice a day, before and after effluent sample collection. A field blank was collected by placing an open bottle filled with Milli-Q water near the columns to determine the effect of volatile hydrocarbons on the hydrocarbon results obtained. A column blank was collected for each column by pumping Milli-Q water through this system, accounting for the potential hydrocarbon to partition from the tubing. After 5 days of column operation, the reactive materials were collected from the bottom and the top of the 4 columns for SEM and TPH testing.
Figure 8.1 The diagram of column installation in the field test

8.2.2 Sample delivery and analysis

Following the completion of the field tests, liquid samples collected for TPH analysis were stored and transported from Antarctica to Australia in 500 mL amber glass jars with Teflon lined septa caps at 4°C. Liquid samples for ion and nutrient analysis were stored and shipped from Antarctica to Australia in 50 mL plastic Sarstedt tubes at -20°C. Solid material removed from the columns for TPH analysis were stored and shipped back to Australia from Antarctica in 40 mL glass vials with Teflon lined septa caps at -20°C. Materials for microbiological observations were firstly fixed in 2.5% glutaraldehyde in 1M phosphate buffer solution for 4 hours and then stored and transported from Antarctica in 50 mL plastic Sarstedt tubes.

All samples, excluding those fixed in glutaraldehyde, were analysed at commercial laboratories. Analysis of aqueous samples for TPH was conducted at Australian Laboratory Services (ALS) in Melbourne, Victoria, following USEPA standard method 8260 and 8015. Aqueous samples for cations (K⁺, Na⁺, Mg²⁺, Ca²⁺), anions (Cl⁻, SO₄²⁻) and nutrient (NH₄⁺, NO₃⁻, NO₂⁻, organic nitrogen, total Kjeldahl nitrogen, dissolved reactive phosphorus) concentrations were conducted at Analytical Services
Tasmania (AST). Analysis for anion concentrations were carried out using Ion Chromatography (IC) whilst metals were analysed by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Dissolved nutrients in the aqueous samples were analysed by Flow Injection Analysis (FIA) with total nitrogen concentration determined by Kjeldahl Digestion and FIA.

Extraction and analysis of the reactive materials for TPH was conducted in the laboratory of the Australian Antarctic Division (AAD – Australian Government Department of the Environment and Energy) in Kingston, Tasmania. 10g of the reactive material was subsampled into a 40 mL glass headspace vial. To each sample, certified reference materials, laboratory reference material, blanks and blank recoveries, 1000 µL of internal standard was added. The internal standard comprised of 1,4-dichlorobenzene, p-terphenyl, deuterated tetracosane (C_{24}D_{50}) at 50 mg/L and bromoeicosane and cyclooctane at 250mg/L. To the blank recovery, 1000 µL of the spike mix containing 5000 mg/L of SAB in hexane was added. All samples were extracted via tumbling at room temperature for 16 hours using an extraction solvent mix of 1:1 milli-Q: n-hexane. Upon completion, an aliquot of the n-hexane layer was transferred to a GC vial for analysis. The extracts were analysed using an Agilent 7890 gas chromatograph fitted with a flame ionisation detector (GC-FID) with helium as the carrier gas. The GC column was a J&W DB-1 Column (length was 25m, Internal Diameter was 0.25mm and film was 0.25µm). The carrier gas velocity at the injector was 10.5 mL/min while in the column was firstly 1.3 mL/min held for 16 minutes then increased to 3.0mL/min for 30 minutes. The initial oven temperature was 50 °C which was held for several minutes followed by a ramp to 320 °C at a rate of 18 °C/min. TPH was measured using the ratio of the total detector response of all hydrocarbons to the internal standard peak response. This data from the GC-FID was processed using MATLAB software.

SEM testing of solid samples was conducted in Bio21 at the University of Melbourne using the Quanta Cryo SEM. Details of this process are described in Section 3.4.6.

8.3 Results and Discussion

8.3.1 Field test environmental characterization

The field test was conducted in the Contaminated Wastewater Treatment Plant (CWTP), located near the Main Power House (MPH) at Casey Station. The feed water was pumped from a 20 L container following what pre-treatment processes to the columns and replaced every morning during the experimental period. Meanwhile the temperature, pH and EC of the influent were recorded every day and is presented in Figures 8.2 to 8.3.
As shown, the temperature of the influent (Figure 8.2) fluctuated around 11°C, indicating the experiment was conducted at relatively low temperature conditions. The pH of the influent (Figure 8.3) was close to the prevailing soil pH (Freidman, 2016), which was around 9. According to the studies (Das et al., 2011), 6-9 is a suitable pH range for bioremediation processes. Meanwhile, the conductivity of the influent (Figure 8.3) stabilized between 500 to 600 µS/cm, which was also close to that of soil (Freidman, 2016).

Overall, the experimental conditions of field test were close to the real environmental conditions to simulate the adsorption and degradation process of contaminated waste water within the DAZ columns.

Figure 8.2 The temperature of influent in field test
8.3.2 Ion exchange performance

The ion concentrations in the column influent and effluent waters are presented in Figures 8.4 to 8.9. The major cations in the influent were potassium (K) and sodium (Na) and the concentrations of these two cations were all gradually increasing with time.

Upon the comparison of potassium concentration in the influent and effluent of AZ and DAZ columns (Figure 8.4), it can be observed that breakthrough of potassium has not yet occurred and it was all taken up by the zeolite. This is not unexpected due to the high selectivity of K⁺ by zeolite. Based on the ion selectivity of clinoptilolite, potassium was more amenable to exchange the ammonium in the AZ and DAZ compared with sodium, calcium, magnesium (Cooney et al., 1999). It can be speculated that after 450 PV passing, the exchange between potassium in the feed water and ammonium in the reactive materials were still stable.
The exchange of sodium onto the zeolite surface can be interpreted from Figure 8.5. As shown, initially most of the sodium was exchanged however this reduced over time due to the lower selectivity. The total amount of sodium captured by AZ was higher than DAZ (Table 8.1), suggesting surface modification process may change the zeolite surface characteristic, such as the distribution of the exchange sites or effective pore size, resulting in a different exchange capacity (Cooney et al., 1999). After 450 PV of feed water passing, the sodium concentrations in both column effluents were only 0.5 mmol/L less than that of feed water.
The calcium concentration in the influent and effluents is presented in Figure 8.6. For the AZ column, the effluent concentration stabilized at around 0.03 mmol/L during the trial with an influent of 0.2 mmol/L. This indicates that calcium in feed water exchanged with ammonium in AZ throughout the trial. However, the calcium concentration in the effluent of DAZ column started to increase after 300 PV passing, suggesting the ion exchange on the surface of DAZ was gradually decreasing. Difference between the effluents of AZ and DAZ columns might be because the modification process changed the surface characteristics of AZ (Cooney et al., 1999).
The magnesium concentration in the influent and effluent of AZ and DAZ columns are shown in Figure 8.7. The magnesium concentration in feed water stabilized around 0.2 mmol/L and gradually increased to 0.32 mmol/L after 200 PV passing. In the DAZ column, the magnesium concentration in the effluent increased linearly, reaching 0.32 mmol/L after 400 PV passing. This indicates the ion exchange process between magnesium in feed water and ammonium on DAZ surface gradually achieved the equilibrium status and therefore, there was no significant difference of magnesium in influent and effluent. For the AZ column, a different trend was observed. The magnesium concentration in effluent first increased to 100 PV and then stabilized during the 100 PV to 200 PV and finally sharply increased again after 250 PV passing. This trend was similar to the change of magnesium concentration in feed water. It means the exchange between magnesium in feed water and ammonium on AZ surface was continuous during the trial. The different cation capture performance of AZ and DAZ columns can also be observed from Table 8.1, which might contribute to the surface modification.
The mass balance of cation exchange on reactive material is presented in Figures 8.8 and 8.9. Though slight difference may exhibit at beginning period, the amount of cation adsorbed was almost the same as the amount of ammonium released from on the surface of material.
Figure 8.8 The equivalent sorb/release amount of cation on the surface of DAZ. Equivalent amount (meq/L) = ion concentration (mmol/L) × its electric charge

Figure 8.9 The equivalent sorb/release amount of cation on the surface of AZ. Equivalent amount (meq/L) = ion concentration (mmol/L) × its electric charge
Table 8.1 The total cation exchange amount of DAZ and AZ after 450PV

<table>
<thead>
<tr>
<th>Cation exchange amount (mmol/g)</th>
<th>K</th>
<th>Na</th>
<th>Ca</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>DAZ</td>
<td>0.2046</td>
<td>0.2162</td>
<td>0.0634</td>
<td>0.1201</td>
</tr>
<tr>
<td>AZ</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The anion exchange results are presented in Figure 8.10 and 8.11. The chloride in feed water was around 1.2 mmol/L and the sulphate was around 0.14 mmol/L. No changes occurred in chloride and sulphate concentrations in the influent and effluent. This is because the no exchangeable anions were presented in the reactive material. As zeolite is a cation exchange material, this result is within the expectation.

Figure 8.10 The average chloride concentration in the influent and effluent of AZ and DAZ columns
8.3.3 Nutrient release performance

The ammonium concentration in the feed water and effluent of AZ and DAZ columns are presented in Figure 8.12. As shown, there was almost no available ammonium in the influent during the observation period, which was consistent with previous studies (Mumford et al., 2013). The low nutrient concentrate in water would lead to the inefficient bioremediation as the bacteria culture required continuous nitrogen supply to form amino acids, nucleic acids and coenzymes (Hatzinger et al., 2015). However, the ammonium concentration in the effluent of both experimental columns was relatively high and stable even after 450 PV passing. This indicates the ammonium exchanged material has the potential to promote the in-site bioremediation process by continuously providing the nutrients that the microbes need. The concentration gap between the effluent of AZ and DAZ columns always existed, suggesting the surface modification process may change the surface characteristics of AZ via clogging some internal pores and thus influence the ammonium release behavior.
The nitrate and nitrite concentrations in the influent and effluent of AZ and DAZ columns are shown in Figure 8.13 and 8.14. The concentration of nitrate and nitrite in feed water was slightly higher than the previous investigation on the in-situ surface water (Mumford et al., 2013) and soil (Freidman, 2016). No significant difference was observed between the concentrations of influent and effluent, indicating no nitrates were released by the materials, which was as expected. This is because 5 days was not sufficient for microbial culture, and thereby the metabolism would not be very active and no apparent nitrification process was proceeded during the observation period.

Figure 8.12 The average ammonia concentration in the influent and effluent of AZ and DAZ columns
Figure 8.13 The average nitrate concentration in the influent and effluent of AZ and DAZ columns

Figure 8.14 The average nitrite concentration in the influent and effluent of AZ and DAZ columns
The change of total kjeldahl nitrogen in influent and effluent is shown in Figure 8.15. The concentration change was similar to the ammonium concentration change in Figure 8.12, indicating little organic nitrogen was produced in this system. Stable gap between influent and effluent of AZ and DAZ columns was also found during the experimental period.

![Figure 8.15](image)

**Figure 8.15** The total kjeldahl nitrogen concentration in the influent and effluent of AZ and DAZ columns

The dissolved reactive phosphorus concentration in the influent and effluent of AZ and DAZ columns is presented in Figure 8.16. No apparent difference was found between the influent and effluent after 450 PV passing. Little dissolved reactive phosphorus was presented in the feed water and little was taken up by the reactive material. This may indicate minimal microbial activities occurred. The reason for that is the dissolved reactive phosphorus is essential to cell division and metabolism in microbial growth. If there were sufficient accessible phosphorus, bacteria can utilize them to form nucleic acids, nucleotides, phospholipids, lipopolysaccharides or teichoic acids (only gram-positive bacteria) (Freidman, 2016), which are crucial components for microbial activities.
8.3.4 Hydrocarbon adsorption behaviour

In addition to ion exchange and nutrient release performance, the hydrocarbon adsorption behaviors of the materials were also investigated. As described, hydrocarbon concentrations in the feed water and effluent were all tested by Australian Laboratory Services (ALS). Figure 8.17 presents the petroleum hydrocarbon concentrations in range of C\textsubscript{10}-C\textsubscript{36} in the influent and effluent of AZ and DAZ columns. Other components, such as Trimethylbenzene, Isopropylbenzene, Styrene, Butylbenzene, Propylbenzene, Isopropyltoluene, Benzene, Ethylbenzene, Naphthalene, Toluene, Xylenes were below the detection limits, even in the feed water.

The concentration of C\textsubscript{10}-C\textsubscript{36} in solution fluctuated around 210 µg/L in the feed water and in the effluent of AZ column, the value was always close to that of influent. In the effluent of DAZ column, the breakthrough and saturation points were reached between 6-16 PV passing (Zone A). After 100-120 PV passing (Zone B), the DAZ column was still saturated, where no significant difference was observed between the concentration of influent and effluent. However, the concentration in the effluent of DAZ columns started to decrease after 200 PV (Zone C), which was lower than that of the
The difference between influent and effluent of AZ and DAZ columns after 200 PV (Zone C) suggests other processes occurred in the DAZ columns besides the conventional physical or chemical adsorption. As the field blank was below the detection limit and the influent and effluent were sampled at the same time, evaporation was not a significant factor.

Besides analyzing the variation of hydrocarbon concentration between the influent and effluent, it is also helpful to detect the components adsorbed to the reactive material, which was conducted in the laboratory of the Australian Antarctic Division (AAD – Australian Government Department of the Environment and Energy). The Gas Chromatograph (GC) chromatogram of the components extracted from the surface of reactive materials from the inlet and outlet of columns are presented in Appendixes 8.3 to 8.10. The components that above the detection limits are showed in Table 8.2 and the corresponding calculated ratio of components are presented in Table 8.3. The small molecular hydrocarbon peaks noticed in GC chromatogram (Appendixes 8.3 to 8.10) are not presented in Table 8.2 as their concentrations are very low and less than the method detection limit.

Upon comparison of the GC chromatogram in Appendixes 8.3 to 8.10, differences may be observed...
between AZ and DAZ, and between the materials in the different parts of one column. Compared the chromatograms of AZ and DAZ columns, there are peaks (19.5 and 26 minutes) showed in the chromatograms of all DAZ columns (Appendixes 8.4-8.9), which are absent in that of AZ column (Appendixes 8.10 and 8.11). The possible components were the DPDSCI coating that extracted from the surface of zeolite, rather than C_{36} (Lubricant), as the shape of these peaks were different to the reference (Appendix 8.3). The reason for that is the DPDSCI molecular might have similar structure to the film of GC column, the higher affinity would cause longer retention time, which might coincide with the time that C_{36} peak presented.

In the columns (A to C) containing DAZ, the material close to the inlet of the column always presented more intensive peaks, from 8 to 13 minutes, compared with the material close to the outlet of the column (Appendixes 8.4-8.9). In the extraction blank (Appendix 8.1), no significant hump was observed in this range, while in the spiked blank (Appendix 8.2), the peaks were large and distinct. The peaks came out in this period belong to hydrocarbons in range of C_{10} to C_{18}. This indicates that there were more lighter alkanes present on the surface of DAZ near the inlet than the outlet of the columns. However, no distinguishing peaks in this range were observed on the material of AZ column. This suggested that the surface modification by DPDSCI indeed enhances the hydrocarbon adsorption ability of natural zeolite as more hydrocarbon was adsorbed on the surface of DAZ compared with AZ. Additionally due to the low hydrocarbon concentration in the feed water, the material near the outlet of DAZ column was not saturated and still possessed the sufficient ability to capture more hydrocarbons.

The results from the GC (Table 8.2) indicate that few components on the surface of reactive material in DAZ column are above the detection limits and it was apparent that nothing existed on the surface of reactive material in AZ column. From triplicate DAZ columns, it can be observed that higher concentrations of detected components presented on the surface of reactive materials close to the inlet of column rather than outlet, which is consistent with the GC chromatogram.

To evaluate the mechanism of hydrocarbon loss during the trials, several chemical fuel indices were calculated. In the natural environment, the natural attenuation of hydrocarbons are mainly through the evaporation and biodegradation processes (Snape et al., 2006). Different types of hydrocarbons have different fates in these processes, due to their structural characteristics. Some components are found to be more volatile but more resistant to biodegradation, such as the light acyclic isoprenoids (i-C_{13}, i-C_{14} and i-C_{15}) in kerosene or diesel, they would evaporate more easily and can be compared with the heavier isoprenoids such as i-C_{16} and pristane (Snape et al., 2005). Whilst some other
components possess similar evaporative characteristics but are known to degrade differently. For example, the straight chain alkanes ($n$-C$_{12}$, $n$-C$_{13}$, $n$-C$_{14}$, $n$-C$_{15}$, $n$-C$_{16}$ and $n$-C$_{17}$) are found to be more easily degraded compared with the branched isoprenoids (Pond et al., 2002). Therefore, the ratios from $n$-C$_{12}$/i-C$_{13}$ up to $n$-C$_{18}$/phytane can be regarded as indices to evaluate the extent of in-situ biodegradation (Gill et al., 1989). Through the comparison with reference hydrocarbon concentrations and their biodegradation indices in soil (Snape et al., 2006), if the experimental ratios decreased significantly, it indicates more extensive biodegradation occurred.

As the pristane/phytane ratio varies from different fuel source, it can be used to determine the extent of specific fuel spills (Snape et al., 2006). The major petroleum hydrocarbon presented in the contaminated water at Casey Station is Special Antarctic Blend (SAB). The result obtained from the surface of the reactive materials were 1.27 and 1.44 (Table 8.3), which were not that close to the reference fuel (6.17) measured same time. This indicates that the lighter alkanes on the surface of DAZ might be changed during the trial. As most of the hydrocarbons presented on the surface of reactive material were below the detection limit, thereby only $n$-C$_{17}$/pristine produced a significant result. Upon the comparison with referenced SAB, a small reduction of $n$-C$_{17}$/pristine was found, indicating mild biodegradation happened on the surface of DAZ.

Overall, through the analysis of hydrocarbons in the effluent of each column and on the surface of reactive material, it can be concluded that 1) the surface modification by DPDSCI would help to enhance the hydrocarbon adsorption of natural zeolite; 2) with the combination work of DPDSCI and ammonium presented on the surface of reactive material, biodegradation process was motivated as the hydrocarbons were gradually degraded.
Table 8.2 The hydrocarbon components extracted from the surface of reactive materials in AZ and DAZ columns

<table>
<thead>
<tr>
<th>Component (mg/kg)</th>
<th>Columns</th>
<th>DAZ 1 (A)</th>
<th>DAZ 2 (B)</th>
<th>DAZ 3 (C)</th>
<th>AZ (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Outlet</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
<td>Outlet</td>
</tr>
<tr>
<td>C8</td>
<td>0.05</td>
<td>0.05</td>
<td>0.06</td>
<td>&lt;0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>C9</td>
<td>0.02</td>
<td>0.03</td>
<td>0.03</td>
<td>0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C10</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C11</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C12</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C13</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C14</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C15</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C16</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C17</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C18</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C19</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C20</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C21</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C22</td>
<td>0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>C23</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C24</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C25</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C26</td>
<td>0.02</td>
<td>0.03</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C27</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>C28</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>i-C13</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>i-C14</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>i-C15</td>
<td>&lt;0.02</td>
<td>0.04</td>
<td>&lt;0.02</td>
<td>0.05</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>i-C16</td>
<td>&lt;0.02</td>
<td>0.04</td>
<td>&lt;0.02</td>
<td>0.05</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Pristane</td>
<td>&lt;0.02</td>
<td>0.02</td>
<td>&lt;0.02</td>
<td>0.03</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Phytane</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>Resolved (C9-C18, SAB range)</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Resolved (C9-C28, DRO range)</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
<td>&lt;20</td>
</tr>
<tr>
<td>Resolved (C9-C36, Lube range)</td>
<td>50</td>
<td>28</td>
<td>39</td>
<td>44</td>
<td>16</td>
</tr>
<tr>
<td>Resolved (C9-C40, Total range)</td>
<td>56</td>
<td>35</td>
<td>52</td>
<td>46</td>
<td>&lt;32</td>
</tr>
</tbody>
</table>
Table 8.3 The ratio of hydrocarbon components for reactive materials in different columns (the blank cell means the at least one of the components was not detected)

<table>
<thead>
<tr>
<th>Marker Ratio</th>
<th>Columns</th>
<th>DAZ 1 (A)</th>
<th>DAZ 2 (B)</th>
<th>DAZ 3 (C)</th>
<th>AZ (D)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Outlet</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
<td>Outlet</td>
<td>Inlet</td>
</tr>
<tr>
<td>Pristane/phytane</td>
<td>1.27</td>
<td>1.44</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C_{12}/i-C_{13}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C_{13}/i-C_{14}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C_{14}/i-C_{15}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C_{15}/i-C_{16}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C_{17}/pristane</td>
<td>0.93</td>
<td>0.60</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C_{18}/phytane</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

8.3.5 Microbial attachment

After disassembling the columns, some distinct black points were observed on the surface of AZ and DAZ. The reactive materials from bottom of AZ and DAZ columns were collected and fixed in glutaraldehyde in 1M phosphate buffer solution. After dehydration by acetone, the materials were tested by SEM. The cell attachment on the surface of reactive materials is shown in Figure 8.18. At the same magnification, the bacteria on the surface of DAZ (Figure 8.18b) was more robust compared with AZ (Figure 8.18a). Also the cell number on the surface of DAZ under one horizon was more than that of AZ.

Furthermore, the filamentous Extracellular Polymeric Substances (EPS) can be observed from some single bacteria (Figure 8.19a) and there are always some by-products (smaller than 1µm) existing near those single bacteria (Figure 8.19b). These by-products were speculated to be the excreted cellular products, such as protein, produced from bacteria activities (Sutherland, 2001).

The SEM images showed the bacteria activity on the surface of DAZ was more active than on the AZ, indicating DAZ provided more suitable living environment. This may include more hydrocarbon as a food source and stable ammonium release as a nutrient supply. However, the biofilm or uniform EPS layer in previous studies (Freidman, 2016) was not found in this field test. The exhibition and variation of EPS matrix structure was dependent on the microbial cells present, their physiological status, the nutrients available and the prevailing physical conditions (Sutherland, 2001). Due to the short time that the experiments were conducted over and low hydrocarbon concentrations in the feed water, it was possible that not many EPS or biofilm was formed on the surface of reactive material.
8.4 Conclusions

A field test was completed in the Contaminated Wastewater Treatment Plant at Casey station, Antarctica. The temperature of feed water was 11°C, the pH was 9 and EC was between 500-600 µS/cm. The ions presented in influent included potassium, sodium, calcium, magnesium, chloride, sulphate. Of these, potassium and calcium interacted mostly with ammonium present on the surface of material. The ion exchange for AZ and DAZ was different due to the surface modification by DPDSCI. The ammonium release of both materials was very stable even after 500 PV passing. However, this might be negatively impacted by the surface modification process, as the ammonium
release of DAZ was always 1 mmol/L lower than that of AZ.

The hydrocarbon adsorption ability of DAZ was more effective than AZ as the TPH concentration in the effluent of AZ column always very close to the influent while the TPH concentration in the effluent of DAZ column was much lower especially before 16 PV and after 150 PV passing. For the period between 0-16 PV, the TPH was adsorbed on the surface of DAZ through the physical adsorption therefore the concentration in the effluent was lower. During the 16-150 PV, the adsorption process reached saturation and few microbes were cultured on the surface of reactive material, thus the TPH in effluent was similar to that in influent. After 150 PV passing, the TPH concentration in effluent started to decrease and the probably indicated the start of biodegradation.

GC results of the components extracted from the reactive material showed that hydrocarbon was adsorbed and higher concentrations were detected on the surface of materials closed to the inlet of the DAZ column. The biodegradation indice (n-C_{17}/pristine) suggested that biodegradation had already proceeded and the hydrocarbon began to degrade on the surface of reactive material. However, due to the limitation of experimental time and low concentration of influent component, more distinct results cannot be obtained from this field test.

The SEM micrograph of column materials confirmed that bacteria grew better on the surface of DAZ. However, due to the lack of microbes in feed water, there was little bacteria observed and extensive biofilm and EPS were not found.

Overall, the field test successfully proved the ion exchange between contaminated groundwater and column materials, the stable nutrient release and good hydrocarbon adsorption capacity of DAZ and its promotion towards in-site biodegradation.
Chapter 9
Conclusions and Recommendations
9.1 Conclusions

From the preliminary work of literature review and laboratory test, it can be concluded that:

1) DPDSCI was successfully grafted to the surface of natural zeolite. The functional groups of DPDSCI was observed on the surface of zeolite via TGA and FT-IR analysis.

2) Compared with natural zeolite, DPDSCI coated zeolite possessed a higher toluene adsorption capacity in both batch and column tests, even under low temperatures. The regeneration of DPDSCI coated zeolite was confirmed in batch and column tests, indicating that the toluene adsorption on this material is reversible, and therefore accessible to microbial populations for biodegradation processes.

3) The Langmuir isotherm fitted the adsorption isotherms, suggesting a monolayer and homogeneous adsorption process occurred. Meanwhile, thermodynamic analysis confirmed the interactions between hydrocarbons and DPDSCI coated zeolite were mainly Van de Waals interactions with some enhancement of hydrophobic bonding and \( \pi-\pi \) electron stacking interactions.

4) Reactive transport modelling in column tests presented good agreement between the experimental data and model prediction, suggesting the ADRE equation with Langmuir equilibrium isotherm could well simulate the toluene adsorption on DPDSCI coated zeolite at various temperatures and flow rate conditions.

5) Upon the comparison with DPDSCI coated zeolite, DPDSCI coated ammonium exchanged zeolite possessed similar toluene adsorption capacity at the same experimental conditions. Additionally, it also exhibited stable ammonium release in both batch and column tests. Regeneration tests indicated that the ammonium release ability of DPDSCI coated ammonium exchanged zeolite may be recovered via ammonium conditioning and toluene may be washed off and toluene adsorption capacity not negatively impacted.

6) The Langmuir isotherm fitted the toluene adsorption process of DPDSCI coated ammonium exchanged zeolite. However, with potassium concentration in the aqueous phase increasing, the maximum adsorption capacity calculated by the Langmuir isotherm also increased. The possible explanation may be that the higher ionic strength of the solution decreases the toluene solubility, causing the toluene to be adsorbed onto the hydrophobic surface of DPDSCI coated ammonium exchanged zeolite, resulting in enhanced adsorption capacity. For the reactive transport modelling in column tests, not as good agreement between experimental data and modelling was obtained,
suggesting that the ionic strength of the aqueous phase may have slight influence in the modelling of the ADRE equation.

From the field test, it can be concluded that:

1) The DPDSCI coated ammonium exchanged zeolite possessed a good ion exchange capacity. Compared with ammonium exchanged zeolite, the ion exchange processes were different. The possible reason may be the surface modification would alter the surface characteristic of ammonium exchanged zeolite.

2) The ammonium release of ammonium exchanged zeolite and DPDSCI coated ammonium exchanged zeolite was both very stable even after 500 PV passing. However, this may be negatively impacted by the surface modification process, as the ammonium release of DPDSCI coated ammonium exchanged zeolite was always 1 mmol/L lower than that of ammonium exchanged zeolite for the same influent.

3) The hydrocarbon adsorption ability of DPDSCI coated ammonium exchanged zeolite was more effective than ammonium exchanged zeolite. Through analysis of the components adsorbed to the surface of the reactive materials after trial, it was found that concentrations of hydrocarbons were higher on the material close to the inlet of DPDSCI coated ammonium exchanged zeolite column. The biodegradation indice \((n\cdot C_{17}/\text{pristine})\) suggested that biodegradation was occurring on the surface of the DPDSCI coated ammonium zeolite.

4) The SEM micrograph of the reactive materials confirmed that higher population of bacteria grew on the surface of the DPDSCI coated ammonium exchanged zeolite compared with ammonium exchanged zeolite.

Overall, extensive investigations were conducted on the performance of DPDSCI coated natural and ammonium exchanged zeolite under various environmental conditions in batch, column and field tests. The promising results showed that DPDSCI coated ammonium exchanged zeolite possesses good and reversible hydrocarbon adsorption capacity, long-term stable nutrient release ability, good regeneration performance and as such had the potential to be used in situ to promote adsorption and biodegradation processes. This indicates this material can be viewed as an alternative choice for the reactive material applied in PRBs in cold regions.
9.2 Recommendations

1) Due to time limitations for the field test, low TPH concentration in the feed water, it is recommended that further field scale tests can be conducted before wide spread application of this material. It is not necessary to repeat them in site, but large flow cells are needed. Under suitable conditions, such as longer experimental time, adequate TPH in feed water and appropriate amount of bacteria in system, the hydrocarbon adsorption and degradation performance on the surface of DPDSCI coated zeolite can be more detailed investigated.

2) The reactive transport modelling towards the adsorption process of DPDSCI coated ammonium exchanged zeolite was not perfect when addition ions were presented in solution. A multicomponent adsorption model is needed to account for changes in adsorption due to the changes in ionic strength or alter competing ions.
Reference


Freidman, B. L. (2016). *The development and contribution of bio-reactive materials for petroleum hydrocarbon remediation in the Antarctic*. (PhD), University of Melbourne,


comparison with a continuous adsorptive barrier. Desalination and Water Treatment, 57(48-49), 23372-23381.


Appendix
Appendix 3.1 Calibration curve for the analysis of Toluene by HPLC at 220nm wavelength

\[ y = 16.858x \]
\[ R^2 = 0.9972 \]

Appendix 3.2 Calibration curve for the analysis of Toluene by HPLC at 254nm wavelength

\[ y = 3.3544x \]
\[ R^2 = 1 \]
Appendix 3.3 Calibration curve for the analysis of K by ICP-OES

\[ y = 21515x \]
\[ R^2 = 0.9993 \]

Appendix 3.4 Calibration curve for the analysis of Total NH₄⁺ by UV-Vis

\[ y = 2.81x \]
\[ R^2 = 0.9998 \]
Appendix 5.1 CXTFIT code for axial dispersion coefficient determination

The CXTFIT code is developed by the U.S. Department of Agriculture to estimate the solute transport parameters using a nonlinear least-squares parameter optimisation method. This software can be downloaded through the U.S Department of Agriculture’s website at https://www.ars.usda.gov/research/software.

The following code is an example of the CXTFIT used in this thesis to determine the $D_l$ and $\bar{v}$. The description of input and output parameters and files are referred to the CXTFIT manual (Toride et al., 1995) and Woinarski’s thesis (Woinarski, 2004).

```
1
*** BLOCK A: MODEL DESCRIPTION ****************************************************
INVERSE PROBLEM
RELATIVE CONC. VS. TIME (MIN) AT 12.5 CM. UNITS: CM, MIN
INVERSE MODE NREDU
  1                1
MODC  ZL (BLANK IF MODE=NREDU=1)
  3
*** BLOCK B: INVERSE PROBLEM ****************************************************
MIT ILMT MASS
  150            1            0
*** BLOCK C: TRANSPORT PARAMETERS *********************************************
V D R Mu
  0.6          1        1         0
  100         100     999    999
*** BLOCK D: BVP; MODB=0 ZERO; =1 DIRAC; =2 STEP; =3 A PULSE *****************
MODB (Reduced Conc. & time) =4 MULTIPLE; =5 EXPONENTIAL; =6 ARBITRARY
  0
*** BLOCK E: IVP; MODI=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODI
  1
  1.0
*** BLOCK F: PVP; MODP=0 ZERO; =1 CONSTANT; =2 STEPWISE; =3 EXPONENTIAL **
MODP
  0
*** BLOCK G: DATA FOR AN INVERSE PROBLEM **************************************
INPUTM =1; T,C FOR SAME Z
  1
  12.5
TIME CONC (Give "0 0 0" after last data set.)
  0    1.0000
  4    1.0000
  8    0.9924
 12    0.9524
 16    0.8389
 24    0.4292
 28    0.2854
 32    0.1745
 36    0.0867
 40    0.0425
 44    0.0317
 48    0.0146
 52    0.0161
 56    0.0088
 60    0.0082
```
Appendix 5.2 MATLAB code for the prediction of solute transport in column tests

MATLAB was used to calculate the results from Equation 7 and Equation 8 based on the initial conditions, such as influent concentration, temperature, flow rate and particle porosity. Before applying the already defined function PDE in MATLAB, the Equation 7 and 8 need to simplified into appropriate form. The simplification steps are as followed:

Equation 8: \[
\frac{\partial q}{\partial t} = \frac{\partial}{\partial x} \left( \frac{q_{\max K_l}}{1+K_l C} \right) \frac{\partial C}{\partial t}
\]

Equation 7:
\[
\frac{\partial C}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x} - \frac{p_b}{n} \frac{\partial q}{\partial t}
\]
\[
\rightarrow \frac{\partial C}{\partial t} + \frac{p_b}{n} \frac{\partial q}{\partial t} = D_l \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x}
\]
\[
\rightarrow \frac{\partial C}{\partial t} + \frac{p_b}{n} \frac{q_{\max K_l}}{1+K_l C} = D_l \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x}
\]
\[
\rightarrow \left[ 1 + \frac{p_b}{n} \frac{q_{\max K_l}}{1+K_l C} \right] = D_l \frac{\partial^2 C}{\partial x^2} - \bar{v} \frac{\partial C}{\partial x}
\]

In this thesis, the code contained three Parameterizing Functions: bcfun, icfun and pdefun and one major program: main. The bcfun was for the definition of the boundary conditions, the icfun was for the definition of the initial conditions and the pdefun was for the definitions of the components in the PDE. The following code is an example used in this thesis to calculate the result of effluent/influent in the column test based on the initial conditions.

**Main.m**

```matlab
clear all
clc

global qm db Kl DL vs n c0 Kd

vs=0.1366*0.4151/3600;                                                % superficial velocity, m/s
db=2.0613E6;                                                                    % dry bulk density, g/m3
n=0.4151;                                                                           % porosity

%------------T=20 oC--------------
data=importdata('T20C.mat');
T=20;                                                                                   % temperature
C0=25.82;                                                                           % constant input concentration, g/m3
DL=0.812E-6;                                                                     % axial despersion coefficient, m2/s
%--Langmiur----
Kl=7.2087E-4;                                                              % Langmuir constant, m3/g
qm=12.7795E-4;                                                         % max zeolite conc, g/g

% data=importdata('NaClExpData.mat');
%----------------------------------
% data=importdata('NaClExpData.mat');
%----------------------------------
t_Exp=data(:,1)*60;
c_Exp=data(:,2);

m=0;

x=linspace(0,0.5,100);
t=linspace(0,45000,50);
sol = pdepe(m,@pdefun,@icfun,@bcfun,x,t);
u = sol(:,:,1);
c1cal=u(:,25)/c0;
```

125
plot(t_Exp,c_Exp,'o',t,c1cal);
title('Concentration at sampling points');
legend([Exp. Result', 'Cal. Result L=12.5']);
xlabel('Time t/min')
ylabel('C/C0')
results=[t' c1cal];

Bcfun.m
function [pl,ql,pr,qr] = bcfun(xl,ul,xr,ur,t)
global c0;
pl=ul-c0*(1-exp(-t/1E-20));
ql = 0;
pr = 0;
qr = 1;

icfun.m
function u0=icfun(x)
u0=0;
end

Pdefun.m
function [c,f,s] = pdefun(x,t,u,dudx)
global qm db Kl DL vs n c0 Kd;

% ----------Langmuir model----------
c=1+(db/n)*((Kl*qm)/(1+Kl*u)^2);
%----------------------
f=DL*dudx;
s=vs/n*dudx;
end
Appendix 8.1 The chromatogram of extraction blank (no fuel)

Appendix 8.2 The chromatogram of spiked blank (with SAB added)
Appendix 8.3 The chromatogram of Lubricant
Appendix 8.4 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the outlet of DAZ column (A)
Appendix 8.5 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the inlet of DAZ column (A)
Appendix 8.6 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the outlet of DAZ column (B)
Appendix 8.7 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the inlet of DAZ column (B)
Appendix 8.8 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the outlet of DAZ column (C)
Appendix 8.9 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the inlet of DAZ column (C)
Appendix 8.10 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the outlet of AZ column (D)
Appendix 8.11 The chromatogram of the components extracted from the surface of reactive materials and the corresponding fuel signal. The material was sampled near the inlet of AZ column (D)
Minerva Access is the Institutional Repository of The University of Melbourne

Author/s:
Ma, Junchao

Title:
Development of contaminant removal material suitable for implementation in cold regions

Date:
2018

Persistent Link:
http://hdl.handle.net/11343/212534

File Description:
Complete thesis

Terms and Conditions:
Terms and Conditions: Copyright in works deposited in Minerva Access is retained by the copyright owner. The work may not be altered without permission from the copyright owner. Readers may only download, print and save electronic copies of whole works for their own personal non-commercial use. Any use that exceeds these limits requires permission from the copyright owner. Attribution is essential when quoting or paraphrasing from these works.